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# Scientific Research ABSTRACTS

Volume 1a

## ICC 2009

## XIV INTENATIONAL CLAY CONFERENCE

# XIV INTERNATIONAL CLAY CONFERENCE ICC 2009

Castellaneta Marina (Taranto), Italy
June, 14-20, 2009

# Scientific Research Abstracts

## Volume 1a

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# PREFACE

These two volumes contain the oral and poster contributions to the 14th International Clay Conference held in Castellaneta Marina (Taranto, Italy) from 14 to 20 June 2009. The meeting was organized by the *Associazione Italiana per lo Studio delle Argille* - onlus (AISA, the Italian Association for the Study of Clays), on behalf of the *Association Internationale pour l'Etude des Argiles* (AIPEA - International Association for the Study of Clays). Volume I includes the contributions submitted as oral presentations. Poster contributions are collected in Volume II.

The scientific program of the meeting included 6 plenary lectures, 42 keynote lectures, 24 invited presentations, 408 oral and 548 poster contributions. All the contributions were revised by 74 international experts, many of them being the conveners of the 43 sessions dealing with the eight themes of the Conference: Bio-Clays Interface & Life's Origin, Ceramics & Engineering, Geology & Geochemistry, Health & Environment, Mineralogy & Crystallography, Nano & Porous Materials, Soils & Sediments, Miscellaneous. Our sincere thanks go to these colleagues who devoted their time to the 14th ICC.

Our heartfelt thanks go to the many people who worked hard to organize the scientific and social events as well as to the Institutions and business enterprises, which supported the meeting. We owe a special thank-you to the delegates, more than 700 coming from 51 Countries, who contributed to make the 14th International Clay Conference a memorable event.

Saverio Fiore
Chair, 14th ICC

# PLENARY LECTURES

# EXTRATERRESTRIAL CLAYS, AS RECORDERS OF POTENTIAL HABITABILITY: THE CASE OF MARS."

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It has long been considered that if life ever emerged, other than on the Earth within the solar system, the most likely candidate would be Mars, the Red planet. With the space missions, the question of extraterrestrial habitability entered its scientific era, with dedicated approaches and actual measurements performed. However, until recently, no clear evidence was found that Mars ever harboured habitable conditions, at least in having hosted conditions capable of sustaining surface liquid water. In particular, hydrated minerals recording an early warm and wet Martian environment have long been searched for, unsuccessfully.

The situation changed drastically, with the discoveries made by the presently orbiting Mars missions, ESA/Mars Express and NASA/Mars Reconnaissance Orbiter: their hyperspectral imagers OMEGA and CRISM respectively have identified and mapped hydrated phyllosilicates in a variety of sites within the most ancient terrains. They likely trace and locate, in space and time, episodes while Mars maintained perennial water. These mineralogical findings open new windows to explore planetary habitability.

A totally renewed history of Mars is now being built, enlightening in particular its early era dominated by the heavy bombardment that affected all planetary bodies along the first hundreds of millions years. We will present the relevant data that might account for similar early developments of Mars and the Earth, while terrestrial life emerged. We will then present scenarios to account for the potential divergence of the evolutionary paths of these planets.

# THE ROLE OF CLAY MINERALS IN CARBON DIOXIDE SEQUESTRATION

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Carbon dioxide capture and sequestration (CCS) in deep geological formations has emerged over the past ten years as an important component of the portfolio of options for reducing greenhouse emissions. Large and tectonically stable sedimentary basins can provide geological formations with sufficient pore space to accommodate large volumes of $CO_2$. They contain vast volumes of inter-layered sedimentary rocks of different textures and compositions that provide both the pore volume to sequester the $CO_2$ and seals to trap the $CO_2$ underground. Within sedimentary basins, depleting oil and gas reservoirs, saline aquifers and coal beds are all options for sequestering $CO_2$. Suitable formations are expected to be deeper than 800 m, have a thick and extensive seal, sufficient porosity to contain large volumes of $CO_2$ and enough permeability to permit injection of $CO_2$ at high flow-rates. Four mechanisms can contribute to retention of $CO_2$ for long periods of time: structural, solubility, capillary and mineral trapping.

In the case of saline aquifers, successful geologic sequestration is dependent on the seal or cap rock that prevents leakage of $CO_2$ from the injection horizon. The original depositional setting (e.g. grain size, laminar fabric, organic matter) and any subsequent diagenetic alteration (e.g. cementation) are key factors controlling the quality of a seal. Seal rocks are typically fine textured shales, mudstones and carbonates. The fine texture results in very small pore spaces and pore throats, which have low permeability to the flow of any type of fluid. The abundance, size, distribution and composition of the clay fraction in the seal rock can play an important role in determining its transport properties (e.g. wetting, diffusion, capillary-entry pressure, porosity, permeability). Furthermore, clays present in the seal and the injection formations (typically sandstones) may participate in reactions with $CO_2$-rich brines leading to the release of major, minor and trace elements.

This presentation will address the general concept of geological sequestration and describe current activities underway world-wide to test the feasibility of storing large amounts of $CO_2$ in the subsurface. Specific examples of pilot tests involving $CO_2$ injection into different geological settings will be discussed. Results will be presented on mineralogical, compositional and textural characterizations of potential seal and injection-formation rocks with emphasis on the clay fraction. Novel porosity and pore-network characterization tools such neutron scattering will be introduced along with a discussion of how complex $CO_2$-rich fluids interact with the clay-rich nano-environment based on molecular-level modeling. Future research needs will be described that point to the importance of understanding sequestration behavior over a wide range of length and time scales.

**Keywords:** geological sequestration, carbon dioxide, clay fraction.

# CLAYS AND MUDSTONES SINCE 1556

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Clays and clay-rich sedimentary rocks, or mudstones, are by far the most abundant type of sediment. For this reason alone a survey of the history of development of thought and study of them is of interest. One of the first authors to consider historical developments in mudstone studies was Millot (1964), who divided the topic into three parts: initial chemical study, use of the X-ray and modern studies. Additional work by Grim (1953, 1988) and Bergaya et al. (2006) relate specifically to clays. We describe here in the form of a timeline a summary of the key ideas and developments in the history of the study of both clays and clay-rich sediments. In 1556, Agricola published posthumously the first detailed description of a mudstone, but it was not until 1747 that the term shale was formally defined by William Hooson. A review of the world literature since Hooson's time shows a slow, steady increase in activity in the study of clays and mudstones during the 1800s, then a decline during World War II, followed by a return to the pre-war level. This was followed in the 1990s by a slight decrease in activity. The trends are similar for both conceptual advances and for new techniques. A notable increase in the studies of clays and mudstones in the 1920s was led by new technologies that expanded observations down to the angstrom level with powder X-ray diffraction, and up to the formation scale with down-hole geophysical logging and seismic reflection. A "Golden Age" of clays and mudstones ensued from 1922 to 1939. Technological development began this expansion, but conceptual developments caught up within a few years and thereafter the two moved forward together at about the same rate. Thus, for mudstones at least, it would appear that the major breakthrough was stimulated by new instrumentation rather than by new ideas. A comparison with a similar compilation for igneous and metamorphic rocks shows the same three phases – an early slow phase, then an intermediate rapid phase punctuated by the Second World War, and a final slower phase. But in the case of the crystalline rocks the rapid phase begins much earlier, in the 1880s. We suggest that the common techniques of that time, the petrographic microscope and wet chemical analysis, were well suited for crystalline rocks, but the breakthrough for clays and mudstones had to wait for the arrival of new technologies. Three additional observations can be made about the cumulative trend and stepwise curves. First, there was the interruption by World War I with only one paper published between 1914 and 1922, and it was only in 1923 that Max von Laue's 1912 discovery that crystals diffract X-rays was applied to clays by Assar Hadding. Following World War II, however, the transfer from the science used in war technologies was rapid, and greatly benefitted the earth sciences in general and the study of clays in particular. Equally important was the influx of war veterans into the earth sciences after World War II, particularly in North America. And finally, the Golden Age of mudstones from 1922 to 1939 continued into and through the Depression years, perhaps suggesting that intellectual momentum is hard to suppress.

# ROLE OF CLAY MINERALS IN CONTROLLING THE FATE OF DIOXINS IN THE ENVIRONMENT

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Our collective research efforts are centered on understanding the environmental fate of aryl hydrocarbon receptor ligands (AhRLs). AhRLs include dibenzofurans, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and dioxins. The most toxic of these ligands are the class of compounds known as polychlorodibenzodioxins (PCDDs). These chorlinated planar tricyclic aromatic ether compounds are among the most harmful compounds known to man due to their exceptional toxicity and carcinogenicity. Induction of AhR-dependent gene expression in mice, for example, can occur at aqueous concentrations < 10 pM of 2,3,7,8-TCDD.

Both urban and rural soils in localized areas throughout the world are contaminated with PCDDs. Elevated risks for certain types of cancer have been observed in a few of these areas where soil contamination is one of the potential pathways of exposure. Soil organic matter would seem to be the logical sorptive phase for the strongly organophilic PCDDs and their association with hydrophilic clay minerals would, at first glance, seem tenuous. However, recent evidence has established some connectivity between PCDDs and clay minerals that will be presented.

One such link relates to elevated levels of PCDDs found in prehistoric clay deposits in the United States and in Germany. These clay deposits contain elevated concentrations of PCDDs exhibiting unique homologue profiles not associated with anthropogenic processes. The congener patterns found in these prehistoric clay deposits are unique to clays. Furthermore, the presence of PCDDs in these clays pre-date any anthropogenic inputs and suggests a common natural geologic mechanism to account for their origin.

Current research is directed along three lines of attack. The first is examining the role of clay minerals as regulators of the adsorption, and long term fate of dioxins. We have found that dioxin analogs show a surprising dependence on the nature of the exchangeable cation and nature of the clay itself. The second area seeks to understand the molecular mechanisms of dioxin sorption to clay minerals. Finally, using an array of natural and synthetic materials, we seek to elucidate the bioavailability of dioxins sorbed to clay minerals.

**Keywords**: Dioxins, clay minerals, sorption, molecular mechanisms, biovailabiliy.

# THE ROLE OF CLAYS IN THE ORIGIN OF LIFE

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Prebiotic chemistry plays a central role in the investigation of the possible scenarios of the early chemical environments. Its goal is to shed light on the events involved in the synthesis of initial biomolecules and on the self-organization processes that led the last common ancestor. Since Bernal's analysis of the physical basis of life, several prebiotic scenarios invoking clays have been proposed (1). Accordingly, both the surface and, possibly, the interlamellar spaces of clays might serve as microenvironments (or micro-reactors) to concentrate organic building blocks for life-related syntheses such as the formation of peptides and polynucleotides (2). Because of their favorable physical and chemical properties, such as high surface area and large adsorption and ion-exchanging capacity, montmorillonites are widely employed as catalysts in the synthesis of fine-chemicals and drugs under mild experimental conditions. Remarkably, montmorillonites catalyze the aldol condensations of formaldehyde into sugars ("formose reaction") (3). Their role in the preparation of oligonucleotides up to the length of small ribozymes has been reported after adsorption of a template on the mineral surface and repeated incubations with activated nucleotides (4). It is also relevant that nucleobases which are not normally intercalated into montmorillonite, such as thymine, are taken up through specific molecular recognition processes based on hydrogen bond pairing with partner molecules localized in the interlamellar region. Cairns-Smith has pointed out the possibility that imperfections in a growing crystal lattice are replicated upon crystal growth. The fact that biopolymers formed in the montmorillonite microenvironment could be pre-ordinated by the information encoded in the charge distribution of the layers suggested for clays a role in a "rudimentary pre-biological evolution process". Of additional relevance are the template and the shielding properties proposed for clays (5) and their catalytic properties in the synthesis of nucleobases. (6). Taken together, these data suggest that clays played an important role in the origin of life.

**Keywords:** Prebiotic synthesis, nucleic acids, clays.

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# ONE DIMENSIONAL STRUCTURE OF EXFOLIATED POLYMER-LAYERED SILICATE NANOCOMPOSITES: A POLIVYNYLPYRROLIDONE (PVP) CASE STUDY

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The classical modeling of powder X-ray diffraction patterns of lamellar structures is applicable only to periodic or quasi-periodic structures. For non-periodic structures another approach is necessary. X-ray diffraction patterns of non-periodic structures contain relatively small amount of information, therefore some initial assumptions are necessary. In case of an exfoliated polymer-layered silicate nanocomposites it is possible to assume the chemical composition and the thickness of the clay layer but the structure of polymer remains unknown. A new approach, which can be used to solve the structure of the polymer is proposed. This approach is based on modeling of $LpG^2$ factors recorded from oriented samples in order to obtain the one dimensional structure of polymer.

In case of polivynylpyrrolidone (PVP) adsorbed on smectite it was found that, although $LpG^2$ factors for various smectites are quite different, the structure of polymer is not affected by the charge of smectitic layer, nor by the location of this charge in the tetrahedral or octahedral positions. There is an enhancement of the polymer concentration at distances closer to the clay layer, and it seems that PVP chains that are directly bonded to the surface are more rigid, while the outer parts - more flexible. It was also possible to obtain the thickness of the polymer layer adsorbed on the surface. The generalized configuration of PVP on smectite can be used as a model for other surfaces of smectitic character, e.g. the surface of illite fundamental particles.

# BIO-CLAYS INTERFACE & LIFE'S ORIGIN

## BC1 • CLAYS & BIOMOLECULES: FROM THE ORIGIN OF LIFE TO MEDICAL APPLICATIONS

## BC2 • CLAYS - LIVING ORGANISMS INTERACTIONS

# BIO-CLAYS INTERFACE & LIFE'S ORIGIN

## SESSION BC1

## *Clays & Biomolecules: From the Origin of Life to Medical Applications*

# PROTEINS AND CLAYS: MECHANISMS OF INTERACTION

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Proteins have generally a strong affinity for all types of interfaces found in soil, particularly clay minerals (Quiquampoix, 2008). The affinity for various types of interfaces originates in the flexibility of the polypeptide chain and in the diversity of the 20 amino acids that can be classified on an electrical scale as positively, neutrally or negatively charged and on a hydrophobic scale from polar to non-polar. These properties give rise to a large variety of interactions with soil surfaces, relationships that may be dominated by enthalpic or entropic contributions to the free energy (Quiquampoix, 2002). The strong and often largely irreversible adsorption of proteins on the mineral phase of the soil has important consequences (Quiquampoix and Burns, 2007) on their resistance to breakdown and functional activity (for example, catalylic for enzymes, infectious for prions, toxic for Bt proteins). An important question is the determination of possible changes of conformation of the adsorbed protein. NMR and FTIR spectroscopies are useful to answer this question since they respectively give information on the interfacial area of the surface of contact of protein-clay and on the secondary structure of adsorbed proteins. Soft proteins, such as bovine serum albumin, are more prone to the first mechanism, whereas hard proteins, such as $\alpha$-chymotrypsin are more prone to the second. In addition to electrostatic forces, hydrophobic interactions are also implied in the interaction of proteins with clays. The hydrophobic interactions can result from an electrostatic exchange of the hydrophilic counterions on the clay surface leaving a hydrophobic siloxane surface. The rearrangement of the protein structure on the clay surface can be facilitated when hydrophobic amino acids come in contact with the hydrophobic siloxane layer and remain shielded from the water molecules of the solution. If this rearrangement is accompanied by a decrease of ordered secondary structures, it would result in an additional increase in conformational entropy, lowering the Gibbs energy of the system. The combination of all these different subprocesses is responsible for the irreversible aspects of the modifications of conformation on clay surfaces.

**Keywords:** Protein, Clay mineral, Adsorption.

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# BIOSIGNATURES PRESERVATION POTENTIAL AND HABITABILITY IN PHYLLOSILICATES VS. IRON-RICH ENVIRONMENTS AS MARS ANALOGUES

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Phyllosilicates have been identified on the surface of Mars by the OMEGA-Mars/Express [1], the Mars Reconnaissance Orbiter (MRO) instruments, HiRISE and CRISM, as well as inferred from rover observations in Gusev Crater [2]).

A better understanding of the preservation potential and habitability in phyllosilicates and hematite-rich materials, achieved by studying analog sites, will therefore provide critical information in support of next decade missions landing site selection e.g., 2009 Mars Science Laboratory (MSL), the ESA Pasteur ExoMars.

We present geochemical ($\delta^{13}C_{org}$, $\delta^{15}N_{total}$, CN ratios) and microbiological proxies i.e., Adenosin-Triphosphate (ATP-based biomass) and Limulus-Amebocite-Lysate (LAL-based biomass) from a suite of phyllosilicate and iron-rich environmental samples collected from a variety of environments e.g., Rio Tinto (Spain), Death Valley (CA, USA), Atacama Desert (Chile), and the California coast.

Phyllosilicates-rich zones (47-74 wt.%) from the Rio Tinto (RT) region can preserve up to 10-time higher amount of organics ($C_{org}$ = 0.23 wt.%) than the embedding hematite/goethite-rich (34-89 wt.%) rocks i.e., $C_{org}$: ~0.05 wt.% [4]. Organics entrained from surface soil horizon (litter layer) are rapidly oxidized within the shallow hematite/goethite-rich rocks i.e., $C_{org}$ drops from 3-11 wt.% to <0.05 wt.%, but preserved in smectites/illite minerals where conditions are more conducive [4]. ATP luminometry-based biomass was detected in some oxidized-rock samples where roots materials were present i.e., ~$10^4$ to $10^6$ cell/g (750-1245 RLUs).

Geochemical and microbiological analyses of relevant analog environments are underway to confirm the biogeochemical trends observed in the Rio Tinto. Preliminary results show that oxidized, goethite-rich, sandstone (Purisima formation, CA) have higher ATP-based and LAL assay-based (Gram negative) biomass contents i.e., 35.05 Endotoxin Units (EU)/mL (~$2.0 \times 10^7$ cell/g) and up to 3891 RLUs (Relative Luminosity Units). These are higher values than those determined from the overlying clays units i.e., 22.0 EU/mL (~$1.3 \times 10^7$ cell/g) and up to 1143 RLUs.

**Keywords:** Mars analogs, biosignatures, biomass.

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# STUDY ON THE INTERCALATION AND RELEASE OF Zn-PCA- SAPONITIC BENTONITE

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In recent years, in the field of pharmaceutics and cosmetic products there has been a growing demand for means such as: creams, lotions, gels to reduce bacterial activity on the body and also ingredients for anti-ageing products. Zinc is one of the essential trace elements for any living body. In fact, zinc compounds have been reported to be effective not only as inhibitors of bacteria growth, but also as sebum inhibitors. In this context, Zn-compounds can inhibit 5a-reductase activity and especially behave as important precursors of catalytic reaction in the cells. To reach this goal, zinc must be suitable to be absorbed by living cells. Since the solubility of zinc salt is usually low, making it difficult to add zinc compounds to pharmaceutics and cosmetics, it is hard to obtain positive effects from many zinc compounds. To overcome this problem we have synthesized a soluble zinc salt utilizing an organic acid: L-Pyrrolidonecarboxilic acid (PCA), that has been detected as an intermediate in many biosyntheses and in the transport of amino acids through cell membranes[1].
Considering the wide uses of clay materials for cosmetic purposes[2], and the affinity of clay minerals for Zn and for many organic compounds, in this work we report a study on the interaction between Zn-PCA and a natural bentonite.
The clay is characterised by trioctahedral smectite (saponite), with a few carbonates (mainly dolomite) and quartz; the occurrence of zeolites (such as phillipsite) and feldspars is possible at trace level.
After bentonite - Zn-PCA interaction, spectroscopic data (Infrared) indicate the occurrence of PCA in the silicate matrix. X-ray diffraction analyses does not show traces of crystalline PCA, whereas the 001 spacing of saponite changes (increase of the 001 space by augmenting the Zn-PCA loaded), suggesting that the organic component enters into the interlayer space of the smectite.
To explore different condition of smectite-PCA interaction, the synthesis of Zn-PCA has been developed also by a new method. The kinetic release of Zn-PCA-saponite has been studied too, in order to design a new Zn releasing clay, which a tailored release kinetic adjusted by synthetic parameters modification. The intercalation compounds were characterized by XRD, FT-IR, TGA and ICP-AES.

**Keywords:** Zn-PCA, Intercalation, saponite, drug release.

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# LYSOZYME SORPTION ON SMECTITE

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The interaction of hen egg white Lysozyme (HEWL) with Na-saponite was examined using sorption, structural and spectroscopic methods. Three different independent methods were used to determine the amount of HEWL sorbed. The BCA assay method was used to measure the loss of protein from aqueous suspension and to determine the equilibrium concentration of protein in solution after equilibration. The amount of lysozyme sorbed on the clay surface was also measured directly by mass loss analysis using TGA and C and N analysis. All three methods provided consistent data at low to medium surface loading of protein up to a surface concentration of 400 mg of lysozyme /g of clay. Lysozyme sorption was accompanied by the release of 9.5 $Na^+$ ions for every molecule of HEWL sorbed, indicating the HEWL was sorbed predominantly through ion exchange. The d-spacing of the HEWL-saponite complex increased to a value of 4.2 nm consistent with the crystallographic dimensions of HEWL of 3 x 3 x 4.5 nm. FTIR and Raman analysis of the amide I region of the HEWL-Sap films prepared from water and $D_2O$ showed little perturbation to secondary structure of the protein. The water sorption isotherms revealed that the HEWL-Sap films were hydrophilic but the amount of water sorbed was somewhat less than that of the Na-saponite.

**Keywors:** Protein, sorption, smectite, lysozyme, saponite, FTIR, thermal analysis.

# IMMOBILIZATION OF TRYPSINE AND CHYMOTRYPSINE IN MG-AL AND ZN-AL LAYERED DOUBLE HYDROXIDES

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Enzymes display very selective molecular recognition and catalytic properties and then are very attractive alternative biological materials to traditional chemical catalysts or sensors. However enzymes are very sensitive to structural denaturation, decomposition reactions and slight changes of pH or temperature, which often rapidly inactivate them. Consequently, immobilization of enzymes by host structures and particularly layered inorganic materials is seen as an efficient method to preserve or even optimize their activities, biomimicking the enzyme-clay complexes of soils. Such bionanocomposite systems are strongly investigated for the realization of a new generation of smart biohybrid materials for sensing devices, recognition systems and nanoreactors with many potential industrial developments. Layered Double Hydroxides (LDH) also referred as anionic clays of general formula $[M^{II}_{1-X}M^{III}_{X}OH)_2]^{x+}[X^{q-}_{x/q}.nH_2O]$ display unique anionic exchange properties, a wide range of chemical composition in both layer and interlayer domains including electroactive systems, adjustable textural properties with particles size from nanometer to micrometer scales and soft chemistry preparation methods. They are then very appropriate materials for the immobilization of enzymes which often bear an overall negative charge and appear capable to preserve their native integrity[1]. We will present here an overview of the recent data we have obtained on the encapsulation of trypsine, a-chymotrypsine and Bovine Serum Albumine by Mg-Al and Zn-Al Layered Double Hydroxides. Various soft chemistry processes such as adsorption, coprecipitation, delamination/restacking have been investigated and compared. Effect of chemical composition and charge density of the LDH as well as the state of nanostructuration on the Enzymes-LDH interactions will be discussed in relation to the structural and morphology properties of the various biohybrid materials. Finally the catalytic performances of the bionanocomposites will be presented.

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# THE REASON WHY BIOMOLEULES ARE ALL HYDROPHILIC AND CLAY-AFFINITIVE

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Urey and Miller's synthesis of organic molecules for life's origin assuming atmospheric gases of $H_2$, $CH_4$, $NH_3$ and $H_2O$ are very well known. However, recent geo-scientific research suggests that the composition of the early atmosphere was not reducing, but slightly oxidizing being made up of $N_2$, $H_2O$ and $CO_2$, a mixture in which natural synthesis of organic molecules is difficult. How biomolecules necessary for life's origin were prepared, was, thus, a fundamental question. On that, the authors proposed a possible scenario named "the big bang of organic molecules" [1], and the scenario has recently been supported by shock recovery experiments [2]. The experiment simulates that oceanic impacts of ordinary chondrites, the most common type of meteorite, on the early Earth may have formed organic compounds in a great abundance, variety and complexity. Ordinary chondrite contains iron and carbon. Water and nitrogen are on the Earth. Those are elements essential to form organic compounds. Great frequency of meteorite impacts is well known as "late heavy bombardment" during 4.0 to 3.8 Gyr ago. It was, thus, quite probable that organic molecules were prepared by such events that occurred only in the early history of the Earth.

The formation mechanism of organic molecules suggests the reason why biomolecules are all hydrophilic and clay-affinitive: Organic molecules formed in post-impact plumes were in a great variety because they were produced by hydrocracking of solid carbon having graphite-like bondings. They were finally accumulated in the early ocean. In them, hydrophobic molecules have to float on the surface of ocean in contact with the $N_2$, $CO_2$ atmosphere and under strong irradiation by ultraviolet light. They would, therefore, be decomposed. On the other hand, hydrophilic and clay-affinitive molecules could have survived an environment of strong UV radiation and photolysis because they would have been dissolved in water with subsequent adsorption on clay particles that were finally deposited on the seabed [3]. This may have been the first natural selection of organic molecules that formed far bigger molecules such as proteins and nucleic acids in further evolution.

**Keywords:** Biomolecule, hydrophilic, clay-affinitive.

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# INVESTIGATING THE LAYER STRUCTURE OF ILLITE/SMECTITE MIXED LAYER AS A MODEL FOR SELF-REPLICATING SYSTEM

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Clay mineral surfaces were suggested by Bernal (1951) to be ideal for the concentration and polymerization of amino acids, etc. Hartman (1998) proposed that Fe-rich clay mineral surfaces were sites where amino acids could be synthesized from CO2 and N2 by photochemical means. Synthesis of amino acids would be preceded by the fixation of CO2 into oxalic acid and later into a reverse citric acid cycle and that the oxalic acid would be a catalyst for the synthesis of Fe-rich saponite. In this study, saponite was synthesized from a gel containing stoichiometric Si/Al3+, Mg2+ and Na+-oxalate as a catalyst. As the synthesis was carried out in air, the ferrous ion was eliminated. To test if rectorite might act as a seed for the synthesis of saponite, synthetic mixtures were produced by adding pure rectorite to the saponite gel at 80oC for periods of 1 and 3 months. XRD patterns of air-dried and EG solvated pure saponite showed very weak peak intensities. HRTEM images of the synthetic saponite after treatment with octadecylammonium cations (nC=18) showed predominantly clusters of disorganized, single 2:1 silicate layers and sequences of curved to planar 2:1 silicate layers having expanded interlayers with a d-spacing of ~2.5-2.8 nm. XRD patterns of the saponite-rectorite mixtures after nC=18 treatment suggested a physical mixture of a smectite-group mineral and rectorite. This was supported by the HRTEM images which showed disruption of the large coherent sequences of rectorite into smaller sequences of double layers or even single double layers. It appears also that the newly formed saponite layers have grown between the interlayers of the larger rectorite particles causing them to split apart. This suggests that the rectorite layers do not act as seeds for the synthesis of the saponite layers; rather the rectorite is dissolved and serves as the source for Al3+ and Si4+. As the dominant form of saponite in both the pure samples and in mixtures was similar to the structure of mixed-layer illite-smectite, it appears that the synthesis of the saponite layers was due to each clay layer surface seeding the next layer. This is similar to the template for the catalyzed polymerization of nucleic acids.

**Keywords:** Illite-smectite, Saponite, Rectorite, n-Alkylammonium cations.

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# RELATIONSHIP BETWEEN NANOMORPHOLOGY AND SURFACE POTENTIAL OF CLAY AND LAYERED MINERALS AND INTERACTIONS WITH BIOMOLECULES

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The objective of the present work deals with the characterisation of the surface potential of various layered minerals for origin of life research and side nanotech applications such as the control of DNA, nucleotides and cells adsorption. A critical factor in the imaging of biomolecules and biomolecular processes is the nature of the substrate on which the biomolecule is adsorbed. In the past, the underlying assumption, derived from current models of biomolecules' adsorption, is that the substrate surface plays a "passive" role in the process and functionalization is required before or during the deposition. Several techniques have been developed to tailor the adsorption of biomolecules according to different experimental requirements. These include the functionalization of the surface with self-assembled monolayers, the use of ligand-receptor complexes and the regulation of the buffer conditions. Our experiments showed clearly that the above assumption is not completely correct for layer silicates because very similar atomic flat crystals, as in the case of muscovite and biotite, presented very different affinity to DNA and protein adsorption [1]. Furthermore, it was found that chlorites have the ability to nanoconfine the deposition of nucleotides and long DNA molecules on particular areas (brucite-like) of the surface [2,3]. This effect became even more interesting when it was noted that some DNA strands (single and double) could be stretched between two brucite areas and that AFM nanolithography of brucite layers can be performed effectively. The stretching was shown to be produced by the anisotropy of the surface potential and therefore can be considered an active process induced by the surface. The molecules were also shown to be "suspended" between the two brucite areas with very small interactions with the underlying surface but with the possibility of interactions with surrounding enzymes.

**Keywords:** Layer silicates, DNA, Origin of life.

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# PHOSPHATIDYLCHOLINE-CLAY SYSTEMS AS ARTIFICIAL LIPID MEMBRANE SUPPORTS OF BIOLOGICAL SPECIES

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Clay minerals showing either layered (e.g. montmorillonite) or microfibrous (e.g. sepiolite) morphology are specially useful for assembling biological species, resulting in stable and functionalized bio-hybrid materials[1]. Phosphatidylcholine (PC) is the main constituent of cell membranes[2], showing important features, such as its environmental friendliness and the ability to form artificial bilayered membranes, of interest for immobilizing biological species. PC has surface active properties and its zwitterionic structure makes it prone to electrostatic interaction with clay minerals. In this way, it has been recently reported the use of clay-liposomes in which the mineral particles are externally covered by a planar PC bilayer[3].

In this communication a new type of clay-PC materials is introduced, displaying lipid molecules associated to the surface of sepiolite or to the internal surface of montmorillonite. Controlled adsorption of PC molecules on $Na^+$-homoionic montmorillonite or sepiolite was carried out from methanolic and ethanolic solutions. PC intercalation in montmorillonite causes an interlayer swelling of ca. 4.4 nm, which is compatible with an intracrystalline PC arrangement in form of an artificial lipid bilayer being protected by the rigid silicate framework. From the adsorption isotherms in sepiolite it can be deduced the formation of a phospholipid bilayer, favoured by the presence of silanol groups on the external surface of the clay that make possible hydrogen bonding interactions. The resultant materials show a biocompatible interface which give rise to various potential applications for agricultural, clinical and biotechnological purposes. Examples may be sequestration of fungi produced mycotoxins, such as aflatoxin or deoxynivalenol, as shown in a preliminary study[4]. These PC-clay systems are also useful to accommodate membrane enzymes, such as cholesterol oxidase, the resulting systems being active phases of novel biosensors.

**Keywords:** bio-hybrid materials, phosphatidylcholine, biosensor.

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# SIMPLEST BIOMODELLING SYSTEM: NATURAL GEL - MONTMORILLONITE

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Montmorillonite, with its significant complexity and heterogeneity of crystal structure, dynamism in varying conditions, is often considered as a model for some biological structures including information matrix in abiogenesis, the catalyst in synthesis of biomolecules of possible gene predecessor. The montmorillonite gel from the hydrothermal fluorite deposit Palat in Bulgaria can be considered as a simplest biomodelling system.

The gel represents homogeneous jelly-like snow-white mass. The dispersed phase are two-dimensional (length 15 mcm, width 0.4-0.8 mcm) thin-banded individuals of Ca, Mg-montmorillonite, the dispersion medium – strongly mineralized water of chloride-sulphate-bicarbonate calcium-natrium composition.

According to nuclear magnetic resonance data, there are at least two types of water: similar to zeolite with relaxation time 8.3 msec, and stronger-bonded with relaxation time 1 msec. The density of the gel is 1.07-1.10, pH 9.4, electric charge of montmorillonite particles is negative. The gel includes crystals of fluorite and pyrite and also numerous bacterial cells of elongated form with the size 0.2-1.4 mcm. At ageing of the montmorillonite gel in the depressurized state, i.e. during natural gradual removal of dispersive phase at a continuous X-ray control of its structural state, the strictly orientated "maturing" of montmorillonite occurs from structurally unstable system of fragmentary ordered two-dimensional crystal bands with superperiod by axis about 120Å through intermediate 80, 60, 22, 17, 15-angstrem phases to rather stable smectite with $d_{001}$-12.6Å.

In natural gel-montmorillonite the presence of amino acids is determined, which spectrum (Glu, Gly, Ala, Val, Leu, Tyr, Phe, His, Lys, Arg) essentially differs from the corresponding spectra of sedimentation montmorillonite clays and closer to amino acidic composition of abiogenic hydrocarbon ordered structures. The formation of amino acids, and possibly of other biomolecules, is resulted from the catalytic action of montmorillonite on the structure of organic substance of bacterial genesis.

Montmorillonite and other minerals undoubtedly play an important role in the formation of biomolecules, complex ones as well, including RNA oligomers, and also in the origin of biofunctions; however the prebiological structures should be formed for the origin of life and formation of protoorganisms, which are possibly supermolecular ordered hard hydrocarbons (our concept of mineral organismobiosis). (RFBR and RAS, ESD RAS program support)

**Keywords**: montmorillonite, abiogenesis, biomineral systems.

# BIO-CLAYS INTERFACE & LIFE'S ORIGIN

## SESSION BC2

## *Clays - Living Organisms Interactions*

# BIONANOCOMPOSITES BASED ON CLAYS AS SUPPORT OF MICROORGANISMS

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Bionanocomposites are an emerging group of bio-nanohybrid materials resulting from the assembly at the nanometric range of nano- or micro-particulate inorganic solids and biopolymers (1-2). Of particular interest are the synthetic bionanocomposites prepared by combination of polysaccharides, proteins, nucleic acids and other biological materials with smectites or microfibrous clay minerals. This type of materials is similar to conventional polymer-clay nanocomposites except that the polymer is a natural product that does not derive from petroleum. As clay-based bionanocomposites become from natural components, they are ecologically acceptable materials being known as green nanocomposites. In addition, they can be often regarded as biocompatible materials, which is of great significance in view to applications from regenerative medicine to the development of new substrates to immobilize living entities.

We introduce here recent results describing new bio-hybrid materials in the frontier of biological and mineral worlds. The hierarchical porosity of certain bionanocomposites can be profited for cellular growth within these materials. Algae (*Chlorella*) and cyanobacteria (*Anabaena*) are able to colonize macroporous bionanocomposites based on sepiolite and chitosan prepared by a procedure developed in our group, while bionanocomposites based on sepiolite associated to the anionic polysaccharide xanthan gum are able to bind to Influenza virus nanoparticles (3). The most salient feature of these last types of bio-hybrids is their bioactivity allowing application as an effective low-cost vaccine adjuvant that increases the immune response against Influenza viruses compared to virus alone. Experiments carried out in mice demonstrate that the virus-bionanocomposites induce the formation of specific antibodies and the subsequent protection against influenza. The novel system here reported may be potentially useful to control human and avian Influenza, but also other mucosal-entry viruses as HIV.

**Keywords:** bionanocomposites, sepiolite, virus.

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# TRANSFORMATION OF CLAY DUE TO ACTIVITY OF ALKALINE CYANOBACTERIA MICROCOLES CHTHONOPLASTES AND RHABDODERMA LINEARE

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The aim of the study was to investigate the possible transformations of illite and bentonite SWy-2 in laboratory experiments during the growth and fossilization of alkaline cyanobacteria *Microcoleus Chthonoplastes* and *Rhabdoderma lineare*. Cyanobacteria, also known as blue- green algae, are oxygenic photoautotrophic organisms. At the present time, cyanobacteria create relict communities in extreme ecological conditions; regions with hydrothermal activity, hypersaline reservoirs and alkaline lakes. Besides organic matter, bacterial mats contain minerals components; carbonate, silica, Fe and Mn oxides/hydroxides, clay minerals, phosphates, and sulfides.

The experiments with cyanobacteria and clay minerals have been undertaken with and without light. Cyanobacteria were incubated for 7, 14, 28 and 60 days at 28°C. Control bottles without cyanobacteria were incubated at the same conditions. The fossilization process was studied using scanning electron microscopy (SEM). Mineralogical investigations included X-ray diffraction, XRF and magnetic measurements. Biological activity parameters of cyanobacteria in the presence of clays were also determined. Cyanobacteria affect the properties of the studied clays. They influence the properties of iron compounds, which are present as impurities in all the studied clay minerals. Both dissolution and precipitation processes of iron compounds were observed. The data show that the biochemical transformations observed has a multi-step nature. The initial samples differ from the later precipitates and one mineral can substitute for another. These processes relate to the conditions of the medium (temperature, pH, redox conditions, rate of Fe oxidation, presence of inhibitors; organic matter, Si and etc). This conclusion applies to transformations of layer silicates as well as Fe oxides (hydroxides). The clay incubation with *Microcoleus chthonoplastes* and *Rhabdoderma lineare (*two cyanobacterial cultures with different morphological and physiological properties) resulted in different transformation trends. The observed processes were fast and completed within the first 40 days of the experiments.

**Keywords**: Cyanobacteria, illite, bentonite, iron oxides.

# TRANSFORMATION OF CHLORITES BY PRIMARY BIOLOGICAL AGENTS – A REVIEW

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Several published studies generalized that chlorites in the bio interaction zone (rhizosphere soils) are transformed into 2:1 minerals with different cation exchange capacities. We wish to review several studies on chlorite – bio mineral interaction and assemble the data in an overview of the current state of the knowledge. Examples from our work will be used as examples to demonstrate the differential chlorite breakdown in water-rock and biologically-mediated pathways. Bacteria, fungi of different species and mosses give similar results. Some of the new clays are fully smectitic, expanding with glycol treatment in the Ca – saturated state, while others show a high intensity 001 peak that is not affected by glycol treatment. Most of all, the material present is affected by potassium saturation forming different hydration states in mixed layered phases or as individual units or minerals. The different reactions to laboratory treatment indicate dissimilarity in charge site and intensity on the 2:1 layers but the overall pattern is one of transformation of chemically inert minerals (high temperature chlorite) to clay minerals with high exchange capacities. The extracted magnesium from the chlorites is probably important for the growth of soil organisms most often in symbiosis with higher form of plants. Biotic processes appear to transform the whole mineral units in a rather homogeneous manner compared to the formation of interstratified (alternating layers) mineral in the water-rock interaction pathway. At any rate, these reactive high charge clays left after the biologically-mediated reactions are strong potential sites for magnesium (and potassium) capture and storage to meet the nutritional requirements of plants and organisms.

**Keywords:** rhizosphere soil, 2:1 clays, magnesium storage.

# INVESTGATIONS INTO CLAY MINERAL FORMATION IN A TEMPERATE ENVIRONMENT

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Porosity and permeability in deeply buried petroleum reservoirs can be enhanced due to the presence of iron-rich chlorite cements that inhibit quartz cement growth. Understanding the origin and distribution of iron-rich chlorite will aid prediction of anomalously good reservoir quality in the deep subsurface. Iron-rich chlorite is not a primary mineral but forms due to the replacement of early diagenetic precursor minerals, such as iron-rich 7Å berthierine. It has been previously demonstrated that berthierine forms grain coats in estuarine and deltaic settings due to animal sediment interactions. This means that environment-specific animal populations may also have a major effect on localisation on growth of these clay minerals.

Using the Dee estuary, North-West England, as a study area, sediment and water samples were taken from a variety of environments in order to understand the fate of suspended iron in the estuary. Sediment samples were taken using a range of coring materials and analysed using XRD and FTIR. Water samples taken were analysed using IC and VA.

Further animal-sediment experiments have been re-initiated in order to understand clay growth on a variety of sediment types representative of those found in the Dee estuary. Analysis of the sediment and water following these experiments has been carried out using XRD, FTIR, IC and VA. These analyses will be continuously repeated in order to determine changes in the controlled environment as berthierine evolves.

**Keywords**: Chlorite clay formation; Sediment grain coats; Animal-sediment interactions.

# ADSORPTION OF L-LYSINE ON MONTMORILLONITE AND REACTIONS AT 80 ºC

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It has been suggested that smectite may have had a role in the origin of life by concentrating organic molecules, such as amino acids, within its interlayers and then catalyzing polymerization reactions that originated peptides and proteins. We investigated the adsorption and reaction of lysine (Lys) on Na-montmorillonite (SWy-1). Several concentrations of Lys (0.025-0.4 M) were tested. The adsorption isotherm is of S-type (Giles' classification), indicating cooperative adsorption with increasing Lys adsorption. The adsorption mechanism changes from cation exchange (with proton transfer) to Lys-Lys interaction. XRD and FTIR data allowed us to create a model for Lys configuration in the interlayer sites. First, Lys cations are at an angle (<90º) to the smectite layers, with interstitial water; then, progressively, molecules are adsorbed as zwitterions, adopting a 90º angle with the layers and driving water out of the interlayer. We chose the complex from 0.05 M Lys for the hydrothermal experiments since that strikes a balance between representing natural conditions and having enough adsorbed Lys to allow subsequent analyses.

Lys-smectite complexes (with L-, D- and racemic Lys) were reacted at 80ºC for 10 days in different moisture conditions: open tubes, closed tubes, closed tubes with added water. Then, Lys was displaced from the smectite using 0.1 M $CaCl_2$, and studied with circular dichroism (CD) to analyse optical activity. The smectite was analysed using CHN elemental analysis for non-desorbed Lys. CD spectra were dependent on the solution pH, which was controlled by Lys protonation state. The Lys protonation state was altered by the adsorption-desorption process, inducing an increase of the $Lys^+/Lys^\pm$ ratio (or pH change from ~10 to ~8). CD and CHN analyses show that the thermal treatment in a moist state causes stronger smectite-Lys binding and FTIR spectra suggest that this is caused by more or stronger hydrogen bonds between $–NH_3^+$ Lys groups and smectite basal oxygen atoms. The changes of Lys protonation state and Lys-smectite binding strength may be relevant to pre-biotic reactions. CD did not detect changes of Lys optical activity (transformations between L and D forms).

**Keywords:** Adsorption, FTIR, Lysine, Montmorillonite, Pre-biotic reactions, X-ray diffraction.

# ULTRAFINE CLAY MINERALS AND HUMAN HEALTH: THE EXAMPLE OF PODOCONIOSIS

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Podoconiosis is a geochemical form of elephantiasis resulting from long-term barefoot exposure to irritant volcanic red clay soils. It is a chronic and debilitating disorder, highly prevalent in Ethiopia where it affects at least 1 million people (Desta et al., 2003). This non-communicable, preventable disease has contributed to Ethiopia's economic burden (Tekola et al., 2006) and has resulted in widespread social stigmatism of people displaying podoconiosis symptoms. Despite this, the condition has been severely neglected, and the components of the clay soils that cause oxidative stress, inflammation and blockage of the lymphatic lumen have not been identified. In this paper, we summarize what is known to date surrounding the pathogenesis of podoconiosis and report preliminary results of soil analysis. Future research directions are indicated.

Colloid-sized particles of aluminium, silicon, magnesium and iron have been found in the tissues of individuals living on red clay soils (Price and Henderson, 1978). Soils in endemic areas contain a significantly higher proportion of particles <5µm in diameter compared with neighbouring non-endemic areas (Price and Plant, 1990). We analysed soil samples from three podoconiosis-endemic sites in southern Ethiopia using a field emission SEM (after thoroughly drying and light grinding to break down aggregates). The soil consisted almost entirely of fine submicron particles present as aggregates; large mineral particles were very rare.

The potential for such ultrafine particles to cause inflammation is related to both their surface reactivity and their surface area, and it is plausible that they pass through cell walls, cause oxidative stress, and initiate the inflammatory processes seen in podoconiosis. Further work to characterize the individual particles within the aggregates is required to better understand the components of the soil contributing to podoconiosis in areas such as Ethiopia.

**Keywords:** Elephantiasis, Podoconiosis, Ultrafine.

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# ROLE OF STRUCTURAL FE (III) FOR BACTERIAL DEVELOPMENT IN EXTREME CONDITIONS IN DEEP CLAY-RICH ENVIRONMENTS

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Since the discovery of oceanic hydrothermal ecosystems in the '80s, the existence of active deep-sea or continental biospheres raised great interests among biologists and geologists. These findings demonstrated the adaptability of microorganisms and their capacity to find the necessary energy for their survival even in hostile environments. New results open the question of the existence of microbial activities in deep and confined environments and thus questioned confinement sustainability involved in high-level nuclear wastes (HLNW) disposal.

The question of bacterial activity within a waste disposal site remains open (Poulain, 2006; Stroes-Gascoyne et al., 2007; Mauclaire et al., 2007). A critical issue is the possible energy sources in clay environments for the development of microorganisms.

In the case of geological disposal of HLNW, two electron donors can be considered: organic matter of clay-rich environments and hydrogen produced by corrosion in anoxic conditions or radiolysis. One electron acceptor could be structural Fe (III) in clay minerals. Both energy sources have been studied and used in short-term experiments in the scattered environment (batch) over reactivity clay-bacteria through the use of crystal chemistry tools. In order to understand interaction between clays minerals and bacteria, the role of structural Fe (III) has been analysed as the only electron acceptor in our system. Experiments have been conducted at 40°C with a synthetic solution close to the interstitial water of argillite representative of future possible geological disposal.

Finally kinetic studies of redox metabolism bacteria model, the ferric-reducing bacteria "*Shewanella putrefaciens* strain MR-1" show availability of Fe (III) in clay-rich environment for bacterial development.

**Keywords:** argillite of geological storage, $H_2$, organic matter, ferric reducing bacteria.

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# LAYER SILICATES MINERALIZING MICROBIOTA IN PROCESS OF HYDROTHERMAL ALTERATION OF BASALT PILES IN ICELAND

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Clay minerals are widespread in the upper low temperature zone of altered basalts in Iceland. The most widely occurring are smectites and celadonite which is equally extensive and locally dominant.

By optical investigation, the entire variety of clay mineral microtextures aggregates may be classified: (1) rims in gas bubbles and another cavities, and on the walls of fissures; (2) accumulations that resemble – so called “sedimentation levels”; (3) “threads” that branch off or form occasional knotted fibrous aggregates; (4) worm-like growths on the surface of rims or “sedimentation levels”; (5) spheres, globules, aggregates of balls and globules; (6) bud-like masses composed of separate rounded or oval bodies. Electron scanning microscope shows a range of microtextures. Only two of the studied microtextures, worm-like and ball microtextures can be confidently attributed to the biochemical activity of micro-organisms.

The worm-like microtextures range from fractions of a millimeter to 0.5 mm, or rarely over 1 cm. They show delicate twists and offshoots. Even at low magnification the scanning electron microscope detects clear concentric zones and a distinct central rod. The rod sometimes shows round lengthwise canals (one or several). Fossilization of the biogenic object is confirmed by the sectional type of the central rod’s structure. The ball-like structures range in size from 2 – 5 to 10 μm. Three types of ball-like structures, depending on the shape of the composing crystals, can be distinguished: (1) ball-like structures on the surface of the rod which are always to be found in its hole; (2) ball-like bodies located in the vacant space in between worm-like structures composing of large plank- and bar-like crystals; (3) balls bristling with needle-like crystals.

In some worm-like structures and their complicated intergrowths, there are presence of numerous round, oval or irregularly shaped holes which have smooth shapes formed by needle- and plank-like crystals. Tiny holes with smooth shapes occur in some leafy-like clay mineral crystals.

The above patterns of microtextural elements suggest that layer silicates were formed around and on some material that dissolved and disappeared later. It is probable that such material could have been living organic matter, most likely bacterial or fungi nature.

Judging by the data available, the studied layer silicates were formed in low mineralized ground solutions. Apart from clearly biomorphic structures, the responsibility of the organic matter in clay mineral formation is supported by a variety of holes and canals that are to be found in the dense mass of clay substance.

**Keywords:** layer silicates, bacterial, microtextures.

# THE ROLE OF BIOMINERALIZATION IN THE ORIGIN OF SEPIOLITE AND DOLOMITE IN THE MIOCENE BASIN OF MADRID (CENTRAL SPAIN)

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Sepiolite is a mineral frequently found with dolomite, Mg-smectites or palygorskite in the so-called Intermediate Unit of the Miocene sediments of the Madrid basin. This study describes sepiolite-rich layers, up to 90 % concentration, in marl-clay sediments, either with gypsum, chert (micro-crystalline quartz) or dolomite, in the same sequence within 2-3 m of each other. These sediments have dolomite aggregates resembling mineralized microorganisms (biolithes) with ovoid morphologies and with spherical to tubular voids inside. The regular size and relative uniform shape of the biolithes has to be related by a spatially-constrained mechanism: the shape and size of the microorganisms for instance. The light isotopic signature for carbon ($\delta^{13}C_{VPDB} < -7.5$) confirm the organic source for carbon. Concentration of sepiolite is observed when the presence of dolomite is minimised. Dolomite in sepiolite-rich layers is in the form of irregular, partially dissolved, biolithes or as fully recrystallized isolated crystals. Thus, a general process of dolomite dissolution and recrystallization is linked to sepiolite formation.
The studied materials have been formed in shallow lake environments or floodplains depending on the prominence of dissolution-precipitation originated sediments, with desiccation periods (carbonates, gypsum), or alternative wet periods. These are characterized by the presence of sedimentary clays, rich in hydrous micas and dioctahedral smectites. Potassium depletion in the detrital components and the observation of organic-rich reduced sediment (U and sulphides concentration), at interfaces with sepiolite (oxidized), are evidence for biological activity at the sepiolite interface. A theoretical concentration of a Mg-Ca-$SO_4$-$HCO_3$ water in the presence of dissolved silica, after the reduction of sulfates, predict the coexistence of sepiolite and dolomite and did not excluded a syngenetic origin. The role of biomineralization in the formation of these high grade sepiolite deposits can be based on (1) specific organic-inorganic interactions, and (2) on the highly porous nature of this biogenic dolomite, considered to be a sepiolite precursor during the diagenetic evolution of these sediments.

**Keywords:** sepiolite, dolomite, biomineralization, Madrid Basin.

# THE WORM GUT; A NATURAL CLAY MINERAL FACTORY AND A POSSIBLE CAUSE OF DIAGENETIC GRAIN COATS IN SANDSTONES

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Using a series of experiments, it is shown that the formation of clay minerals can occur biologically via the process of sediment ingestion by worms. Specimens of lugworm, Arenicola marina, were fed a mixture of sand and unweathered, crushed Icelandic basalt in experimental tanks that simulated an intertidal, shallow-marine, sedimentary environment. The basalt was entirely free of clay minerals. Faecal casts, collected and separated into a <2 µm fraction, were analysed using X-Ray Diffraction and Fourier Transform Infrared spectroscopy. The faecal samples were found to have lost plagioclase feldspar due to dissolution reactions and to contain newly-formed clay minerals (kaolinite, illite and a 14Å clay) not present in the original or control samples. The experiments show that macrobiotic processes induce rapid clay growth. These clays coat sand grains and may be the precursors to porosity-preserving chlorite coats found in sandstones.

**Keywords:** clay mineral, faecal cast, lugworm, FTIR, weathering.

# CERAMICS & ENGINEERING

## CE1 • CLAYS IN ARCHAEOLOGY & CULTURAL HERITAGE

## CE3 • CLAYS IN TRADITIONAL CERAMIC INDUSTRY

## CE4 • COLLOIDS & RHEOLOGY

## CE5 • DESICCATION AND FRACTURE IN CLAY

## CE6 • HETERO-MODULUS CERAMICS FOR TECHNICAL APPLICATION

## CE7 • MODIFIED CLAYS & NEW APPLICATIONS

## CE8 • PROCESSING AND PROPERTIES OF CERAMIC MATERIALS

# CERAMICS & ENGINEERING

## SESSION CE1

## *Clays in Archaeology & Cultural Heritages*

# THE EFFECT OF CARBONATE CONTENT OF CERAMICS RAW MATERIALS IN THE TEMPERATURE OF BROMINE VOLATILIZATION

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In multivariate studies, where the geochemistry of archaeological shards is compared with possible raw materials to infer on provenance, is important to choose the best discriminatory elements and exclude from the database those with concentrations significantly affected by firing (volatilization). Several works, including this one, concluded that firing had no effect on most of the elements in the fired clays, with the main exception of bromine (Br) (Cogswell et al., 1996); therefore Br is considered unsuitable for provenance studies. However, this element is still important in archaeometry, as he may possibly inform about the using of pottery or the post depositional history. In fact, Br is usually associated with organic matter that can be incorporated in the ceramic pastes during its use and burial.

The main objective of this study is to infer a possible correlation between the temperature of Br volatilization and the carbonate content of the clays, in order to confirm if all Br found in ceramics is not inherit from the original raw material and could be interpreted merely in the archaeological point of view.

We studied 94 clays from the Algarve (Portugal), probably used as raw materials of ancient ceramics found near roman kilns in the region (Trindade, 2007). Six samples were selected, representing the compositional variability observed and was studied the effect of temperature on elemental concentrations of the test pieces (mild and compressed clays) fired to 300-1100ºC. Chemical analyses were done by instrumental neutron activation analysis (INAA). Chemical composition of natural clays was also used to search for a correlation between Br and Ca-Mg (in carbonates) in 3 types of clays: non-carbonate, calcite-rich and dolomite-rich clays.

We observed correlation of Br with carbonates, indicating a dependence of bromine volatilization on decarbonation reactions (~ 800-900ºC) in calcareous clays, while in non-calcareous clays Br volatilized at much lower temperatures. This suggests that the Br found in ceramics can be clearly attributed to processes operating after their production if non-calcareous clays were used. On the contrary, the presence of Br in ceramics can be justified simply by a firing temperature not high enough to complete decarbonation reactions and consequently to produce Br volatilization. So, careful interpretations about the Br in the pottery are required.

**Keywords**: bromine, clays, firing.

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# BRONZE AGE RAW MATERIALS: AN ANALYTICAL AND EXPERIMENTAL APPROACH

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Bronze Age "impasto" pottery from several sites in Modena area (Northen Italy) has been investigated to identify the raw materials and the manufacturing technique. This pottery production is a low-medium specialized one and generally locally performed. Nearly 200 pots from 6 sites have been selected and 38 clays and other sediments from different geological units in the area have been collected (Cardarelli et al. 2007). Several posts have been reproduced in an experimental exercise in the Parco Archeologico e Museo all'aperto della Terramara di Montale (Brodà et al. in press). Pots and sediment have been analysed using different techniques: petrographic analysis (OM), chemical analysis of major, minor and trace elements (WDS-XRF) and X-ray powder diffraction (XRPD). The impasto pottery is characterized by a coarse texture and is tempered with grog, calcite and calcareous sand. The OM examination allowed to divide the samples into 6 different groups. The Digital Image Processing has been used to define the granulometry: the matrix (clay and silt) is 71-97%, the clasts represent 1-22% and the voids are 1-12%.

The XRPD results confirm the mineral composition observed by OM: quartz, albite, k-feldspar, illite (muscovite) are present in every sample; amphiboles and calcite are present only in some samples.

The chemical composition shows a good discrimination among the pottery from different archaeological sites but the sediments are difficult to compare. Pots are characterized by a low content of CaO. Raw materials show a great variability in terms of CaO and granulometry (clay fraction between 18- 55%).

In order to identify the raw materials and to understand the influence of the temper in the ceramic paste composition some new samples have been specifically prepared mixing clays and different amount of temper (Day, Kiriatzi 1999).

According the experiment's results some problems linked to the difficulty of a close matching between ancient coarse pottery and actual raw materials are discussed.

**Keyword**: "Impasto" Pottery, Bronze Age, tempered clay.

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# TWO-DIMENSIONAL NMR CORRELATION OF LONGITUDINAL AND TRANSVERSE RELAXATION TIMES IN ANCIENT CERAMICS

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A novel methodology in the framework of Cultural Heritage studies, based on 2D correlation of proton relaxation times[1], is employed as a nuclear magnetic resonance (NMR) non-invasive fingerprinting tool for ancient ceramics. This study aims at investigating whether the most relevant firing-induced changes in ceramics, in terms of both pore space properties and paramagnetic mineral structures, could be used as markers of the firing process, i.e. of ceramics themselves.

Archaeological ceramics are made up of naturally available clays, which upon firing undergo relevant modifications of pore distribution and chemical transformations of iron-bearing species, producing mineral structures with different magnetic properties. $^1$H-NMR relaxometry is an efficient method for studying porous ceramics, since spin-lattice ($T_1$) and spin-spin ($T_2$) relaxation times for protons of water filling the pore space of high surface-to-volume ratio $(S/V)$ systems can be written as $T_{1,2} \approx \rho_{1,2}^{-1}(V/S)$, where the longitudinal ($\rho_1$) and transverse ($\rho_2$) surface relaxivities are due to the nuclear magnetic interactions at water-pore wall interface. Being $T_2$ relaxation also affected by spin-dephasing in presence of high field gradients at pore and sample scale, $T_1$-$T_2$ correlation maps[2] are expected to show the interrelation between ceramic structure and firing technology, allowing to separate the information about pore size $(V/S)$ from that about magnetic composition, carried by $(\rho_2/\rho_1)$ and by the spin evolution-time-dependence of $T_2$. The potentiality of this method is first illustrated for reference ceramic samples, prepared with different paramagnetic compositions, firing temperatures and soaking times, in order to tackle the problem of model-ceramics selection. Then, the method is tested on medieval ceramic findings of unknown manufacture, revealing the efficiency of 2D maps as NMR fingerprint of thermal and compositional history of ceramics, in agreement with archaeological dating.

**Keywords**: Two-dimensional NMR, relaxation correlation map, archaeological ceramics.

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# PROVENANCE OF CALCITE TEMPERED "SERRA D'ALTO" COARSE WARE IN SOUTH EASTERN ITALY: PRELIMINARY RESULTS

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Forty samples of Mid-Late Neolithic "Serra d'Alto" coarse pots (V millennium BC) tempered with spathic calcite were analyzed by petrographic, mineralogical and chemical methods to confirm the hypothesis of widespread technological models of production in different areas in south eastern Italy. The analyzed samples were excavated in different archaeological sites across Tavoliere Plain, Murge Plateau and Bradanic Through areas, namely Masseria Fragennaro, Cala Colombo, Santa Barbara, Sette Ponti, Masseria Candelaro and Grotta Scaloria (Apulia) and Trasano (Basilicata).

Almost all the coarse wares were produced using eluvial or colluvial deposits in a carbonatic area tempered with speleothemic calcite. The amount of calcite temper seems to be quantized according to different recipes. LA-ICP-MS analysis of over 30 spathic calcite inclusions per thin section revealed some chemical homogeneity within the same sample and interesting differences among samples from the same site with different pottery fabric.

Although the number of the analyzed samples was not sufficient to clearly define characteristic fabrics or reference groups, our preliminary results suggest that the calcite tempered Serra d'Alto coarse ware was produced in different sites, starting from different raw materials and using different processing. The strong similarities in technological processes in different sites clearly show a large network of middle-distance exchange of formal and technological production techniques between many Neolithic communities, located in different geographical areas of South Eastern Italy. LA-ICP-MS analysis of calcite inclusions seems to be a promising route to discriminate the provenance of these ceramic vessels.

**Keywords:** Serra d'Alto ware, calcite temper, LA-ICP-MS.

# ARCHAEOMETRICAL STUDY OF CELTIC CERAMICS FROM MONTE BIBELE (BOLOGNA)

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The ceramic samples, presented in this work, come from the archaeological excavation in Pianella di Monte Savino, territory of Monte Bibele, near Bologna. Here a Celtic village was founded during IV-II sec. b.C. Even though the extension of this village is 7000 $m^2$, no traces of furnaces have been found, only ruins of houses and streets.

By considering that, it seems important to characterise the ceramics finds in order to recover information regarding the provenance of the raw materials and the technological processes that were used.

Twenty-three ceramic samples (in the majority open shapes) previously distinguished in two macroscopic groups have been selected for archaeometrical characterisation. The first group includes ceramics with red paste and black slip, and second one ceramics with grey paste. All the ceramics present a very fine paste.

The results of mineralogical and chemical investigations show that non calcareous raw materials were used for these ceramics. The presence of argillaceous minerals in the phases composition seems to indicate a firing temperature less than 800°C.

As regards the provenance of the raw materials, the absence of calcareous mineral phases and their products could support a non local origin of these ceramics by considering that the clayey deposits outcropping in this area are with calcite and dolomite.

# ELECTRON MICROPROBE ANALYSES ON ANCIENT CERAMICS. CASE STUDIES FROM ROMANIA

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Electron Microprobe Analysis (EMPA) is a widely applied technique in geological sciences, e.g. mineralogy and petrology. It has several advantages for the research of mineral-based materials, including ceramic and glass artefacts. The main benefit for the ceramic analysis is the possibility to identify components with a wide range of size, independent of their nature as primary minerals or firing products.

The identification of mineral components of the matrix can be very difficult, as it represents a more or less homogeneous mixture of extremely fine-grained compounds, usually smaller than the focused beam diameter. The use of a defocused beam (20 microns) may result in an average composition of matrix for the irradiated area. The most important problem is the frequently observed low sum of the quantitative analyses. This is due to the porosity of samples, the incomplete dehydroxylation during the firing, or the rehydration and/or rehydroxylation during the burial.

The EMP studies performed on Late Bronze Age ceramics from Ilisua, Transylvania (Romania) revealed a highly porous ceramics, composed of an illitic-kaolinitic matrix and various clasts (fragments of minerals such as quartz, feldspars, micas, ilmenite, pyroxenes, garnets, zircon or amphibole, as well as fragments of various rocks i.e. volcanic tuffs, andesites, basalts, rhyolites, granodiorites, sandstones, quartzites, micaschists, gneisses, amphibolites). Bioclasts, soil aggregates and four different types of ceramoclasts (potshards) are also present.

Additionally, several new phases, most likely formed during the firing process, were identified: K-feldspar, An-rich plagioclase, silica glass. They are metastable phases, with often a non-stoichiometric composition, thus difficult to characterize in terms of mineralogy. Frequently they are "contaminated" with elements such as e.g. additional Fe, K, Al or P trapped inside the new lattice. The distinction among the primary and the secondary (firing) phases can be also relatively difficult, as the same mineral may occur as both.

The detailed knowledge of the mineral phase composition based on EMP analyses allows the classification of shards, and improves greatly the identification of the raw materials and their provenance, as well as the reconstruction of the technological conditions of firing.

**Keywords:** EMPA, Bronze Age ceramics, Romania.

# TEMPERATURE EVOLUTION INSIDE A POT DURING OPEN FIRING

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Problem: There are very few experiments dealing with the temperature evolution of a ceramic object during an open firing. Gosselain's (1992) ethno-thermometric approach, based on the measurement of the inside and outside surface temperature, showed considerable variations in the same firing and for the same pot. However, nothing was said about the temperature evolution in the core of the objects and the prograde mineralogical changes.

Experimental: To answer these questions, three experimental firings were conducted, each involving 10-15 pots. They were shaped by coiling from a calcareous clay (10.63 wt.% CaO), tempered with crushed Carrara marble (400 g for 1 kg clay/grain size:1.5-3mm). Four to seven Ni/NiCr thermocouples were put in direct contact on the outside and the inside surface of one pot per experiment, as well as in the core, along one or two cross-sections through the object. These thermocouples are well adapted for thermometric measurements, since they can be exposed to temperatures up to 1200°C. After shaping and before firing, the objects were dried at 100°C. They were then put on a dry, clayey floor in a house of the "Neolithic village" of Glétterens and covered with straw and finely cut wooden branches. The fuel was set on fire at the top. Wood was added during the firing when the flames were dying out. The temperature evolution for each thermocouple was automatically recorded during the entire firing session. The pots were removed after about 30 minutes at peak temperature.

Results: The maximum temperature recorded in each firing, reached after 12-22 minutes, was different (800, 900 and 990°C). The temperature curves show a wide scatter when comparing the three firings. The range of the thermic variation within one single firing can be as high as 350°C, and up to 220°C on a specific cross-section. The lowest temperature is not systematically recorded in the core of the object, as generally expected. The mineralogical evolution is quick and consistent with previous firing experiments on calcareous clays (Maggetti 1982).

Discussion: (1) Our experiments confirm Gosselain's and Maggetti's results; (2) Archaeometric identifications of ancient firing temperatures must be aware of the considerable temperature variations for the same open fired ceramic object, and (3) Core temperatures can be even higher as the external parts of the same object

**Keywords**: Experimental Firing, Ceramics, Temperature evolution.

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# SOUTH ITALIAN PROVENANCE OF ROMAN AMPHORAE SHIPPED TO THE HERODIAN KINGDOM IN THE LIGHT OF PETROGRAPHIC AND CHEMICAL INVESTIGATIONS

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The paper presents the results of a petrographic and chemical (INAA, ICP-OES) study of 125 Roman amphorae (second half of the first century BC) discovered in the Herodian palaces in Jericho, Cypros, Masada, Herodium, the port city of Caesarea Maritima, and a luxurious villa in Jerusalem.

The basic aim of the presented research was to separate groups of amphorae with common mineral and chemical compositions. The obtained results were supposed to provide answers to the following questions:

(1) which of the amphorae were made in the same area and perhaps even in the same ceramic workshop?

(2) from where were those amphorae imported?

(3) are there imitations (copies) of original shapes among them, perhaps produced on the territory of Palestine? and

(4) do the typological similarities among the amphorae coincide with a similarity in their petrographic and chemical compositions?

The chief source of knowledge about the potential provenance of the distinguished petrographic groups of amphorae was geological and archaeometric articles published on the subject to date.

The results obtained were confronted with a typology of amphorae (Dressel 2-4, Dressel 7-12, Dressel 21-22, Lamboglia 2).

Ultimately, 13 petrographic-chemical groups of amphorae were distinguished. It is highly probable that the two "black sand-pyroxene" groups A and B, the two "pumice-phyllite" groups C1 and C2, and the "devitrified glass - coarse pyroxene" group D have a common south Italian provenance, respectively: Campania or Latium (A, B), Calabria (C1, C2) and Apulia (D), possibly representing different pottery workshops, four of which produced Dr 2-4 forms.

The tentative workshops 1 (Group A) and 2 (Group B) also produced the Dr 21-22 types. No. 3 (Group D) produced Lamboglia 2 and probably also copies of the Dressel 7-12 type. The "pumice-phyllite" group C1 suggests another Italian workshop for the Dressel 2-4 form, probably in Calabria, which was shipped to the Herodian kingdom and found particularly in Jerusalem and Cypros.

**Keywords**: Roman amphorae, petrography, INAA, Herodian kingdom.

# CLAYEY MATERIALS USED FOR CERAMIC MANUFACTURE IN ANCIENT SICILY

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It is well known that mineralogical, petrographic and chemical analyses can be used to determine where archaeological ceramic findings were produced (provenance studies). The classification of a ceramic paste and its assignment to a specific production centre can be faced in a easier manner if local raw materials are studied in combination in terms of mineralogy, chemical composition and textural aspects. To identify with a satisfactory accurateness the source of the clayey raw materials used in a given production centre need an “integrated approach” where geology, mineralogy, petrography and chemistry are uniformly involved.

Archaeological excavations in Western and Central Sicily, especially those which were accomplished in the last 25 years, brought to light kilns and apposite facilities designed for ceramic manufacture in a number of sites, attesting the relevant impact of this craftsman activity on the ancient economic history of this area of the Mediterranean region. The geological predisposition of the territory, being characterized by several clayey formations, certainly made straightforward the development of such a millenary productive tradition of ceramic ware. Nevertheless testimonies about the antique ceramic production in this part of Sicily are still relatively disjointed. The attempts to reconstruct a representative outline of the most important centers of ceramic manufacture during the antiquity seem to be complicated by the multifaceted succession of historic and social-economic events.

The present research was aimed to a detailed study of textural, compositional and technological properties of 9 clayey formations cropping out in the territory of Western and Central Sicily, which were already recognized to have been employed as raw materials for ceramic production in antiquity or could have been potentially used for the same purpose. Several compositional and textural markers for distinguishing local ceramic products were successfully pointed out.

**Keywords:** archaeological ceramic, provenance studies, Sicily.

# ROLE OF SALT CRYSTALLIZATION IN WEATHERING PROCESS OF ANCIENT BRICKS

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Weathering is a group of processes that leads to decay or degradation of materials upon their exposure to the surrounding environmental conditions. The most dominant factors in the environmental damage of the buildings, more precisely of bricks as their constitutive part, are water and soluble salts. The pore size distribution of the primary form of bricks is the dominant factor for their further decay. The crystallization pressure is higher in materials with small pores than in ones with larger ending with minerals precipitation in the body of bricks and salts crystallization on the surface of brick walls.
The object of our investigation was the examination of bricks collected from the church of Bodjani Monastery, North of Serbia – 18th centuries, where salt crystallization and high level of humidity, above 90%, are present as the dominant degradation parameters. The aim of this work was the investigation of the existing connection between raw materials composition and their decomposition due to the water absorption – moisture action. On the base of the used methods (x-ray diffraction, pH –value measurements, SEM-EDS, DTA/TG and Hg-porosimetry) and hystorical data of the church, the degree of structure damage of the examined materials was determined. Experimental research was carried out in order to connect moisture content in the brick body with the salt crystallization process, primarily sodium sulphate- thenardite. Our work is a contribution to a better understanding of the salt crystallize mechanisms (transition between thenardite and mirabilite and thenardite reprecipitation) and durability decrease of the porous ancient bricks. The degree of destruction of the examined materials could be an essential background for the future procedures for the restoration of the church of Bodjani Monastery.

**Keywords:** cultural heritage, historical bricks, salt crystallization, moisture.

# MULTI-TECHNIQUE APPROACH FOR THE CHARACTERISATION OF STRUCTURAL CHANGES OCCURRING IN CLAY FIRING PROCESSES

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The thermal decomposition of clay is one of the most studied ceramic reactions. In fact, a complete description of these processes can be very useful both for optimizing industrial processes and to investigate ancient firing technologies. The study of the clay and of its thermal modifications is both interesting and difficult due to its complexity and variability. In order to find and to test a useful scientific methodology able to follow the many different processes, which occur with the increasing of the temperature, a modern carbonatic clay coming from Deruta (Umbria, Italy) was fired at different temperatures ranging from 600 to 1100° C. A multi-technique approach was required in order to obtain detailed information. XRF analysis was chosen for elementary information and SEM-EDS for morphological study. XRPD was useful for the study of the different phases together with MAS and MQ-MAS-NMR experiments which allow the following of structural changes of both crystalline and amorphous phases occurring during the firing. Moreover Mössbauer and Raman techniques gave information about iron-rich phases. Thanks to this methodology it was possible to follow the clay thermal reactions and to find markers for the different temperatures.

Therefore we decided to apply this methodology also to a clay found during the excavation of a ceramic kiln in Deruta dated XVI-XVII. The archaeologists consider this clay very similar to that used for the very famous Renaissance majolica. Thus, thanks to this study, it was possible to understand more about the ancient firing technique.

# THE EARTH IN THE ARCHITECTURE OF THE HISTORICAL CENTRE OF LAMEZIA TERME

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In Calabria, as in other regions of Italy, it is difficult to verify the consistence of the earthen building patrimony because the plasters, that almost always dresses the buildings hangings, do not allow to see the underlying material. Only when the layer of external covering starts to be detached for decay phenomena, the real nature becomes visible.

Nevertheless in the common language, the term “*casedde*” indicates the houses realised in earth and the term “*casini*” or “*turri*” the houses realised in stone or in bricks. This made it possible to estimate, even though approximately, the presence of this kind of material, also in absence of a visual check.

In the case of buildings with more than a floor, realised with different technologies and different materials, the survey of the earthen building patrimony is very complex. This is the case of the historical centre of Lamezia Terme (Catanzaro-Italy), on the Tyrrenian coast. The ancient nucleus of the town (in the fraction of Sambiase), is an example of urban centre in which there are buildings of 4 -5 floors, completely or partially realized in earth bricks (*adobe*) connected with a mortar made of clay and lime.

In the present study the mineralogical, physical and mechanical characterization of *adobe* samples coming from seven different buildings in bad state of conservation has been carried out. Also samples of local earth have been analysed for comparison. The analyses made it possible to verify the absence of any mixing intervention in the earth excepting for the addition of straw. Besides the type of composition made it possible to understand the observed decay phenomenologies.

**Keywords**: earth, building material, adobe.

# CHARACTERISTICS OF CLAY IN ANCIENT POTTERIES FROM WIANGKALONG KILN SITE, NORTHERN THAILAND

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Wiangkalong was one of the major ceramic production sites in Lanna, a once famous kingdom in northern Thailand during 1296-1558 A.D. The potteries were produced between the 14th - mid 16th centuries; their shapes and designs resembled those of the Chinese Yuan (1280-1368 A.D.) and Ming (1368-1634 A.D.) dynasties. Both scanning electron microscope (SEM) and X-ray techniques, namely XRD and XRF, were employed to study clay minerals in these ancient ceramics in order to determine the kiln sites from which they were produced. Illite and sillimanite were found in one of the ceramics studied, which represent characteristics of ancient potteries made in Wiangkalong.

**Keywords:** Clay characterization, Thai ancient pottery, Wiangkalong.

# CERAMICS & ENGINEERING

## SESSION CE3

*Clays in Traditional Ceramic Industry*

# THE ROLE OF CLAYEY MATERIALS IN CERAMIC INDUSTRY: HOW TO USE THEM AS MINOR COMPONENTS IN OLD AND NEW PRODUCTS FOR DIFFERENT APPLICATIONS?

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Traditional ceramic industry demands annually huge tonnages of non-renewable raw materials, which are being extracted and consumed at exponentially growing rates. The scarcity of some ceramic raw materials in countries with a long tradition in this specific industrial sector means increased costs related with its transport from long distances. Transportation costs are capital, labour, and energy dependent, causing long-term price fluctuations and business instability. Therefore, a strategy needs to be devised to enable using low grades of clayey materials, or self-generated inorganic sludges of a similar nature, as well as residues derived from other industries such as mining and mineral processing, etc., without sacrificing the final properties of the products, or even improving their physical or aesthetical properties. This will help preserving mineral resources, reducing the environmental burden created by the accumulation of industrial residues in land fill and contributing for a sustainable development.

The used of low grade clayey materials can be hampered by the correct use of synthetic and organic additives in ceramic manufacturing in order to improve process efficiency, minimise losses (waste) and improve product performance via a superior microstructure. ADOPTIC is a European collective research project aiming at providing a comprehensive information and support via the web for SME manufacturers seeking to broaden their knowledge and used of additives.

A review about the past-present, and future perspectives on how to continue using clayey materials in a "wise" manner will be presented. Different approaches will be proposed, including (i) the reformulation the traditional compositions, replacing clayey materials by industrial sludges of a similar nature; (ii) how to make use of processing aids to improve the plasticity and the mechanical green strength to enable using low plasticity clays; (iii) how to improve the wet processing ability of difficult raw materials based on smectite and montmorilonite clay minerals. Innovative and smart solutions that enable achieving complementary targets will be suggested aiming at hold and new products for different applications. The role of the processing additives in reducing scrap, increasing yields and product performance will be highlighted.

**Keywords:** Clayey materials; processing additives; sustainable development.

# EFFECTS OF PROCESSING ADDITIVES ON CURRENT PLASTIC FORMING TECHNIQUES OF TRADITIONAL CERAMIC PRODUCTS

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In the present work we report the study of the effects of processing additives on a low plasticity earthenware ceramic paste, which is rich in kaolin to facilitate drying, but the consolidated green products usually have insufficient mechanical properties to be handled in the steps subsequent to plastic forming and often crack. This increases the production costs and the percentage of rejected products along the process.

The effects of adding different amounts of additives on the plastic behaviour and on the green and fired properties (thermal behaviour, shrinkage, density, bending strength and water absorption) were studied aiming at solving this problem.

The plasticity of the pastes was evaluated through stress/strain curves under compression tests and by the Pfefferkorn method. The results obtained revealed that enough plasticity is conferred by adding total amounts of processing additives less that 1 wt%, while significant improvements in the mechanical properties of the green and sintered bodies were also obtained.

The results are very promising enabling to work with kaolin richer earthenware pastes, preferred for their better whiteness, while keeping a high quality of the processing and a high level of the final properties.

**Keywords**: Plastic forming, processing additives, earthenware.

# CHEMICAL, MINERALOGICAL AND TECHNOLOGICAL ANALYSIS OF THE REGOLITHIC CLAY COVERS FROM THE REGION OF ALFENAS, MINAS GERAIS, BRAZIL, AIMING TO EVALUATE ITS USE IN THE CERAMIC INDUSTRY

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The region of Alfenas, in the state of Minas Gerais, Brazil, is predominantly constituted of Pre-Cambrian rocks with well developed alteration profiles in association with colluvial and alluvial sediments. No study to date has examined in detail its potential use in the ceramic industry. The scarce knowledge of its mineralogical and technological properties limits its value and consequently its industrial use. Until now, these clay materials have been used in a rudimental manner, in small scale in the fabrication of red tiles.

The present study aimed at analyzing these clays mineralogically (by X-ray diffraction), chemically (major and minor elements by X-ray fluorescence and organic carbon analysis) and technologically (pressing granulometric distribution; mechanical resistance; water absorption, apparent porosity; linear firing shrinkage; color of firing and others) in order to better understand the raw material and develop adequate technological applications. The results showed that the clays originating from the alteration of schists and gneisses have a high percentage of sand and silt (around 20%) and are comprised mainly of kaolinite and, secondarily of quartz, muscovite, goethite and gibbsite. These results were corroborated by X-ray fluorescence data that showed a $SiO_2$ content from 60 to 70%, $Al_2O_3$ from 14 to 18% and $Fe_2O_3$ from 1 to 5%. The firing temperature tests of 850°C (for traditional ceramics) and of 1020°C (for bricks and tiles) resulted in products with a range of color between yellow and red due to the minor or major presence of goethite, respectively. Additionally, the predominance of kaolinite makes these materials less plastic and more refractory and in turn more adequate for their use in the traditional ceramic industry.

**Keywords**: kaolinite, alteration profiles, traditional ceramic industry.

# OPTIMISED LOCAL SOLUTIONS FOR CERAMIC WHITE-WARES FORMULATIONS; THE ADVANCED CHARACTERISATION AND DESIGN OF CLAY BLENDS

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For many ceramic white-ware applications a blend of individual clays is used in order to achieve the correct balance of plasticity, strength and rheology required for the fabrications process. In addition, the incorporation of clay minerals local to the production facility is preferred for economic reasons. This study aims to show how the results from careful characterisation of individual clays can be combined to optimise the performance of the final clay blend for its use in a specific application. Emphasis will be placed on materials testing and rheological measurements.

# APPLICATION OF MIXTURE DESIGN ON THE EFFECT OF CLAY CONCENTRATION IN TILE CERAMIC BODY COMPOSITION

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Clays are fundamental components in many materials. Among them, the traditional ceramic materials such as: tiles, sanitarywares, tablewares, bricks. In body composition, they are always together with other components such as quartz, feldspars, calcium and magnesium carbonates, in different percentages. The chemical reactions where clays are involved during the firing are complex and the results are not always linearly correlated with the percentages of each raw material. For this reasons, the modelling of such systems has always been considered very complicated and substantially not practicable so their effects have been widely studied, but more from a qualitative than a quantitative point of view. When more parameters are involved with or without interactions among them, DOE approach is an efficient method. In particular, Mixture Design is one of the DOE's techniques in which each experimental run is constrained such that when summed across the factors, the factor levels are constrained to sum to a constant [1].

In this work, the possibility of applying the statistical technique of Mixture Design was tested in order to relate, according to mathematical models, the effect of the concentration of clay and other components on some basic properties for traditional ceramics. In particular, a typical formulation for the production of porcelain stoneware tiles was studied. The considered properties after firing were: linear shrinkage and density, porosity, colour, cleanability, resistance to deep abrasion and chemical attacks. Mathematical models will be presented for each property and their adherence to the experimental data will be checked. In conclusion, a final evaluation of this mathematical-statistical approach with respect to its ability in optimizing the formulation on multiple properties will be presented.

**Keywords**: modelling, DOE, optimisation.

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# EFFECT OF SINTERING ON THE PHASE FORMATION AND MICROSTRUCTURE OF KAOLINITE PORCELAIN STONEWARE TILES

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Porcelain stoneware tile (PSW) is a vitrified ceramic building material obtained by high sintering of kaolinitic clays, quartz and feldspar. PSW are characterized by a very compact microstructure and high performances as covering tiles in construction systems for buildings. The commercial interest in PSW is accompanied by a scarcity of research to determine the relationship of mineralogy and microstructure on the technological properties of fired products. This work shows the phase formation and the microstructure evolution by SEM/EDX of a standard PSW body during firing (500º-1400ºC range). Micro-regions of varying chemical composition are present at low sintering temperatures, including quartz grains, pure kaolin agglomerates and feldspar-enriched clay regions. On heating, these regions react to form a glassy phase and different types of mullite. Primary mullite (type-I), formed from the pure clay agglomerate relicts and composed of aggregates of very small crystals, is detected in SEM observation on samples fired at 1200ºC. Secondary mullite (type-II and type III) composed by elongated needle-shape crystals derived from feldspar-clay relicts at above 1200ºC. Moreover, a new morphology in mullita growth, composed by packing of type-III needle crystals has been detected in the 1250º-1280ºC range for these covering porcelainized tiles.

# CERAMIC COOKWARE

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One of the most important properties of a stove-top ceramic cookware is having low thermal expansion coefficient to prevent cracks upon heating. In this paper, ceramic body with low thermal expansion is made from kaolinite clay, talcum, and zircon. After firing at 1250 and 1300 ºC, its physical properties, phase, thermal expansion and thermal shock resistance are analyzed. XRD measurement shows that the body after firing consists of cordierite. Low thermal expansion glaze is also developed to be utilized with such a body. Glaze is fired at a temperature of 1250 ºC. Thermal expansion coefficient and crazing resistance are also measured. Finally, a cookware sample with low thermal expansion is successfully developed from this method and is able to be used on stove-top.

**Keywords:** Ceramic cookware, Kaolinite, Cordierite.

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# IMERYS: THE RIGHT CLAY FOR EVERY APPLICATION

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Imerys is a world-wide supplier of clays and is able to provide each type of clay for every ceramic use: tiles, sanitaryware, tableware as well as earthenware like roof tiles and bricks.

For each ceramic product, ball clay is the key raw material from a technical standpoint and it provides a very specific and different added value according to each application.

This presentation will explain the main parameters required for ball clays according to the single application and will show Imerys' dedicated offer. This offer is the answer to market requirements analysed by Imerys marketing, R&D and production teams according to the different deposits.

**Keywords:** specific clay, ceramic application, Imerys 'offer.

# THE RELATIONSHIP BETWEEN COMPOSITION-SINTERING BEHAVIOUR OF PORCELAIN STONEWARE TILE

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Porcelain stoneware tile is a product having extremely high technical specifications, as it shows a high bending strength value and low water absorption (usually <0,1%). The sintering of porcelain stoneware tiles occurs by viscous flow sintering and sintering rate is controlled by glassy phase viscosity. The aim of the present study is to investigate the relationship between composition-sintering behaviour of porcelain stoneware tile formulations in order to lower sintering temperatures and/or firing cycles. Furthermore, it also involves the development of formulations with acceptable whiteness by incorporating low cost local clays. Glassy phase composition of a standard porcelain tile was taken as a reference and modifications of the glassy phase composition were made by using Seger formula. Alkali and earth alkali ratios, alumina and silica content were all modified in a systematic manner. Hot stage microscopy was used to analyze thermal behaviour of the glassy phases, and glassy phase compositions with lowest softening points and viscosities were determined. New porcelain stoneware body formulations were prepared based on these glassy phase compositions. Firing temperature, sintering range and firing shrinkage of the body formulations were investigated with an optical dilatometer. It was observed that it was possible to lower maximum sintering temperature of a technical porcelain tile down to 1185°C and also shorten the firing cycle to 35 minutes. Moreover, when the whiteness of reference formulation is taken into consideration the obtained values of L* are quite remarkable. It was possible to develop bodies having high whiteness values at commercially acceptable levels with using local clays instead of Ukrainian clay.

**Keywords**: porcelain tile, sintering, composition.

# UKRAINIAN BALL CLAYS: MINERALOGICAL CHARACTERIZATION AS A KEY TO EXPLAIN THEIR OUTSTANDING TECHNOLOGICAL PROPERTIES

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Ball clay is defined as “a fine-grained, highly plastic, mainly kaolinitic, sedimentary clay, the higher grades of which fire to a white or near white colour in an oxidising atmosphere”. Ball clays are traditionally used in ceramic production, i.e. tableware, sanitaryware and extensively in tilemaking. In particular, they are the most important component of porcelain stoneware bodies, used to manufacture big slabs up to 3 m$^2$. Technological requirements of ball clays are ever stricter in terms of plasticity, rheological behaviour, workability in the green state, refractoriness and firing colour. The best performance achieved in the industrial production of porcelain stoneware tiles is with ball clays coming from Ukraine, which turned to be a world because wide benchmark of their peculiar mineralogical, granulometric and technological properties. This work is aimed at understanding the reasons the outstanding ceramic properties of these raw materials. Seven Ukrainian ball clays, currently used in industrial ceramic production, were selected and their chemical analysis, particle size distribution, rheological behaviour, specific surface, plasticity and methylene blue index were determined. The mineralogical composition was investigated by SEM-TEM and XRPD performed on both randomly oriented bulk samples and oriented <2μm and <0.2μm fractions. Compared with conventional ball clays, the Ukrainian raw materials are characterized by abundant clay minerals, mostly kaolinite (poorly ordered) and randomly interstratified illite/smectite (expandable component <15%), and low content of quartz. The kaolinite-to-I/S ratio is low and I/S terms turn to be predominant in the colloidal fraction. This mineralogy, together with fine particle size, implies plasticity, specific surface and methylene blue index higher than classic ball clays; moreover, rheological properties are suitable easily dispersible in water and much less active than artificial blends added with bentonite in order to improve plasticity. Firing behaviour is satisfactory for easy sintering and light colour. Overall, the Ukrainian ball clays unrivalled performances are due to the occurrence of moderately active clay minerals, such as disordered kaolinite and illite-rich I/S interstratified, with fine particle distribution: a mix hard to be reproduced by mineralogical treatments.

**Keywords:** ball clay, technological properties, ceramic behaviour.

# CERAMICS & ENGINEERING

## SESSION CE4

## *Colloids & Rheology*

# STRUCTURAL FEATURES AND RHEOLOGY OF CLAY PARTICLE DISPERSIONS

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Numerous are the particle characteristics and structural features which affect the rheological properties of clay dispersions, especially when dispersed in aqueous media, in a interconnected manner, more markedly than for other colloidal systems or nanodispersions.

Indeed, the disperse phase concentration is the primary factor governing the viscous response of dispersions, its deviations from Newtonian behaviour and the viscoelastic properties whose importance becomes more and more remarkable with increasing concentration. Its role is strongly related to the clay particles features, i.e. to their dimensional factors (size and shape) and, even more, to the surface charge heterogeneity which results into interparticle (attractive and repulsive) interactions highly dependent on nature and composition of the dispersing phase. Even small changes in pH and ions concentrations can produce significant variations in interaction potentials of particle faces and edges, and, hence, lead to a good state of dispersion or, alternatively, to different aggregation modalities (edge-face, edge-edge or face-face), as highlighted in several studies on aqueous montmorillonite suspensions. Accordingly, stable clay dispersions show liquid-like properties with shear-thinning character with the onset of shear-thickening at high concentrations, while plastic behaviour and marked time-dependent (thixotropic and viscoelastic) properties appear with the formation of an aggregated particle network.

The complex interplay among particle concentration, dimensional features and interactions clearly emerges from investigations carried out on aqueous dispersions of laponite nanoparticles, which undergo pronounced changes in their rheological properties even at very low concentration owing to sol/gel or sol/glass transitions induced by changes in ion and/or particle concentration or to the structural effects produced by polymer addition, such as bridging flocculation.

Organically modified phyllosilicates dispersed in polymeric matrices can give origin to very peculiar nanocomposite structures with intercalated or exfoliated morphology owing to the expansion of the sheet silicate structure, the polymer intercalation into the gallery space or to particle exfoliation into lamellar subunits. In the latter case a three-dimensional network pervading the whole system from wall to wall can be formed even at low organoclay concentration, and, thus, a neat transition is observed in the rheological behaviour of the nanodispersion, which exhibit marked shear thinning and viscoelasticity. The role of interparticle interactions and particle diffusivity are sensibly reduced because of the organic nature of the matrix and its relatively high viscosity, and then shear-induced structural processes can result into specific not-reversible rheological properties.

# CLAY IMPACT ON THE PROPERTIES OF GRANULAR MIXES: A RHEOLOGICAL STUDY

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The influence of small amounts of clay on granular suspensions as debris-flow materials or fresh concrete is badly understood due in part to the difficulty to obtain well defined flow curves. A new experimental approach for analyzing granular suspensions based on the limitation of settlement in high viscosity matrices (HV45 Emkarox) was used in order to appreciate the effect of three clays, montmorillonite, illite and kaolinite, on the rheological properties of clay-containing granular mixes. The flow curves revealed that the addition of small amounts of clay materials strongly influence granular suspensions, the intensity of this influence depending on clay type. The yield stress strongly increased with montmorillonite and illite whereas kaolinite showed no effect. Comparative studies on clay suspensions in this high viscosity medium indicated that a correlation can be made between clay-liquid interaction and clay effect on granular mix. Clay impact can then be interpreted as corresponding to the trapping of water by clay particles. This hypothesis was confirmed by the non influence of an hydrophobic uncharged montmorillonite derived from a Hoffman Klemen treatment. Tentative modeling of the curves in term of effective volume fraction will finally be described taking into account the anisotropy of such particles.

**Keywords**: clay, granular mixes, rheology.

# SODIUM PYROPHOSPHATE – BENTONITE SUSPENSIONS FOR USE IN LIQUEFACTION MITIGATION

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Liquefaction of loose granular soils is an important cause of damage to civil infrastructures during earthquakes, and there is great interest in the development of methods for reducing the susceptibility of sand deposits to this phenomenon. Recent research (El Mohtar et al. 2008) indicates that the liquefaction resistance of sand is greatly enhanced in presence of small percentages (~3% by mass of the sand) of bentonite in the soil pores. This effect is ascribed to the nature of the pore fluid formed under these conditions: a concentrated bentonite suspension with gel like structure, suggesting that permeation of a sand deposit with a bentonite suspension may represent an effective approach to liquefaction mitigation. Practical application of this method requires that the rheology of the bentonite suspension be engineered so that on the short term the suspension has properties that allow its permeation inside a porous medium; but that once inside the sand pores, it regain the gel-like nature, which ensures its effectiveness in mitigating the effects of cyclic loading.

The work presented here explored the use of sodium pyro-phosphate (SPP) to modify the rheology of bentonite suspensions prepared using a commercial Wyoming sodium-bentonite. A Physica MCR 301 Rheometer was utilized to investigate the changes in the flow and viscoelastic properties of 10% bentonite suspensions treated with SPP (at dosages ranging from 0% to 5% by mass of the bentonite,) over time. It is found that even small additions of SPP impact the rheology of the suspensions, and that the effects are more marked as the SPP% increases. At early ages suspensions with SPP $\geq$ 0.5% are shown to be suitable permeation materials, based on permeation tests conducted through laboratory prepared sand columns. Compared to the bentonite-only suspension, these materials display a significantly reduced storage modulus, an increased loss modulus, minimal yield stress, and little to no thixotropy.Over time the rheology of all SPP treated bentonite suspensions evolves significantly, and after 7 months of ageing all the suspensions display a gel-like structure; the greater the SPP %, the more delayed the formation of the gel. Preliminary results from tests conducted on sand treated with a 10% bentonite and 0.5% SPP suspension demonstrate the effectiveness of the treatment in increasing the resistance of the sand to liquefaction.

**Keywords:** liquefaction, bentonite, sodium pyrophosphate, rheology.

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# ZEOLITE-CLAY SUSPENSIONS: RHEOLOGICAL AND SINTERING BEHAVIOR

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Zeolites are known as hydrated crystalline aluminosilicates having three dimensional skeleton structures. Zeolites are utilized in several industrial applications (adsorbent, catalyst, ion exchanger, etc.) due to their unique characteristic properties. The use of zeolite rich rocks as a substitute material in ceramic production has been gained attention in last few years because of their high $SiO_2$ and $Al_2O_3$ content, availability in large deposits, and low-cost. The purpose of the study is to determine the effect of natural zeolite addition in slip for ceramic tiles production by evaluating the rheological behavior and microstructural properties of the sintered products.

The ongoing experimental study involves the characterization of natural zeolite and the raw material of slip, determination of rheological behavior of slips w/wo natural zeolite and microstructure of slip-cast sintered bodies. Natural Zeolite and slip raw material was supplied from Gördes Region, Western Anatolia and from a ceramic tile manufacturer, respectively. The chemical composition of the materials used was determined by Inductively Coupled Plasma Emission Spectrometer (ICP). The slips were prepared by adding various amounts of natural zeolite ranging from 0-50wt% to commercially used ceramic slip having constant solids content of 60wt%. Rotational rheometer was used to evaluate the rheological properties of slips w/wo natural zeolite by steady shear (flow, viscosity, and thixotropy) and dynamic shear rheological (stress and frequency sweep) techniques. The slip cast greenbodies were sintered between 1000-1400$^{o}$C. The crystal and microstructure of the materials and sintered bodies were determined by X-Ray diffraction (XRD) and Scanning Electron Microscopy (SEM), respectively. The sintering behavior was determined by using dilatometer and density measurements.

The addition of natural zeolite modified the rheological behavior of the slips. After determination of linear viscoelastic region, the microstructure of the slips was evaluated by frequency sweep tests. The sintered bodies have darkened as the sintering temperature was increased due to impurities of the natural zeolites.

**Keywords:** natural zeolite, ceramic, rheology.

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# EFFECT OF ORGANIC MODIFICATION AND CHEMICAL FUNCTIONALITY ON EXFOLIATION

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Relative viscosities of a series of clay alcohol suspensions were employed to assess the influences upon montmorillonite exfoliation. Much research within the polymer industry is focused on the development and production of polymer-clay nanocomposites. To produce such nanocomposites by an *in situ* polymerisation process, a stable and highly exfoliated suspension of the desired clay in a liquid monomer must first be generated.

Production of a stable and exfoliated monomer-clay suspension is dependent upon many attributes of the clay, dispersing monomer and other potential organics within the system.[1] A number of glycols, bi-functional and mono-functional alcohols were employed to assess the factors influencing dispersant behaviour. All dispersants within the study were Newtonian fluids, however stable clay suspensions exhibit non-Newtonian shear-thinning behaviour. If a highly exfoliated suspension is produced there is also potential for a house of cards structure to form, resulting in a delay in the normal shear thinning behaviour, observed as a regime change within the viscosity profile.[2] Observation of the viscosity profile whilst varying the dispersants allows the dominant influences in platelet exfoliation to be identified. Attributes of the dispersant which were examined were polarity, permittivity and molar mass. The organic surface modifiers were also capable of influencing exfoliation by altering the hydrophobicity of the platelet surface. The structural composition and surface concentration of the modifiers were therefore also examined.

Within suspensions based on the bi-functional alcohols, it was observed that the relative viscosity was dependent upon both dispersant polarity and permittivity. The relative viscosity of mono-functional alcohol suspensions however were observed to behave in the opposite manner, favouring a lower permittivity. Clay surface modifiers were also observed to directly influence the relative viscosity through both the surface concentration and structural composition.

**Keywords**: viscosity, montmorillonite, alcohol.

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# THE ELECTRO-RHEOLOGY OF SUSPENSIONS OF SYNTHETIC SMECTITES IN OIL

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We have studied the effect of an external DC electric field (E ~ kV/mm) on the rheological properties of colloidal suspensions made by suspending synthetic smectite crystallites in a silicon oil. Under application of an electric field E greater than a triggering value, the particles assemble into chain- and/or column-like structures in the oil. At E = 0, the steady state shear behavior of the suspensions, at the particle fractions Φ investigated here, is Newtonian-like. Under application of a sufficiently large electric field, their rheology changes dramatically as a result of the changes in the microstructure: a significant yield stress is measured, and under continuous shear the fluid is shear-thinning. We study samples made respectively with laponite and fluorohectorite particles. The suspensions' rheology is studied as a function of Φ, for various strengths (including null) of E. We perform three types of rheology tests: (i) standard steady shear tests, (ii) standard disruption tests (under steady shear stress), and (iii) rheology bifurcation tests. In the latter tests, the bifurcation in the rheology when letting the system flow and evolve under a constant applied shear stress is characterized, and a yield stress is estimated as the applied shear stress at which viscosity bifurcation occurs. The steady shear flow curves (under fixed strain rate) can be scaled with respect to E, onto a master curve. In the case of laponite, they can also be scaled as a function of Φ. The scaling is consistent with simple scaling arguments. The shape of the master curve accounts for the system's complexity; it approaches a standard Herschel-Bulkley model at high Mason numbers for both systems. For all samples, the corresponding dynamic yield stress is measured to scale as $E^{\alpha}$, with $\alpha \sim 1.8$ for laponite and $\alpha \sim 1.9$ for fluorohectorite. For laponite, it also scales as $\Phi^{\beta}$, with $\beta \sim 1.0$. Standard disruption tests bifurcation tests provide similar scaling laws for the yield stress: $\alpha \sim 1.8$ for laponite and $\alpha \sim 1.6$ for fluorohectorite. For laponite, the β exponent is measured to 1.7 from disruption tests, and 0.6 from bifurcation tests. The results from the three types of measurements are found to be reasonably consistent with each other. The differences in the rheology of laponite and fluorohectorite samples are attributed to the difference in the shape of the particle aggregates. The study also proves that ER fluids can be studied in the framework of thixotropic fluids, by focusing on their rheology bifurcation.

**Keywords:** Clay suspensions, electo-rheology, yield stress, rheology bifurcation.

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# BENTONITE COLLOID STABILITY IN GRANITE GROUNDWATERS: EXPERIMENTS AND MODELLING

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The erosion of the compacted bentonite buffer/backfill material in a repository for high level nuclear waste in crystalline host rocks will strongly depend on the ground water geochemical conditions. Based on model calculations it is assumed that a decrease of [$Me^{2+}$] concentration below the critical coagulation concentration (CCC) leads to the detection of colloids from the bentonite backfill material and transport in a fracture. Therefore, in this study, colloid stability measurements are conducted for a bentonite (Febex, Almeria, Spain) colloid suspension by varying ionic strength, pH and type of electrolyte ($Na^+$ and $Ca^{2+}$, $Mg^{2+}$) to determine the stability ratio $W_{measured}$ and hence the CCC for the investigated systems. The dynamic light scattering technique (PCS) is used to investigate the time-dependent colloid aggregation behaviour. The values for the measured stability ratio ($W_{measured}$) increase with decreasing ionic strength, as expected. A pH independent CCC could be determined for $CaCl_2$ at approx. 1 $mmol \cdot L^{-1}$ in agreement with literature data. The CCC for the NaCl system shows a pH dependent CCC with ascending values from 10 to 625 $mmol \cdot L^{-1}$ for pH 6 to pH 10, respectively.

A DLVO-theory approach is used to calculate edge-edge, edge-face and face-face interaction energy for the bentonite platelets [1]. The total interaction energy barrier ($V_{max}$) calculated was used to derive the theoretical stability ratio $W_{DLVO}$. Measured Febex bentonite bulk zeta-potentials ($\zeta$) are used as colloid face potential and the colloid edge charge was estimated based on the aluminol to silanol- ratio given by the Febex bentonite structural formula [2] using measured $\zeta$- potentials of pure silica and $\alpha$-alumina. The calculated $W_{DLVO}$ values follow in general the same trend as the $W_{measured}$. A sensitivity analysis for $W_{DLVO}$ by varying the colloid face potential entered in the DLVO approach to obtain the best fit for $W_{measured}$ revealed a maximum deviation of $\leq \pm 12$ mV of the measured Febex bentonite $\zeta$- potentials which is slightly higher than the $\zeta$- potential analytical error.

The work was conducted in the framework of the Grimsel Test Site Phase VI project “**C**olloid **F**ormation and **M**igration” and the BMWi project “Kollorado”.

**Keywords:** Bentonite Colloid Stability, DLVO-Theory, Critical Coagulation Concentration.

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# ELECTRORHEOLOGICAL PROPERTIES OF ORGANICALLY MODIFIED LAPONITE: INTERCALATION ADSORPTION AND WETTABILITY

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Cethyl-Trimethyl-Ammonium Bromide (CTAB) modified synthetic laponite has been synthesized by an ion exchange method and characterized by simultaneous small-angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy dispersive spectrometry (EDS), atomic force microscopy (AFM), thermal analysis and rheometry. Through the formation of the organoclay, the properties of clay change from hydrophilic to hydrophobic. Morphology our results show that the hydrophilic particles are aggregating easily, where the suitable CTAB modified laponite can get near monodispersed nanoparticles due to its hydrophobic properties. It is proposed that CTAB is intercalated and adsorbed onto the laponite partially depending on the substituted concentration of the surfactant cation exchange capacity (CEC) (0.5CEC to 6CEC). The electrorheological (ER) effect has been investigated for suspensions of CTAB modified laponite dispersed in silicone oil. The two-dimensional SAXS images from ER bundles of CTAB modified laponite exhibit marked anisotropy SAXS patterns, giving a measure for laponite particle alignment within the ER structure. An optimum electrorheological effect can be attained at a particular CEC substituted concentration. On the basis of the structure analysis and dielectric measurements, we attribute the enhancement of ER activity to the improvement in the dielectric properties that show an increase in the dielectric constant and the dielectric loss at low frequency and their regular optimum change with CTAB modification.

**Keywords:** Electrorheological effect, Wettability, Organoclay.

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# KAOLINITE FLOCCULATION STRUCTURES, RESULTS FROM CRYO-SEM AND SYNCHROTRON BASED TXM INVESTIGATIONS

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Effective flocculation and dewatering of mineral processing streams containing clays (particularly kaolinite and smectite platelets often <200 nm in lateral dimension) has become increasingly urgent. Release of water from slurries in tailings streams and dam beds (often >75 wt%), for recycle and reduced make-up water consumption, is usually slow and incomplete. To achieve fast settling and minimization of retained water, individual particles need to be bound, in the initial stages of thickening, into large, high-density aggregates, which may sediment more rapidly with lower intra-aggregate water content.

Quantitative cryo-SEM and TXM image analysis shows that the structure of aggregates formed before flocculant addition has a determinative effect on these outcomes. Without flocculant addition, 3 stages occur in the mechanism of primary dewatering of kaolinite at pH 8: During settling, the sponge-like network structure with EE and FF string-like aggregates, limits dewatering because the steric effects in the resulting partially-gelled aggregate structures are dominant. With flocculant addition, the internal structure and networking of the pre-aggregates is largely preserved but they are rapidly and effectively bound together by the aggregate-bridging action of the flocculant. The effects of initial pH and Ca ion addition on these structures are also analysed. Graphs of partial void contributions also suggest that it is not total porosity that dominates permeability in these systems but the abundance of larger intra-aggregate voids.

Knowing that flocculant addition has little influence on the intra-aggregate structure, and that it is in filtration, it isto control the aggregate structures prior to the flocculant addition in order to improve both settling rate and final solids density.

**Keywords:** Kaolinite, Microstructure, Flocculation.

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# NANO-STRUCTURE OF CLAY GELS

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Smectite and kaolinite are common ingredients of tempered climate soils. To understand better the unusual behavior of clays investigations were undertaken using transmission X-ray microscope with 60 nm tomography resolution has been installed at beamline BL01B SWLS “X-ray Microscopy” NSRRC in Taiwan.

A snapshot from 3-D reconstruction of TXM of a kaolinite suspension where a dense network of colloidal kaolinite particles supports a larger kaolinite stacked crystal of few µm in lateral dimension. Individual colloidal size particles are well visible in higher magnification, however distinctive string-like spongy and highly oriented structure is well visible when carefully observing the 3-D reconstruction and especially in this reconstruction when rotating image on different angles.

In 3-D, TXM reconstruction the Na gel structure in water is revealed. In micrograph elongated montmorillonite sheets forms cellular network 0.6 to 1.5 µm in diameter. The Ca gel cellular structure show much smaller cells dimensions 300-600 nm. The average distances measured between smectite sheets was around 450 nm which is less than half of the cells dimension measured in Na-montmorillonite.

From the plot in AFM results can be found that long range repulsive forces have been detected from distances ~1000 nm of the surface separation in case of Na-montmorillonite where in case of Ca-montmorillonite repulsive forces were detected from distance ~400 nm. This fact has crucial importance on how microstructure of Na- and Ca-montmorillonite differs in dilute water gel and how it trigger swelling phenomenon in the smectite rich soils.

Our TXM investigations reveal swollen cellular structures (cellular tactoids) in aqueous montmorillonite gel with void diameters on the micrometre scale. This forms thick gel cellular tactoids in Na-montmorillonite with cells up to 1-2 µm in diameter or coagulated aggregates in Ca-montmorillonite with cells of around 0.4 µm in diameter. The nature of long distance repulsive forces, which look similar to electrostatic repulsion, and are responsible for enormous swelling, remain uncertain however, elastic interactions cannot be rule out.

**Keywords:** Smectite, Gel, Colloids.

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# CERAMICS & ENGINEERING

## SESSION CE5

## *Desiccation and Fracture in Clay*

# MEMORY OF CLAY PASTE AND ITS APPLICATION TO CONTROL CRACK PATTERN

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We experimentally find that clay pastes have memories of external mechanical fields, such as flow and vibration. It is difficult to observe these memories inside clay pastes directly, but we find that, by drying these pastes, the memories in pastes can be visualized as macroscopically anisotropic desiccation crack patterns.

For example, a water-poor clay paste has a memory of vibration. This fact is visualized by drying water-poor clay paste after it is vibrated horizontally in one direction for a short period. When it is dried after the initial vibration, lamellar crack pattern appears with these directions all perpendicular to the direction of the initial vibration. We consider that the initial vibration produced a longitudinal density fluctuation along the direction of the initial vibration.

On the other hand, a water-rich clay paste has a memory of flow. When a water-rich clay paste is vibrated, it is easily fluidized, and the resultant desiccation crack pattern has a structure which is similar to the flow pattern that we observed at the initial vibration. That is, the directions of desiccation cracks become parallel to the flow direction.

Then, why can a water-rich clay paste have a memory of the flow direction? The shape dependence plays an important role here, because due to its plate-like shape of clay particles, a flow can induce directional ordering of plate-like particles. Also, the dilute network structure can be elongated along the flow direction.

A morphological phase diagram of desiccation crack pattern is presented as a function of a solid volume fraction and strength of the initial vibration to understand the mechanism of memory effects. We find that, between a liquid-limit and a plastic-limit where clay paste behaves as a visco-plastic fluid, there exist three regions, one with a memory of vibration, the second with a memory of flow, and the other without any memory inside, and also transitions between these regions.

We consider that these memories in clay pastes are sustained as microscopically anisotropic network structures of clay particles inside pastes, which can be observed by ultra small angle neutron scattering experiments.

By using these memory effects of clay pastes, we find that we can imprint flow and vibration patterns into pastes, and control to make various crack patterns, such as cellular, lamellar, radial, ring, spiral, and so on.

**Keywords:** Memory, Desiccation crack pattern, control.

[1] Nakahara A., Matsuo Y. (2005). Imprinting memory into paste and its visualization as crack patterns in drying process. J. Phys. Soc. Jpn. 74, 1362-1365.

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# THE CATION-DEPENDENCE OF THE DESSICATION CRACKING PATTERNS OF SMECTITE PASTES

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The ability of a clay pasty body to withstand cracking upon drying depends on both material-independent and material-dependent parameters. Among the former are the imposed evaporation rate and/or moisture gradient in the clay body and the mechanical properties of the clay-support interface. Among the later are the interparticle attractive forces and the aggregation state of the individual clay lamellae.

The present work is an investigation of the cracking behaviour of twenty cation-exchanged montmorillonite samples obtained by filtering aqueous suspensions. The cracking behaviour was correlated to several structural parameters not only of the dry clay deposits (X-ray correlation lengths, nitrogen surface area) but also of the parent suspensions (water-accessible surface area measured by NMR) and the filtration cakes (permeability).

The results show that, counter-intuitively, the clay cakes which withstand the best the drying stress without cracking are those in which the inter-lamellar forces are the weakest. This may be interpreted in terms of mesoscale plasticity.

**Keywords:** cracking, plasticity, order propagation.

# ROUGNESS OF FRACTURES IN LAPONITE GELS DETERMINED FROM MAGNETIC RESONANCE IMAGING

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In this work we have determined the roughness of fractures in soft transparent clay gels. The gels were prepared by dispersing synthetic Laponite in de-ionized water. A novel way of identifying roughness exponents through the use of Magnetic Resonance Imaging has been developed. By recording the $^1$H signal from vertical MRI slices of the clay gel, a mapping of the clay–air interface is possible. Conventional methods of extracting height profiles for roughness determination, such as laser- or stylus profilometry are unsuited for this kind of gel, due to the gels transparency and softness. From the one-dimensional MRI height profiles, the roughness exponent was calculated using established numerical methods (see e.g. [1]).

Fracture surfaces were obtained by a controlled removal of filter paper attached to the surface of the gel, a method similar to [2]. For fracture surfaces created with Mode-I fracturing, the roughness exponent has been found to be 0.56 (+0.05, -0.07), with no observable dependency between fracturing speed and roughness. On the other hand, when combining Mode-I and Mode-II fracturing, a velocity-dependent roughness in the direction perpendicular to the fracture propagation direction is revealed. We argue that these observations can be accounted for by considering the shear thinning behavior of Laponite gels.

**Keywords**: Clays, Gels, MR Imaging, Roughness.

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# CRACK PROPAGATION IN A THIN LAYER OF DRYING PASTE

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In the uniform drying process of a thin layer of paste, a quasi-two-dimensional crack pattern with T-shape intersections is formed with gradual shrinkage of the sample. In a conventional approach, we regarded a layer of paste as a network of linear springs with a shrinking natural length to investigate such crack patterns [1]. However, the fracture patterns can be affected by the rheological property of paste. The actual growth process of individual cracks in this process is quite different with the brittle fracture of completely-dried paste. The motion of a crack tip is slow enough to be observed with the naked eye, and the failure cross sections exhibit distinctive patterns with fine stripes known as plumose structures.

We investigated crack propagation induced by evaporation of water from the open surface of a layer experimentally and measured crack speeds in a controlled experimental condition. In this presentation, we report the results on calcium carbonate pastes mainly [2]. Cracks grow at approximately constant speeds except near the boundaries. We found that the crack speed is an increasing non-linear function of the drying rate and, in particular, cracks stop growing when evaporation of water is prevented.

We confirmed that cracks are created at the volume fraction of water which is independent of the drying rate, and pastes are in capillary states at that time. In addition, we estimated the tensile stress acting on the lateral boundary of a layer from the measurement of the displacement of a flat spring. The stress increases with drying and does not depend practically on the drying rate. In ordinary homogeneous materials, cracks are generally unstable once they start to grow with an increase of tensile stresses. We infer that plastic deformation arises to prevent cracking in the vicinity of crack tips in half-dry paste. We discuss the fracture mechanism responsible for the drying-rate dependence of the crack propagation.

**Keywords**: crack speed, drying paste, plastic deformation.

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[2] So Kitsunezaki. (2009). Crack Propagation Speed in the Drying Process of Paste. Submitted to J. Phys. Soc. Japan.

# CRACK PATTERNS IN DESICCATING LAPONITE – PEO COMPOSITES

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Polymer-clay composites have many practical applications and are a subject of current interest [1]. The formation of crack networks in clay layers shows several interesting features [2], so a study of crack formation in clay-polymer composites promises to reveal new results. We present here experiments conducted to observe the desiccation crack patterns in layers of laponite RD and polyethylene oxide (PEO). Aqueous solutions of a definite concentration of laponite and PEO are prepared, by stirring for different periods of time in a magnetic stirrer. The samples are left to dry under ambient conditions of temperature and humidity. It is observed that when the stirring time is about 30 minutes, the desiccating samples yield a network of cracks. If the stirring time is 10 - 22 hours then the layers of laponite-PEO seem to desiccate as a continuous film with fewer and fewer v-shaped cracks instead of yielding any definite crack pattern. This phenomenon is valid for different concentrations of laponite and polyethylene oxide. Leaving the samples to desiccate for a longer period of time does not affect the nature of cracks in the two cases.

**Keywords:** Laponite, PEO, Cracks.

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# CERAMICS & ENGINEERING

## SESSION CE6

## *Hetero-Modulus Ceramics for Technical Application*

# EFFECT OF STRUCTURAL PARAMETERS ON STRENGTH AND THERMAL STRESS RESISTANCE OF HETERO-MODULUS CERAMIC COMPOSITES

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Mechanical characteristics, thermal stress resistance and habits of fracture of heterogeneous composites on the basis of a brittle carbide matrix with carbon particles at force and thermal loading are observed. The thermal stress resistance is estimated on mean-integrated temperature drop $\Delta T_m$ at a non-stationary loading of disks 35 mm in diameter by a lateral surface heated in the bath of melted tin. Zirconium and niobium carbides with different contents of a carbon component in the form of carbon black (up to 5 wt. %) and in the form of mineral scaly graphite inclusions of grade KLZ by a size of 50-150 μm (up to 10 wt. %) are used as objects for studies. Carbide-diamond composites prepared by blending powders of zirconium carbide with synthetic diamond of ACM grade with average sizes of particles 0.2, 0.6, 6, 17 and 50 μm are also investigated.

Introduction of each view of carbon inclusions in the carbide matrix invariably reduces strength and modulus of composites and increases the strength variation from 20% for ZrC to 28 and 35% for the composition with carbon black and graphite respectively. Design values of modulus are compared with experimental measurements. Carbon black and diamond inclusions in comparison with graphite cause a less sharp drop of strength and greater decrease of a modulus. The effective surface energy $\gamma = K_{1c}/2E$, computed on measured values $K_{1c}$ and modulus E, is diminished with increase of the contents of carbon black and it does not vary practically with the introduction of graphite. Thermal stress resistance $\Delta T_m$ with increase of the contents of carbon inclusion up to 5 wt. % is increased two to three times in case of use of carbon black, or remains without modifications for composites with graphite.

Temperature dependences of thermal stress resistance are investigated by induction heating method. The thermal stress resistance of ZrC composites with modification of temperature from room temperature to emersion of micro-toughness at 1700 K remains at stationary value; the further heating increments the value $\Delta T_m$ to three times at 2500 K.

Improvement of the mechanical characteristics of the ceramics, with the elimination of structural defects by technological curing or by optimization of compaction and sintering parameters are considered. Increase of thermal stress resistance by modification of surface stressed state is observed.

**Keywords:** Thermal stress resistance, Carbide hetero-modulus composites, Fracture.

# OBTAINING OPPORTUNITIES OF BORON CARBIDE POWDERS BASED HETERO-MODULUS CERAMICS

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Nowadays, materials researchers show an increasingly more interest in elaboration of various hetero-modulus ceramics, which represent a combination of ceramic matrix with the high modulus of elasticity and additional components possessing essentially low modulus of elasticity. Applicability of boron carbide $B_4C$ as a matrix for hetero-modulus ceramics is determined by its high melting point, high values of hardness and modulus of elasticity, and also chemical stability against aggressive environments. The possibility of replacement in $B_4C$ natural boron by its neutron transparent ($^{11}B$) and neutron absorbent ($^{10}B$) isotopes makes it even more interesting to application in nuclear energy industry for neutron shielding goods etc. However, fields of boron carbide application is limited to its brittleness, what is a caused by rigidity of the B−B and B−C covalent bonds realized in crystalline lattice. Disposition towards fracturing and low impact toughness constrain opportunities of boron carbide to be used. Therefore, solving of the problems of decrease in rigidity, increasing in impact toughness and thermal resistance of the $B_4C$-based products gets a special urgency.

In the present work, there are considered features of technological process of the synthesis of boron carbide super-dispersed powders with carbon inclusion. Boron anhydride and glucose serve as initial materials for the technology, which includes deposition of water-solute reacting components on the preliminary heated substrate and provides with $B_4C$ and C in form of super-dispersed powders. Blending agents react by means of carbothermal reduction and subsequent graphitization process, and the product obtained as a result of final thermal treatment show presence of both boron carbide, as well as free carbon. Studies carried out allow making of some conclusions how it is possible to tune properties of the obtained material in dependence of requirements: by changing the system composition, by doping with special impurities; by modification of the technological conditions (like the temperature of deposition, thermal treatment process, substrate material, and deposition environment). Obtaining of the boron carbide super-dispersed powders with carbon inclusion applying simple technology seems rather attractive. Such powders will allow lowering of the pressing temperature and making anisotropic products, obtaining compositions of $B_4C$ with $sp^3$-structured carbon and various alloying elements. Main advantage of the proposed approach is an opportunity of obtaining of the super-dispersed composite powders with uniformly distributed components formed in the process of synthesis.

**Keywords**: Boron carbide, Carbon, Superdispersed powders.

# HETERO-MODULUS MATERIALS IN SIC- SI - C SYSTEM

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Hetero-modulus composite materials concept was developed under direction of Prof. Frantsevich in the Institute for Problems of Material Science, Kiev, Ukraine as far back as 50-ies of the last century. Actualization of this problem was connected with tasks of development of high-temperature materials working under extreme conditions of shock cycling heating of more than 2000K and contact with supersonic oxidizing gas blasts. Under these conditions satisfactory behavior even of the highly refractory metallic alloys was impossible because of their catastrophical oxidation and erosion. Moreover, there were made new requirements to the materials on the ground of the fast development of rocket and space engineering where light materials with low density were relevant.

These tasks solution was found by composite materials based on refractory compounds and low density matters development. The matter is primarily about silicon carbide (SiC) and graphite. Each of these materials does not have the full essential complex of properties providing their operability under above mentioned conditions. Thus silicon carbide having high modulus of elasticity, high-temperature strength and high resistance to oxidation is incapable to resist to dynamic thermal and mechanical load – the material is brittle and has low thermal shock resistance, and graphite being thermal resistant material has low modulus of elasticity, is easy to oxidize under the temperatures higher than 800 K and has low erosion resistance. At the same time, due to specific lamellar lattice graphite has shock-absorbing, dissipative characteristics. Therefore the idea of material combining these two phases appeared. The family of the materials in SiC – Si – C system with regulated phase ratio and crystallite size was obtained by methods of powder metallurgy and ceramic technologies. The technology was based on reaction sintering when SiC formation occurs as a result of melted silicon and graphite interaction. The possibilities of dissipative characteristics regulation in consequence of phase composition change were really effective since each phase has distinctly differing modulus of elasticity ($E_{SiC}$ = 300 GPa; $E_{Si}$ = 105 GPa; $E_{graphite}$ = 5,5-6,5 GPa).

On the basis of above mentioned ideas we have developed industrial technology of self-bonded silicon carbide (SiSiC) and siliconized graphite manufacturing with maximum size of the final products up to 600 mm.

Work under structure improvement of SiSiC materials directed on nano-sized components usage and purposed on surface quality and enhancement of product properties is progressively continued.

**Keywords**: Silicon carbide, Graphite, Reaction sintering, Hetero-modulus ceramics.

# CORUNDUM MATRIX COMPOSITES WITH HETERO-MODULUS NANO-PARTICLES WITH HIGH THERMAL SHOCK RESISTANCE

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The advances in science and technology make higher and higher demands against mechanical and thermal properties of high performance technical ceramics and ceramic matrix composites. Because of these circumstances several kind of ceramic materials and ceramic matrix composites are developed with high values of mechanical strength and hardness.[1-2] Most of these ceramics have microstructure of relatively "big" crystals with high rigidness and have strong inclination to nick, pitting, and rigid facture, but only a few of them have the required level of Young's modulus and thermal shock resistance in the same time. To increase significantly the Young's modulus of ceramics and ceramic matrix composites several methods and techniques are developed till today.[3-5]

Applying the well-known alumina powders for matrix and using different oxide and non-oxide ceramic nano-particles as additive materials, and investigating the impact of nitrogen atmosphere on sintering,[6] the authors successfully developed new corundum matrix composite materials, reinforced with particles of submicron and nano-sizes. Thanks to the used special compacting pressure distribution and sintering technologies, these new developed corundum matrix composite materials are "reinforced" not only with the mixed nano-particles, but with $Si_2ON_2$, SiAlON and AlN particles of submicron and nano-sizes, and having excellent mechanical properties and thermal shock resistances.

Analytical methods applied in this research were laser granulometry, scanning electron microscopy, X-ray diffraction and energy dispersive spectrometry. Digital image analysis was applied to microscopy results, to enhance the results of transformations.

**Keywords**: Corundum matrix composites, Thermal-shock resistance, Hetero-modulus ceramics.

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# HETEROGENEOUS DESIGN IN CERAMIC SYSTEMS

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Phase diagram (PD) is the main device for heterogeneous design (HD).[1] Along with the well-known and wide-spread molecular and structural designs, HD - as a new approach in solid state chemistry - opens up new opportunities for multiphase materials engineering.

When projecting PD geometrical elements in the direction of concentration simplex, we divide the phase regions beneath into thermodynamically unstable fragments. The lowest isothermal section of the sub-solidus regions is a PD base, divided into the concentration fields with unique crystallization schemes and microstructures.[2-4]

HD means to use different types of PD models (with and without the thermodynamic parameters) to simulate any type of equilibria (stable, metastable, spinodal) and to elaborate for this purposes the algorithms of multidimensional computational geometry and visualization.[5-7] Regularities of PD geometrical characteristics transformation, depending of solid solubility, polymorphism, properties of binary and ternary compounds, and PD dimension have been considered.

The term “genotype” is offered to take into account the whole variants of microstructures which can be realized at definite thermodynamic conditions. HP can be used to predict the microstructure of multiphase materials and to decipher their genotype, which is determined by PD geometrical construction.

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**Keywords**: Phase diagrams, Microstructures, Heterogeneous Design.

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# RIDGE-EFFECT OXIDATION BEHAVIOUR OF TITANIUM CARBIDE BASED HETERO-MODULUS CERAMICS WITH DIFFERENT GRAPHITE CONTENT

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Recent studies on oxidation kinetics of the TiC-graphite hetero-modulus ceramics (HMC) led to the discovery of a temperature-pressure-dependent phenomenon, which was termed the ridge effect. The oxidation rate of the carbide-carbon HMC rises to a maximum at ridge values of oxygen pressure or temperature, but then it declines with subsequent growth of oxidation parameters. The ridge values mark a change in the prevailing mechanism, as while the ridge parameters traversing the values of apparent activation energy $Q$ or order of reaction $m$ change its sign. The oxidation mechanisms are essentially different within the range of oxygen pressures and temperature and can be systematized by special ridge temperature – ridge pressure diagrams.[1-4]

The isothermal-isobaric oxidation of series of hot-pressed TiC – C (graphite) HMC materials with graphite content varied from 7 to 41 vol. % was studied at temperatures of 400–1000 $^0$C and pressures of 0.1-80 kPa in oxygen atmosphere with mass flow rate of gas about 0.1 g min$^{-1}$ using a TGA microbalance as well as chemical, optical microscopic, XRD, EMPA, SEM and EDX analyses of oxidized samples.

The obtained experimental results are interpreted by plotting of the ridge parameter diagrams for the materials with different graphite content to analyze the effect of carbon on oxidation behaviour of carbide-carbon HMC. The developed approach allows preparing the protective scales on the surface of substrate by means of special pre-oxidizing technique.

**Keywords**: Titanium carbide, Graphite, Hetero-modulus ceramics.

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# SYNTHESIS OF FIBROUS PHASE OF BORON NITRIDE FOR HETERO-MODULUS CERAMICS

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In this contribution the recent results on a synthesis of the fibrous structures of boron nitride are presented. Light-induced catalyst-free heating of fine-grained graphite-like h-BN powders was performed for the synthesis. The new structures of boron nitride were produced in the flow of dried and purified nitrogen in an optical furnace.

Scanning electron microscopy (SEM) micrographs revealed a variety of structural features that apparently developed in response to the interaction of BN plume with ambient nitrogen.

The surface of the heated compacted h-BN samples, surface of titanium, silicon and quartz substrates were carefully studied and analysed. X-ray Diffraction (XRD) measurements demonstrates the presence of the pure boron of different modifications, hexagonal phase of BN, two boron-enriched tetragonal phases ($B_{51.2}N$ and $B_{25}N$) in investigate materials depending on experimental conditions.

Complicated structure and phase composition of fibrous structures (whiskers) formed on the surface of heated samples of compacted graphite-like h-BN powders were studied by transmission electron microscopy (TEM). It was shown that whiskers are multi-walled boron nitride nanotubes covered by polycrystalline sheath. Phase composition of the surface of whiskers is homogeneous boron nitride enriched boron. A small amount of oxygen was only detected in the initial part of the whiskers growth on the surface of heated sample of compacted graphite-like h-BN powders.

The process of synthesis, formation and growth of fibrous structures in an optical furnace was analyzed and understood.

**Keywords**: Boron nitride, Fibrous structures, Light heating.

# COMBUSTION SYNTHESIS OF SIALON–BN HETERO-MODULUS CERAMIC COMPOSITES

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SiAlON based ceramics have high strength, excellent wear and corrosion resistance. BN-based ceramics have high thermal shock resistance, low friction coefficient and good machinability. SiAlON–BN composites are capable to combine these properties in desirable proportion. All of these make possible consider such composites as one of the most promising structural material for various fields of up-to-date engineering. Accordingly the developing of advanced methods for its production is promising task of up-to-date materials science. The aim of the present work is to study the regularities of infiltration assisted combustion synthesis of SiAlON–BN ceramic composites. The objects of investigation are composites with general formula of sialon phase $\beta'$-$Si_{6-z}Al_zO_zN_{8-z}$ (where $z = 0 \div 4,2$) and up to 40 wt.% of BN content. The main factors affecting the density and phase composition of synthesized SiAlON–BN composites are revealed experimentally: nitrogen pressure in the reactor, bulk density and composition of initial reaction mixture. Optimum conditions for synthesis of high-density composites are realized under nitrogen pressure about 100 MPa in the reaction mixtures enriched in oxides (synthesis of highly substituted β′-sialons). In this case infiltration assisted combustion occurs in a layer-by-layer mode and accompanied by the significant shrinkage of sample. The synthesized machinable SiAlON–BN ceramics exhibit excellent resistance to thermal shock and to the action of metallurgical melts and have good tribological characteristics.

**Keywords**: Sialons, Boron nitride, Combustion synthesis, Hetero-modulus ceramics.

# MATERIALS OPTIMUM DESIGN OF HOT-PRESSED CARBIDE-GRAPHITE HETERO-MODULUS CERAMICS

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The transition-metal carbides are real champions among the variety of materials concerning their melting points (up to 3950 ºC for HfC) and hardness (up to HV 40 GPa for TiC), so because of these properties they are candidate materials for many modern engineering applications in aerospace industry and nuclear engineering.[1] To avoid the dramatic effects caused by brittleness of the carbides is a key problem of materials engineering design for a long period of time. The earlier engineering solutions in this way, which were connected with development of ceramic-metal composites (cermets), cannot be useful in the range of temperatures higher than 2000 ºC. The generally imperfect impact tolerance and low thermal-shock resistance (TSR), which are inherent to the transition-metal carbides, can be improved noticeably by the addition of a low-modulus phases such as graphite or boron nitride,[2] and this is without considerable restrictions to the applications at ultra-high temperatures, because the eutectic points in the TiC – C, ZrC – C and HfC - C systems are positioned close to 3000 ºC.

Densified TiC-, ZrC- and HfC-based hetero-modulus ceramics (HMC), containing 10-40 vol. % of low-modulus phase in the form of particulate graphite, were prepared by high-temperature hot pressing. The microstructure, flexural and compressive strength, impact resistance, fracture toughness, hardness, thermal expansion and elastic characteristics were investigated for clear understanding the composition-property correlations and anisotropy of this type of ceramic composites. Different TSR parameters for the HMC were estimated on the basis of the obtained experimental data.

It is exemplified by the TiC – C HMC that the graphite volume content in the materials has an opposite impact on the different TSR criteria. The parameters, which characterise the resistance to crack propagation and/or further cracking, are growing with the increase in graphite content, whilst the parameters, which are responsible for crack initiation, decrease in this case. Novel principles of materials design for the composition selection/optimization in the refractory carbide – graphite HMC are considered.

**Keywords**: Carbides, Carbon, Hetero-modulus ceramics.

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# THE MORPHOLOGY AND FORMATION MECHANISM OF SIC IN 3-DIMENSIONAL NEEDLED C/C-SIC BRAKING COMPOSITES

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Carbon fibre reinforced carbon and silicon carbide dual matrix composites (C/C-SiC) is a new type of high performance brake materials and possess a series of outstanding advantages such as low density, good high temperature resistance, high strength, good oxidation resistance, excellent friction properties, and low sensitivity to service environments. In the present study, the C/C-SiC braking composites were fabricated by the combination of chemical vapour infiltration (CVI) with liquid silicon infiltration (LSI). The preform was prepared by three dimension needling method and the volume fraction of carbon fibre was 30%. The preform was densified by chemical vapour infiltration to form porous carbon/carbon (C/C) composites. Then, the porous C/C composites were converted into C/C-SiC during LSI, in which silicon carbide matrix was formed by the reaction of carbon and melt silicon. Results show that two different areas of SiC exist there. A zone of coarser micro-β-SiC grains between 5 and 20 μm at the SiC/Si interface, and they usually form inside the pores of carbon fibre reinforced carbon (C/C) preform like around the needling fibres and among the C/C bundles. The other is a fine nano-SiC layer with dimension of 100-500 nm at the SiC/C interface. From these observations, reaction mechanisms governing the siliconization of porous C/C preforms are proposed. After an initial reaction of carbon with liquid silicon, an initial continuous SiC layer formed on the Si/C interface, and the subsequent formation of SiC is controlled by diffusion of C and/or Si through the already formed SiC layer. The results show that the C/C-SiC braking composites possessed excellent braking performance and wear resistance. Micro-β-SiC could enhance the debris ploughing action to increase the friction resistance. Nano-SiC could help to form the friction film.

**Keywords**: C/C-SiC composites, Silicon carbide, Liquid silicon infiltration, Formation mechanism.

# CERAMICS & ENGINEERING

## SESSION CE7

## *Modified Clays & New Applications*

# CATION EXCHANGED SMECTITES: PREPARATION AND CHARACTERIZATION

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Smectite clay minerals, as bentonite and montmorillonite, are layer silicates that are notable for their tendency to expand and hydrate upon exposure to water. The swelling process is driven in great part by hydration of exchangeable cations that reside between the negatively charged clay layers.[1,2] Furthermore, it is also demonstrate that the nature of these interlayer-cations could have an important role on the exchange process with organic molecules (as surfactant, organic contaminants).[3] Generally, smectites play an important role in many environmental and engineered systems. For example, swelling and ion exchange properties of smectites impact the transport and bioavailability of both ionic nutrients and pollutants in the environment.[4]

The present study show the first step of the research highlighted to the investigation of the role of the nature of exchangeable cations, present in the interlayer and on the surface of bentonite minerals, on sorption of organic molecules. In particular, the experimental preparation and characterization of a natural bentonite and a standard montmorillonite (as comparison) exchanged with different inorganic cations ($Cs^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$) is presented. The characterization include, X-ray powder diffractometry (XRD), transmission electron microscopy (TEM), thermal analysis (TGA, DTA), cation exchange capacity (CEC) and Fourier transform infrared spectroscopy (FTIR). The results obtained demonstrate the radical influence of the different inorganic cations selected on the physico-chemical characteristics of the correspondent homoionic bentonite, including hydration and thermal behavior.

**Keywords:** Smectite minerals, bentonite, cation exchange.

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# OXIDATIVE PILLARING OF THE SYNTHETIC MICA FERROUS TAINIOLITE

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Layered compounds may easily be modified by exchanging interlayer ions. Pillaring the interlayer space of 2:1-layered silicates by large molecules or oligomers in particular represents a facile and appealing route to microporous hybrid materials [1]. With respect to thermal stability these pillared inter-layered clays (PILCs) certainly are inferior to zeolites, especially when organic molecules were used as pillars. Nevertheless, PILCs possess a number of peculiarities that renders them an interesting class of porous hybrid materials in their own right.

1. While isomorphic substitution in zeolites is limited to a few elements, in layered silicates it is not restricted to the tetrahedral layer only. Most interestingly, transition metals in the octahedral layer lead to attractive physico-chemical properties like magnetism or electrical conductivity [2].
2. The intercalation of molecular pillars into layered silicates results in porous hybrid materials with pillars being part of the inner pore surface. This way, interesting properties like catalytic activity or chirality can easily be introduced into the pore volume by choosing the corresponding pillar.
3. In contrast to established porous materials like zeolites, mesoporous silica based materials, or metal organic frameworks, the pore shape and size of PILCs are not predetermined during the synthesis of the host structure. Instead, pore shape and size of the PILCs are determined by both, the dimensions and shape of the utilized pillar and the pillar density in the interlayer space which may be varied by adjusting the valence state of the transition metals in the structure.

Starting with a synthetic mica, ferrous tainiolite $Cs(Fe^{2+}{}_2Li)Si_4O_{10}F_2$, a facile synthesis of the microporous PILC $Me_2DABCO$-tainiolite by intercalating the molecular pillar $Me_2DABCO^{2+}$ (N,N-dimethyl-1,4-diazabicyclo[2.2.2]octane) was developed [3]. Oxidative conditions during the pillaring reaction promoted a significant reduction of the layer charge into the regime of smectites. Thus, ahighly charged and dense material could be converted to a well crystalline, course-grained hybrid material with a narrow pore size distribution in the range of micropores.

**Keywords:** PILC, Porosity, Intercalation.

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# NATURAL SMECTITES DELAMINATION BY MECHANICAL GRINDING

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The interest devoted to clay in catalysis as support has continued to grow over the years. Smectite clays are the group of clay minerals that are able to expand in presence of water. Their important thermal stability, cation exchange ability and resistance to poisoning make them interesting candidates in the field of catalysis. In addition to these advantages, their low cost have made this type of materials a prime target to be used as support. However, when these clays are exchanged by metal polycations developing catalytic activity, the internal aspects of tactoids are scarcely accessible to the reactive molecules during the catalytic act. This fact limits considerably the catalytic activity of these matrices and restricts remarkably the use of clay as a support in catalysis. The detachment or separation of clay layers, more commonly called delamination improves significantly the access to the layer facets of clay, increases the surface area and facilitates the dissemination of catalyst active sites.. In this context, several processes are proposed in order to delaminate the clay layers. However, the classical ones remain long, complicated and expensive especially in terms of reagents and equipment.

In the present work, we are interested in the possibility of smectite clay delamination by mechanical grinding. This method is very advantageous due to extremely simple run and very low cost. Two natural smectites were used in this study: a montmorillonite (Wyoming, USA) and a Saponite (Cabañas, Spain). Both clays were grinded with a disc grinder (THEMA) for varying durations. The properties of obtained solids have been studied by physisorption of nitrogen at 77 K, X-ray diffraction (XRD), thermogravimetric analysis and thermal differential (TGA/DTA), nuclear magnetic resonance (MAS NMR) of $^{29}$Si and $^{27}$Al, Infrared spectroscopy (FTIR), Laser seizer and transmission electron microscopy (TEM).

The study showed a partial clay layers delamination leading to an improvement in the specific surface areas by layers sliding on their facet's plan for short grinding times. However, for relatively long mechanical processing times, the structure sheets of the clay seems to be completely destroyed because of a weakening of the interlayer bonds and the departure of octahedral aluminium after dehydoxylation. These phenomena reduce the specific surface of these matrixes, destroy the microporosity and induce an early glass transition in the case of saponite clay. It has also shown that mechanical resistance decreases with aluminium rates in the octahedral layer. This fact induces a much better mechanical resistance in the case of saponite compared to montmorillonite.

# Fe/Al/Mn MODIFICATION OF ALUMINOSILICATES: MECHANISM AND KINETICS OF SURFACE PROCESSES

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Adsorption of As, Se and Sb oxyanions on natural clay materials (often inferior for another use) has got into increasing concern for economical end ecological reasons. However, aluminosilicates are not selective sorbents for anionic contaminants thanks to a low $pH_{ZPC}$. A simple Fe/Al/Mn surface pre-treatment of initial material can significantly improve their sorption affinity to oxyanionic contaminants, including arsenites and arsenates, selenites and selenates and antimonites and antimonates, respectively.

The pre-treating methods included $Fe^{II}$, $Fe^{III}$, $Al^{III}$ and $Mn^{II}$ modification. Mineralogically pure clays were used for surface changes study – two kaolins from West Bohemia with the high content of kaolinite (>80 %), bentonite (Riedel de Haën, Germany) content mostly montmorillonite and standard Ca-rich montmorillonite SAz-2 (Arizona, USA).

The adsorption efficiency of modified sorbents increased significantly for all investigated systems (to >90 %) by the initial As/Se/Sb concentration of 10-40 mg $L^{-1}$, and the solid-liquid ratio 0.5-8 g $L^{-1}$. The mechanism and kinetics of surface processes depended on the structure of raw material (steric properties, chemical and mineralogical composition, specific surface), and applied treating method associated with Fe/Al/Mn chemistry. The quality of initial solution (pH, As/Se/Sb concentration) was also significant. The characteristic changes on the sorbent surface during the pre-treating processes were checked up with infrared spectroscopy and voltametry of microparticles.

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**Keywords:** aluminosilicates, adsorption, As/Se/Sb oxyanions.

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# USE OF KAOLIN IN PREPARATION OF GEOPOLYMERS

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“Geopolymeric” materials has found increased application in various fields, such as decorative stones, fire-resistant materials, thermal insulating products, toxic wastes containers, as well as soft attempts in archaeological and architectonical conservation.

The increase of interest towards these types of products is due to their low cost and the low temperature of production process. In addition, no high thermal gradients, that could cause stresses in the products, are reached.

The geopolymers are alumina-silicate materials, obtained from the reaction between silicon and aluminium-rich raw material and a very high basic alkaline solution (ph=12), sodium or potassium silicate in particular. The Si-Alrich raw material can be represented by kaolin, which is treated at temperature of 750°C in order to obtain an extremely reactive material known as metakaolin. The metakaolin reacts with alkaline solution that furnishes a “polymerizant” components. The result is an amorphous or semi-crystalline product with particles of nanometric dimension. In this geopolymerization process the “natural” compound, represented by kaolinite, is very important, because it gives the structure to the geopolymer. The mechanical, thermal, acoustic and other characteristics of geopolymers are influenced by the Si/Al ratio.

In order to obtain a suitable product, it is necessary to characterize the raw material. For this purpose, two commercial kaolins (BS4 and Bal-Co) have been characterised before and after the thermal treatment for their activation. The specific surface, the crystalline phases through XRD and thermal analyses, the chemical composition and the grain size have been determined. With the aim to verify the most suitable temperature for obtaining a very reactive product, the clay materials have been fired at two different temperatures: 750°C, according to the literature, and 650°C, a value close to the minimum temperature for the formation of metakaolin.

**Keywords**: kaolin, metakaolin, geopolymer.

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# THE EFFECT OF TITANIA/SILICA RATIO ON SOLID ACIDITY OF TITANIA-SILICA SOL PILLARED CLAY

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The oxide sol pillared clays with the solid acid are expected to use for the catalyst of chemical recycling of the poly-lactic acid. There is a report that the commercial acid montmorillonite (K10) actually used to decompose the poly-lactic acid to oligomer[1].In this work, titania-silica sol/montmorillonite composites with variety of titania/silica ratio were prepared to investigate the effect of the titania/silica ratio of 10:1, 9:2, 8:3, 7:4, and 6:5. The composites were synthesized by reaction of titania-silica sols prepared from alkoxides with natural montmorillonite at laboratory temperature. The obtained composites showed the slight expanding and broadening of basal reflection in XRD, corresponding to the intercalation of titania-silica sol particles into the montmorillonite sheets, and disordered stacking of exfoliated montmorillonite and titania-silica sol particles. The specific surface area ($S_{BET}$) of composites measured by $N_2$ adsorption ranged from 227 to 298 $m^2/g$ and greatly increased compared with that of montmorillonite (6 $m^2/g$). The pore size of obtained composites showed almost same value about 3 nm. The $NH_3$-TPD spectra of the composites were consisted of an overlapped peak. The deconvoluted peak temperatures were about 190° and 290°C. The amount of solid acid measured by $NH_3$-TPD method showed 277-381 μmol/g in the obtained composites and were higher than of the commercial acid montmorillonite, K10 (85 μmol/g), which was synthesized by the acid treatment of montmorillonite. Among the composites, the sample with titania:silica = 9:2 showed the highest acid amount (381 μmol/g), which was about 4.5 times higher than K10.

**Keywords:** Pillared clay, Titania-silica sol, Solid acidity.

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# KINETIC MODEL FOR CATION EXCHANGE CAPACITY OF BENTONITE VIA ACTIVATION BY SODIUM CARBONATE

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Smectites are one of the largest and most important classes of the phyllosilicate clay-mineral group. The cation exchange capacities (CEC) and high specific surfaces of bentonites make them suitable for cationic absorption processes. Bentonites, which contain high percentages of smectite, are greatly affected by thermal treatment. Therefore, the study of physico-chemical variations in bentonite structures as a function of temperature has got a great importance. Nowadays, the cation exchange in bentonite structure resulted in numerous applications in ceramics, nanocomposite materials, oil drilling, waste isolation and the metal and paper industries.

In this work, activation of a typical bentonite by sodium carbonate has been studied. Activation processes were performed at three temperature levels of 55, 75, 96 ºC and different activation times. The values of cation exchange capacity of activated samples were measured by methylene blue test. Thereafter, a modified kinetic model was presented for cation exchange capacity for Na-bentonite. Furthermore, the activation energy and frequency factor were calculated by using experimental data. In the next part of work, bentonite activation was carried out at different concentrations of soda. Therefore, the effect of soda concentration on kinetic parameters was investigated. Finally, the optimum activation time to achieve the maximum value of cation exchange capacity at various temperatures and soda concentrations were calculated using a mathematical model. The obtained kinetic parameters confirmed that the activation energy remains constant with increasing soda concentration, but the number of active sites significantly increases depending on the soda concentration.

**Keywords:** Bentonite, Activation, Sodium Carbonate.

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# SOLID-STATE INTERCALATION OF MIXED LIGANDS IN Zn(II)-MONTMORILLONITE

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The intercalation of organic guest species into layered inorganic materials is the excellent way of fabricating organic-inorganic hybrid materials. Clay minerals such as montmorillonite provide attractive features due to their large surface area, ion exchange property, adsorptive property and swelling behavior. The immobilization of mixed ligand metal complexes into the interlayer space of montmorillonite is worth investigating for fabrication of novel photofunctional hybrid systems, which exhibited high photoluminescence efficiency and thermal stability. The novel electroluminescence hybrid materials, such as Znqb- and Znqp-montmorillonites (q =8-hydroxyquinoline, b=2,2´-bipyridine, p=1,10-phenanthroline), were investigated by solid-solid reactions between Zn(II)-montmorillonite and two types of ligands (8-hydroxyquinoline and 2,2´-bipyridine or 1,10-phenanthroline) at ambient conditions. Zn(II)-montmorillonite was prepared by a conventional ion exchange method. The incorporation of 8-hydroxyquinoline and 2,2´-bipyridine or 1,10-phenanthroline into Zn(II)-montmorillonite was carried out by solid-solid reactions. The intercalation of two different ligands into interlayer spaces of Zn(II)-montmorillonite and *in situ* complex formation were proved by powder XRD, TG-DTA, FT-IR, UV-Vis and photoluminescence spectroscopies. The basal spacings of Znqb- and Znqp-montmorillonites after the reactions were ca. 1.8 nm. The improved thermal stability of the complexes can be expected by the immobilization on the clay. The absorption spectra of products with two ligands were significantly changed relative to that of Znq-montmorillonite. The intercalation compounds exhibited the PL band at 503 nm. The photoluminescence intensity of Znqb-montmorillonite was higher than that of Znqp-montmorillonite, showing that the emission intensity of Znq complex in montmorillonite can be improved by co-coordination with 2,2´-bipyridine.

**Keywords:** Intercalation, Montmorillonite, Optical Properties.

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# PREPARATION OF CADMIUN SELENIDE-ORGANOMONTMORILLONITE HYBRIDS

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The intercalation of guest species into layered inorganic solids has attracted increasing attention from a wide range of scientific and industrial sphere. Among possible layered solids, the smectite group of layered clay minerals has been studied widely for organization of guest species because of their attractive features such as large surface area, swelling behavior, adsorptive and ion exchange properties. The immobilization and/or surface modification of photofunctional metal complexes or semiconductor particles such as CdSe were investigated in order to stabilize the complexes or particles as well as modify the useful optical properties for a great potential in the fields of electroluminescence and light-emitting devices. The intercalation of CdSe into the interlayer space of organically modified montmorillonite was prepared by a conventional and solid-solid reactions between hexadecyltrimethylammonium ($C_{16}H_{33}(CH_3)_3N^+$)-montmorillonite and CdSe at room temperature. The amounts of the added hexadecyltrimethylammonium ion and CdSe particle were just equal to the cation exchange capacity (119 meq/ 100g clay) of montmorillonite. The intercalation compounds prepared by conventional and solid-solid reactions were orange and red products, respectively. The as-synthesized products were characterized by powder X-ray diffraction, thermal analysis, UV-visible and photoluminescence spectroscopies. Powder X-ray diffraction and thermal analysis data supported the intercalation of CdSe nanoparticles in hexadecyltrimethylammonium-montmorillonite. The optical features of the intercalation compounds obtained by conventional and solid-solid reactions reflected the difference in organizing CdSe nanoparticles. The formation of CdSe in the organically modified montmorillonite is useful for tailoring the optical properties of semiconductor particles.

**Keywords:** CdSe, Intercalation, Montmorillonite.

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# Na-4-MICA MODIFIED BY ALKYL-AMMONIUM IONS

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The adsorption of cationic surfactants on clays at the solid-liquid interface is of great interest and fundamental importance due to the wide spread use of these compounds in both household and industrial activities, and to the occurrence of layer silicates in soils, subsoils, and sediments. Na-4-mica is a highly charged expandable sodium fluorophlogopite firstly reported by Gregorkiewitz, which has been described as a trioctahedral mica-type and has recently received much attention. These swelling micas, which have not yet been intercalated with organic matter, could be valuable for the decontamination of soils and residual waters. In consequence, our main aim in this contribution is to study the intercalation of Na-4-mica samples with alkylammonium ions and to establish a relation between the arrangement of these interlayer molecules and the physico-chemical properties of this interesting new mica. Organomicas were prepared by a cation-exchange reaction between Na-4-mica and the $C_{12}$, $C_{14}$, $C_{16}$ and $C_{18}$ akylammonium ions obtained from their primary amines after reaction in HCl solution. Long-range order structural characterisation of synthesized samples was carried out by XRD and variable temperature XRD. Both MAS NMR and FTIR, were employed to investigate the local order of tetrahedral sheets of the mica and the molecular arrangements of interlayer organic species. Rational series of basal X-ray reflections were obtained for the whole series of systems analysed with basal spacing values of up to 46.02 Å. These basal spacing were increased during the heat treatment of samples, a reorganization of the organic molecules being inferred from variable temperature XRD results. $^{29}$Si MAS NMR results showed a chemical shift displacement in all the organomicas, compatible with a rearrangement in the structural pseudohexagonal cavities caused by the incorporation of the ammonium polar heads. $^{13}$C and $^{1}$H MAS NMR and FTIR data indicate a paraffin-like structure for all the organic molecules with a tilting angle dependent on the chain length. Moreover, organic molecules adopt an all-trans configuration, although a considerable gauche conformation was observed for the $C_{12}$ shortest chain. For the first time Na-4-mica has been intercalated with alkylammonium ions with even number of carbon atoms between 12 and 18. The high-charge of micas layer determines a close-packed interlayer structure with the polar ammonium heads forming crown ethers-like interactions with the hexagonal cavities and the all-trans hydrocarbon tails forming paraffin arrangements. These new materials are potentially useful for decontamination of polluted soils and fluids.

**Keywords**: Na-4-mica, alkylammonium, organo-clay.

# INORGANIC FOAMS PREPARED FROM VARIOUS CLAYS IN SITU. TEXTURAL PROPERTIES

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Geopolymers are amorphous three-dimensional alumino-silicate binder materials, which were first introduced to the inorganic cementitious world by Davidovits in 1978. Geopolymers may be synthesized at room or slightly elevated temperature by alkaline activation of aluminosilicates obtained from industrial wastes, calcined clays, natural minerals or mixtures of two or more of these materials. Under a strong alkaline solution, aluminosilicate reactive materials are rapidly dissolved into solution to form free $SiO_4$ and $AlO_4$ tetrahedral units. Geopolymer concretes are based on compounds that are generally produced from one or more solid components (binders) and one or more liquid components (activators), which react together to form strong, durable materials. Some binders such as PVA fibres or fly ash have been used by extrusion technique but not in batch preparation like concrete. Furthermore a few work has been devoted to the feasibility of synthesized foam of geopolymer without organic additives. Amongst the different families of geopolymers, those based on potassium exhibit modified thermal and mechanical properties due to the larger size of the potassium ion compared to sodium.

The aim of this work was to prepare the geopolymer foams based on potassium polysialate, industrial waste and various types of clay. The influence of used clays has been illustrated by structural data determined by ATR spectroscopy and SEM characterization correlated to their thermal properties verified by flash laser method.

The materials were prepared from the solution containing kaolinite, illite or monmorillonite and KOH pellets dissolved in potassium silicate. The mixture was then transferred to a sealed polyethylene mould and placed in an oven at 70°C during 24 hours. The properties of material depended on the nature of clays. We have studied the influence of crystallochemistry of clays, i.e. structural and chemical alteration, as well as their BET specific surface area values. The last parameter acted upon the elementary attack of potassium silicate associated to KOH, which was investigated by ATR and XRD analyses.. The loss of the clay structure was partial for kaolinite, a higher for illite and the highest for monmorillonite. The SEM observations clearly show this behaviour inducing textural modification, notably on sample containing kaolinite where the blocky tactoids were organized along the pores. Moreover, these inorganic foams have potential use as a building material, since they have a thermal behaviour as insulating materials.

**Keywords:** Geopolymer, Building material, Stability.

# ENHANCING BRONSTED ACID SITE ACTIVITY OF ION EXCHANGED MONTMORILLONITE BY MICROWAVE IRRDIATION FOR ESTER SYNTHESIS

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A microwave synthesis represents a major break through in synthetic organic chemistry. This technique brings about a dramatic change in the way chemical synthesis is performed. Effect of microwave results not only in the reduction of reaction time from hours to minutes but also in the knowledge how to reduce side reactions and improve reproducibility. The unique feature of microwave synthesis of esters is that it can be carried out even in the absence of solvent. In the present work an attempt has been made to study the esterification of butanol with different aliphatic acids over cation exchanged clays under microwave irradiation. The metal cations had hydration sphere around them and possesed the property to dissociate the coordinated water in the hydration sphere. This resulted in the clay catalyzing the esterification. A microwave irradiation has been found to enhance it.

$Na^+$ montmorillonite (raw clay) was inactive while cation exchanged clay ($Al^{3+}$ montmorillonite) dried at 110 $^0$C showed 80 % conversion to ester during 30 minutes under microwave irradiation conditions. The results were compared with conventional heating using autoclaves. The effect of concentration of reactants, amount of catalyst, reaction temperature and time on the yield of butyl acetate has been investigated. The esterification of butyl alcohol with butyric acid, hexanoic acid, octanoic acid and decanoic acid has also been studied. It was observed that as the length of the carbon chain increased, ester yield decreased. Microwave irradiated esterification was faster resulting in higher yields in shorter time. Factors like the time of irradiation, a catalyst type and its amount, the molar ratio of reactants and the polar nature of the solvent influenced the yield of product similarly to the conventional method of reflux esterification. Microwave irradiation is beneficial for carrying out clay catalyzed reactions in an efficient way.

**Keywords:** $Al^{3+}$ Montmorillonite, Microwave irradiation, Alkyl esters.

# ORGANIC MODIFICATION OF A BRAZILIAN SMECTITE CLAY

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The clays of smectite group exhibit a variety of properties that make them interesting to be used in a great range of applications: their particles have naturally small dimensions with average size smaller than 2 μm, they have a large specific surface area and their individual layers are reactive. Also it is possible to exchange the ions present between the layers by organic cations. The method to change the metallic cations by organic cations has a strong influence on the structure and properties of the resultant organophilic clay. A review of the main procedures adopted for the cation exchange reaction reported in the literature was realized in this work and showed that the studies do not reach a consensus regarding the ideal conditions to prepare an organophilic clay. Therefore, the objective of this work was to study systematically the structural changes of organically modified smectitic clays by different methods. A Brazilian smectite clay was modified using two different ammonium quaternary salts with one and two long alkyl chains. The preparation methods included the principal parameters described in the literature [1,2]: clay particle size, mixing time of clay/water dispersion, mixing time of clay/water/organic cation system, temperature for cation exchange. To check the most effective preparation methods, the resultant organoclays were characterized by XRD, DTA (to determine the organic cation content), and by Foster swelling test. It was also evaluated the variation of basal spacing values of organoclays when heated in the temperature range of 25-500 ºC, by XRD. The results showed that the temperature for cation exchange and the clay/water dispersion mixing time are the key parameters of the preparation method. It was observed, that the arrangement of the salt chains within the organoclays will change, when the temperature increases, depending also on the salt structure and concentration, and the water amount within the organoclays.

**Keywords:** Organophilic clay, Preparation methods, Ammonium salt conformation.

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# WIDE ANGLE X-RAY SCATTERING STUDIES OF GUIDED ASSEMBLED ORGANOCLAY ELECTRORHEOLOGICAL SUSPENSIONS

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We have studied surfactant modified clay in silicone oil using wide angle x-ray scattering (WAXS). The electrorheological suspension of organic modified clay was synthesized by the combination of ion exchange and liquid-liquid phase transfer method. Firstly, different clays (Na-fluorohectorite, kaolinite, laponite and montmorillonite) modified with Cethyl-Trimethyl-Ammonium Bromide (CTAB) were synthesized by the ion exchange method. Through the formation of organoclay, the properties of clay change from hydrophilic to hydrophobic which is suitable for the transfer from the aqueous phase to the organic phase. Secondly, a liquid–liquid phase transfer method was employed in order to prepare novel organic modified clay/silicone oil suspensions. The transfer process was identified by the rapid change of colour of the aqueous and organic phases. For different clay and CTAB substitution, the CTAB molucules are thought to lay either parallel to the host layers forming lateral mono- or bilayers, or radiate away from the surface forming extended (paraffin-type) mono- or bimolecular arrangements, or adsorb onto the surface of clay layers. The three-dimensional WAXS images from chains of CTAB modified clay under a DC external electrical field exhibit marked anisotropy patterns. The dynamic formation of chain for organoclay ER suspensions and unmodified clay ER suspensions, respectively, have also been investigated, which may provide new evidence for the enhancement of ER effect.

**Keywords:** Organoclay, Intercalation, Electrorheological effect.

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# CERAMICS & ENGINEERING

## SESSION CE8

## *Processing and Properties of Ceramic Materials*

# HOW INNOVATION IN CERAMIC PROCESSING IS CHANGING BALL CLAY REQUIREMENTS

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The main technological advances occurring in the last decade in ceramic tile manufacturing will be outlined and their effect on ball clays will be overviewed: use, technical requirements and future expectations.

Ball clays are expected to fulfil, along with the classical requirements for whitewares, the rapidly changing exigencies driven by innovation in tilemaking, involving development of new products (e.g. porcelain stoneware bodies consisting of less than 40% clay) or processes (i.e. novel shaping and decoration techniques) or both (the so-called “product-process”, such as 4 $m^2$ ceramic slabs).

From this standpoint, ball clays are requested to play an even more specialized role, with emphasis on their rheological properties, technological behaviour during the shaping and drying stages, and microstructural evolution during firing. All these features depend in a complex way on the intrinsic characteristics of clays (i.e. mineralogy, particle size distribution, surface activity, etc.).

Therefore, clay suppliers are therefore facing the challenge to go beyond blending, trying to design and engineer new clay products tailored on the ceramic industry demand.

**Keywords:** Ball clay, Ceramic tiles, Technological behaviour.

# EFFECT OF GRAIN SIZE ON THE QUALITY OF POTTERY CLAYS

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Mixture of the right proportion of expanding and non-expanding clays to improve plasticity (moldability) of clays used in the pot industry of Malaysia is yet to be well investigated. In addition, little is known about the choice of the right clay size to reduce the contents of undesirable compounds such as $Fe_2O_3$, $Al_2O_3$ so as to improve the strength of pots and roofing tiles in the country. The objective of this study was to investigate how selected chemical properties of pottery clay relate to grain size of Nyalau series ((Typic Paleudults). Soil samples were refined into 63, 25, and 20 µm using size grading method. The mineralogical composition of the samples was determined using X-ray diffraction. The chemical composition of the samples was also determined using standard procedures. Firing was done at 500 to 1000 $^{o}$C) in an electric kiln at a heat rate of 5 K/min and the cracking behaviour of the samples recorded. The clay with particles 63 µm had the best working quality and this was so because the clay particles had the lowest amount of $Fe_2O_3$, $Al_2O_3$ and $SiO_2$. As result, the clay with particles 63 µm was selected to produce pot at 800 $^{o}$C with a firing time of 5 hours. The quality of Malaysian pots can be improved upon proper grading of the clay particles.

# MICROSTRUCTURE OF CLAY-CHAMOTTE CERAMIC COMPOSITES

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Two kaolinitic refractory clays mined in Cameroon and two calcined clays (chamottes) with a large grain size (0.1–4 mm) were used to realize clay-chamotte ceramics. Clay-chamotte compositions containing various quantities of chamotte (0–50 wt %) were shaped and sintered at 1200–1350°C. The structural characteristics of composites indicated the presence of quartz from the initial clay, cristobalite and mullite. SEM observations revealed very heterogeneous microstructures where porosity is weakly distributed and large pores are entrapped at the vicinity of large chamotte and quartz grains. In general, the global porosity increases with the chamotte content. A specific interpretation of the matrix role on the global sintering behaviour reveals that only a part of the matrix acts effectively. Since the most part of the global porosity is within the matrix, it is distributed in matrix zones, which participate effectively to sintering and in inert matrix zones where larger pores occur. The global mechanical strength is controlled by the matrix behaviour, but the high porosity of this phase is unfavourable to high strength values. Besides, the occurrence of larges pores and local cracks at large grain interfaces from thermal stresses are critical flaws, which reduce the mechanical strength.

**Keywords:** Clay, sintering, ceramic-composite.

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# STAGES OF TRANSFORMATION OF VEGETAL ADDITIVE MATERIALS UPON CLAY MIXTURE FIRING

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To increase the porosity of clay-bricks, various additive materials are mixed with the clay minerals. These materials will decompose during firing and create voids, closed pores in the fired body. In the last decades much attention was paid to additives which decompose by oxidation, thus release additional heat during firing. Organic, vegetal waste materials are of this type.

Recent studies involving sawdust, rice husks and sunflower seeds hull evidenced that the original skeletal structure of vegetal material is preserved in fired bodies [1]. The thermal reactions involved in the transformations of clay minerals and vegetal materials were characterized by differential thermal analysis. Raw clay samples, raw additives and mixtures were analysed. Based on these results, sequential firing of samples was set up, to observe the stages of transformation. In this research, three main transformation stages were considered, generally overlapping with the reactions of clay minerals.

The first stage is between 40˚C and 200˚C and is of endothermic nature. This stage produces the shrinkage of additive grains, the starting of pore formation. The geometry of grain is preserved and is identical with the geometry of the created pore. The second stage is between 200˚C and 500˚C and is marked by a strong exothermic reaction. In this stage the oxidation of organic compounds is finished and the non-organic part of vegetal material will be reorganised in order to form the remnant of the grains. The transfer of substance from clay into the additive samples is questionable. The third stage is between 500˚C and 720˚C, showing only a few small endothermic reactions, at different temperatures. These reactions are assumed to be in relation by the reorganisation of the remnants of pore forming additive grains. However, the remnants do not possess any crystalline structure according to observations by optical microscopy.

Analytical methods applied in this research were optical microscopy in polarised light, scanning electron microscopy and energy dispersive spectrometry. Digital image analysis was applied to microscopy results, to enhance the results of transformations.

**Keywords:** Vegetal additive materials, Transformation on firing, Remnants of additives.

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# MECHANICAL PROPERTIES OF TEXTURED CERAMICS FROM MUSCOVITE-KAOLINITE ALTERNATE LAYERS

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An organized network of mullite anisotropic crystals embedded in a silico-aluminate matrix material is obtained at interfaces of sintered alternate layers of muscovite and kaolinite minerals. The nucleation and growth of mullite anisotropic crystals occur preferentially along the muscovite basal planes through topotactic reaction with the high temperature form of muscovite.

Simultaneously to structural transformations, dehydroxylation of muscovite induces an exfoliation process, which is temperature and time dependant. The kinetics of this process was controlled using an appropriate thermal cycle and uniaxial load. During sintering, the control of mullite size is mainly dependent to temperature, and the addition of a small quantity of low temperature liquid phase also favors the growth of mullite. But liquid induces the weakening of the organization degree of the mullite network. To characterize microstructural characteristics, techniques of Quantitative Texture Analysis (QTA) and SEM were performed.

Flexural strength, Young modulus and fracture toughness are closely related to size and organization degree of the mullite network. In general, mullite length favors the increase of strength and fracture toughness. But a high organization degree of the mullite network favors the occurrence of interconnected crystals and increases mechanical properties.

**Keywords:** Muscovite, Kaolinite, Mullite, Textured ceramics.

# THE EFFECT OF BINDER MIXING ON TECHNICAL PARAMETER OF CERAMIC RASHIG RINGS

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Ceramic Raschig rings are very appealing for high performance applications in chemical and petrochemical process such as absorption, distillation, catalytic bed due to their mechanical and corrosion resistance. However, prediction and control the properties of ceramic Raschig rings are necessary to produce reliable material for above applications. Therefore, the microstructural improvement of ceramic body can be affected the reliability of Raschig rings. In the manufacturing of ceramic products, binders are normally used to improve the physical and mechanical characteristics of green body. Nowadays, mixtures of binders are commonly used to increase the homogeneity of body during the shaping process. In this investigation the mixture design method was used to obtain the best combination of CMC (carboxyl methyl cellulose), PVA (poly vinyl alcohol) and kaolin to maximize the compressive strength and reliability of final products. Firstly, different combination of binders was used to shape the ceramic specimens and then the dried body sintered at 1270˚C to obtain the dense Raschig rings. The statistical Weibull theory was used to study the compressive strength data distribution. Thereafter, Weibull modules were analyzed by mixture design method. The results show that the maximum reliability is achieved when 0.72 % CMC and 0.27% PVA were added to kaolin.

**Keywords:** Binder, Ceramic Raschig Ring, Mixture Design Method.

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# FRICTION PROPERTIES OF CLAY COMPOUNDS

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Heavy-clay products which made of brick-clay differ from each other in respect of their properties. As the production method is similar it is obvious that the difference is caused by the varying mineral composition. Composition acts not only on properties of products but on production process.

During forming, machines (crusher, extruder...etc) are in continuously connection with clays having different composition and plasticity. It follows from this that dies have a considerable abrasion load and the wear is the result of friction. Beside wear of shaping dies, friction plays an important role in developing extrusion pressure [1]. Friction coefficient is altered by several parameters as moisture and mineral contents, pressure developed in and around the clay body, forming velocity in shaping die, temperature, surface quality...etc.

Some previous works [2] have been examined friction properties of clay minerals with only one component (e.g. pure kaolin-water mixtures) or mined clay [3]. However clay used for production of traditional heavy clay products consist sometimes more than ten components with different features. Opening agents and other pore forming materials are often added to the compound. These materials decrease lamination during extrusion [4] and also have an influence on friction [1,4,5]. Clays were selected with high flake type clay minerals content, opening agents and pore forming materials were added to it. Moisture content was also varied. The investigation was performed on special tribometer up to the flow limit of a compound.

Aims of this study is to examine the effects of technological parameters and different mineral composition (different compounds) on friction coefficient. Results show changes in value of friction coefficient and correlation of examined parameter.

**Keywords:** Clay compounds, Opening agent, Friction coefficient.

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# CORRECTION OF CRITERIA FOR CLAY DRYING SENSITIVITY ON THE BASIS OF BIGOT`S CURVE

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Behavior of ceramic raw material (especially heavy clay) during drying process was one of widely discussed subjects. Method by Frenchmen A. Bigot and V. Badin is mostly in usage. They constructed an instrument which records linear shrinkage as a function of mass loss, which is graphically represented by Bigot`s curve. For a long time this was the only way to group clays on the basis of drying susceptibility, according to the obtained critical point.

New findings in clay drying processes, especially “fast drying” process which is being developed in order to decrease energy consumption, indicate that clay drying criteria must be updated. Drying behavior of different clays which underwent different regimes are presented in this work, by means of traditional Bigot`s curve criteria. Unexpected conclusions are drawn, which are not compatible with sensibility clays criteria: weak susceptibility clays (<7 % humidity in critical point) are inappropriate, while extremely susceptible clays (>10 % humidity in critical point) are adequate for “fast drying” process.

**Keywords:** drying, clay, Bigot`s curve.

# ANALYSIS OF PRE-TREATMENT EFFECTS FOR THE REMOVAL OF TITANOFERROUS IMPURITIES FROM CHINA CLAY BY FROTH FLOTATION

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China clay for paper coating requires high brightness besides other specifications. Ultrafine titanoferrous minerals are detrimental impurities which reduce the brightness of clay. Froth flotation, which is used for the removal of this impurity (titania removal), has been a topic of great interest to many. In 1969 Cundy, for the first time, introduced a high shear energy pre-treatment before flotation and this is continued until today. Though the collector chemistry has been studied well, pre-treatment aspect is ignored. The present study is an attempt towards the same.

Processed Mamuara china clay from India was subjected to pre-treatment at three increasing shear levels (1, 2 and 3) before subjecting to flotation. The feed sample measured a brightness of 83.4%ISO. The 'titania removal' by flotation increased when the 'intensity' (shear rate and shear frequency) and 'time' of pre-treatment are increased. Again, the titania removal was optimum at a particular ratio (3:1) of shear agitation time with the collector (HSC time) and shear agitation time with the dispersant (HSD time). The shear frequency was more influential for titania removal than the shear rate and at higher shear frequencies pre-treatment time and flotation time considerably reduced. It could be shown that the overall effect due to 'shear pre-treatment' is higher that that with 'increased collector dosage'.

A modeling study shows that the experimental data for pre-treatment at shear level 2 and 3 fits the equation $R = Rx\,(1-e^{-kx})$ where, Rx stands for the max. titania removal and k stands for the rate of pre-treatment. Whereas Rx increases with HSC/HSD time ratio for both shear levels, rate of pre-treatment attains a constant value with the increase in HSC/HSD time ratio. Again, Rx values are always greater for shear level 3 than shear level 2 for all the values of HSC/HSD time ratios.

**Keywords**: Titanoferrous minerals, Reverse froth flotation, High shear pre-treatment.

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# INVESTIGATION OF THE CLAY MATURING PROCESS AS BASIS FOR PROPERTY-ENHANCING UTILIZATION AND CONTROL OF MICROBIOLOGICAL REACTIONS

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Although clay maturation is applied intuitively in ceramic industry for hundreds of years, the process is not fully understood yet and far from being controllable. Microbiological activity as well as homogenization of the water surrounding the clay-particles is supposed to be responsible for enhancement of plasticity, but detailed elucidation is still necessary. The first aim of this interdisciplinary research project is therefore to investigate the reactions and processes during aging of clay systematically.

Two model clays (W1, W2 from different deposits in the Westerwald, Germany) with similar chemical composition, but with distinctly different rheological behaviour and plasticity, have been selected for examination of the maturing process. A comprehensive characterization program is carried out over a period of several weeks: qualitative and quantitative changes in chemical, mineralogical, microbiological and technological characteristics of the clays are recorded. Special emphasis is placed upon processing properties: by extrusion on a laboratory vacuum press, parameters such as radial pressure in the pressure head and quality of the extruded product are examined in correlation to maturation time. Furthermore, the structural coherence of the extruded material is analyzed by rheological methods (creep test and amplitude sweep). Variations in pH, conductivity, release of soluble salts, and microbiological activity were also examined within the investigation period.

The results show that comprehensive characterisation, including new methods developed within the project, helps to explain the aging process. Based on the findings of the described investigation program, the second project phase targets at drawing conclusions for quality assurance systems and developing methods to selectively utilize and control these maturation processes.

**Keywords**: clay maturing, characterisation of ceramic masses, plasticity.

# INTRODUCING OF BIMORGH KAOLIN INDUSTRIAL APLICATIONS IN NORTHEAST OF IRAN

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Bimorgh Kaolin mine located in the east of Iran and in Khorassan Razavi province. From geological viewpoint rock exposes in this area consist of Jurassic shale and sandstones, Cretaceous lime stones, Andesite, Basalt, Tuff, Argillite and volcanic breccias with the age of Neogene. Faults in this area have northeast – southwest strike and tectonic activities caused to increasing of alterations in volcanic rocks and forming of Kaolin mineral. Mineralogy and chemical composition of samples investigated by XRD and XRF analysis and have been compared with the similar samples of Halak Abad mine in the east of Iran, Zenoz mine in the west of Iran and Diamond mine in England. Analysis show that amount of silicon oxide in Bimorgh mine is high and is about 70 percent and amount of Aluminum oxide is about 14 percent. Remarkable increasing of SiO2 in chemical composition of Bimorgh and Halak Abad mines in the East of Iran is accompany more with the decreasing of Al2O3 between Zenoz mine in the west of Iran and Diamond mine in England, as average amount of Al2O3 in Bimorgh and Halak Abad Kaolin is 14.23 and 17.77 percent and in Zenoz and Diamond mine is 16.02 and 35.4 percent. Other difference is amount of Titanium oxide in Bimorgh and Halak Abad Kaolin that these amounts are 4.14 and 0.7 percent while this amount is less than 0.05 percent for Zenoz and Diamond mines. This point has been caused to decreasing in decoction color quality of ceramic primary material in Bimorgh and Halak Abad Kaolin. Other difference in chemical composition is Potassium oxide. Potassium oxide has flox role in ceramic productions. Amounts of Potassium oxide in Halak Abad mine is similar to Diamond mine and is about 3 percent and is more than Bimorgh mine (1.96 %) and Zenoz mine (0.12%). This point has been cause to decreasing of deforming in ceramic production in Halak Abad and Diamond mines than Bimorgh and Zenoz mine. Mineralogy comparison of Bimorgh Kaolin and Halak Abad, Zenoz and Diamond mines show that minerals of Bimorgh mine consist of Quartz, Kaolin, Calcite, Montmorionite, Crystobalite and Beidilite and amounts of Kaolin mineral is about 25 percent in Bimorgh mine while this amount is 28 percent in Halak Abad mine, 35 percent in Zenoz and 84 percent in Diamond mine. Super quality of Diamond Kaolin is because of difference in amount of Kaolin mineral than others. Base on physical test best application for Bimorgh Kaolin is using of it in ceramic and tile body.

**Keywords:** Kaolin, Industrial Application, Chemical & Physical Analysis.

# INVESTIGATION OF A LIGHT-WEIGHTED HUMIDITY CONTROLLING MATERIAL WITH MICROCELLULAR PORE STRUCTURE

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Our lifestyles are demanding improved and more comfortable living environments in order to reduce allergic conditions and other technical problems. For instance, symptoms of atopy and asthma are caused by tick and fungi, which grown well in high humidity. Alternatively, a build-up of static electricity occurs in low humidity, which can be harmful to electric devices. Generally, in an attempt to control the relative humidity of our environment, air-conditioning equipment has been used; however, this method has the associated problem of high energy consumption. Therefore, there is a strong need to develop harmless inorganic materials which have humidity control and high water adsorption capacity. Recently, natural inorganic materials such as allophane, sepiolite and diatomite were commercialized due to harmless property and low cost for humidity controlling tile in the building material. In particular, light-weighted materials are of technological interest because of their potential use in building materials that require scale-up in tile size as well as good insulating and noise proof characteristics.
The humidity controlling ceramic materials was developed by applying the phenomena of dew condensation in the capillary. It is said that the humidity range which human feels comfortable is from 40 to 70% in relative humidity. In this study, the ceramic tile using natural soils such as clay, diatomite for interior wall was investigated. This product per one square meter adsorbed and desorbed humidity about 300g. In particular, we had introduced novel processing routes for fabricating microcellular ceramics tile using hollow microsphere as a pore former. The microcellular pores in the humidity controlling ceramic materials showed the superior properties such as light-weight, heat insulation and sound absorption.

**Keywords:** Humidity, Microcellular, Adsorption, Surface area.

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# CHARACTERISATION AND ANALYSIS OF MECHANICAL PROPERTIES VERSUS POROSITY IN CLAY CERAMICS

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Different kinds of ceramics with controlled porous size, shape and spatial arrangement have been realized for this study.

- Some heterogeneously distributed porosity have been realized. Matrix ceramics can be describe as an initial cubic stacking of spheres, before densification. After the sintering, the obtained porosity is then non-spherical, and distributed around the spheres.
- Some homogeneously distributed porosity have been realized. The porosity is constituted of small and spherical pores.
- Some intermediary ceramics are also synthesised. The two previous types of porosity coexist.

A comparative study of mechanicals and thermals properties is proposed based on theses three microstructures, with preexistent modelisations.

- Some mechanical tests on flexural or compressive strength will be analysed relatively to the Ryshkewitch's modelisation and the followings.
- Some thermal tests on thermic conductivity will be analysed relatively to the Hashin and Shtrikman's modelisation and some others.

At the end, a finite element modelisation of porosity impact on material properties will be realised, enlightening the effects of the main factors which leads to the variation of properties with porosity.

**Keywords:** Porosity, Mechanical properties, Thermic properties.

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# FABRICATION AND CHARACTERIZATION OF FLOOR TILES FROM COAL GANGUE AND COAL FLY ASH

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Coal gangue is a kind of solid refuse derived from the mining or processing of coal. It was usually piled up on the ground, which polluted the environment seriously. Some coal gangue is a kind of resource that consists mainly of kaolinite, as well as a few quartz and other minerals. Therefore, this kind of coal gangue was used as the main raw material to prepare the floor tiles in this paper. Powders of coal gangue, coal fly ash, quartz, feldspar and montmorillonite were milled in mixture, pressed into specimens and sintered at different temperatures. The obtained tile samples were characterized by phase composition, microstructure, water absorption, shrinkage on firing, density and strength. It is revealed that the tiles are composed of the glass phase, small amount of quartz and mullite. The water absorption, shrinkage, density and strength of the samples change with the sintering temperature. The optimum physical properties may be obtained in sample sintered at 1180 oC. When the sintering temperature exceeds 1180 °C, the water absorption increases gradually with the sintering temperature increasing, but the shrinkage, density and strength of the samples decreased correspondingly.

**Keywords:** Coal Gangue; Coal fly ash; Wall and Floor Tiles.

# IMPROVING TECHNOLOGICAL PERFORMANCES OF BALL CLAYS: THE CASE-STUDY OF CERAMIC RAW MATERIALS FROM PATAGONIA (ARGENTINA)

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Ceramic industry has known a considerable product and process innovation, that fostered the development of novel typologies and applications implying new technological requirements for ceramic raw materials. The latest innovation in tilemaking is particularly stressing properties like powder flowability, ability to densify during dry pressing and to toughen green tiles. Thus the technological requirements of ball clays are ever stricter in terms of plasticity, dispersion in water, rheological behaviour, workability in the green state, refractoriness and firing colour. This work is aimed at improving the technological performances of conventional ball clays by taking as benchmark the highest quality raw materials on the market. A case study was undertaken on ball clays from Patagonia (Argentina) which offer a wide range of technological behaviour and mineralogical composition. Different clays were selected and the main characteristics in terms of mineralogical and chemical composition, particle size distribution, rheological behaviour, specific surface plasticity, methylene blue index, colour and ceramic behaviour were determined. Appropriate mixtures, designed adding highly plastic materials (rich in expandable clay minerals) to moderately plastic clays were targeted on the benchmark. Porcelain stoneware formulations, containing improved ball clay mixes, were experimented at a laboratory scale, simulating the industrial tilemaking process. Technological properties and behaviour were measured on both semi-finished and finished products and compared with reference bodies made up with the benchmark. The improved ball clays behave in porcelain stoneware bodies like the best raw materials currently utilized, although modest changes of technological behaviour occur in the mechanical properties, water absorption and whiteness of the fired products.

**Keywords:** Improved ball clays, Technological performances, Ceramic behaviour.

# GEOLOGY & GEOCHEMISTRY

## GG1 • BENTONITE: GENESIS, PROPERTIES AND USES

## GG2 • CLAY MINERAL ASSOCIATION OF THE CRETACEOUS - PALEOGENE AND PALEOCENE – EOCENE BOUNDARY EVENTS

## GG3 • CLAY MINERALS AND FLUID FLOW THROUGH FAULTS

## GG4 • CLAY MINERALS & CLIMATE CHANGE

## GG5 • CLAYS IN GEOLOGICAL PROCESSES

# GEOLOGY & GEOCHEMISTRY

## SESSION GG1

## *Bentonite: Genesis, Properties and Uses*

# A K-AR STUDY OF THE PELLIGRINI LAKE BENTONITE (MALARGÜE GROUP), NORTHERN PATAGONIA: CAN THE AGE OF MONTMORILLONITE FORMATION BE DETERMINED?

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We discuss the application of the K-Ar radiogenic isotope technique for determining the age of bentonite formation in the Upper Cretaceous (Malargüe Group) rocks of the Pelligrini Lake, Northern Patagonia. Electron microscopy reveals a mixture of two K-bearing minerals in these samples: an authigenic montmorillonite clay that contains interlayered $Na^+$, $Mg^{2+}$ and $Ca^{2+}$ ions, together with small quantities of $K^+$ and a biotite mica of detrital origin. The calculated age values of 17 clay-sized fractions separated from the bentonite, and associated volcaniclastic shale and pyroclastic ash lithologies, range between 63 to 117 Ma. The ages of these two components can be extrapolated from a K-Ar value versus % montmorillonite linear regression curve. The intercept at 0 % montmorillonite yields a detrital biotite age of ~126 Ma and the 100 % montmorillonite end-member indicates an authigenic age of 63 ± 3 Ma. Based on the mineralogic and isotopic variations, we demonstrate that the original ash was mixed with detritus of the Lower Cretaceous age and that bentonite formation and closure of the isotopic system was complete 4-10 Ma after the age of sedimentation. These relationships imply that the bentonite has successfully remained closed to fluid-rock interaction for the past 63 Ma; a relationship much desired in the construction of clay-based barriers in planned underground radioactive waste deposits.

**Keywords:** Bentonite, Isotopic dating, Genesis.

# RELATIONSHIPS AMONG PEDOGENESIS, MINERAL COMPOSITION, CHEMICAL AND PHYSICAL PROPERTIES OF BENTONITE DEPOSITS IN THE QUAZVIN PLAIN, NW IRAN

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Bentonites are important for numerous industrial applications but their properties vary depending on their genesis. Bentonites of different origins differ in their mineralogy, chemical composition of individual minerals, surface properties, rheology and texture.

The bentonites located in the Quazvin province, in N.W.Iran consist of bentonitised tuff of volcano-sedimentary origin. They are made up of horizontal layers of interbedded epiclastic tuffs with volcanic bentonitised material which have been subjected to hydromagmatic activity. The beds of volcanic ash-tuffs have been devitrified by hydrothermal solutions giving rise to bentonites and sodium-silica-rich residual fluids which have partly crystallized as cristobalite.

Twenty fine bentonite samples (37-56% Mont.) from the Quazvin sediment series with bentonite sites were collected and their mineral composition, particle size distribution, specific surface area, cation exchange capacity, swelling, adsorption and migration rate of different substances were studied.

The results indicate a predominantly meteoric origin of the fluids responsible for the transformation of pyroclastic rocks into bentonites at temperatures ranging from 30 to 90˚C. The contact zone of bentonites affected by highly concentrated saline solution exhibits mineralogical changes. High salinity and high temperature also remarkably influence the technical parameters of bentonites and reduce, for example, the cation exchange capacity or microporosity. We found that some characteristic properties of these bentonites are mainly determined by montmorillonite content but others depend on their origin. The montmorillonite content determines the cation exchange capacity and caesium ion sorption properties.

**Keywords:** Tuffogenic Bentonite, Hydrothermal Solutions, Mineralogical Changes.

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# MINERALOGICAL CHARACTERISATION, ORGANOPHILIZATION AND OIL ABSORPTION PERFORMANCE TEST OF A BRAZILIAN BENTONITE

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The Boa Vista region, Paraíba State of North-eastern Brazil, is by far the largest Brazilian bentonite producer. Mineralogical characterization of the main bentonite types indicate that montmorillonite, quartz and cristobalite are the main minerals, and kaolinite, illite/muscovite, feldspar, anatase, goethite and possibly jarosite may also be identified through X-ay diffraction.

Due to high CEC and surface area – 106 meq/100 g and 94 m$^2$/g, the highest among analysed samples, the “chocolate” bentonite was characterized in detail, and the surface of a fine (< 2 μm) fraction was modified aiming at the removal of organic contaminants from oil production waters.

Chemical analysis, X-ray diffraction, Mössbauer, $^{29}$Si and $^{27}$Al MAS-NMR, and FTIR spectroscopies, as well as DTA/TGA converged to an iron-rich montmorillonite. Its surface was modified by the quaternary ammonium salts DDTMA (dodecyltrimethylammonium chloride) and BTMA (benzyltrimethyl-ammonium chloride).

The effective intercalation of the organic salts was confirmed by the displacement of the 001 XRD reflection, from 15 Å (13 Å after Na homoionization) to 18 Å and 16 Å, respectively after DDTMA and BTMA incorporation, as well as by FTIR, DTG and elemental carbon determination. DDTMA incorporation has been more effective than that of BTMA. Furthermore, $^{13}$C MAS-NMR spectrum of the DDTMA-modified montmorillonite shows only interlayer organic compound (i.e., after short contact time), and none on the surface.

Hydrophobicity and organophillicity of the modified montmorillonite was assayed through contact angle measurement, a novel quick, low-cost and reliable method to measure surface modification performance. The non-modified clay displayed a contact angle of 18° with water, increasing to 59° modified with DDTMA, but of only 30° with petroleum. Less effective intercalation of BTMA allowed the contact angle to increase only to 22° with water, i.e., still quite hydrophillic. Direct absorption measurements confirmed the good performance of the DDTMA-modified clay.

**Keywords:** Organophilization, Iron-rich montmorillonite, Surface modification.

# COMPOSITION AND ORIGIN OF RIO DO RASTO BENTONITE (BAÑADO DE MEDINA QUARRY, URUGUAY)

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Bentonite beds inside the Rio do Rasto Formation (Permian sequence of Paraná Basin) have been described for long time ago. They have been identified in small occurrences distributed in a wide area that extends from South Brazil to North Uruguay. Until now, the knowledge on that material indicated a non economical bentonite associated to discontinuous beds rarely with a metric thickness. This scenario starts to change when boreholes drilled close to Bañado de Medina reveal anomalous and continuous bed of bentonite with thickness until 6.5 meters. Our aim is to present preliminary results in order to study the occurrence, the mineralogy and chemistry of this bentonite and its probable economical applications. Detailed description shows depositional structures and discontinuities that are helpful for explaining the anomalous thickness and also for reconstructing the environment of deposition. The preservation of this bentonite section was related to the existence of normal faults that limit the occurrence and produced vertical movement of blocks, promoting a protection of this bentonite section against subsequent erosion process. The Permian age of the bentonite increases the difficulties to preserve original volcanic textures. The use of detailed petrography by separation of primary minerals, mainly quartz, feldspar and zircon associated to isotopic studies (Sm/Nd in whole rock and U/Pb in zircon) and chemical analysis (trace and rare earth elements) permitted to establish the age and composition of original volcanism, but also to correlate with Gondwanic volcanic events. The Bañado de Medina bentonite displays a high purity and a monomineralic composition, formed by Ca-montmorilonite. Detailed treatments of the montmorilonites through calcium and potassium saturation (clay fraction), followed by X-ray difractometer decomposition in Gaussian and Lorentzian elementary contributions were carried out. Results show Al-montmorilonite and mainly with low charge components. Technological tests involving measure of cation exchange capacity, water adsorption and swelling, expansibility, viscosity and ability to generate organophylic compound will be presented trying to determine the appropriate industrial use of this bentonite.

**Keywords:** Bentonite, Bañado de Medina, Uruguay.

# BONDING OF AFLATOXIN $B_1$ TO SMECTITE

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Aflatoxin $B_1$ ($AfB_1$) is the most potent carcinogenic, hepatotoxic, teratogenic, and mutagenetic aflatoxin produced by the *Aspergillus flavus* and *A. parasitcus* fungi. Since the finding of its toxicity to animals and humans in the 1960's, significant efforts have been made to prevent the growth of the molds during crop growth, harvest, and storage. The occurrence of aflatoxins, however, appears to be unavoidable due to drought or poor storage conditions. Several remedy or management strategies have been implemented to reduce or to eliminate the toxicity of aflatoxins in animal feed. Using clay minerals, particularly natural smectite-rich bentonite, it has been demonstrated that it is an effective and economic way to reduce the toxicity in numerous animal trials. Studies of using clays in human diet to alleviate aflatoxicosis have started in the last three years. The results from animal feed and human diet trials suggest that using clay in the contaminated feed or diet is promising. It also suggests that a thorough understanding of the reaction between the toxin and the clay minerals is needed. This is not only important for selecting appropriate clays or to modify clays as binders but also to understand the physiology of the toxin and clays after ingestion. The objective of this study is to reveal the bonding mechanism of aflatoxin $B_1$ to smectite. The <2 μm clay fraction of a bentonite from Gonzales, Texas, USA was separated and used in the study. Smectite (montmorillonite) is the major mineral in this fraction. A minor amount of opaline-CT is present as well. Two aflatoxin B1-smectite complexes were prepared in acetonitrile and water respectively. Intercalation of aflatoxin B1 into smectite occurred in the complex prepared in water. The aflatoxin-smectite complexes were saturated with $Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Al^{3+}$, $La^{3+}$, $Mn^{2+}$, $Ni^{2+}$, or $Cu^{2+}$. After removing excess salts from the suspensions by washing with water, the complexes were dried on ZnS discs and their infrared spectra were recorded with a 1 $cm^{-1}$ resolution. The infrared bands of smectite did not shift after adsorbing aflatoxin $B_1$. On the contrary, the in-phase vibrations of the dicarbonyl bonds of aflatoxin $B_1$ showed a greater than 26-$cm^{-1}$ shift from 1750 $cm^{-1}$ in pure aflatoxin to 1723 $cm^{-1}$ in the complexes. Furthermore, this shift was affected by the exchangeable cations: from the monovalent cations $Na^+$- and $K^+$-saturated complexes to the transition heavy metal $Ni^{2+}$- and $Cu^{2+}$- saturated complexes, the carbonyl band shifted from 1734 $cm^{-1}$ to 1685 $cm^{-1}$, i.e., a nearly 50-$cm^{-1}$ shift. The shifts suggest that the transition metal cations weakened the carbonyl bond more than the monovalent cations did. We conclude that the major bonding mechanism in the adsorption of aflatoxin $B_1$ to smectite is the ion-dipole interaction and coordination between the exchangeable cations and the carbonyl groups of aflatoxin $B_1$.

**Keywords:** Aflatoxin $B_1$, Smectite, Bonding.

# EXCHANGEABLE CA$^{2+}$ OF GYPSIFEROUS BENTONITE

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The performance of bentonite buffers is of interest in case of disposal of high level radioactive waste (HLRW). Models are used to understand transport processes; however, these models require input data of exchangeable cations which are frequently affected by dissolution of soluble minerals in the bentonites. One of the challenges is the occurrence of gypsum, which is present e.g. in MX 80.

Three new methods were tested all based on typical CEC complexes. The complex solutions were pre-saturated with respect to calcite and gypsum since both minerals frequently occur in gypsiferous bentonites and the methods were called Cu-trien$_{\mathbf{5xCcGp}}$, CoHex$_{\mathbf{CcGp}}$ and AgTU$_{\mathbf{CcGp}}$. Six bentonites (all calcareous, three of them also gypsiferous with gypsum concentrations of < 1 wt%), a Greek bentonite without these soluble Ca-minerals, admixtures of this Greek bentonite with additional calcite and/or gypsum, and a pure calcite were used to test the methods. The exchange solutions were added to sample powders in batch experiments of 2 h each, followed by centrifugation and dilution of the clear supernatant for ICP analysis.

Results show that the reference values of the non gypsiferous bentonites could not be found by any of these new methods. One reason is of course the very high starting concentration of Ca$^{2+}$ in the solutions which increases scattering. Plausible values for exchangeable Ca$^{2+}$ values of gypsiferous clays can be obtained by a combination of two separate results: 1) calcite saturation (e.g. AgTU$_{\mathbf{calcite}}$, Dohrmann, 2006) and 2) quantification of gypsum (e.g. by combination of Rietveld refinement using the AutoQuan® and the smectite model of Ufer et al. (2008) and elemental sulphur analysis for verification of small gypsum concentrations).

Result 1) is free of error caused by calcite dissolution; however it is still wrong because it contains a lot of Ca$^{2+}$ from gypsum dissolution. Result 2) is used to subtract the theoretical Ca$^{2+}$ portion of gypsum from result 1) assuming that gypsum is completely dissolved during the exchange experiment. This is believed to be a realistic assumption because gypsum is approximately 10 times more soluble in e.g. AgTU than calcite.

Using this combined procedure the sum of exchangeable cations is very close to the CEC (within < 5 %) which is a satisfying step forward. The resulting Ca$^{2+}$ saturation (in % Ca/CEC) of the three bentonites ranges from 1-46 % and there is no clear correlation with calcite or gypsum content or with exchangeable cations.

**Keywords**: Bentonite, Exchangeable Ca$^{2+}$, Gypsum saturation.

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# QUARTZ CRYSTAL SIZE DISTRIBUTION OF THE ORDOVICIAN MILLBRIG K-BENTONITE

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Crystal size distribution (CSD) analysis has been applied to quartz crystals of the Ordovician Millbrig K-bentonite, which represents one of the largest known fallout ash deposits in the Phanerozoic Era, to establish crystal growth histories and conditions in the magma chamber prior to eruption. Specific CSDs were examined for crystal growth conditions. All Millbrig samples exhibit lognormal concave-down shapes in agreement with previously reported CSDs on large silicic systems but in contrast to more mafic systems characterized by linear CSDs. Concave down CSDs are possibly an intrinsic property of phenocryst growth in large volume silicic magmas as documented in the literature (Bindeman, 2003). Quartz crystals of the Millbrig must have been produced by surface-controlled, size-dependent growth with a minor Ostwald ripening component, which could have easily changed to supply controlled growth due to a limited supply of nutrients, as the crystals grew larger. CSDs were also used to examine the possible origin of multiple ash beds in the Millbrig. These ash beds appear to be a product of a series of separate eruptions that represent separate magma layers or batches, each with slightly different crystal growth conditions.

**Keywords:** K-bentonite, crystal size distribution, Millbrig.

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# CHARACTERIZATION OF BENTONITE CLAYS OF BOA VISTA (BRAZIL)

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In Northeastern part of Brazil, surrounding the locality of Boa Vista (Paraíba State) there are several bentonite quarries which constitute the most important deposits of Brazil. Mineralogical studies involving the most significant occurrences account for the dominant presence of smectite and kaolinite, followed by feldspar and silica minerals as quartz and cristobalite. In general, in this region, bentonite profiles have as substratum granite gneiss rocks or sandstones normally with ferrification or volcanic rocks covered by bentonitic clays, partially reworked by an upper siliciclastic fluvio lacustrine sequence. In some places, the top of the profile is covered by volcanic rocks and volcanic agglomerates. The recognition of volcanic material (breccia, lava flows and loose or welded glass fragments) in the same profile where bentonite is found corroborate to a straight genetic relationship between clays and volcanism in Boa Vista bentonite. In some places bentonite is associated to an intermediate geomorphological surface, between an older one that is in the top of the area and the recent base erosion level. Inside this intermediate surface it is possible to find erratic agate blocks with at least 30 cm of diameter. Detailed studies of clay samples saturated with magnesium indicate that the smectite is a Ca-montmorilonite with a basal spacing of 15Å (air dried) that expands to 17Å (solvated with ethylene glycol) and 060 reflection near 1,490 Å (dioctahedral type). This smectite is pure, without any evidence of interstratified and vermiculite. By infrared spectroscopy, samples from Cubati occurrence show the presence of dickite, a kaolin mineral that suggests the alteration under the influence of warm water. Considering the association of these clays with volcanic material, with large lateral spread of clay horizons and the purity of the Ca-montmorilonite composition, make acceptable a model to these clays as originated by alteration in situ of ash and tuffs in terrain depressions with interstitial water warmed by the Tertiary magmatism. The main episode of bentonitic alteration is associated directly with volcanic rocks, which belong to Tertiary (Miocene to Oligocene). It is possible to correlate magmatism type and bentonite using information about primary minerals distribution and the concentration of rare earth and trace elements. Additionally, characterization of the high and low charge nature of montmorilonite will be discussed and the relationship of the capacity of exchange cations and technological properties.

**Keywords:** bentonite, Boa Vista, Brazil.

# MINERALOGY, PETROGRAPHY AND GEOCHEMISTRY OF THE FAXINAL COALFIELD TONSTEIN, AN ALTERED VOLCANIC-ASH LAYER

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Mineralogical, petrographic and geochemical analyses were performed in a tonstein layer interbedded with coal seams in the Faxinal coalfield, Rio Grande do Sul, Brazil. The integrated interpretation of the results indicates a volcanic origin for this kaolinitic claystone bed. The studied tonstein is an almost monomineralic rock, composed essentially of highly crystalline authigenic kaolinite. Scattered in the kaolinitic mass, primary pyroclastic minerals occur, including euhedral beta-quartz paramorphs and quartz splinters, idiomorphic zircons, apatite, allanite, and sanidine pseudomorphs, as well as large kaolinite "accordions" generated by replacement and expansion of mica flakes (Simas, 2008). These are considered as a restricted suite of volcanic minerals which were preserved during diagenesis. The primary minerals and the geochemical characteristics of low-mobility elements indicate a rhyodacitic to rhyolitic ash composition, and the field relations indicate a volcanic air-fall origin, similar to that of the Candiota coalfield tonsteins (Formoso et al., 1999). The tonsteins interbedded in coal seams indicate episodes of tephra sedimentation during the deposition of the Lower Permian (Sakmarian) coal-bearing sequence in the southern Paraná Basin (Guerra-Sommer et al., 2008 a,b).

**Keywords:** Faxinal and Candiota Tonsteins, High crystallinity Kaolinite, Volcanic air-fall origin, Lower Permian of Paraná Basin.

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# BENTONITE OCCURENCES IN NEW SOUTH WALES, AUSTRALIA

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New South Wales, Australia, has widespread occurrences of bentonite that are exploited for use in domestic markets including civil engineering applications, foundries, pet litter, stock feed and soil improvement. Bentonite deposits of commercial importance principally occur near Scone, north eastern New South Wales, and at Arumpo, south western New South Wales. Total production from these sources in recent years has been about 30,000 tonnes per annum.

Although there are numerous bentonite deposits, they are currently economic to mine at only a few places. At Arumpo, high purity Na-Mg bentonite resources exceeding 70 million tonnes have been identified in the Pliocene Loxton-Parilla Sands in the Cainozoic Murray Basin. The Permian Singleton Coal Measures, in the north western part of the Sydney-Gunnedah Basin, has extensive deposits of mainly Ca-Mg bentonite. The most important deposit, Cressfield, near Scone, has bentonite resources of several million tonnes.

Specific weathering and redepositional processes involved in bentonite formation are poorly understood. Apart from ash composition, waters of varying salinity appear to primarily control bentonite evolution. Distinctive Na-Mg bentonite occurrences at Arumpo developed in marginal marine settings containing saline to brackish waters. In contrast, the Sydney-Gunnedah Basin has Ca-Mg bentonite deposits that formed in mainly alluvial environments.

**Keywords:** Bentonite, Scone, Arumpo.

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# GEOLOGY & GEOCHEMISTRY

## SESSION GG2

## *Clay Mineral Association of the Cretaceous - Paleogene and Paleocene – Eocene Boundary Events*

# MINERALOGICAL SHIFTS AT THE PALEOCENE-EOCENE THERMAL MAXIMUM (PETM) EVENT, SVALBARD

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Two sections of the Paleocene – Eocene succession of Svalbard have been analysed sedimentologically, mineralogically and micropaleontologically in this study, which is a part of the long term pACE (paleo Arctic Climate and Environments) project. The pACE is aiming at reconstruction of important changes in Arctic paleoenvironmental and paleoclimatic conditions during the Paleocene-Eocene greenhouse episode and the subsequent transition to Eocene-to-modern icehouse conditions (~ 55-40 million years ago). (http://www.wun.ac.uk/pACE/index.html).

The studied shallow marine, siliciclastic, succession displays a transition from delta plain through nearshore/inner shelf to outer shelf settings, across the Paleocene – Eocene transition. The Paleocene part of the successions is dominated by sandstones and siltstones, while claystones are the dominate lithology in the about 520 m thick Eocene succession. Biofacies analyses and carbonate starvation suggest basin-wide brackish water conditions during deposition of the whole succession.

The clay mineralogical changes across the boundary has been analysed in detail and they may reflect both original variations in the source rocks, climatic effects, grain size-controlled variations or be the result of diagenetic and weathering reactions. The shift towards finer grained, more kaolinite-rich sediments from Paleocene and into the Eocene will be discussed.

**Keywords:** PETM, Mineralogy, Svalbard.

# PRESERVATION OF ORGANIC CARBON WITHIN THE INTERLAYER SITES OF SMECTITE WITHIN MILLINEAL SCALE CYCLES OF A CRETACEOUS OAE

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Continental margin sediments constitute the dominant sink of organic carbon resulting from the interface of terrestrial and marine processes and facilitated by accommodation space. Here we show the importance of terrestrial processes sensitive to rapid shifts in continental climate strongly influencing burial of organic carbon and the associated development of ocean anoxia in a Late Cretaceous (Coniacian "oceanic anoxic event 3") black shale from a deep water setting in the tropical Atlantic. Sediments recovered from ODP 959 from West Africa document a systematic variation of mineralogical feedback between continental climate change, redox change across the entire water column and organic carbon preservation and burial in deep water sediments in the middle Cretaceous tropical Atlantic.

TOC up to 16% developed repetitive cycles over meter scales of the core coinciding with movement of the intertropical convergence zone (ITCZ) on precessional time scales (~22 kys) (Beckmann et al., 2005) and associated freshwater and nutrient runoff from tropical Africa. We analyzed clay mineral composition in four of these cycles at cm scale and observe a strong relation ($r=0.81$; $n=105$) between TOC and the concentration of 2:1 (smectite) clay minerals in the sediment. This relation suggests a control of organic enrichment by clay minerals over these abrupt changes in TOC as occurs in modern continental margin sediments through organic carbon preservation by mineral surfaces. Since the detrital clay minerals in these sediments are a product of terrestrial weathering conditions, the mineral surface preservation provides a direct link between organic carbon preservation in marine sediments and changes in hydrology and soil formation on land that track changing climate. Changes in terrestrial soil forming conditions in tropical west Africa during the late Cretaceous thus affected a strong influence on organic carbon burial patterns in deep water Atlantic sediments and provide evidence of a strong continental feedback between terrestrial climate change and carbon burial.

**Keywords:** Smectite, Cretaceous black shale, Paleoclimate.

# CLAY MINERALS OF THE CRETACEOUS AND PALEOGENE SEDIMENTS FROM THE LOMONOSOV RIDGE, ARCTIC OCEAN (BASED ON IODP-302 DATA)

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Deposition of sediments in the Arctic Ocean is strongly influenced by the worldwide climate changes. This work is based on a detailed study of the clay fraction (<2 mkm) of sediments collected during the IODP Leg 302 (ACEX) on the Lomonosov Ridge. This work is focused on the sediments from the bottom part of the core M0004A, deposited from Cretaceous to Eocene time. The following methods were used: X-Ray diffraction, infrared spectroscopy, thermal analysis, scan electron microscope, chemical analysis. Sediments formed in different climatic conditions are characterized by specific composition of clay fraction. Illite-tobelite-smectite mixed-layered clay minerals were found by the XRD modelling in SYBILA software at the Cretaceous sediments. This mineral variety can indicate a possible oil and gas potential (Drits et al., 2002) of the Arctic Cretaceous sedimentary rocks. Smectite predominants in warm periods of Paleocene and Eocene time. Neritic (coastal) environments at the PETM were changed to lagoon and freshwater channels conditions at Eocene time. Sediments at the 48.5-48.8 Ma are characterized by the presence of unique Azola species (Brinkhuis et al., 2006). Ordered di-octahedral Na-smectite, predominated in the sediments, was formed as in-situ transformation of ash or volcanic-clastic material which was probably delivered to ACEX site from the Svalbard. Temperature at the Arctic Ocean was decreasing after termination of Azola phase and first seasonal ices might be appeared since 44 Ma (Moran et al., 2006). It's indicated by extremely changes in smectite contents. Smectite material could be transported into sedimentary basin by the surface currents which were blocked during periods of seasonal short-lived ices. After a long hiatus (44 22 Ma) ice conditions became dominated in Arctic. This work was supported by grant of the President of Russian Federation for young scientists MK-2780.2008.5

**Keywords:** Arctic Ocean, IODP-302, Cretaceous-Paleocene sediments, Source of clay minerals

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# ENVIRONMENTAL AND CLIMATIC CONDITIONS ACROSS CRETACEOUS-TERTIARY TRANSITION IN THE CAUVERY BASIN, SOUTH INDIA: EVIDENCES FROM CLAY AND BULK MINERALOGICAL DATA

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The close of Mesozoic era marks the beginning of an eventful phase in the geological history in terms of global climatic deterioration that left imprints on faunal and floral distribution and on the sedimentary deposits and established an abrupt boundary separating the Cretaceous from the Tertiary virtually everywhere in the global stratigraphic record. The presence of abrupt $\delta^{18}$O and $\delta^{13}$C changes associated with the K/T boundary at number of localities found to be precede the K/T boundary as defined by the worldwide iridium anomaly. These anomalies raise questions on the relative timing of biotic and isotopic events near the K/T boundary and their relevance to the impact scenario.

The Upper Cretaceous-Paleocene succession is exposed in the Ariyalur-Pondicherry depression of the Cauvery basin, South India. Previous studies document the occurrences of strontium, Ba, and stable isotope anomalies that predate the KTB. A composite stratigraphic profile representing a continuous stratigraphic record of Maastrichtian-Danian strata was constructed by Systematic field mapping. Twenty four (24) rock samples were analyzed for strontium isotope, stable isotopes, major and trace elements and clay mineralogy. Both mineralogical, geochemical and isotopic data are utilized as a supportive evidence to the interpretations on bulk and clay mineralogy.

Calcite and quartz are the dominant minerals identified in these siliciclastic and carbonate deposits and followed by the presence of clay and detrital minerals in the order of decreasing abundance viz., species of Ca, Na, Illite - montmorillionite, illite, kaolinite, smectite-kaolinite and smectite. Albite, beryl, biotite, Ca-flouroapatite, grossularite, muscovite, orthoclase, and topaz. Presence of unaltered mineral species of these indicates lesser or absence of chemical weathering, proximity to source rock and quick burial in the depocenter. Dolomite identified in association with carbonate deposits suggest secondary in origin. Occurrences of goethite, limonite, and siderite suggesting siliciclastic deposits being deposited in flood plains and coastal plains with the prevalence of dry hot climate that promoted oxidation of Fe and precipitation as iron oxides. Analysis of stratigraphic variations of mineralogical composition of the studied section confirms the interpretations on sedimentary history of the area deduced through facies analysis and study of geochemical and isotopic profiles.

**Keywords :** K/T boundary, Siliciclastic, Meteoric-phereatic.

# COSMOGENIC NI IN THE CRETACEOUS-PALEOGENE BOUNDARY CLAY AT BLAKE NOSE (NW ATLANTIC)

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The Cretaceous-Paleogene boundary (KPB) sequence at Blake Nose Plateau recovered by Ocean Drilling Project (ODP) Leg 171B (site 1049, hole A, core 17X, section 2) contains the biogenic calcite-poor spherule-rich bed marking a late Cretaceous asteroid impact. The nature and geochemical composition of this bed imply that it originated mainly from the target rocks of the Chicxulub impact site (Yucatan Peninsula, Mexico), the site of the presumed asteroid impact.

Mineralogical analyses reveal that the carbonate-free fraction of the spherule bed is mainly (>95 %) composed of (cheto-type) dioctahedral smectite. In the layers below and above the spherule bed, the predominant clays are smectite, illite and kaolinite.

Ni in the whole-rock smectite samples and their carbonate/smectite fractions of the samples studied was analyzed by inductively coupled plasma-optical emission spectrometry. The spherule bed shows strongly enhanced concentrations of Ni within the calcite fraction (up to 165 ppm) and the smectite concentrate (up to 300 ppm).

We reason that these Ni enrichments represent the sudden and rapid airfall of high cosmogenic Ni into ocean surface on Blake Nose Plateau. The source of the metal was probably the Chicxulub impacting (carbonaceous) C1chondrite-type body (CM2).

**Keywords**: Cretaceous-Paleogene, Blake Nose, nickel.

# FALLOUT AND BOUNDARY CLAY OF THE CRETACEOUS/PALEOGENE (K/T) BOUNDARIES OF CARAVACA (SPAIN), CERBARA (ITALY) AND BJALA (BULGARIA)

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The impact of Chicxulub, Yucatan (Mexico) was a global event having a short-time and a long-time component, i.e. fallout and boundary clay (Eder & Preisinger, 1987). The fallout is characterized by iridium, spherules, glasses, shocked quartz, and Ni, Cr-rich magnesia-ferrite spinels etched by sulfuric acid during its flight. The amount of sediment and its distribution are dependent on the distance from the impact crater. The well analyzed Cretaceous/Paleogene (K/T) boundaries Caravaca, Cerbara and Bjala are situated at different distances from the impact crater: ~ 7400 km, ~ 8800 km and ~ 9800 km, respectively. Through earth rotation the analyzed samples lie along circle segments from Chicxulub to Caravaca, Cerbara and Bjala indicating the ejecta of a single impact. The boundary clay is characterized by transported minerals like quartz and feldspars, authigenically formed minerals like smectite, as well as biominerals like Mg-calcite and greigite ($Fe_3S_4$). The samples were analyzed by scanning X-ray diffraction (Bruker Analytical X-ray System) and scanning electronic microscopy (XL30, ESEM-Philips), neutron activation analysis, $\delta^{13}C$ and $\delta^{18}O$ analyses, and the nannofossils and foraminifera contents. The K/T boundary of Bjala and the partially reworked depositions lying in CHRON 29R will be discussed in detail. The study of this K/T-boundary with high resolution scanning X-ray diffraction in combination with scanning electron microscopy reveals the chronological sequence of the K/T-event in the fallout as well as in the boundary clay. The spherules settled before the iridium peak and glasses reacted to smectite. Partially etched single crystals of Ni, Cr-rich magnesia-ferrite spinels in connection with the determination of iridium by neutron activation analysis indicate when and where the formation of the spinel took place. The biomineralization of sulfate-reducing bacteria by greigite gave us information about the duration of the sulfuric acid rain. The reoccurrence of algae led to the formation of Mg-Calcite in the boundary clay and indicated the end of the K/T event.

**Keywords**: K/T-boundary, Fallout, Boundary clay.

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# THE REDDISH "IMPACT" LAYER OF THE BASAL FISH CLAY AT CRETACEOUS-PALEOGENE BOUNDARY, HØJERUP (STEVNS KLINT, DENMARK)

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*Abstract***. –** The marine-shallow Cretaceous–Paleogene boundary section at Højerup-Fish Clay consists of a very thin reddish smectite-rich carbonate-poor ("impact") layer overlain by a black marl. Similar reddish layers are found in the shallow-marine boundary sections at Agost in Spain and El Kef in Tunisia. The deposition of the "impact" layers at Højerup, Agost and El Kef occurred simultaneously and lasted for several decades to a century at most. Smectites of the "impact" layers of the boundary sections at these three locations are probably detrital and redeposited from adjacent coastal areas. Conceivably, a small part of these smectites is authigenic and derived from the nano-size glasses. The microspherules and nano-size glasses of the "impact" layer at Højerup are likely reworked and redeposited at or near the Cretaceous-Paleogene boundary simultaneously with smectite.

**Key words:** Cretaceous-Paleogene, Fish Clay, Impact layer.

# HE CRETACEOUS-PALEOGENE BOUNDARY CLAY BEDS IN THE WORLD OCEANS: EVIDENCE FOR THE GLOBAL ACIDIFICATION OF OCEAN SURFACE

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The Cretaceous-Paleogene boundary (KPB) represents one of the most dramatic turnovers in the fossil record for marine calcareous plankton (mainly coccolithophores and foraminifera) that formed calcite deposits that gave the Cretaceous name. In the world oceans more than 90 % of calcareous plankton was extinguished at that boundary; this mass extinction appears to have been sudden and inevitably led to the catastrophic collapse of the whole oceanic life.

The KPB sections of the deep- and shallow-marine settings throughout the world are characterized by a relatively thick biogenic calcite depleted/clay-rich interval, so-called the boundary clay. Various paleontological, mineralogical and geochemical data as well geological data all apparently support a genetic relationship between the deposition of this clay and the asteroidal impact at Chicxulub (Yucatan Peninsula, Mexico).

Because the impact target at Chicxulub is a predominantly carbonate-rich marine sedimentary rock combined with some minor sedimentary anhydrite (calcium sulfate), an immense amount of acid-forming gas $CO_2$ was instantaneously released into the atmosphere accompanied with lesser amount of another acid-forming gas $SO_2$. According to theory, the massive amount of impact-derived atmospheric $CO_2$ would accumulate globally in ocean surface, since this gas enters ocean water by air-ocean exchange. The net geochemical effect of this accumulation would be a decrease of the ocean surface pH (leading to an “acidification”) and $CaCO_3$ saturation state, causing primarily a large decline in $CaCO_3$ precipitation induced by calcareous plankton. In my opinion, the excessive impact-generated $CO_2$ in the atmosphere was perhaps a critical factor in forming the boundary clays at deep- and shallow-marine sites worldwide. If this is a true, then experimental data and observations would indicate that the impact-released $CO_2$ accompanied by the acidification of ocean surface/$CaCO_3$ undersaturation lasted only a few decades at most.

**Keywords:** Cretaceous-Paleogene, boundary clay, global acidification

# GIGANTIC BIOGENIC MAGNETITE IN BOUNDARY CLAYS AT THE PALEOCENE-EOCENE THERMAL MAXIMUM

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Clay-rich sediments of the Paleocene-Eocene boundary contain important evidence of a 100- to 200-ky interval of atmospheric and oceanic perturbations that resulted in 5-9oC abrupt global warming also known as Paleocene-Eocene Thermal Maximum (PETM). The discovery of exceptionally large biogenic magnetite crystals in kaolinite-rich clay sediments from the boundary clay in a borehole at Ancora, N.J., sheds some light on environmental conditions during the PETM. These sediments were deposited at subtropical paleolatitude in the Atlantic Coastal Plain of New Jersey. Aside from abundant bacterial magnetofossils, electron microscopy reveals novel spearhead-like and spindle-like magnetite crystals up to 4 µm long (eight times larger than magnetite produced by magnetotactic bacteria) and elongated hexaoctahedra up to 1.4 µm long. Similar to magnetite produced by magnetotactic bacteria, these single-crystal particles exhibit chemical composition and lattice perfection consistent with a biogenic origin. The oxygen isotopic composition of individual particles also supports a low temperature aquatic origin. Electron holography indicates single-domain magnetization despite the large crystal size. In a few cases we observed apparently intact, tip-outward spherical assemblages of spearhead-like particles that possibly represent the preserved original biological arrangement of these crystals in a hitherto unknown magnetite producing organism. We suggest that the development of a thick suboxic zone with high iron bioavailability – a product of dramatic changes in weathering and sedimentation patterns driven by severe global warming - resulted in diversification of magnetite-forming organisms, likely including eukaryotes.

**Keywords:** Biomineralization, PETM clay, Magnetofossils.

# CLAY MINERALOGICAL VARIATIONS IN THE BOLE HORIZONS FROM THE EASTERN DECCAN VOLCANIC PROVINCE: DURATION OF DECCAN VOLCANISM AND K/Pg BOUNDARY

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The Deccan Traps in India record vast accumulations of basaltic eruptions over a short time span, straddling Cretaceous/Palaeogene boundary (KPg, age ca. 65 Ma), coeval with an interval of global environmental changes and a major contributor to the K/Pg mass extinction. The clay minerals associated with intra-volcanic bole horizons of varied colors were analyzed, their relative abundance group these bole horizons into seven distinctive groups. The lower succession is dominated by dioctahedral iron rich montmorillonite, formed under alkaline conditions with alternate wet and long interval of dry seasons. The mixed layer clays predominate in the middle succession, formed by transformation of montmorillonite under cold or temperate climate. The halloysite is formed by the alteration of Mg poor volcanic glasses under conditions similar to montmorillonite with more humidity. The presence of palygorskite and montmorillonite at two stratigraphic levels (top of 5th and 21st lava flows), suggest prevalence of arid climate. The kaolinite found in the upper sequence (above 25th lava flows), indicates a warm, humid, tropical or subtropical climate towards waning stage of Deccan volcanism. Clay minerals show distinct microstructures and microaggregates. The smectite associated with these boles is rich in iron content. Most of these clays are dioctahedral type, show balance between net layer and interlayer charges. The interstratified illite-smectite (I/S) mixed layers containing variable proportions of montmorillonite. Illite contains sheet-like, well oriented microaggregates. The parallel stacks of chlorite sheets show chlorite/smectite (C/S) mixed layers. Progressive enrichment of Fe and depletion of Al ions with the advancement of kaolinization process is observed. High order of structural and compositional maturity observed in these bole clays, indicate long a hiatus between the two volcanic episodes.Translating the production time estimates of clays associated with the 21 bole horizons, it is assessed that the minimum time required for their development would be approximately 5.34 my. The cyclic changes in the climate, favouring longer duration of volcanic activity. Late Maastrichtian Lameta beds post-date Deccan volcanism to 70 Ma or earlier to this. Considering the formation of bole clays in terms of time, it is possible that the volcanic activity started much earlier in the late Maastrichtian, continued after 65 Ma or or even later, supporting longer duration of Deccan volcanism and consistent with the geomagnetic polarity timescale.

**Keywords:** Deccan volcanism, Intra-volcanic bole horizons, Clay minerals.

# GEOLOGY & GEOCHEMISTRY

## SESSION GG3

## *Clay Minerals and Fluid Flow through Faults*

# CLAYS AND CLAY MINERALS AS MARKERS OF FAULTS ACTIVITY IN GEOLOGICAL SYSTEMS

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Clays and clay minerals are of the greatest importance for the study of faults because of their impact on strain, rupture, fluid circulation and water-rock interactions over a large range of time-space scale. A significant part of the “message” recorded within clays and clay minerals can be read using a multi-scale approach which combines structural, textural and crystal-chemical- methods.

At the nanometer scale, crystal-chemistry records $P/T/\mu_x$ conditions under which crystallized clay minerals in response to chemical disequilibrium between percolating fluids and minerals. At the same scale, radiation induced defects which persist in the structure of clay mineral record past circulation of radio-elements bearing fluids and confirm the potential of clay mineral as natural dosimeter. Variations of structural and textural properties (morphology of particles, type of layer staking, polytype…) of the illites (10 – 1000 nm) related to fault controlled circulations of fluids result from nucleation/growth kinetics and may be indicative of a change in the flow regime, and/or a change of saturation state of the infiltrating solution vs illite. At a larger scale (1 – 100 µm), the arrangement of clay aggregates within fault gouge (texture of a clay matrix), depends on the shear intensity which controls the textural anisotropy of clay. In its turn, the textural anisotropy partly conditions the permeability tensor within the fault, assisting the flow parallel to the fault plane. At the scale of the textural heterogeneities (spatial arrangement of clay matrix and clasts, 1 mm to 10 cm), the porosity distribution of clay cements determines the connectivity of transport paths along the fault plane. Fluid pressure distribution along these paths regulates also the mechanical disequilibria which are responsible of seismic activity. These complexes paths can be visualised ought to new techniques of rock impregnation by resins such as $^{14}C$ or $^{3}H$ labeled MethylMethAcrylate (in situ or laboratory). Advection/diffusion transport of solutes within these paths is retarded by lateral diffusion within the rock matrix porosity producing long terms fluid/mineral disequilibria around fault which form clay-rich alteration halos (scale 1 cm – > 1 m). At the field scale, past circulations of fluids related to fault activity led to typical zoned patterns of alteration in the hosted geological formations. The observed change of clay mineralogy in such fault systems depends on the variation of both $P/T/\mu_x$ conditions and fluid/rock ratio with increasing distance from the major flow channels.

# CHANGES IN SEAL CAPACITY OF FRACTURED CLAYSTONE CAPROCKS INDUCED BY DISSOLVED AND GASEOUS $CO_2$ SEEPAGE

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Claystone caprocks are often the ultimate seal for $CO_2$ underground storage when residual $CO_2$ gas reaches the reservoir top due to buoyancy. Permeability changes of a fractured claystone due to seepage of $CO_2$-enriched brine and water vapor-saturated $CO_2$ gas are investigated. Results show that brine flow induces a large porosity increase (up to 50 %) in the vicinity of the fracture due to dissolution of calcite and quartz, while permeability remains unchanged. Conversely, cyclic flows of $CO_2$-brine and $CO_2$-gas increase the fracture aperture abruptly after each gas flow period, producing a progressive decrease of the caprock seal capacity. Aperture increase is controlled by decohesion of the clay framework within a micrometer-scale-thick layer induced by $CO_2$-gas acidification. Results show that hydraulic aperture increases linearly with duration of the preceding $CO_2$-brine flow period, emphasizing the kinetic control of the quartz grains dissolution during the brine flow periods.

**Keywords**: $CO_2$ storage, Fractured claystone, Dissolution, Permeability.

# TERTIARY TECTONICS OF NORTH-WESTERN SARDINIA AND ITS BEARING ON KAOLIN DEPOSITS GENESIS

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The north-western part of Sardinia experienced widespread calc-alkaline volcanic activity, embracing the Oligocene and part of Miocene. This volcanism is related to the subduction of insubric oceanic crust beneath the south European palaeomargin (Downes et al., 2001). It generated thick volcanic and volcano-sedimentary sequences ranging in composition from basalt to rhyolite. The arc-related geodynamic context favoured hydrothermal alteration strongly controlled by faulting.

The role of district-scale brittle tectonics in the formation of hydrothermal deposits in NW Sardinia has not been investigated; despite, along with lithological factors, it acts as a prime controlling factor (Sibson, 2003). District-scale fault systems allow the formation of a plumbing network, which ties deep structural levels with near-surface horizons, where epithermal alteration and related deposits form, depending on the composition of the protolith and on its primary and acquired porosity (Neubauer et al., 2005).

A number of Neogene hydrothermal kaolin deposits in the district of Romana (NW Sardinia) have been studied focussing on their tectonic context, their structural setting, compositional, lithological and stratigraphical features of the parent rocks.

Faults related to the Miocene tectonics controlled the cyclic hydrothermal systems that led to four different types of kaolin deposits differing both in shape and composition. Such variety depends on the lithology of the parent rock and on the fault array which controlled cyclic hydrothermal system. The wider deposits generated in correspondence of, fault controlled, repeated hydrothermal eruptions that enhanced the fluid-rock interaction.

**Keywords:** Kaolin, Hydrothermal eruption, Sardinia.

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# CLAY NANO-COATINGS AND THEIR ROLE IN FAULT-CREEP ACTIVITY ON THE SAN ANDREAS FAULT AT THE SAFOD DRILLHOLE IN PARKFIELD, CALIFORNIA

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The San Andreas Fault Observatory at Depth (SAFOD) drill-site situated near Parkfield, California offers the opportunity to investigate the role of in-situ, fault-related mineralization along an active strike-slip plate boundary. Samples from two fault zones at around 3066 m and around 3300 m measured depth have been investigated by X-ray diffraction, electron microscopy and Ar-Ar dating analysis. We found localized, thin precipitations of hydrous mixed-layered clay minerals in all fault rocks, which grow preferentially on fracture clasts as polished and occasionally slickensided displacement surfaces. These heterogeneously distributed sub-micron thin films (nano-coatings) are of particular interest due to their localization on fracture surfaces, large surface areas, cation exchange possibilities, clay hydration state, and preferred orientation produced by substrate-controlled growth. Ar-Ar dating of the illitic coatings reveal an "older" fault strand (8 Ma) at 3066 m measured depth, and a "younger" fault strand (5 Ma) at 3295 m measured depth. These ages imply that the fault zone initiation is at least 5 Ma and 8 Ma old and that the recent creep activity at ca. 3300 m measured depth reflects a stage of fault reactivation. We propose that the majority of the slow creep occurs on such nano-coatings, accommodated by a combination of 1) slip along particle surfaces, 2) displacement along hydrated smectitic phases (primarily illite-smectite and chlorite-smectite), and 3) intracrystalline deformation of the clay lattice, associated with repeated dissolution and growth. The presence of enhanced concentrations of smectite in both illite-smectite and chlorite-smectite phases is proposed to contribute to fault weakening, with renewed cataclasis creating nucleation sites for neomineralization on grain surfaces during faulting. Our observations reveal the ultrathin hydrous clay coatings along displacement surfaces of the Parkfield section of the San Andreas Fault play a key role in influencing weak fault and creep behavior as opposed to talc/serpentine phases at these depths.

**Keywords:** SAFOD, Nano-coating, Fault-creep.

# COMPACTED BENTONITE EROSION UNDER GRANITE GROUNDWATER CONDITIONS

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The Colloid Formation and Migration (CFM) experiment at the Grimsel Test Site (Switzerland) will investigate the bentonite erosion/colloid generation at the interface between a compacted bentonite block in contact with a water conducting shear zone under controlled near- natural ground water flow velocities. In order to evaluate which geochemical as well as hydraulic parameters might influence in the integral in situ experiment an accompanying laboratory program has been set-up to investigate the processes of colloid generation, stability and transport independently and perform a mock-up test as an integral lab experiment.

In this study, colloid generation from compacted bentonite pellets under variation of ionic strength, pH, degree of compaction, bentonite cation composition and flow velocity are performed. As electrolyte solutions NaCl, $NaHCO_3$, $CaCl_2$ and ground water from the Grimsel Test Site (GTS GW), Switzerland are used. The experimental setups allow to investigate purely diffusion controlled conditions as well as investigations at flow velocity of $3.3 \cdot 10^{-6}$ $m \cdot sec^{-1}$ at the bentonite – ground water interface. The generated colloids are quantified by means of Laser-induced breakdown detection (LIBD), Photon Correlation Spectroscopy (PCS) and Al-signal (ICP-MS).

Increase in bentonite colloid concentration of contact waters is observed for the $NaHCO_3$ and GTS GW contact solutions immediately after contact and a plateau value of 7.1 and 9.3 $mg \cdot L^{-1}$ is reached after 17 or 90 days, respectively. For concentrations of $CaCl_2$ below the critical coagulation concentration CCC ($[Me^{2+}]$ ~1mmol) a slow increase in colloid concentration to a plateau of 5.3 $mg \cdot L^{-1}$ after 250 days is observed, whereas for contact water solutions above the CCC no colloid release or bentonite erosion within 377 days could be quantified. After exchange of the contact water solution a neo-formation of bentonite colloids was observed in the $NaHCO_3$ and GTS GW system, reaching again a concentration plateau. Further studies on the exchanged contact water clearly show colloid aggregation kinetics in solution indicating a dynamic equilibrium in these experiments. The results will be discussed in light of cation exchange processes and DLVO theory approaches.

The work was conducted in the framework of the Grimsel Test Site Phase VI project "**C**olloid **F**ormation and **M**igration" and the BMWi project "Kollorado".

**Keywords:** Bentonite erosion, Gel layer, Colloid.

# GEOLOGY & GEOCHEMISTRY

## SESSION GG4

## *Clay Minerals & Climate Change*

# MECHANISM OF LATE GLACIAL TO HOLOCENE CLAY MINERAL TRANSPORT IN A FJORD SYSTEM ACROSS THE SOUTHERNMOST ANDES (53°S)

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Characteristics and changes of the clay mineral transport pattern from the partly glaciated and superhumid mountain range of the Southern Andes at 53°S towards the westward Pacific and eastward foreland has been investigated for the period from the Late Glacial to Present day. This part of the Andes is affected whole year-round by southern hemispheric westerlies, producing precipitations up to 10 m/year. Ten 3-8 m long piston cores and numerous gravity cores were taken along a fjord transect which document the sedimentation of clay minerals over more than 120 km distance towards both side of the Andean mountain range. Age determinations ($^{14}C$ and $^{210}Pb$) and tephra chronology give an age frame for the sediment cores which were further investigated concerning magnetic susceptibility, grain sizes, geochemistry and XRD clay mineralogy. Our results show that Late Glacial proglacial lakes on both sides of the Andes were characterised by very low clay settling times, resulting in a long distance transport of a chlorite-rich clay fraction, derived from mafic Jurassic to Cretaceous lithologies, exposed in the central part of the Andes. The amount of the chlorites in the sediment could be correlated with the Fe-Mg content of the clay fraction. The transport and deposition of clay minerals from partly exposed granodiorites of the Patagonian Batholith was characterised by higher illite contents and could be correlated with the potassium content in the clay fraction. The marine transgression to the western fjord system at around 14,000 years caused a more rapid clay flocculation and a decrease in the long distance transport, so that the sedimentation became autochtonous at most sites, associated by a strong decrease in the sedimentation rates. To the east of the Andes the long distance clay mineral transport was partly controlled by thermohaline characteristics of a semihaline fjord system, which was reconstructed based on the chlorinity of the pore water of the clayey sediments. The eastern fjords are characterised by pronounced eastward superficial low salinity currents which can reach velocities of up to 20 km/day during stormy periods. A northward migration of the westerly wind belt during the Neoglacial produced a decrease in the average westerly wind component during the Neoglacial after 5000 years B.P in the southernmost Andes. Such a decreasing westerly influence can explain the drop in the long distance eastward clay mineral transport in the middle to late Holocene. Subordinate kaolinite contents (up to 10 vol.-%) in some sediments seem to be related to the Holocene alteration of granodiorites which were covered by peat with very acid (pH 3-4) soil water. Our results should help to improve paleoenvironmental and paleoclimate interpretations of sediment cores and to better trace sediment pathways in this very remote area at the southern tip of South America.

**Keywords**: Clay mineral transport, Andes, Paleoclimate.

# LATE CARBONIFEROUS PALYGORSKITIC PALEOSOL: KEY TO PENNSYLVANIAN CLIMATE

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Paleosols are useful proxies of past climates. Here we report the properties of a Late Carboniferous (308±2 My) (semi)arid carbonaceous and weakly gypsiferous palygorskite paleosol discovered in Moscow region (Russia*)*. This paleosol contains inborn organic carbon (TOC) – 0.5 - 1.5 % from its clay fraction (Alekseeva et al., 2009). Soil profile contains four layers: (1) *Ts* (resedimented terrestrial clay); (2) *Ti* (*in situ* terrestrial clay); (3) brecciated and calcretized marine limestone at transition to *Ti*; and (4) a marker horizon of brown chert at 0,9-1,1 m depth from the paleosol top (Kabanov , 2005). Clay fraction (< 2 μm) was separated by sedimentation from the insoluble residue after carbonate dissolution with buffered acetic acid mix. Its mineral composition was investigated by X-Ray diffraction and the elemental concentrations by XRF. The organic matter (OM) has been studied by a range of methods: chemical, FTIR spectroscopy and solid-state CP/MAS $^{13}C$ – NMR. Surface micromorphology of detrital sand-sized (0.25 - 0.10 mm) quartz was examined by SEM. Additionally the magnetic properties measured at room temperature have been obtained: magnetic susceptibility (MS), anhysteretic remanence (ARM), incremental acquisition of magnetic remanence (IRM), demagnetization, and a high-field IRM (HIRM). The discovered Pennsylvanian-age paleosol is the earliest known palygorskitic paleosol and the earliest known aridisol retaining inborn OM. Palygorskitic matrix, shallow pedogenic carbonate horizon, presence of minor sepiolite, opal and gypsum, chemical weathering indices, and magnetic properties of the studied paleosol consistently attest to (semi)arid well-drained pedogenic conditions with less than 300 mm annual precipitation. The TOC content in clay fraction is as much as in the modern, Quaternary, and Pliocene arid soils. The OM contains predominantly fulvic acids. $^{13}C$ – NMR spectra show the presence of alkyl- and aromatic carbon and polysaccharides. The FTIR and $^{13}C$ - NMR spectra are similar to those from modern and Holocene aridland soils. The observed remarkable preservation of OM is explained by the creation of true covalent bounds with Si-OH groups of acid-activated lattice of palygorskite which makes OM resistant to diagenesis.

**Keywords**: Late Carboniferous, paleosol, palygorskite.

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# EVOLUTION OF CRUST- AND SOIL FORMATION AND SEDIMENTATION FROM LATE CRETACEOUS TO QUATERNARY (THE BAIKAL REGION)

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The Baikal region is a moderate climatic zone embracing the Baikal Foredeep (BF) and Baikal Rift (BR). This region underwent dramatic transformations in time (from Cretaceous to Quaternary) and space (Platform and Rift). Climate and tectonic are the main regulators of weathering and sedimentation. Small boggy lakes and very deep lakes developed in BF and BR, respectively. In BF, the thickness of Cretaceous to Quaternary sediments is of about 700 m, while in BR is about 7500-8000 m. In the period from late Cretaceous to early Oligocene (70-30 Ma) the region appeared as a peneplain, climate was humid subtropical or tropical and kaolinite-laterite formed through weathering. Correlated sediments are red-coloured humid products. In BF they host coal and boxite, fire-proof, refractory clay while in BR boxite, Fe/Mn ores, highly siliceous formations, kaolin, phosphorite. From late Oligocene to early Pliocene (30-3.5 Ma) the climate changed into a arid–semi-arid Mediterranean type. The original peneplain began dismembering. In BF the weathering formed montmorillonite; correlated sediments are semi-arid terrigenous and chemogenous-deposits. In BR, the weathering formed kaolin-hydro-mica, and since the middle Miocene, also hydro-micaceous-montmorillonite and red-color montmorillonite. The sediments of BR are mostly carbonate-devoid polymictic terrigenous deposits. In the intra-rift uplifts in the lakes and bogs, carbonate-gypsum and montmorillonite deposit could form, while in the large lakes carbonate-devoid terrigenous sediments were present. Montmorillonite rich silts deposited in the lagoons. On-shore, red coloured carbonate polymictic diluvium and soils of Mediterranean type (Red clay) developed. From late Pliocene to Quaternary (3.5–0 Ma) the climate became moderately cold, with alternation of glacial and inter-glacial periods; the weathering was mostly physical. On-shore, in late Pliocene, soils were basically brown-reddish calcareous and pedosediments (Reddish clay). At the end of Pliocene, tundra soils developed. In BF depressions reduced, while in BR very deep depressions formed. In Lake Baikal, some features of sedimentary diagenesis are similar to those common in the sediments in the oceans. Deposits of the methane gas hydrates and oil are found in bottom sediments of Lake Baikal. On the lake's bottom, mud volcanoes and hydrothermal discharges are present. Baikal Rift can be considered as the model of the initial stage of continental basin transformation into the oceanic one.

**Keywords:** Weathering crust, Soil formation, Sedimentation, Cretaceous–Quaternary, Baikal.

# CLAY MINERALS AS POSSIBLE PALEOCLIMATIC INDICATORS FOR RIO DA PRATA BASIN

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Rio da Prata Basin is located on the central portion of South America, with an area of approximately 3000 km$^2$. Geology consists mainly of Quaternary volcanic rocks, Cretaceous tholeiitic basalts, Cretaceous sandstones and a thick layer of Quaternary sediments (DePetris et al., 2003). Climate is affected directly by cold polar fronts coming from the south. Strong El Niño events tend to block these fronts; a fact which is associated with intense rain falls in southern Brazil (Martin et al., 1993).
Clay mineralogy was studied in a marine sediment core collected at the Brazilian Shelf (33°48'18"S and 52°17'40"W), from the mud accumulation called Depressão do Albardão. Mineralogical analyses were carried out with a PANalytical diffractometer, model X´PERT PRO MPD (PW 3040/60). Semi-quantification of the four major clay mineral groups was performed according to the methodology proposed by Biscaye (1965). Samples for dating the core are being processed. Granulometry was determined with a CILAS laser granulometer, model 1064.
The quantities of the four main clay mineral groups obtained for superficial sediments from Depressão do Albardão agree with the data from Biscaye (1965) for the shelf sediments under influence of the Prata Basin, and also agree with the abundances found by DePetris (2003) for sediments in suspension in the Rio Paraná – the main affluent of the Rio da Prata. Clay mineralogy, associated with Rare Earth Elements interpretation, confirms that the provenance of these sediments is Rio da Prata basin.
The origin of chlorite is associated to the Andean tributaries of the basin, which mainly contribute with the sedimentary load of the Rio Paraná (DePetris et al., 2003). It is suggested that clay mineral assembly variations along the core, as well as other parameters, e.g. the kaolinite/chlorite ratio, could be used for inferences about more humid periods for the tributary regions of the basin.

**Keywords:** Paleoclimate, Clayminerals, Prata Basin.

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# MINERALOGY OF PLIOCENE AND QUATERNARY ALLUVIAL SEDIMENTS OF THE PANNONIAN BASIN: A QUANTITATIVE APPROACH

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Mineralogical composition of fine-grained alluvial sediments in thick sedimentary sequences of the central region of the Pannonian Basin is reviewed embracing long time spans during the Pliocene and Quaternary. Published data and data of unpublished X-ray diffraction analyses of a total of about 150 samples were considered. The analyses were carried out in the Geological Institute of Hungary, Budapest. All data were revised and recalculated in a uniform system in order to obtain comparable results. Compositional relations were described in a qualitative manner by Viczián (2002). In the present study quantitative data were grouped according to the genetic significance of clay minerals and were reviewed in triangular diagrams.

The dominant clay minerals in the bulk sediment are smectite, illite/smectite, illite and chlorite. In the <2 μm fraction the same minerals occur, however, expanded phases are more dominant. Triple mixed-layer illite/smectite/chlorite and kaolinite of various degree of disorder may appear.

Clay minerals are essentially detrital, depending on the catchment areas of rivers in various areas of the surrounding Carpathians and Alps. Sub-basins of the Pannonian Basin differ in degree of disorder and quantitative proportions of clay minerals and quantitative relations of other phases like calcite, dolomite, quartz and feldspars. Source areas and transport directions were relatively permanent. In the South Tisza Basin and Maros Alluvial Fan well crystallised detrital phases prevail while in the Körös Basin more mature sedimentary material of lesser degree of crystallinity, higher kaolinite and very low carbonate contents can be found.

The clay, carbonate and feldspar minerals deposited may have been modified by flow systems of ground water causing ion exchange and partial dissolution. Amorphous iron hydroxides underwent diagenetic crystallization and reduction producing from amorphous “limonite”, in a downward sequence, more ordered goethite and finally siderite or pyrite. No diagenetic K-fixation and illitization occurs in this shallow level, however, some kind of palaeo-pedological illitization may have occurred in the sediments.

It is remarkable that the large climatic variations during the Pleistocene seem to have no significant effect on the composition of the alluvial sediments while contemporaneous loess and red clay deposits covering the surrounding hilly areas are highly dependent on climatic factors.

**Keywords:** Alluvial clays, Pliocene, Quaternary.

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# GEOLOGY & GEOCHEMISTRY

## SESSION GG5

## *Clays in Geological Processes*

# CLAY MINERALS AND ASSOCIATED PHASES RELATED TO THE DEPOSITION OF UNCONFORMITY-TYPE URANIUM DEPOSITS

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Unconformity-type uranium deposits consist of high-grade and high-tonnage ore bodies, hosted in strongly argillized rocks, occurring on both sides of basal unconformities between oxidized Proterozoic conglomeratic sandstones and reduced metamorphosed crystalline basement rocks. The host-rock alteration sequence determined for both Canadian and Australian unconformity-type deposits is as follows: illite (+ kaolin) ± Sr-LREE-bearing aluminum phosphate-sulfates (APS) in background sandstones well above the unconformity, illite + sudoite + APS ± illite/sudoite mixed-layer minerals in alteration halos on both sides of the unconformity, and illite + sudoite ± Fe-Mg chlorite ± APS ± apatite deeper in the basement. The main stage of uranium deposition was associated with the chloritization processes (sudoite and/or Fe-Mg chlorite). The clay mineral sequence and the transition of APS to apatite are interpreted to be the result of an increasing degree of interaction of the basement rocks with infiltrating acidic and oxidizing basinal brines at about 150-200°C. In turn, these fluids were neutralized and reduced by their ongoing interaction with iron-bearing minerals of metamorphic origin. Several signatures of the proximity of the uranium ore bodies have been characterized in the clay minerals and associated phases of the alteration halo:

—“Hairy” illite of the 1Mt polytype crystallized close to the structures which drained the solutions and host the uranium ore bodies, whereas coarse-grained diagenetic illite with hexagonal platy shape ($2M_1$ polytype) or lath-like flaky shape (1Mc polytype) predominate outside of the alteration halo.

—Fine-grained and disordered Fe-bearing sudoite crystallized close to the ore bodies, whereas well-ordered Fe-poor sudoites crystallized elsewhere.

—Trioctahedral chlorites are chemically zoned ($0.10<X_{Fe}<0.70$), often with a spherical habit, in response to periodic changes in the oxidation state of the solution during crystallization.

—APS are also chemically zoned with coupled substitutions of LREE for Sr and P for S, respectively. The main chemical variation of the APS consists of increasing florencite end-member with increasing proximity to uranium mineralization.

These results demonstrate that clay minerals and associated phases have recorded the conditions which prevailed at the moment of the uranium deposition through their texture, crystal-structure, and/or crystal-chemistry. Hence these minerals are promising tools for prospection for unconformity-type uranium deposits worldwide.

**Keywords:** Clay minerals, APS minerals, Unconformity-type uranium deposit.

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# LOW TEMPERATURE ALTERATION OF TRIOCTAHEDRAL MICAS TO BEIDELLITE IN A KARSTIC ENVIRONMENT

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The variety of minerals observed in the weathering products of trioctahedral micas from igneous rocks suggests that Mg-rich phyllosilicates alter to several products under different weathering conditions due to differences in the composition of the altering fluids. We investigated the weathering products of a phlogopite-rich volcanoclastic deposit in a karstic environment (Grotta del Cervo, Pietrasecca, Italy) by using XRD, FTIR, CHN elemental analysis, EMPA, optical and scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDS). We outline different stages of volcanic glass weathering and show evidence for the growth of mixed-layer phlogopite-beidellite at the edge and on the basal surface of phlogopite phenocrysts.

Fine phlogopite crystals show alteration to mica-smectite with 1-4% smectite. SEM-EDS observation of large phlogopite crystals shows progressive in-situ alteration of mica layers towards beidellite (dioctahedral, Al-rich smectite). The loss of octahedral Mg from the phlogopite precursor indicates that water chemistry controlled the composition of the neoformed phase, even though the alteration mechanism appears to be a solid-state transformation.

Seemingly, the local environments where the transformation reaction takes place in the glass and the mica have different characteristics. Glass dissolution starts by penetration of protons (with cation exchange) and water within the glass, which may result on the transformation process taking place within the glass grains (very near the surface) and thus, controlled mainly by glass chemistry. At the very initial stages, the carbonate-rich water from the surrounding limestone and the proton exchange process favour a slightly alkaline pH that led to glass alteration first to smectite and then to zeolite minerals. Alteration of the phlogopite crystals probably takes place from the outer surface (edges of the layers, primarily) and the well-flushed conditions favour water chemistry control on the composition of the resulting phase. This is the reason why vermiculite, usually observed as a weathering product of phlogopite, was not detected.

**Keywords:** Beidellite, Phlogopite, Solid-state transformation.

# TRACING GEOCHEMICAL PROCESSES USING RADIATION- INDUCED DEFECTS IN KAOLINITE: A REVIEW

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It is known from early studies of the mid-70's that kaolinite contains radiation-induced defects detected by Electron Paramagnetic Resonance spectroscopy (EPR). They are differentiated by their nature, their production kinetics and their thermal stability. One of these defects is stable at the scale of geological periods and provides a record of past radioactivity, as reported in several studies from about 20 years. Based on artificial irradiations, a methodology has been proposed to determine the dose cumulated by kaolinite since its formation (paleodose).
Two main applications are derived from the determination of the paleodose in kaolinite-containing systems:
—1) in open systems, the paleodose can be used to derive equivalent radioelement concentrations responsible for the defects, provided that the age of kaolinite formation can be constrained. This allows quantitative reconstruction of past transfers of radioelements in natural systems, an important issue for the long-term safety assessment of high-level nuclear waste repositories. Several different geosystems have been studied. A case study will be detailed for the Nopal I U-deposit (Chihuahua, Mexico), hosted in hydrothermally-altered volcanic tuffs and considered as analogue of the Yucca Mountain site (USA). Using few geochemical assumptions, an equivalent U-content was calculated from EPR and was compared to the present U-content. This revealed past accumulation of uranium in the mineralized zone and past leaching in the present barren rock.
—2) in closed systems, the paleodose can be used to date the kaolinite, provided that the constant dose rate can be assessed. This was applied to lateritic soils and continental detrital sediments of the Amazon Basin (Brazil). U is mostly incorporated in resistant minerals such as zircon: this suggests a closed system, providing a constant dose rate. The average ages derived from paleodoses vary from more than 20 Ma (sediments) to 6 Ma (soil surface). These results suggest that kaolinites cannot be in equilibrium with present day waters. Models assuming the dynamical equilibrium of kaolinites with local physical-chemical conditions prevailing in lateritic soils are thus questionable. Alternatively, these findings bring strong support for the use of the isotopic composition of kaolinites to decipher continental climates of the Past.

**Keywords:** Kaolinite, Defect, Uranium.

# MINERALOGICAL, GEOCHEMICAL AND SR-PB-ND ISOTOPE STUDIES OF SEDIMENTARY KAOLIN DEPOSITS IN EGYPT: IMPLICATIONS FOR THEIR SOURCES AND ORIGINS

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Cretaceous continental sedimentary kaolin deposits of economic significance occur in the Sinai, Red Sea and Aswan regions, Egypt. Carboniferous sedimentary kaolins are present only in the Sinai. We present here a combined mineralogical, geochemical and the first Pb-Sr-Nd isotope study on the kaolins to better understand origins and ultimate sources of the clays.

The Cretaceous kaolins share some geochemical characteristics, such as high $TiO_2$ (1.3-3.8 wt.%), Zr (450-1500 ppm), and Nb contents (50-190 ppm) in the clay fraction, that distinguish them from sedimentary kaolins in other parts of the world. High Zr, Hf, Nb, and Ta contents are associated to anatase, while Sr, Pb and REE are hosted mainly by clay-sized phosphate minerals. The $^{87}Sr/^{86}Sr$ ratios (0.7072-0.7088) and $\varepsilon_{Nd(0)}$ values (-3.9 to -2.6) are quite uniform, while slight differences in Pb isotope ratios are noted between the Sinai and Aswan kaolins.

The unique pisolitic flint clays at Kalabsha, Aswan area, were formed by deferration and resilicification of lateritic sediments, as indicated by low trace element contents, LREE depletion, positive Ce anomaly, geochemical homogeneity, and unusually high kaolinite crystallinity. The overlying plastic kaolins were not formed by reworking of the pisolitic kaolins, but probably derived from the saprolites underlying the lateritic crusts in the source area.

The Carboniferous kaolins (Khaboba, Hasbar) are distinct by the presences of illite and alunite in veins and disseminations. The clays are characterized by lower Zr and Ti contents, higher $^{87}Sr/^{86}Sr$, $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ and lower $^{143}Nd/^{144}Nd$ ratios as compared to the adjacent Cretaceous kaolins indicating a clearly different and more crustal source.

**Keywords**: Kaolin, Egypt, Isotopes.

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# GEOCHEMISTRY OF MIXED LAYER ILLITE-SMECTITE MINERALS FROM A TRIASSIC RIFT-RELATED EXTENTIONAL BASIN (ANTALYA UNIT, KEMER-KUMLUCA, SW TURKEY)

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Tauride-Anatolide Platform or Tauride-Anatolide Composite Terrain (TACT) is an Alpine continental microplate containing numerous tectonostratigraphic units deposited during the Cambrian to Tertiary time interval, which has been sliced and shortened due to latest Cretaceous Alpine closure of the northern and southern branches of Neotethys. Antalya Unit, one of the allocthonous units from TACT, has critical regional tectonic importance because of the presence of rifting remnants during Triassic time (Robertson and Woodcock, 1981). In this study, geochemical characteristics of smectite and mixed-layer illite-smectite (I/S) minerals with different ordering (R, reichweite) from Antalya Unit were investigated. Paleozoic-Mesozoic sedimentary rocks from Antalya Unit mainly contain calcite, dolomite, quartz, feldspar and phyllosilicates (I/S, kaolinite, chlorite, illite, chlorite/smectite and chlorite/vermiculite). I/S were found in all of the sequences from Cambrian to Cretaceous, but smectites was only detected in Late Triassic-Cretaceous. R0 I/S is found only in early diagenetic Middle-Late Triassic-Cretaceous units of Alakırçay Nappe (rift sediments), whereas R1+R3 and R3 I/S in late diagenetic/low anchimetamorphic Cambrian-Early Triassic units of Tahtalıdağ Nappe (pre-rift sediments). Illite crystallinity and illite contents in I/S reflect increasing diagenetic grades together with the increasing depth. Major, trace and rare-earth (REE), and stable isotopes (O and H) element compositions were investigated on two smectites (dioctahedral and trioctahedral) and five I/S (dioctahedral) minerals. Total layer charge and interlayer K increase, whereas tetrahedral Si and interlayer Ca decrease from smectite to R3 I/S. Trace and REE concentrations of I/S minerals are higher in pre-rift sediments than those of rift sediments, except P, Eu, Ni, Cu, Zn and Bi. According to chondrite normalized values, REE patterns of I/S in both pre-rift and rift sediments were clearly separated from each other. $\delta^{18}O$ and $\delta D$ values of smectites and I/S smectites represent supergene condition and show decreasing $\delta^{18}O$ whereas increasing $\delta D$ values with increasing diagenetic grades. Lower $\delta D$ values of I/S (-95 to -100 $\delta D_{SMOW}$) are characteristics in rift sediments, but pre-rift sediments have relatively higher values (-69 to -76 $\delta D_{SMOW}$). Geochemical characteristics of Triassic units indicate that the rifting was started in the end of Anisian (Middle Triassic).

**Keywords:** Clay mineralogy, Major and trace elements, REE, Isotopes.

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# MECHANISM OF FORMATION OF FE-MONTMORILLONITE IN DEEP SEDIMENTS (PACIFIC OCEAN, COSTA RICA MARGIN)

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Iron-rich smectite is commonly described in the diagenetic fraction of deep sea sediment. It occurs as millimetric to centimetric aggregates dispersed in the sediment, or as coating of sedimentary particles or nodules. In specific environments, Fe-rich smectite is considered as the glauconite precursor and both minerals are commonly associated (e.g.[2]). The aim of the study is to determine the factors that allow the formation of Fe-rich smectite and its probable transformation into glauconite. The study combines a detailed mineralogical investigation on natural samples and a chemical modelling of the mineralogical reactions.

TEM observations and EDX analyses have been carried out on microtomed samples of millimetric to centimetric green grains of Fe-rich smectite that were described in sediments from the Costa Rica margin by Gaudin et al. (2005). These grains are widespread in pelagic calcareous sediments and are associated with pyrite. An accurate mineralogical investigation indicated that smectite is $Fe^{3+}$-montmorillonite, with the following structural formulae $(Si_{3.94}Al_{0.04}Fe_{0.02})$ $(Fe_{1.42}Mg_{0.68}Mn_{0.02})$ $O_{10}$ $(OH)_2$ $(K_{0.11}Ca_{0.11}Na_{0.07}$ $nH_2O)$ [1]. The TEM investigation of the green grains displays that pyrites are partially dissolved and are surrounded by amorphous or very poorly crystallized Fe-rich particles. Smectite grows from an amorphous precursor and its formation implies the input of Si, O, K, Na and Ca. These results suggest the dissolution of sedimentary phases like volcanic glasses, siliceous microfossils and silicates.

The thermodynamical modelling of fluid-sediment interactions using the geochemical modelling code PhreeqC have been carried out. Hypothesis concerning the precipitation of Fe-smectite as glauconite precursor have been tested, using the mineralogical and pore water compositions of the sediment, and calculating thermodynamical constants of additional smectites. Simulations first confirme that the green grains are the result of pyrite alteration by sea water circulation in sediments under oxidizing conditions. Besides, the smectite area extent is controlled by the kinetic of pyrite dissolution and fluid migration. The absence of aluminium in the Costa Rica margin system explains the formation of such a Fe-rich montmorillonite instead of glauconite.

**Keywords:** $Fe^{3+}$-montmorillonite, TEM-EDX, Geochemical modelling.

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# CLAY FABRIC–THE ASSEMBLY OF CLAY PARTICLES

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Clay Fabric, defined as the spatial distribution, orientation, and particle-to-particle relationships of less than 4 µm solid particles (mainly clay minerals) in fine-grained sediment, determines the characteristic of the microstructure and properties of sediments/soils, and provides pore space for interstitial water, gas, and organic matters both living organisms and their products. Clay fabric research is of crucial importance in geology, mineralogy, biogeochemistry, and materials science, however, investigation of this field has been slow in advancing due to technical difficulties and heretofore lack of high powered instrumentation. This paper presents unique novel methods and technologies of studying clay fabric and its various applications to geological, mineralogical, biogeochemical, soil science, and civil engineering research. The development and recent highlights of clay fabric research during the last a few decades will also be reviewed.

High-resolution characterization of clay particle size, mineralogy, and shape (morphology) is critically important for understanding clay fabric. Historical difficulties of measuring individual clay particles (domains/assemblies) especially smectite, have been overcome using specially developed environmental-cell transmission electron microscopy (EC-TEM) and high-resolution TEM techniques. Other techniques, such as cryo-TEM and TEM tomography also have recently provided excellent characterization of fundamental characteristic of clay fabric.

Samples from various depositional environments depicting individual clay particles have been studied. Traditionally, researchers believed that smectite was characterized by a platy fluffy morphology. EC-TEM has discovered that of different shapes (spherical-like, platy, elongated rod-like, needle, triangular, and polygon shape) of nano-size clay particles exist. Recent studies show that the thinnest individual smectite particles range between 4 to 10 nm with the mode of 5 to 6 nm. This thickness corresponds to ~ 4 to 5 unit cell layers and is unique to the development of smectitic clay fabric. Results of clay fabric TEM observation of marine sediments from Middle-America Trench, Mississippi Delta, Pacific Basin, California Continental Slope, and Baltic Sea revealed many characteristics of the depositional environment. Depositional environment, pore water geochemistry and biological/organic interactions play important roles in the formation and diagenesis of clay fabric and ultimately the fundamental sediment properties. Clay nanofabric synthesized and studied in the laboratory contributes to the understanding of the developmental history of clay fabric in natural environments and also provides useful and important applications in materials science and related disciplines.

**Keywords:** Clay fabric/assembly and environment, Clay nanostructure, (EC-) TEM.

# STATISTICAL ANALYSIS OF GEOCHEMICAL DATA. A TOOL TO DISCRIMINATE THE ORIGIN OF KAOLIN DEPOSITS IN PATAGONIA, ARGENTINA

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The numerous kaolin deposits located in Patagonia Argentina have been formed by either hydrothermal, meteoric or sedimentary processes. The primary origin has been established from $O^{18}$ and D isotopic composition of the main minerals, kaolinite and/or dickite and, as defined by Dill et al. (1997), from the behaviour of certain elements during the alteration.

Considering that in all the primary deposits, the fresh rocks are similar in age and composition, the purpose of this work is to determine which are the chemical elements that better characterize the kaolins and allow to differentiate their origin.

To handle the great amount of variables per sample, a statistical multivariable study was used. The Principal Component method permits to define, on one hand the variables that better characterize each deposit and, on the other hand, the correlation between them. Once worked with all the elements, those that were not explained in the first two components (which represents 75% of the total variance of the model) were discarded. Doing so, the contents of $Fe_2O_3$, $P_2O_5$, LOI, Sr, Y, Zr, V, Pb, Hf, Rb and REE were used. The results show that the first two components allow a clear separation between the hydrothermal and meteoric-sedimentary deposits. The first component indicate that $Fe_2O_3$, Y, Rb, U and HREE are more abundant in the meteoric-sedimentary deposits, whereas, Sr, Pb and V are in the hydrothermal deposits. The second component shows that $P_2O_5$ and the LREE are enriched in the hydrothermal and Zr in the meteoric sediments. In the meteoric deposits and their transported products (sedimentary deposits), most of the elements show the same geochemical behaviour, emphasizing the idea that the sedimentary processes have little influence in the mobilization of the analyzed elements. Data suggest that there is an enrichment in Y-HREE during weathering and a depletion during hydrothermal processes.

The obtained data can be plotted in binary diagrams (Ce+La *vs.* Y+Yb+Lu), $P_2O_5$ *vs.* Y, $P_2O_5$ *vs.* Zr, $P_2O_5$+Sr *vs.* Zr) were the field of the hydrothermal deposits is well separated from the field of the meteoric ones.

**Keywords:** Kaolin, REE, Patagonia.

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# CHLORITE IN THE SUBSURFACE: A SYNTHESIS

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The depositional environment of detrital clay minerals and their development during diagenesis helps understanding of porosity and permeability preservation in deeply buried petroleum sandstone reservoirs. Grain-coating chlorite cement results from burial and diagenetic alteration of primary or early diagenetic minerals and acts to impede quartz cement growth during subsequent stages of diagenesis.

Literature suggests that chlorite can form as a result of deposition of clay minerals in a range of sedimentary environments including shallow marine and deep-water settings (iron-rich chlorite), as well as in association with evaporites (magnesium-rich chlorite) [1]. A compilation and synthesis of the depositional environment and characteristics of chlorite from published literature is presented to enable a quantitative understanding of these controls.

The diagenesis of clay minerals in the subsurface results in the formation of a suite of minerals which includes chlorite, illite, smectite and kaolinite. These clay minerals frequently occur as grain coats in reservoir sandstones. A statistical analysis of the relative proportions, habit and origin of each of these minerals as described in published literature was undertaken. From this analysis a quantification of detrital versus authigenic chlorite found in the subsurface, as well as the morphology of diagenetic clay minerals has been produced.

A synthesis of the proportions of each type of chlorite in different environments will improve understanding of the depositional controls on their origin and distribution and aid exploration and appraisal strategies. While a statistical analysis of diagenetic clay minerals may provide an insight into the origin of chlorite and chlorite pre-cursor minerals. Future work aims to understand the origin as well as the distribution of chlorite precursor minerals in modern-day shallow marine settings.

**Keywords:** Chlorite diagenesis, Sedimentary environments, Grain-coating clay.

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# MINERALOGICAL, PETROGRAPHICAL AND GEOCHEMICAL EVOLUTION OF THE HYDROTHERMAL KAOLIN-ALUNITE DEPOSITS: DUVERTEPE DISTRICT, BALIKESIR, TURKEY

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Düvertepe District, situated in western Simav Graben, includes the largest hydrothermal kaolinite+alunite deposits of Turkey. Tectonically active Simav Graben extends about 80 km long in northeastern area of Aegean region and advanced argillic alteration zones constitute for major alunite (+/- kaolin) deposits at the eastern end and kaolin (+/- alunite) deposits at the western end of the graben. Upper Miocene calc-alkaline volcanic rocks (rhyolitic and andesitic lavas and tuffs) associated with Aegean magmatism and N-S extentional Aegean tectonism is widespread in the region. The parent rocks of kaolinite and alunite occurrences are rhyolitic tuffs and rhyolitic-rhyodacitic tuffs consist of quartz, alkaline feldspar, biotite and muscovite phenocrystals and pumice. Epithermal kaolin+alunite mineralizations was the result of intense hydrothermal alteration of rhyolitic-rhyodacitic tuffs under acid-sulphate-rich geothermal solutions and these mineralizations commonly occurred along small faults which cut almost vertically to the E-W trending Simav Graben.

SEM studies show that these kaolinite crystals show well-formed hexagonal shapes and alunite crystals show idiomorphic rhombohedral forms. Needle-shape and stubby to long tubular structure with open-ends halloysites are also determined in some alunite samples. XRD studies revealed that mineralogical composition of kaolinite (+/- alunite) deposits consists of kaolinite (1T polytype) + alunite + quartz and that alunite deposits consist of alunite + opal-cristobalite/tridymite + quartz with minor halloysite. Si and S inputs along fault zones are common because they are the products of ascending origin of geothermal solutions. Silicification becomes more intense upward; for instance, funnel-shape silicification at the top of fault zone, silica precipitation or replacing with surrounding rocks is commonly observed features in the field. Also, silica gossans above the kaolin deposits are the result of spraying and infiltration of Si-rich geothermal waters on rhyolitic lavas and tuffs. These silica gossans are the striking features on the exploration of hydrothermal kaolin deposits in Düvertepe District.

**Keywords:** Hydrothermal alteration, Alunite, Simav Graben.

# GEOLOGY, MINERALOGY, GEOCHEMISTRY AND GENESIS OF THE TAŞOLUK KAOLINITE DEPOSITS IN PRE-EARLY CAMBRIAN METAMORPHITES AND NEOGENE VOLCANITES OF AFYONKARAHISAR, TURKEY

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The Taşoluk kaolinite deposits of Afyonkarahisar (western Anatolia) are hosted by both pre-Early Cambrian sericitic mica–chlorite schists and Neogene volcanites, the latter comprising tuff and agglomerate. These units have been affected by hydrothermal alteration controlled by faults resulting in complex, irregular, lateral mineralogical zonation. The occurrence of a siliceous cap on altered schists and in claystone, quartz veins in schists and tuffs, and development of explosion cones and pit fillings indicate that alteration in both the schists and the volcanites is due to hydrothermal processes. Altered schists have generally high (locally low) iron contents. Claystones are generally silicified and have low iron contents. Kaolinite predominates south and west of Taşoluk, whereas high Fe+Ti-bearing illite + kaolinite predominate in other altered sections. The kaolinite exhibits a stack micromorphology within altered schists, and the altered volcanites record *in situ* precipitation, derived from a mechanism of paired dissolution and precipitation. Illite fibres coexist with kaolinite, smectite, chlorite, mica and sericitized feldspar in particularly altered schist, revealing that the illite formed either authigenically or by conversion of smectite to illite. Relative increase in Cr+Ni and decrease in Sr+Ba in the kaolinite deposits and the schistose host-rock related to the upper level of the kaolinite deposits, as well as in volcanic parent rocks, result from the alteration of chlorite, mica, and feldspar in the sericitic mica-chlorite schists, and feldspar, glass shards and schist fragments in the volcanites. An extensive faulting, fracturing and hydrothermal activity during Late Miocene-Pliocene volcanism episode favourably contributed to the development of kaolinite deposits under acidic environmental conditions. With regard to industrial applications, the low-Fe kaolinized schists are suitable for use in refractories and paper coatings, while the claystone is suitable for use in ceramics and in the white-cement industry.

**Keywords:** Illite, Kaolinite, Hydrothermal alteration, pre-Early Cambrian schist, Neogene volcanites, Siliceous cap, Afyonkarahisar, Western Turkey.

# MINERALOGICAL AND CHEMICAL PROPERTIES OF PALYGORSKITE OCCURRENCES IN THE MIOCENE TO PLIOCENE BOUNDARY (ISKENDERUN BASIN), SOUTH OF TURKEY

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After the termination of Messinian crisis in the East Mediterranean region, brakish water conditions took place due to heavily fresh water dilutions. Drastic changes of the hydrological conditions of these basins involved establishment of oligo – mesohaline environments, called *Lago–Mare.* The Iskenderun Basin which is located to eastern part of the Mediterranean, consisting of mainly claystones and carbonates together with coarse siliciclastics were deposited in lagoon-tidalflat beach complex of the transition interval between Messinian and Zanclean. The white to cream-colored units consist of carbonates (dolomite), and clay mineral (palygorskite), and accessory smectite, quartz and cristobalite were accumulated in a lagoon environment cut by canalized tidal flat conglomerates and sandstones. In the studied sample, palygorskite have been determined by 10.55 Å and 4.48 Å peaks, and also orthorhombic and monoclinic peaks at 4.25 and 4.14 Å in the XRD charts, respectively. This supports that palygorskites were developed in different ratios of the orthorhombic and monoclinic forms. Structural formula of the palygorskite mineral has been calculated as:
$(Si_{7.63}\ Al_{0.37})\ (Mg_{2.40}\ Al_{0.73}\ Fe_{1.01}\ Ti_{0.08})\ O_{20}\ (OH)_2\ (OH_2)_4\ (Ca_{0.02}\ K_{0.02}\ Na_{0.02})\ 4H_2O$. SEM studies show that palygorskites formed as plate crystals which are rimmed by acicular fibers. When the lithology became clayey carbonates, palygorskite was precipitated as fibers resting on the dolomite crystals. Palygorskite did not evolved from alteration of detrital minerals or diagenetic transformation of volcanic glass, illite and chlorite, feldspar or talc because of lack of these mineral associations. The obtained data suggests that palygorskite took place as authigenic mineral within the dolomite–dominated section in where climatic changes were essential factor changing from humid to arid. Dolomites were crystallized in brackish water environment, during mixing of marine and fresh waters. Subsequently increasing fresh water input (source for Al, Si) led to lowering of pH conditions which caused dolomite dissolution (for Mg source); finally palygorskite was precipitated, under basic environmental condition driven by high value of pH (8 to 9).

**Keywords:** East Mediterranean, Lago-Mare, Palygorskite.

# QUICKCLAY AND LANDSLIDES OF CLAYEY SOILS

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We study the rheology of quickclay, an unstable soil responsible for many landslides. We show that above a critical stress the material starts flowing abruptly with a very large viscosity decrease caused by the flow. This leads to avalanche behavior that provides a partial explanation for the instability of this type of soil. Reproducing landslides on a small scale in the laboratory shows that an additional factor that determines the violence of the slides is the inhomogeneity of the flow. We propose a simple yield stress model capable of reproducing the laboratory landslide data, allowing us to relate the landslides to the measured rheology.

**Keywords:** Avalanches, Clayey soils.

# FORMATION OF ALTERATION ZONES AND DICKITE GENESIS IN SINDIRGI-BALIKESIR, WESTERN TURKEY

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Hydrothermal alteration hosted by Miocene calc-alkaline volcanism related to extensional tectonic activity is widespread in Western Anatolia. Simav Graben is the latest product of this tectonic regime and includes a wide range of ore deposits and hydrothermal mineralizations.

Sındırgı (Balıkesir) region is an example of hydrothermal alteration associated to a rhyolitic volcanic dome. The alteration is controlled by faults and fractures. Forty samples were collected from the alteration zones and studied by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), FTIR and FT-Raman spectroscopy. The main mineral assemblages in each zone are: 1. dickite-alunite, 2. dickite-quartz-alunite, 3. quartz-dickite ± kaolinite, 4. quartz-mixed layer illite/smectite-alunite and 5. mixed layer chlorite/smectite-mixed layer illite/smectite-quartz-dickite-alunite. It is concluded that two types of alteration episodes have taken place in the hydrothermal process. The first episode is an intensive acid-type alteration and the second is a neutral-type alteration.

The presence of quartz-dickite indicates a formation temperature at about 160-200°C, transformation of illite/smectite to illite occurs at ~230°C and transformation of smectite to chlorite at ~150-200°C (Reyes, 1990; Karimzadeh Somarin and Ashley, 2004). It is therefore concluded that hydrothermal mineralizations occurred within the range of ~150-250°C in the region.

Hydrothermal minerals occurred after dome emplacement (Cunningham et al., 1991). The presence of alunite and dickite is indicative of an acid sulfate alteration (Choo and Kim, 2004). The dickite was formed by a dissolution-precipitation process in this period. In the first episode, acid-type fluids dissolved the rhyolitic rock and precipitation of dickite took place. In the second episode, fluids of higher pH formed the mixed-layer clay minerals in cracks and fault zones.

**Keywords:** Hydrothermal alteration, Dickite, Mixed-layer clay minerals.

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# LANDSLIDE CLAYS OF THE SENPOJI SLIDE AND OTHERS AROUND AKKESHI BAY, EASTERN HOKKAIDO, JAPAN

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The Akkeshi Bay area faces the Pacific Ocean along the eastern coast of Hokkaido, the northernmost island of Japan. A number of landslide-related disasters have occurred within this area, and the Pirikauta, Tomata, Okimanbetsu, and Senpoji Slides are well known throughout Hokkaido.

The bedrock of the landslides consists primarily of slate, shale, sandstone, conglomerate, acidic tuff, and andesite lava of the 3,000-m-thick Upper Cretaceous to Paleogene Nemuro Group, while the moving material consists of relatively fresh rock, weathered rock, debris, and earth derived from basement rocks, as well as surface soil. Rocks in contact with the slip surfaces of the relatively fresh and weathered rockslide material are mainly shale, with lesser acidic tuff. The landslide clays originated from shale consist mainly of interstratified illite/smectite minerals. On the other hand, those from acidic tuff include relatively large amounts of smectite. Interstratified illite/smectite minerals are formed from smectite by diagenesis, which is adding alkali ions and increasing temperature and pressure. This transformation starts by increasing the alkali ion content and smectite changes to interstratified illite/smectite minerals with g=0 in the early stage of the transformation.

On the basis of porosity values of 2.093-14.820 %, and according to the scheme of Aoyagi and Asakawa (1977), pelitic rocks of the Nemuro Group correspond to the stage of diagenesis to low-grade regional metamorphism. Accordingly, landslides that developed within the Nemuro Group are classified as diagenetic to low-grade regional metamorphic zone landslides. We believe that these landslides were triggered by the swelling of clay minerals such as interstratified illite/smectite minerals and smectite in shale and acidic tuff, during periods of heavy rainfall.

**Keywords:** Landslide clay, Interstratified illite/smectite minerals, Pelitic rock.

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# ALTERATION ZONATION "LOMA BLANCA" KAOLIN DEPOSIT, LOS MENUCOS, RIO NEGRO PROVINCE, ARGENTINA

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Loma Blanca is a kaolin deposit situated 70 km NW of Los Menucos (Río Negro Province – Argentina). The parent rock is a lower Triassic andesite (Vera Formation, Los Menucos Group).

Hayase et al. (1974) proposed a concentric zonation model. From the parent rock outward, three different alteration patterns were recognized. Zone 1 with sericite, chlorite and montmorillonite. Zone 2 with kaolinite and dickite. Zone 3 with dickite, pyrophyllite and alunite-natroalunite and a latter zone 4 with quartz, disseminated sulfides and diaspore.

The relation between the chemical composition of major, minor and trace elements and the mineralogical alteration zonation was evaluated to confirm the genesis of the deposit. $Fe_2O_3$, CaO, $Na_2O$, and $K_2O$ contents decrease from zone 1 to zone 3 whereas $Al_2O_3$ and LOI increase in the kaolinite-alunite zone. In alunite composition sodium prevails to potassium. High Ba, Sr, V and Zr contents were observed principally in zones 2 and 3. Co, Ni, Cu, Zn and Rb are more common in zone 1. LREE are more abundant than HREE in zones 2 and 3. $\delta^{18}O$ in kaolinites range from 10.8 to 13.2 ‰ and $\delta D$ from -83 to -85 ‰.

The mineralogical association (dickite-alunite-pyrophyllite-dispore), the alteration zonation pattern, laterally concentric, the geochemistry of the trace elements, the relation between LREE and HREE and the low $\delta^{18}O$ values, suggest that "Loma Blanca deposit" was formed by hydrothermal processes.

**Keywords**: Geochemistry, Kaolin, Argentina.

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# A CONTRIBUTION FOR THE GEOCHEMICAL ATLAS OF SANTIAGO ISLAND, CAPE VERDE – TOTAL CONTENTS OF REE AND OTHER TRACE ELEMENTS IN THE TOPSOIL LAYER

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At Santiago Island, Cape Verde archipelago, soils, stream sediments and rock samples were collected aiming compiling an environmental geochemical atlas. Santiago is the major island of the archipelago with a surface area of 991km$^2$ and an elevation of 1394 m at Pico da Antónia. The density of sampling was done according to the recommendations of the IGCP 259 – “International Geochemical Mapping”, and a chemical characterization of soils has been performed by ICP-AES after digestion in a modified aqua regia solution (Hernandez, 2008).

In this work the total contents of several elements in soils, namely Sc, Cr, Co, Zn, Ga, As, Br, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th and U, are presented for selected sites of Santiago island. The chemical contents of the whole sample (< 2mm fraction) were obtained by instrumental neutron activation analysis (INAA). Reference samples of sediment and soil (GSS4 and GSD9) from the IGGE from the People’s Republic of China were used as standards and irradiated along with the samples in the core grid of the Portuguese Research Reactor (RPI). Relative precision and accuracy are in general within 5%.

The results obtained contribute to the geochemical characterization of superficial environments of the Santiago Island, and to the establishment of the geogenic sources and other factors in the chemical elements distribution in the topsoil layer. Among the studied trace elements, a special attention is paid to the rare earth elements (REE) distribution in soils from different geomorphological units/ geological formations, and their correlation with the grain size distribution and the present clay minerals. Based on obtained data, statistical analysis was used to propose a range of values representing background concentrations.

**Keywords:** Soils, Cape Verde, Trace elements.

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# EPITHERMAL (AU, CU) DEPOSITS (ca 600 MA) IN SOUTH BRAZIL – CONSTRAINTS FROM CLAY MINERALS AND PHYLLOSILICATES

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Three epithermal deposits of similar age (ca 600 Ma) were studied on their mineralogy and compared between themselves: Lavras do Sul Gold District (LSGD) (Au, Cu), Camaquã Mine (CM) (Cu, Au) and Torquato Severo (TS) (Au). These three deposits are located in the south western part of Rio Grande do Sul state in south Brazil. They distance from each other around 50-80 km, have similar ages but were hosted in different rock types. In the LSGD a detailed study in dioctahedral phyllosilicates (phengite, illite and interstratified illite-smectite) permitted to establish a regional zonation probably associated with erosion levels and linked to vertical temperatures variations (Bongiolo et al. 2008). The mineralized veins crosscut a granitic complex and a volcaniclastic sequence. In the CM several generations of chlorites (diagenetic I and hydrothermal, II and III) were studied and concentrated in order to provide stable isotopes information, temperatures and source of the fluids. Temperatures of 100-150°C were obtained for chlorites I and II (polytype Ib (90°) and IIb), which is in agreement with quartz, carbonates and barite. For chlorite III latest vein-type, temperatures less then 70°C were obtained. The mineralized veins, veinlets and disseminations are hosted by sedimentary rocks (sandstones and conglomerates) of Camaquã Basin. In TS region the hydrothermal alteration is characterized by the occurrence of hydraulic breccias with quartz and carbonate veins that crosscut granitic and trachytic rocks, and are associated with strong chloritization, sericitization and sulphidation (veinlets + pervasive alteration). In some areas propylitic alteration was observed enveloping the vein region. The host rocks are composed of granites and gneisses with later intrusions of trachytes.

These three epithermal deposits have a strong and different structural control (LSGD: EW, CM: NW and, TS: NE and NS). The hosts rocks are not the same but their metallogenetic model is similar. In all three deposits it was not possible to define a high or low sulphidation epithermal genesis. They frequently show both characteristics suggesting different phases of oxidation state of the fluids associated with metal (Au, Cu) deposition in a straight period of the geological time.

**Keywords**: Clay Minerals, Epithermal Deposits, Hydrothermal Alteration.

# RADIATION-INDUCED DEFECTS MEASUREMENTS IN CLAY MINERALS RELATED TO UNCONFORMITY-TYPE DEPOSITS

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Uranium prospect uses classical exploration methods (research of petroleum, minerals, gas...) and methods specifically devoted to the radioactivity and the effect of $\alpha$ – particles on minerals. Thus, these ionizing radiations cause damages in the mineral structure, that we can observe using Electron Paramagnetic Resonance Spectroscopy. Some studies on quartz grains from the meso-Proterozoïc Athabasca basin (Saskatchewan, Canada) and on some clay minerals from recent geological environments (<50 My) (kaolinite/dickite; smectite) were previously realized. This study presents the first unequivocal identification of Radiation-Induced Defects (RID) in kaolinite, illite and sudoite (di-trioctahedral Al-Mg chlorite) constituting the alteration halo surrounding the unconformity-type uranium deposits in the Athabasca basin. The unconformity between meso-Proterozoïc sandstones and Archean basement seems to be the main axe of mineralized fluids circulation. The RID concentrations in samples from about 25 drill holes range from values of regional background (1.02E+17 spins/g) to highest values (7.0E+18 pins/g). Nevertheless, these concentrations are under the concentrations of clay minerals from reference deposits Nopal (Mexico), El Berrocal (Spain) and Coutras (France). Several hypotheses can be proposed to understand this observation:

1) there is a problem of normalization of the RID concentrations in samples from reference deposits;
2) in samples from the Athabasca basin, clay minerals are saturated and no more RID can be created;
3) the thermic history of this basin (200°C during several My) could anneal a portion of RID in the mineral structure.

**Keywords:** RID, Clay minerals, EPR Spectroscopy.

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# ORIGIN OF ENIGMATIC BEDS IN PROTEROZOIC SANDSTONE, ATHABASCA BASIN, SASKATCHEWAN, CANADA

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The Athabasca Group in northern Saskatchewan and Alberta fills a 100,000 km2, 2300-m+ thick basin with three siliciclastic sequences topped by a siliciclastic-shale-carbonate sequence. This reports progress on work to revise, redefine and reposition lithostratigraphic units. Dating rare tuffaceous units may help constrain sequence stratigraphic events, and mineralogical studies may document distal expressions of hydrothermal systems, both related to unconformity-associated uranium deposits.

A 10-cm, medium to dark grey, friable and clay-rich interval with gradational upper and lower contacts was observed in 2007 drill hole ML-015 in the middle of the upper Manitou Falls Formation (Dunlop Member, MFd). In strong contrast to the enclosing fine- to medium-grained competent sandstone, it comprises an unsorted aggregate of highly angular quartz grains with minor to trace mica, zircon fragments, K-feldspar, amphibole, tourmaline, rutile, magnetite, alumino-phosphate minerals, and irregularly-shaped, soft-sediment deformed clay intraclasts that enclose angular quartz. This breccia is marked by a gamma ray anomaly. Several beds, in 2008 drill hole CR-010, about 40 km away, show similar field characteristics and stratigraphic setting to the breccia in ML-015.

Typically the MFd is a pale grey, very pale red or tan, medium- to fine-grained quartz arenite with about 1-3% clay matrix and 2% clay intraclasts, both composed of dickite (+ minor illite), and trace amounts of relatively small, well rounded detrital zircon, tourmaline, and rutile. In contrast, the ML-015 sample contains a felted illite (+ minor kaolinite/dickite) matrix with intraclasts dominated by illite, and rare euhedral detrital zircon grains. The textural and mineralogical attributes suggested an explosive (volcanic or impact) origin – possibly a new tuffaceous layer in the MFd. However, this layer does not contain the classic devitrified glass shards that typify tuffaceous sediments. Faulting and hydraulic fracturing probably generated the highly angular textures and hydrothermal minerals, and may have released the orthoclase, amphibole, and magnetite inclusions from quartz. In contrast, the CR-010 beds are not breccias. They contain intact rounded quartz grains, framboidal pyrite, and their matrix is dominated by kaolinite and dickite, closer to the typical MFd composition. This research focuses on determining the multiple origins of these enigmatic interbeds and their tectonic-hydrothermal overprints.

**Keywords:** Athabasca Group, Breccia, Unconformity-associated uranium deposits.

# MINERALOGY AND GEOCHEMISTRY OF SAPONITE-SEPIOLITE TRANSITIONAL FACIES IN THE NEOGENE BATALLONES BUTTE CLAY DEPOSIT (MADRID BASIN, SPAIN)

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The geology of the Batallones butte is apparently simple constituted by a near-horizontal sedimentary sequence where three major neogene sedimentary units can be differentiated. From bottom to top, these sedimentary units consist of basal green sandy silt to clay facies (Unit I), sepiolite lutites with opal nodules (Unit II) and siliciclastic marlstones, intraclastic clays and strongly silicified limestone top beds (Unit III). The aim of this paper is the mineralogical, petrographic and geochemical characterization of the transition between Unit I and II (facies consisting of saponite and sepiolite) and its relationship with the paleoenvironmental evolution in this area of the Madrid Basin. About fifty samples have been collected from eighth lithostratigraphic sections and boreholes for their textural, mineralogical and geochemical (elements and $\delta^{18}O$-$\delta^{13}C$ in carbonates) study.

Mineralogical analysis (XRD) and SEM studies indicate transitional formation of sepiolite from Mg-smectite, highlighting a progressive increase in the ordering of sepiolite. XRD and petrographic evidences indicate that sepiolite originated first from previous phases, mainly Mg-smectite, by an intrasedimentary mechanism. A later origin by neoformation from solutions or Si-Mg gels is also proposed. The complexity of the sepiolite genesis is attested for the textural evidence of several clay generations. Elemental geochemistry and carbonate stable isotopes ($\delta^{18}O$-$\delta^{13}C$) suggests a change in the hydrochemical conditions from Unit I to Unit II decreasing the salinity (Li, Na) and the Mg/Si ratio but increasing the role played by groundwaters (Si and F input). Under these conditions is favoured the sepiolite formation over other Mg-clays. The presence of seepage-mounds where incipient sepiolite occurs corroborates the role played by groundwaters in the Mg-clays origin.

**Keywords:** Mg-clays, Groundwaters, Authigenesis.

# CLAY GEOCHEMISTRY AND MINERALOGY USED FOR PALEOENVIRONMENTAL RECONSTRUCTION OF THE MINHO ESTUARY RECENT SEDIMENTS

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Minho estuary is located in the northwestern Portuguese coast. Elongated and funnel-shaped, it is partially sheltered from the ocean by a sand spit. Two cores were drilled (close to 30 m depth) in the sand spit, aligned normal to coastline with a distance of 200 m between them. Aiming to improve the knowledge about this estuary, mineralogical and geochemical data defined the lithostratigraphic record, allowing the palaeoenvironmental reconstruction. Mineralogical composition, qualitative and semiquantitative, of the silt (<63 µm) and clay (<2 µm) fractions of the sediments, was determined by X-ray diffraction. SEM-EDAX analyses were performed on selected samples. For geochemical analysis the silt fraction was analysed by Atomic Absorption Spectrophotometry for Fe, Cu, Pb, Zn, Mn, Co, Ni, Cr, Ca and Mg. Radiocarbon data provided ages from Cal BP 13 490 to 13 150 (bottom Core 2) to Cal BP 940 to 720 (top Core 1).

For the fraction <63 µm, a comparative analysis of quartz, feldspars and micas content, as well as some other ratios: fine detritals/coarse detritals and carbonates/detritals were carried out; for the clay fraction (<2 µm), illite, chlorite, kaolinite and smectite contents and the kaolinite/illite ratio were compared, as well as the Esquevin and Kubler indexes for illite. The obtained results allowed to define unformal units along the studied log as well as to put forward paleoenvironmental and paleogeographical considerations. Clay assemblages were used as indicators of marine versus fluvial influence. The obtained data was statistically treated, by univariate and multivariable techniques (Factorial and Discriminant Analysis).

The sediments of the Minho estuary were deposited through a succession of different environments, mostly related with changes in sea-level rise, specially, with the Holocene transgression, regional climate and local forcing factors that occurred since the Late Glacial.

**Keywords:** Mineralogical data, Geochemical data, Clays, Palaeoenvironmental reconstruction, Holocene.

# GLAUCONITE AND FOSSIL PALYNOMORPHS PERMITTED TO RECONSTRUCT THE LIASSIC PALEOGEOGRAPHY JUST BEFORE THE GULF OF MEXICO ORIGIN

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Based on their own lithologic characteristics, redbeds have been considered as azoic and problematic rocks. Nevertheless, Paleopalynology and Inorganic Geochemestry proved to be two very useful sciences in order to place red beds in time and space. During the early last century, in the Mexican NE region, three Mesozoic redbed units were differentiated (Huizachal, La Joya and Cahuasas), chronologically placed from Late Triassic to Late Jurassic. As they were considered the basement of the marine petroliferous sequence in some Mexican Gulf of Mexico sub-basins, it was important stratigraphically to place them properly, where they were found not alone. Since 1969, palynological analyses allowed to place in Middle Jurassic the Cahuasas Formation in the Tampico-Misantla sub-basin. During 1988-2004, the Huizachal and La Joya redbed units, outcropping at the Huizachal-Peregrina Anticlinorium, were palynostratigraphically analysed, resulting the existence of not two but three superposed redbed units, dated and characterized by palynomorphs and palynological residues: Huizachal (Late Triassic) and La Boca (Sinemurian-Pliensbachian) alloformations and La Joya Formation (Middle Jurassic, equivalent in time to Cahuasas Formation). Also, above the base of La Boca Alloformation were found algaceous matter, dinoflagellates and acritarchs, considered as evindences of marine sedimentary condition during Liassic Time. These data were important but, as regionally isolated, it was difficult to use them for regional paleogeographic reconstruction. In order to prove the existence of an ancient marine environment among redbeds, selected rock samples and palynological residues were, from redbed units, by X ray analysed. Successfully, they proved that marine determination was correct, because of the presence of glauconite, dolomite and calcite in some greenish limolites and shales containing also abundant illite, just below the palynological sample with marine palynomorphs. They also proved that the palynological characterization of redbed units was correct, using the mineral and elemental contents obtained from diffraction and fluorescence of X ray analyses. Finally, all these data were used for knowing the paleoclimatic and tectonic conditions during the origin of redbed units and the related marine transgressive-regressive sediments. In order to reconstruct the paleogeographic distribution of these redbeds, they were correlated with other Liassic sequences from the S and SW of Mexico. This correlation allowed know that these units were deposited in a semigraben connected to an Epicontinental Sinemurian Sea, during the Middle Jurassic, invaded from NE by the tethysian waters coming through the Hispanic Corridor across the new Gulf of Mexico, formed by a triple junction origin.

**Keywords:** Glauconite, X ray analyses, Palynostratigraphy, Gulf of Mexico Origin.

# DIAGENESIS OF MALMIAN MARLSTONES, VIENNA BASIN

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Burial diagenetic processes of pelitic sediments have been the subject of mineralogical investigations in Tertiary basins all over the world. Because of oil exploration, the investigations were focused on the Gulf Coast region in the United States. The diagenetic reaction from smectite to illite can be related to petroleum migration processes. The aim of this study is to characterize the diagenetic development of the Jurassic marls of the Mikulov Formation in the Vienna Basin.

The Vienna Basin is located in the NE part of Austria and extends into Slovakia and the Czech Republic. It is a Tertiary pull-apart basin along the junction of the Eastern Alps and the Western Carpathians. The evolution of the basin started during the early Miocene with subsidence along NE trending sinistral faults. It is underlain by alpine thrusted nappes and autochthonous Mesozoic sediments.

The clay mineralogy of 46 core samples from nine different wells was analyzed with X-ray diffraction and quantified. The wells penetrate the Mikulov Formation over a depth range of 1000 m to 8500 m which gives a unique opportunity to study the diagenetic changes of one formation from shallow to deep burial. Also, by following a single formation to depth, it is possible to minimize variations which might result from differences in provenance and depositional environment.

For separation of the <2 μm fraction the carbonate was dissolved with a 0.1 M EDTA-solution before sedimentation. The clay fraction contains a prominent illite/smectite (I/S) mixed-layer mineral, illite, chlorite and kaolinite. The amounts of I/S and kaolinite decrease with depth, illite and chlorite increase with depth. A diagenetic overprint was revealed, involving a gradual transformation of smectite to illite through mixed-layer I/S intermediates. The illite content in I/S ranges from 25% for the shallowest sample to 90% for the deepest sample. The ordering of the mixed-layer I/S changes with increasing depth from R0 (25% illite in I/S) to R1 (60-80% illite) and R3 (90% illite in I/S).

**Keywords:** Diagenesis, Illitization, Vienna Basin.

# ILLITIZATION OF THE EARLY PALAEOZOIC BENTONITES IN THE BALTIC PALEOBASIN

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The Lower Palaeozoic sedimentary sequence of Silurian and Ordovician carbonate rocks in Baltic Basin contains numerous bentonites that are typically classified as K-bentonites. The variation of expandability of the mixed-layer I/S in 115 bentonites samples throughout the Baltic Basin were investigated to study the diagenetic development of Paleozoic sedimentary sections of this old cratonic structure that has recorded an exceptionally stable tectonic regime during last 500 M.y of the geological time.

The clay mineral composition of bentonites is characterized by mixed-layered I/S type mineral and kaolinite except in the Upper Ordovician Katian bentonites where chlorite-smectite (corrensite) mixed-layer mineral occurs. The kaolinite content in studied bentonite clay fractions varies considerably from 4 to 60%. The monomineral mixed-layered I/S composition is characteristic in northern, shallow facies carbonate dominated part of the basin, whereas the kaolinite content increases in central and southern part of the basin characterized by deep water facies zones in transitional and central confacies sediments.

Samples at the northern margin of the basin (present day burial depths <300 m) are characterized by expandability of 15-30%, whereas the expandability increases gradually with the depth. At ~300-400 m depth the expandability is about 35% and it does not change to about 1400 m depth in south-central part of the basin. Further in the south, in deeper part of the basin (>1400 m) the expandability in mixed-layer mineral is gradually decreasing with the increasing depth as it would be expected from normal burial trend. At depths >2000 m the expandability of Ordovician bentonites increases to about 15-20%. The variation of the expandability in the Silurian bentonites shows similar trends. Expandability of the Silurian K-bentonites, however, is in the same depth range, somewhat less compared to the Ordovician beds.

Geological data suggest that the illitization in the northern part of the basin was affected by K-rich fluids in relation to the latest phase of the development of Scandinavian Caledonides ~420-400 Ma. The more illitic I/S in the northern, shallowly buried part of the basin would suggest the K-rich fluid flow direction from north and north-west that agrees with the paleogeographic reconstruction of the elevated Caledonide range in the respect to the Baltic Basin. The illitization in more deeply buried central and southern parts of the basin was probably controlled by normal burial diagenesis.

# GEOCHEMISTRY OF THE EPITHERMAL DICKITE (JEDLINA ZDROJ, LOWER SILESIA, POLAND): ISOLATED $Fe^{3+}$ IONS

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A preliminary geochemical study of a dickite concentrate from the outcropping vein site at Jedlina Zdroj was carried out, employing X-ray powder diffraction analysis, Fourier transform infrared spectroscopy and scanning electron microscopy/energy dispersive spectrometry. The mineralogy of this concentrate is comparatively simple, dickite being the principal component (ca. 91% of total sample) with a minor amount of goethite.

The untreated dickite concentrate showed a complex electron spin resonance (ESR) signal around g=4. Such an ESR pattern has been found frequently for isolated $Fe^{3+}$ ions in a well-ordered kaolinite structure, substituting for $Al^{3+}$ in octahedral sheets. These $Fe^{3+}$ ions were resistant against chemical treatment by cold/hot HCl, but after treatment by the hot HF/HCl solution, their ESR signals disappeared, indicating that they are probably in the dickite structure.

Substantial proportions of $Fe^{3+}$ in the dickite matrix were probably contained in original hydrothermal (acid-sulfate) solution which was diluted by mixing with a groundwater, forming an epithermal solution. Both the goethite and $Fe^{3+}$ incorporated into the dickite structure imply that the epithermal formation solution was oxygenated.

**Keywords:** Dickite, Jedlina Zdroj, $Fe^{3+}$.

# MINERALOGY AND GEOCHEMISTRY OF NICKEL-ENRICHED SAPROLITE FROM JACARÉ DEPOSIT (PARÁ - BRAZIL)

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This work shows that nickel in saprolite of Jacaré Deposit, a world class deposit from Carajás Mineral Province (Brazil) are mainly hold by serpentine minerals. The analysis of saprolite samples using different techniques (optical petrography, X-ray diffraction, scanning electron microscopy with support of energy dispersive spectrometry, Fourier-transformed infra-red spectroscopy and microprobe) indicate that samples are made mainly by serpentines with the following subordinate mineral phases in decreasing order: Fe-Si aggregate minerals (goethite, hematite and quartz), quartz, chlorite (Ni-chlorite and Cr-chlorite), clay minerals, chromite, magnetite, Cr-spinel, talc and Ni-Mn-Fe aggregate minerals. Serpentines occur in different textures (mesh, hourglass, interlocking, veins and minor interpenetrating) and where identified as lizardite, chrysotile and minor antigorite. The main serpentine mineral is lizardite, which occurs in the matrix associated to scarce antigorite, while chrysotile fills the veins. Serpentinization was pervasive, affecting all primary minerals, except for the spinels, which occur as relict Cr-spinel, chromite and minor magnetite. The temperature of serpentinization was around 300°C, as indicated by the different assemblages and textures of serpentine minerals. The absence of metamorphic olivine indicates that temperature of metamorphism was below 400°C. Two chlorite types where identified: Ni-bearing chlorites (type I) that occur in the matrix or veins and Cr-bearing chlorite (type II) that is spatially associated to chromite or Cr-spinel. Talc is a minor and scarce phase and occurs mainly in the matrix. A weathering high-Ni phase is rare, occurring as Ni-Mn-Fe aggregate minerals with botryoidal habit in opaque aggregates. Weathering minerals are also represented by clay minerals (Fe-smectite, probably nontronite) and Fe-Si minerals, corresponding to goethite, hematite and quartz mixtures. Of these, only the goethite and clay minerals contain some Ni.

**Keywords:** Serpentine, Nickel, Brazil.

# THE USE OF CRYSTALOCHEMICAL PARAMETERS OF KAOLINITE TO DEFINE THE GENESIS OF THE KAOLIN FROM THE QUADRILÁTERO FERRÍFERO, BRAZIL

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The Quadrilátero Ferrífero is an important geologic province located in the Minas Gerais State, Southeast of Brazil. The geomorphologic features of this province are related to structural and lithologic controls giving rise to a dome-and-keel like architecture formed by the Archean basement and by the Archean Rio das Velhas and the Paleoproterozoic Minas Supergroups respectively. Keels are made of large synclines which include dozens of kaolin deposits originated from the deposition of lateritic colluvial materials. The kaolinite particles from the different deposits investigated by X-ray diffraction (XRD), differential thermal analysis (DTA), analytical Transmission and Electron Microscopy (ATM and SEM) and infra red (IR) and electron paramagnetic resonance (EPR) spectroscopy analysis showed two different evolutions that highlighted the superposition of two different alteration profiles. In the lower profile the crystals showed a low-defect density typical of a saprolitic kaolinite originated from an *in situ* kaolinized phyllite. In the upper profile, the kaolinite has a high-defect density typical of a pedogenetic origin where the iron content is the main factor controlling crystal properties. Despite the presence of pedogenetic kaolinite crystals throughout the upper profile, they showed appreciable variation in structural defects between the base and the top. IR and EPR spectroscopy showed typical spectra of lower defect density kaolinite at the top when compared to that from the base of the upper profile. Crystal thickness, morphology and size also showed variation between the base and the top where the crystals were small and hexagonally shaped at the base whilst at the top they were bigger, hexagonal and elongated as well as similar to the kaolinite crystals from the lower saprolitic profile. This variation in kaolinite crystal properties at the base and at the top of the upper profile defines this profile as a typical inversed lateritic profile.

**Keywords**: Kaolinite, Pedogenesis, High-defect density, Inversed lateritic profile.

# THERMODYNAMICS OF CLAY DEHYDRATION AND STABILITY WITH T, P AND $aH_2O$: CONSEQUENCES ON THE SISMOGENIC ZONE OF SUBDUCTION ZONES

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Smectites dehydration with increasing temperature or decreasing a $H_2O$ involves two different processes: i) the discontinuous loss of water layers at discrete temperature or $aH_2O$ alternates with ii) the continuous dehydration at constant volume and number of water layers. The stepwise variation of smectite volume during dehydration has important geological implications, because the loss of smectite water layers is accompanied by large and sudden volume changes (about 30% variation at each transition) and release of water (about 150 $kgH_2O/m^3$ smectite). Depending on the nature of the interlayer cation, the loss of water layer can occur at conditions well above the conditions of diagenesis to incipient metamorphism. For instance, Wu et al. (1997) observed from in-situ diamond anvil cell experiments that the $3 \rightarrow 2$ and $2 \rightarrow 1$ water layers transitions of Mg-montmorillonite occurs at $1 < P < 15$ kbar, at 250 and 600°C, respectively. If smectite is stable at such conditions, its dehydration might have important consequences in subduction zones. We propose a macroscopic thermodynamic model that reproduces the experimentally observed $3 \rightarrow 2 \rightarrow 1 \rightarrow 0$ water-layer transitions and associated volume changes as a function of the nature of interlayer cation and $aH_2O$, as well as the stability and compatibility relations of smectite with other minerals at high temperature and pressure condition. The model is used to predict by energy minimizing the stable mineral assemblages and the evolution of clay composition and hydration state for given bulk rock composition. We have calculated the evolution of the volume of sediments and the amount of water expelled during subduction, from the conditions of early diagenesis to high-pressure, low-temperature metamorphism. Strong and abrupt volume changes and water release are predicted to occur within the sismogenic zone up to 350°C.
This result raises the question of the possible contribution of clay dehydration to the < 20 km sismicity of subduction zones.

**Keywords**: Smectites, Dehydration, Subduction zones

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# MÖSSBAUER CHARACTERISTICS OF MIDDLE RIPHEAN GLOBULAR PHYLLOSILICATES (EASTERN SIBERIA) AND GEOLOGICAL SIGNIFICANCE OF THEIR ISOTOPE DATES

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Practice of the employment of globular phyllosilicates as a material for isotopic dating of sedimentary successions has shown that the obtained dates quite often correspond to time of early diagenesis of sediments and are close to their deposition age. However, post-diagenetic processes can produce structure transformation accompanied by loss of radiogenic elements and result in "rejuvenated" dates. The structural simulation together with the Mössbauer data for phyllosilicates enables to estimate, whether the present-day cation distribution is primary or resulted from post-diagenetic transformation of the mineral structure. This technique have been used to assess structure peculiarities of the globular phyllosilicates from the sandstones and siltstones of the Middle Riphean Totta Formation, Uchur-Maya Region, Eastern Siberia.

The results of structural simulation indicate that the pattern of cation distribution in the mineral structure approaches to that originated as a result of post-diagenetic processes. Thus, the K-Ar (861-810 Ma) and isochron Rb-Sr (864±4 Ma) ages (Semikhatov et al. 1989) of glauconites of the Totta Formation do not correspond to the age of sedimentation and hence have no stratigraphical significance.

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**Keywords:** Globular phyllosilicates, Mössbauer spectroscopy, Isotope age.

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# HEALTH & ENVIRONMENT

**HE1 • ASBESTOS MONITORING & ANALYTICAL METHODS**

**HE2 • CLAYS AND NATURAL ZEOLITES IN MEDICAL APPLICATIONS**

**HE3 • CLAYS AS FRIENDLY ENVIRONMENTAL MATERIALS**

**HE4 • CHARACTERIZATION AND REACTIVITY OF AIRBORNE MINERALS AND THEIR EFFECTS ON HUMAN HEALTH**

**HE5 • MOISTURE TRANSPORT THROUGH CLAY**

**HE7• SPECIATION OF TRACE ELEMENTS IN SOILS AND SEDIMENTS**

**HE8 • STABILITY OF CLAY MINERALS IN GEOLOGICAL RADIOACTIVE WASTE DISPOSALS**

**HE9 • THE INTERACTION OF $CO_2$ WITH CLAY MINERALS**

**HE10 • INTERACTIONS BETWEEN CLAYS AND INORGANIC AND ORGANIC POLLUTANTS**

# HEALTH & ENVIRONMENT

## SESSION HE1

## *Asbestos Monitoring & Analytical Methods*

# ASBESTOS MONITORING: PAST, PRESENT, AND FUTURE

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In the past there is no question that occupational exposure to asbestos lead to various diseases, especially asbestosis and mesothelioma. In turn, steps were taken to reduce workplace exposure by monitoring airborne asbestos. Initial air sampling techniques were developed to determine the amount of fibers in the air, and then steps were taken to reduce these numbers. More sophisticated methods to determine fiber type occurring in the air were then developed as it became clear that different forms of asbestos were more harmful (Ross, 1991; Plumlee et al. 2006). The polarized light microscope (PLM) could be used to identify the lager size fractions (i.e., greater a than few microns) of minerals based on routine methods used by mineralogists. However, often asbestos fibers are smaller than the resolving power of the PLM, so the higher magnification of an electron microscope was needed. And for this the transmission electron microscope (TEM) was the logical choice as it could provides both compositional and structural information. At present the state-of-the-art for identifying small amounts (i.e., what is obtained on air filters) of small samples (i.e., micron-sized) is the TEM. Recently concerns shifted from occupational exposure to what could be termed environmental exposure, or often miss-termed as exposure to "naturally occurring asbestos;" what is really meant here is "asbestos occurring in its natural setting" (Gunter et al. 2007). In these settings the concern is often asbestos content of soils or rocks. Because of this bulk methods (i.e., powder XRD, XRF, IR, Raman, etc.) can be used to detect and quantify minerals that might potentially occur in an asbestiform habit. Many of these techniques are well established in the geological community, and require only slight modification to find use in asbestos monitoring. However, the main issue that exists at present is how to define asbestos, especially when it occurs in its natural setting? At present the regulatory community tends to use the so-called counting criteria (which was developed for occupational settings of know asbestos exposures) and using the TEM, while I would propose in the future the geological community needs to take a more active role to develop newer monitoring methods to better fit the natural settings as compared to anthropogenic settings and help to define asbestos.

**Keywords:** Asbestos, amphiboles, analytical methods, environmental exposure.

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# MICROSCOPIC AND SPECTROSCOPIC (RAMAN, LIBS) CHARACTERIZATION OF ASBESTOS MINERALS IN BUILDING MATERIALS FROM ATHENS AREA, GREECE

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Within the frame of the present work the possibility of characterizing building materials containing asbestos using a combination of microscopic and spectroscopic techniques (SEM-EDS, laser μ-Raman, LIBS), has been examined. This is the first attempt to apply a methodology of complementary techniques, separately suggested for the study of asbestos minerals (e.g. Rinaudo et al. 2005, Caneve et al. 2005), with regard to potentially hazardous industrial materials (e.g. asbestos cement) extensively used in Athens area buildings before final ban of all asbestos products after 1st of Jan. 2005 (based on a 1999 EC regulation). Attention was drawn to the application of laser-based techniques due to the existence of both laboratory and portable equipments which can be used for in-situ measurements in the field without sampling or detachment of specimens. The SEM-EDS can be applied to approve the presence of fibrous serpentine minerals by excluding the presence of fibrous or asbestiform amphiboles like tremolite and hazardous crocidolite. However, the identification of the type of common serpentine polymorph (chrysotile, lizardite, antigorite) is rather doubtful. This can be easily and quickly performed using laser μ-Raman even in the field with a portable instrument. On the other hand, the distinction between serpentine and amphibole asbestos can also readily be conducted using LIBS instead of SEM-EDS. In that case the correlation of particular elemental ratios, such as Mg/Mg+Fe, Mg/Si and Fe/Si, can be used as criterion. Crocidolite shows totally different ratios compared to chrysotile and therefore the two asbestos minerals can be identified by taking into account separate areas in the relevant plots.

**Keywords:** Asbestos, Raman, LIBS.

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# THE PATHOLOGIST'S INVOLVEMENT IN THE ASBESTOS INVESTIGATIONS

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The pathologist's involvement in the diagnosis of professional/environmental asbestos exposure disease rises because this specialist studies human and animal surgical specimens, cytological material and/or perform autopsies to define the aetiology of diseases. It is very important to describe all significant pathologies, to prove if there is a causal relationship between them and impairment or death. Quality work is done by a pertinent clinical information, an appropriate interpretation of principal tissue lesions and a correct mineralogical analyses. The pathologist identifies morphological markers of asbestos specific exposure (pleural plaques, covered and uncovered inorganic fibres, mineral particles and specific tissutal reactions) but in some cases it is very difficult to identify the nature of particles without mineralogical analyses. The surveying and counting of asbestos bodies (AB) is the "gold standard". There is a relationship between the number of AB in iron-stained histological section and the AB concentration in digested lung tissue of the same sample. Values of AB = 1-2 for tissue section and AB > 1000 per g of dry lung tissue are usually considered as indicative of nontrivial (usually occupational) exposure [1]. The pathologist selects and handles the biological materials, describes the gross and histological aspect of the tissues and organs and provide the diagnoses. Different information may be obtained depending on the type of human or animal material used, e.g. sputum, bronchiolar-alveolar-lavage, urine, blood, neoplastic or non neoplastic tissue, pleural plaques. Firstly, the investigation begins usually by optical microscopy examination in order to have a general view of the sample, to check where the mineral particles are preferentially accumulated in the tissue and the size of their aggregates. Observation of microscopic sections in parallel and polarized light provides in many cases adequate answers. But in doubtful cases, the biological material must be digested to remove organic matter and concentrate the mineral particles to count AB by light microscopic observation. To investigate the elemental composition of mineral fibres it is possible to use the electron microscopy with chemical microanalyser (SEM and TEM with EDS). Collaboration with other specialists like mineralogists have to be required to acquire such knowledge. In this work the articulated procedure used to create a map of asbestos exposure in Piedmont areas (North-Western Italy Region) and to resolve some medico-legal issues will be exposed.

**Keywords:** asbestos bodies, mineral fibres, mineralogical analyses.

[1] De Vuyst P, Karjalainen A., Dumortier P, Pairon J-C, Monsò E, Brochard P, Teschler H, Tossavainen A, Gibbs A. (1998). Guidelines for mineral fibre analyses in biological samples: report of the ERS Working Group. Eur Respir J, 1416-1426.

# BIOLOGICAL ASBESTOS EXPOSURE ASSESSMENT: NEW PARAMETERS FOR AN OLD MODEL

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Since the 1950s and into this century, a direct means of exposure assessment for "asbestos" and other fibres has been lung-retained fibre analysis, in which fibres are recovered by chemical digestion of pulmonary tissues and then analysed quantitatively by microscopy. This has taken the form of transmission or scanning electron microscopy (TEM or SEM) with energy-dispersive x-ray spectrometry (EDS) for elemental identification. These techniques have had certain problems, both technical and practical. Technically, fibres have been isolated from *human* lung long after inhalation, and samples have often been processed long after acquisition (for example from autopsy tissue). Alterations of fibre in the interim have been little studied. The "leaky sampler" effect, in which fibres which clear more rapidly than other fibres cannot be accounted for, has also been a problem. In addition, increasing requirements for ethical clearance and informed consent have made the acquisition and use of such human samples more difficult.

These problems can be partially addressed through the use of recently exposed animals in habitats of interest as substitutes for human lung. In this paper I present our most recent results from one such area and discuss the use of animal samples generally, with their pros and cons. The area of study is a small subsection of El Dorado County, California. California tumour registry data show a shift of mesothelioma incidence from coastal areas to this and surrounding areas in recent years. A recently published study from the US Geological Survey identified a particular "hot-spot" at a road intersection in the county through bulk sampling and mineralogical and SEM analysis (Lowers and Meeker 2007). Morphology by SEM was asbestiform and "amphibole fibers…fall completely within the tremolite and actinolite fields". We obtained lung samples from four pets – two dogs and two cats – who lived on the immediately adjacent property in the fifteen years preceding the USGS sampling. Tissue from these samples, other pets from other parts of the county, and control animals from the province of Quebec were prepared by chemical digestion and low-temperature ashing and examined by TEM at 13,500 X, with determinations of fibre length, width, and type (by EDS). Results confirmed the presence of high concentrations (from over 100 to over 1000 fibres/ mg dry lung) of long (> 5 um) tremolite-actinolite fiber directly proportional to time of residence and time from last exposure. Lungs of animals elsewhere in the county and in Quebec were negative. Results are relevant to planned housing development in this area. In other locations, wild or domestic animals (for example, goats and cattle) have been utilized for similar purposes. I discuss how best to interpret – and to avoid over-interpretation of – such results.

**Keywords:** asbestos, tremolite, electron microscopy.

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# ASBESTOS EXPOSURES, ASBESTOS-RELATED DISEASES AND FIBER ANALYSIS IN LUNG SAMPLES

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Use of asbestos is now banned in many industrialized countries, but health consequences are still expected for at least two decades. Moreover, exposure to asbestos currently continues in several emerging countries. Asbestos-related diseases are usually the consequence of occupational exposures, but cases occurring from para-occupational, bystander or intra-mural exposures were also reported. In rural areas of several countries, fibres naturally occurring in local soils are responsible for a high incidence of asbestos diseases. Health effects of asbestos include malignant and non-malignant lesions of the lung and pleura, and more rarely peritoneum. It is often necessary to assess past exposures to asbestos for clinical, epidemiological, occupational health or even legal purposes. The difficulties and uncertainties associated with the use of occupational histories, job exposure matrixes or calculations from specific exposure databases have led to investigate the capabilities of fiber analysis in lung samples. Key points related to this topic will be reviewed here. Guidelines about technical aspects of fiber analysis and rules to interpret results were published by a workgroup of the European Respiratory Society (1). Evidence of exposure can be obtained by demonstrating elevated levels of asbestos bodies or fibres by light or electron microscopy in samples of lung tissue, bronchoalveolar lavage fluid or sputum. Relevant data are sought about the fiber types present, their amounts, their sizes, composition and crystalline structure and about their importance as aetiological agent. The measured fiber burdens integrate both phenomena of lung deposition and clearance. Compared to amphibole asbestos, chrysotile has a much lower biopersistance and evaluation of past exposures to this variety of asbestos by analysing lung samples is difficult. Interestingly, chrysotile elementary fibrils are morphologically similar to sepiolite and attapulgite fibrils. There are different dose-response relationships between lung parenchyma and pleura in response to asbestos exposure. The highest cumulative exposures and hence pulmonary asbestos bodies and fibres levels are found in asbestosis. Lower levels, corresponding sometimes to very low cumulated exposure, are usually expected in mesothelioma and in pleural plaques. However, it must be stressed that bronchoalveolar lavage fluid and lung tissue analyses are markers of alveolar and parenchymal retention of fibres, but do not reflect directly the accumulation of fibres in the parietal pleura which is very heterogeneous.

**Keywords:** Asbestos, Lung diseases, Analytical electron microscopy.

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# INDUSTRIAL INERTIALIZATION OF ASBESTOS CONTAINING MATERIALS

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The most common technique to handle asbestos containing materials is the storage in controlled landfills. Deposition of hazardous material, however, is controversial, and ways to convert asbestos into harmless minerals prior to storage have been looked for. Both chemical (f.ex. Sugama et al., 1998) and thermal transformation processes have been proposed (f.ex. Dellisanti et al. 2002). Thermal treatments will transform asbestos into inoffensive phases, either through thermal breakdown or through reactions with the matrix. The published experiments have been made in laboratory size furnaces on small samples. Little information on the influence of the matrix material and heating parameters (sample size, heating gradients, time, max. temperature) on the transformation kinetics are given.

The present contribution presents the results of an industrial scale experiment. Loose, glass fibre based insulation material with 10wt% chrysotile and pieces of porous concrete with 5wt% chrysotile (5-20cm in size) have been treated in an incineration plant. The exit temperature of the rotary kiln was set to 1200°C and a rotation rate of 0.2rpm/min was chosen, which results in a dwell time for the material of 2 hours. Whereas the chrysotile in the loose insulation material was completely transformed, the larger pieces of the porous concrete still contained asbestos (1wt%). The assemblage of new phases formed in the reaction rims of these samples (magnetite *ss*, corundum *ss*) points to peak temperatures well above 1100°C. These rims seem to function as thermal insulation. The result of these industrial scale experiments show, that results from lab size experiments (s. f. ex. Dellisanti et al., 2002) have to be taken with care. For each type of asbestos containing material (size, composition, asbestos concentration etc.), an industrial scale feasibility study is necessary to assure 100% conversion of the asbestos through the thermal treatment.

**Keywords**: asbestos, chrysotile, thermal treatment.

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# REAPPRAISAL OF ASBESTOS REFERENCE MATERIALS

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The chemical and physical characteristics of the asbestos minerals, which are responsible for many types of pulmonary pathologies, are yet debated. The bioassays of asbestos reference materials, evaluated on the basis of the incidence and latency time of tumors, highlighted a different reactivity among different asbestos minerals (Van Oss et al., 1999). Considerable research has been performed to understand the onset of the pulmonary pathogenesis, and many samples were tested in *in vivo* and *in vitro* experiments. In terms of classical concepts of standards the asbestos reference materials are relatively impure, which is somewhat to be expected as they are ores obtained from natural materials. In fact, amphiboles and serpentines are closely associated with different mineral phases and both the preparation and the reproducibility of the standard samples are difficult (Graf et al., 1980; Campbell et al., 1996).

In this work we only investigated the purity of some asbestos reference materials. The reference material we used were the NIOSH and UICC standards. Mineralogical characterization was performed by Optical Microscopy, Powder X-ray Diffraction, and SEM-EDS. The results showed a significant amount of metal oxides (Fe, Ti, Mn, Cr), mainly associated with calcite, quartz, and feldspars. The amphiboles in the reference materials showed both fibrous and non fibrous morphology. The major impurity was concentrated in the fibrous samples of chrysotile, crocidolite and tremolite. In particular the UICC sample of crocidolite is the most impure, containing iron oxides, calcite, apatite, and quartz.

On the basis of these results, it seems necessary to improve the characterization of the asbestos standards with the aim to increase the detailed knowledge of the associated minerals, which could play an important role in the development and/or progression of pulmonary pathologies. To that end, a Rietveld investigation, for a quantitative mineralogical analysis, is also in progress on these materials.

**Keywords:** Asbestos, Reference materials, Carcinogenicity.

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# RAMAN SPECTROSCOPY AND ESEM-EDS: INNOVATIVE TECHNIQUES FOR THE MEDICAL MINERALOGY

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A close scientific collaboration between mineralogists and pathologists is allowing to delve the knowledge on the mechanism for which some mineral species involve effects on the Public Health. In fact, some mineral phases have been considered able to provoke important diseases, especially on respiratory system; some of them have been correlated mainly with occupational exposure – as asbestos and crystalline silica; for others a link with environmental exposure have been found (i.e. fluoro-edenite, erionite). In order to understand the interaction between fibres and cells, many *in vitro* experiments have been performed in order to study the cells response when in contact with the inorganic phases. Another way, is to study the burden of inorganic particles and fibres in the pleural or pulmonary tissues by using different microscopic techniques (SEM-EDS, TEM-EDS). These techniques require a long preparation of the samples, with chemical digestion of the organic matrix and filtration of the inorganic materials on a suitable support. During this preparation, the information about the position of the inorganic phases –intra- or extracellular- is lost.

We describe in this work a study of particles and fibres directly onto the histological sections from pleural and pulmonary tissues of patients affected by important respiratory diseases by means of two innovative techniques: microanalytical environmental scanning electron microscopy (ESEM-EDS) and micro-Raman spectroscopy. Both allow to observe the histological sections without further manipulation of the samples. A procedure allowing to examine exactly the same inorganic phase under the two instrument has been worked out. Applied to the same fibre or particle micro-Raman spectroscopy allowed to identify the vibrating chemical groups or the mineral phase associated to the inorganic grain, when the crystalline structure was preserved by the biological system. The ESEM-EDS characterization, defining the elemental chemical composition of the analysed phases allowed: a) a certain settlement of the mineral phase when the spectroscopic data were unsure; b) to define the chemical elements of the inorganic phases released in the cells.

**Keywords**: Medical Mineralogy, ESEM-EDS, micro-Raman.

# USING POWDER X-RAY DIFFRACTION TO SCREEN FOR ASBESTOS MINERALS OCCURRING IN THEIR NATURAL SETTINGS

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The use of powder X-ray diffraction (XRD) historically has seen little use in determining asbestos content of materials. A significant portion of asbestos identification was related to anthropogenic use of the asbestiform minerals in building products. In the past decade more importance has been given to the exposure of asbestiform minerals in their natural settings. Historically the use of light and electron microscopic techniques has been employed to detect and quantify asbestos content. However, the merits of using XRD result in non-biased quantitation and the analyses of greater amounts of material. Only after significant potential asbestiform minerals are detected by XRD, would microscopic methods be employed to ascertain their morphology. Recent studies have been published in the use of XRD to detect and quantify amphiboles in chrysotile (Addison and Davies, 1990; Gunter et al., 2007) and amphiboles in vermiculite (Sanchez and Gunter, 2006; Gunter and Sanchez, 2008).

Soil samples collected in Italy and the United States were screened for amphibole content, and almost all showed detectable levels of amphiboles based on the presences of the 110 peak. Amphibole-spiked standards and the Rietveld method were used to quantify the amphibole content. Calibrated standards were made using tremolite exhibiting different crystal habits. Quantification of the two methods were then compared. For concentrations greater than 0.5% the spiked standard and Rietveld methods yield comparable results. The use of Rietveld method on samples containing less than 0.5% amphibole performed less reliably. The use of spiked standards work better for low concentrations; however, it is essential to ensure that standards are homogenous. The use of Rietveld-based calibration regressions are also assessed for samples containing less than 0.5 % amphibole.

**Keywords:** Powder X-ray Diffraction, Asbestos, Amphiboles.

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# ASSESSMENT OF RISK FROM ASBESTOS CONTAINING SOILS

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The increasing sensitivity of analytical methods, particularly the use of electron microscopy, means that naturally occurring asbestos can be detected in many soils and minerals, as well as from soil from old industrial sites, where it was present in building structures before demolition. However, the detection of these asbestos components (often <1% w/w) does not necessarily present a risk to health from inhalation of the fibres. A strategy has been developed which measures the ability of the material (soils/mineral etc) to produce respirable fibres in air. The analytical approach is a tiered procedure, first using detailed microscopy, then water release tests, and finally airborne release tests, the latter enabling the soil matrices to be ranked in order of releasibilty, and for the asbestos release to be compared with inhalable and total dust fractions. Finally, the airborne concentration can be used in a human health risk assessment model to produce estimates for excess lifetime cancer risk for residents and workers on the site.

This strategy has been utilised in a number of situations, where asbestos was found to be present in contaminated soil, and these will be described together with the outcomes.

# HEALTH & ENVIRONMENT

## SESSION HE2

## *Clays and Natural Zeolites in Medical Applications*

# CLAY MINERALS ON DRUG DELIVERY

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In drug therapy, it is important to provide therapeutic levels of pharmaceutically active agents to the site of action and maintain them during the treatment. Modified release technologies are employed to deliver active ingredients in a controlled manner, providing some actual therapeutic temporal and/or spatial controls of drug release (1). Most of these strategies assume a new concept of "excipient". Thus, excipients are not only "inert ingredients", but they can also be used by formulators to provide targets of a biopharmaceutical (decreasing or increasing dissolution rate, delaying and/or targeting drug release), pharmacological (prevention or reduction of side effects), technological (taste masking) or chemical (increasing stability) nature. In particular, pharmaceutical grade clay minerals have been extensively applied to delay (extended-release systems) and/or target (site-specific release systems) drug release or even improve drug solubility, because of the good intercalation capacity offered by the clay particles (2). Some properties of natural clays (specific surface area, porosity, hydrophilic character, kind of exchangeable cations) may be modulated to improve their affinity with the bioactive molecules. Clay layers may be also permanently held apart to obtain intercalated structures ('pillared clays') with higher loading capacities (2). Finally, new applications are gaining growing attention in this field, including design of inorganic non-viral gene vectors (3) and hybrid systems of clay particles dispersed in a polymer matrix with new and interesting properties (4). As for example, polymer-clay nanoparticles have been used to improve the cellular uptake of anticancer molecules with limited oral bioavailability (5).

**Keywords:** Drug delivery, clay minerals, polymer clay nanocomposites.

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# MOBILITY OF ELEMENTS INFLUENCED BY INTERACTION BETWEEN ARTIFICIAL SWEAT AND PELOIDS USED IN SPANISH SPAS

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In this research all peloids used nowadays in Spanish spas have been studied. The samples have been characterized mineralogical and chemically, ranging in composition from bentonite to common clay or even peat-clay mixtures. The peloids have been mixed and stirred during 1hour with artificial sweat (EN 1811:1998+A1: 2008) at 45ºC (±2ºC), simulating the thermal-therapy action commonly utilized in the spas. Later the leached extract has been analyzed chemically after centrifugation and separation. In the sweat leached extract the concentration of 31 essential and/or potentially toxic elements has been determined by means of ICP-MS, ICP-AES and AAS.

The main leached elements are Na, Ca, Mg and K, but in smaller proportion are also Si, Sr, Ba, B, Al, Br, Fe, Mo and Mn. Some elements; Ag, Be, Cd, Co, Cr, Hg, Se, Tl, or Th are not leached with the sweat, whilst the lixiviation of others elements including Li or Rb depends of the peloid composition used.

The quantity of the elements after leaching is more related with the composition of the medical mineral water than with the mineralogical composition of the raw material. In those cases in which the mineral water has scarce Na and the peloid is mostly composed of smectites, an important decrease of Na takes place in the sweat. It is also remarkable that some elements including Cu, Ni, Pb, Zn or Rb are ab/adsorbed from the sweat to the peloid removing them from the leached extract.

The content of potentially toxic elements (Hg, As, Cd and Se among others) in the leached extracts is negligible.

**Keywords**: Sweat leaching, Spanish mud therapy, Essential and/or toxic elements.

# PHYSICO-CHEMICAL CHARACTERIZATION OF COMMERCIAL CLAYS USED AS COSMETIC PRODUCTS

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The present study aims the characterization of clay samples available on market for cosmetic purposes, in order to assess the quality of these clay products. A total of 10 cosmetic products (6 powders and 4 pastes) were selected. Samples characterization comprised textural, mineralogical and chemical analysis. Technical properties such as: cationic exchange capacity, exchangeable cations, specific surface area, expandability, consistency parameters, abrasivity index and cooling kinetics have been determined as well.

Grain size distribution was assessed using wet sieving and an X-ray grain size analyzer (Sedigraph 5100 of Micromeritics). All the samples showed high contents of fine fraction and almost all revealed more than 50% of particles <2 µm.

Mineralogical analysis of both fine and clay fractions were carried out by X-Ray diffraction, in random-oriented powders (total sample) and in oriented aggregates (<2µm). According to the results, two groups of samples could be established: Group I - showing a mixed siliceous and carbonated mineralogical composition of total sample and a clay fraction consisting mainly of illite, kaolinite and chlorite; Group II – exhibiting a siliceous mineralogical composition of total sample and kaolinite and smectite as main clay minerals. Concerning the products labeled as “Green Clay”, all samples revealed presence of feldspars and illite as main clay mineral.

Chemical composition was assessed by X-Ray fluorescence and provided the data for major chemical elements: $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $TiO_2$, MnO, CaO, MgO, $K_2O$, $Na_2O$, $P_2O_5$ and Loss-on-Ignition. Trace elements considered toxic such as: As, Sb, Cd, Co, Cu, Pb, Ni, Zn, Se, Te, Tl, and Ba were also analised. Samples of group I revealed higher content of Mg, Ca, K, Sc, V and Sr while samples of the second group showed higher contents of Al, Ga, Pb and U.

The bioavailability of trace elements that can be located in the structure of clay minerals, accessory phases or adsorbed on particles should be taken in consideration.

Regarding technical properties, samples of group I revealed higher abrasive index, and Ca and Mg as main exchangeable cations. Group II samples revealed higher expandability and cooling kinetics than group I.

**Keywords:** Health Care Products, Cosmetic, Clay minerals.

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# MINERALOGICAL AND PHYSICO-CHEMICAL FEATURES OF CLAYEY MATERIALS USED FOR HEALING/AESTHETIC PURPOSES

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The general idea of people about clays is that they are just materials for ceramics production, forgetting that, being the most abundant components of the surface of the "mineral world" they are the minerals showing the greatest diversity of reactions and hundreds of uses. Therapeutic effects of clays are an example of such uses, and although being done since prehistoric times, only more recently properties of clays beneficial to human health are object of interest and study by scientific community.

In Portugal, their application for healing purposes is done outdoor since historical times (on beaches) mixed with seawater, or indoor, usually on thermal centers, mixed with minero-medicinal waters. For people who ignore mineralogical and chemical background, clays are carriers of both beneficial/dangerous factors and physical properties that highlight their importance as therapeutic products.

This study aims the assessment of mineralogical and physico-chemical features of clayey materials used in empirical applications, for healing and aesthetic purposes.

Studied clayey materials are from Mesocenozoic Portuguese geological formations such as: Consolação Beach Jurassic dark marly clays, Penedo Beach Miocene dark clays, Parede Beach Lower Cretaceous dark silty clays, Burgau Beach Lower Cretaceous green clays, Calc-schist alteration products from Ficalho metamorphic complex and Xabrega Miocene clays, which have therapeutic uses through historical times. Also, two green clays for external use on aesthetic masks were studied.

After fine fraction being separated by wet sieving, mineralogical data of fine and clay fractions were obtained by XRD analysis; chemical data of major and minor elements, were obtained by XRF and Flame-Spectroscopy methods; and grain size distribution was assessed using an X-ray grain size analyzer. Cation exchange capacity and physical properties such as plasticity, cooling rates, abrasivity and specific heat were assessed.

Despite having different genesis, these materials exhibit high smectitic content and thus, low levels of hazards, good thermophysical properties (cooling rates and specific heat), good technological properties (abrasivity and plasticity properties) which allow us to conclude their applicability on pelotherapy treatments.

**Keywords**: Pelotherapy, smectitic clays, thermophysical properties.

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# THE *IN-VITRO* PERCUTANEOUS MIGRATION OF CHEMICAL ELEMENTS FROM A THERMAL MUD FOR HEALING USE

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In-vitro experiments have been developed to ascertain whether pelotherapy applications involve the transfer of chemical elements from the healing mud to the human body, across the skin. All the materials used for therapy (raw clay, mineral water and healing mud obtained after maturation) have been characterised from different points of view (mineralogy, chemistry, exchange properties, radioactivity, grain size and microbiology) in order to get an accurate knowledge of the natural media used for therapy and to follow the development of maturation in the spa centre.

A polymineralic silty clay with rather a common mineralogical and chemical composition is used; the mud is matured in a very saline mineral water, of marine origin, for 5 months. Under these conditions the maturation process increases the dispersion of clay particles and allows cation exchange between clays and water, whereas neither microbiological nor mineralogical changes are detectable. In absence of the biologic indicators of mud maturity, the equilibration of clay with mineral water represents an objective quantitative criterion.

*In-vitro* tests have been carried out by using the Franz-type diffusion cells, which show that the transfer of chemical elements across the skin is very well-developed, and also involving many essential or possibly essential elements. The amounts of chemical elements transferred were compared with toxicological guidelines and with world-wide daily requirement models.

No concerns appear from the data, whereas a significant supply of some elements results from a typical application of thermal mud (20 minutes, full body). The elements which have been considered in order to represent a significant supply are Li, Sr, B, I, Rb, Br, Ba, Na, Cl, Se and Ca, some of these are essential nutrients.

**Keywords:** Pelotherapy, Essential elements, Percutaneous, Absorption.

# HEALTH & ENVIRONMENT

## SESSION HE3

## *Clays as Friendly Environmental Materials*

# CHARGED CLAYS: AN ENVIRONMENTAL SOLUTION

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This article canvasses a relatively simple solution to a range of environmental problems that includes the escape of fertilizer elements from agricultural land; terrestrial and aquatic pollution caused by effluents from feedlots, abattoirs, sewage treatment plants, mine-sites etc; and toxicity in drinking water obtained from inappropriate sources. The common denominator linking these problems is the movement of chemical species in ionic (electrically charged) form across biological and non-biological phases, with the receptor phase unable to adsorb the consequences of the transfer. In the suggested technology, negatively and positively charged ions would be attracted to positively and negatively charged substrates similarly to the way iron filings are attracted to a magnet, thereby controlling ionic movement and distribution. The substrates would be positively and negatively charged clay materials.

Nature has provided a mechanism in some situations for controlling the movement of cationic species in soil where certain clay materials have negatively charged surfaces that attract positively charged cations (Ca, Mg, K etc). A prominent group of clays in this process, the smectites, has as one of its members the clay mineral Bentonite, of which there are enormous deposits worldwide. However, there are no large accumulations of positively charged natural clays that would attract anions ($NO_3$, $PO_4$, $SO_4$, $AsO_4$ etc), but it is technically feasible to manufacture Hydrotalcite, a clay material that has this required property and which can be produced from inexpensive sources such as bauxite, magnesite, and even seawater.

The two platforms, saturated with cations and anions, could be used as the basis of a fertilizer industry where the ions would be delivered in slow-release form, and in individual amounts, to suit the requirements of particular crops or the soils on which they are grown. Furthermore, the clays could be used to treat effluent streams (from feedlots, abattoirs etc), converting soluble ions to slow-release forms and returning them to the soil, thus closing the nutrient loop in the food production and consumption process.

Finally, the use of hydrotalcite to remove toxic anions such as arsenic and fluoride from drinking water and mine waste, and to remove phosphate from freshwater bodies, is discussed.

**Keywords:** Charged Clay, Novel Fertilizer, Effluent Treatment.

# ACID ACTIVATION AND BLEACHING CAPACITY OF SOME LOCAL CLAYS FOR DECOLORIZING USED OILS

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The management of used oil is particularly important because of its large quantities generated globally, its potential for direct re-use, reprocessing, reclamation and regeneration, and its detrimental effects on the environment if not properly handled, treated or disposed of[1,2]. The removal of undesirable, highly colored materials of an asphaltic or resinous nature from petroleum fractions through adsorption by acid activated bentonite (Fuller's earth) and bauxite are still the most important commercial application of adsorption refining[3].

Different types of clays found in Iraqi Kurdistan region have been characterized and used as bleaching earth for the decolorization of used lubricating oil. Acid treated and untreated used-lubricating oils were bleached by these clays. The clays were acid activated by mineral acids at various temperatures and time period of activations to optimize the best condition for production of good quality bleaching clay. 2M HCl, 1:15 clay/acid ratio, 800 rpm stirring at 70°C for 2 hours was found to be the optimum conditions. Bleaching experiments were conducted at temperature between 200 and 450°C for 3 hours. Best decolorization results were obtained from Kiffry region clay after acid activation, which was comparable with standard bleaching earth imported from China and Iran. The results were also compared with Standard Fuller's earth. The adsorption isotherms of the bleaching process were studied, and Freundlich equation was more applicable than Langmuir equation for the bleaching process of used lubricating oils by the clay samples. The process is physical adsorption by weak bonds between the dark colored compounds in oil and the clay adsorbent.

**Keywords:** Bleaching clay, Acid activation, Decolorizing.

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# SYNTHETIC ACID SAPONITES: A PROMISING ENVIRONMENTALLY FRIENDLY CATALYST FOR THE TRANSFORMATION OF METHYL EPOXYSTEARATE

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The use of clay minerals has ancient origin and nowadays these natural materials are extensively employed for a great number of environmental and engineering applications. Natural clays are largely available and have low price. However, their use requires several extensive purification steps. Depending on the genesis process and on the provenance site, the chemical composition of natural materials can be extremely variable and this represents a strong limitation in their use especially when surface properties have to be strictly controlled. Lamellar solids with controlled chemical compositions, tunable morphology and enhanced physico-chemical features can be now obtained trough specific synthesis procedure. Among smectites, saponite is arising large interest because of its surface acidity to its thermal stability features[1]. A fine tuning of the concentration and acid strength of surface acid sites can be achieved by optimizing the preparation procedure of saponite materials. After the acid treatment in mild conditions the saponite morphology appeared unaltered (TEM analysis), while (as revealed for the first time by CO adsorption at 100K) different families of Brønsted acid sites are present. Interestingly, these solids contain a significant amount of acid sites whose acidity is similar to that observed in strong acid zeolites. Moreover, the presence of an additional amount of Al-OH species with medium acidity was also observed. The distribution of surface acid sites is strictly dependent on the acid conditions adopted for the activation[2]. Acid activated saponite were tested as heterogenous catalysts for the ring opening of epoxidized fatty acid derivatives, a valuable transformation for the production of precursors of biopolymers. Working under appropriate conditions, after 5 minutes, 90% of the epoxide substrate is converted and the main reaction product is methyl methoxyhydroxystearate, with a 60% of selectivity[3]. Acid saponite, an environmentally benign catalyst, showed higher catalytic performances than mineral acids, such as $H_2SO_4$, widely used for this reaction, showing Brønsted acid sites comparable to those of conventional protonic zeolites, but with a high accessibility, comparable to that of mesoporous materials.

**Keywords:** Synthetic saponite, Surface acid sites, Methyl epoxystearate conversion.

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# ALLOPHANE NANOCLAYS FOR ENZYMATIC IMMOBILIZATION: POTENTIAL USE TO INCREASE THE BIOCATALYSIS OF PHOSPHATE

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Soils derived from volcanic ash, such as Andisols, contain natural nanoparticles. The more important constituent of Andisols is allophane, which is a non-crystalline aluminosilicate. The main characteristics of these nanoparticles are: sphereroidal morphology with an outer diameter of 3.5–5.0 nm, the thick wall (0.7–1.0 nm) is composed of an outer Al octahedral sheet and an inner Si sheet, and defects in the wall structure give rise to perforations of ~0.3 nm diameter[1]. Also, these nanoparticles form stable microaggregates with pores within the nanoscale range and physical characteristics similar to silica nanomaterials (important biocatalysts). Studies have suggested that nanomaterials are more promising clays for enzyme immobilization compared with conventional materials. The aims of this study were: 1) to characterize natural clay and nanoclay from an Andisol; and 2) to evaluate clay and nanoclays as support to immobilize acid phosphatase. An Andisol, denominated as Piedras Negras, taken from Southern Chile was sampled at 0–20 cm of depth, sieved to 2 mm mesh and air-dried. One part of the soil was treated with 30% hydrogen peroxide to remove soil organic matter. The separation of particle-size < 2 μm fractions was performed by sedimentation procedures based on Stoke's law. Natural nanoclays were extracted using the methodology described by Liu et al. (2005). These were characterized throughout energy dispersive X ray, transmission electron (TEM) and scanning electron (SEM) microscopy, and electronic diffraction (ED). The complexes were formed by interaction between acid phosphatase and those materials in study, and used as model systems to simulate enzymatic reactions in heterogeneous environment. The enzymatic activities were measured with p-nitrophenylphosphate (pNPP) as substrate. The kinetics parameters ($V_{max}$ and $K_m$ values) were calculated according to Michaelis–Menten equation. The TEM analysis showed the nanoclay presence (< 50 nm) in the samples evaluated. The occurrence of amorphous and crystalline particles was observed by DE analysis in samples of the clay and nanoclay. The SEM analysis of the immobilized phosphatase revealed cavities of different sizes. The enzymatic activity increased 90 % compared with the free enzyme. Likewise, the kinetic parameters showed that the catalytic efficiency (from 60 to 70 %) and $V_{max}$ (from 110 to 130 %) were enhanced.

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**Keywords:** Natural nanoclays; Allophane; Aluminosilicate.

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# MINERALOGY, GEOCHEMISTRY AND ENVIRONMENTAL ASSESSMENT OF MEDICINAL CLAY FROM SOUTHEASTERN NIGERIA

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Atakiri is the Igbo name given to the medicinal clay deposit in southeastern part of Nigeria. The clay is used for molding pots, building houses, skin protection and edible by pregnant women to aid in child delivery.

The mineralogy and geochemistry of trace elements and the quality parameters of some selected clays regarded as medicinal from southeastern Nigeria were investigated for the first time. The clay samples were collected from three major existing potential mines sites situated in the following towns: Nteje, Umuawulu, and Ogbu. The samples were analyzed using X-ray powder diffraction (XRD), inductively coupled plasma-mass spectrometry (ICP-MS), atomic fluorescence spectrometer (AFS) and scanning electron microscopy (SEM). The concentrations of fourteen potential hazardous trace elements, including Hg, As, Ba, Se, Pb, Cd, Ni, Cr, Co, Mo, Mn, Cu, V, and Zn in coals were determined. To evaluate quality of the proposed analytical method, the GBW standard reference materials; GBW 07312 for sediment was also analyzed. The results obtained with the ICP-MS are in agreement with the GBW certified values. Arsenic speciations as well as persistent organic pollutants (POPs) studies were also carried out.

The mineral composition of the studied clay samples is dominantly made up of chlorite, and barium with minor traces of copper and zinc. The concentrations of the trace elements are relatively low compared to coal, shale and sandstone from the area. However, most of the elements are noted to be associated with sulphide minerals and may be harmful to the people residing in this region. Additional work is necessary to determine the health implications of eating the clay without any processing.

# THE INFLUENCE OF CATION EXCHANGE CAPACITY OF CLAYS ON THE MICROSTRUCTURE OF THE RESULTANT ORGANOCLAYS

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During the last ten years organoclays have attracted great interest due to their wide applications, such as being adsorbents for organic pollutants and constituents in nanocomposites. However, little attention has been paid to the influence of clay characteristics on the microstructure and property of the resultant organoclays. The latter is of high importance to the applications of organoclays.

In this study, three montmorillonites with different cation exchange capacities (CECs) and surfactants with various numbers of alkyl chains were used to prepare organoclays at different surfactant concentrations. A combination of various characterization techniques was applied to investigate the microstructure of the obtained organoclays. Then, p-nitrophenol was chosen as model pollutant to test the efficiency of the organoclays to remove contaminants from water. The present study shows that the basal spacings or d(001) maxima of the organoclays strongly depend on CEC of the used montmorillonite and on the length and the number of the alkyl chains in the surfactants. However, when the same surfactant was used, the d(001) maxima for montmorillonites with different CECs are similar whereas the amount of loaded surfactant within the organoclays increases with CECs. This is very important for the selection of clays to prepare organoclays at low cost. With the increase of the loaded surfactant the basal spacing increases and the stacking of the clay layers becomes regular. The sorption experiments show that the sorption of p-nitrophenol onto organoclays with surfactant loading up to the CEC involves both surface adsorption and partition, whereas p-nitrophenol sorption to organoclays with surfactant loadings greater than the CEC mainly results from partition.

**Keywords:** Organoclays, Microstructure, Sorption.

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# ADSORPTION ABILITY FOR SEVERAL HARMFUL ANIONS OF ZN-FE LAYERED DOUBLE HYDROXIDE

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Layered double hydroxides have attracted attention as a high-capacity adsorption material for harmful anions. The structure is based on brucite-like layers in which some of the divalent cations have been partially replaced by trivalent ions giving positively charged sheets. This charge is balanced by intercalation of anions in the hydrated interlayer regions. The anions are exchangeable and this property can be applied to adsorb harmful anions polluting water and soil. The anion selectivity of LDHs is considered to be affected by the metal ion species and interlayer anion. Many researchers have studied the adsorption behaviour of LDHs for use in cleaning up a polluted environment.

Zn-Fe LDH with sulphate as the interlayer anion is a new type of LDH, as it is composed of a new combination of metal ion species.1) Thus, in this study, Zn-Fe LDH with sulfate as the interlayer anion was prepared by the coprecipitation method, and its anion adsorption ability was examined. The obtained LDH was characterized by powder X-ray diffraction (XRD), simultaneous thermogravimetric and differential thermal analysis coupled with mass spectroscopy (TG-DTA/MS), energy dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS). To clarify the thermal behaviours, the LDH was calcined at 350, 550 or 950 °C for 10 min, and the samples were analyzed by Fourier transform infrared (FTIR) and XRD measurements. Moreover, a comparative study was performed on the adsorption abilities of Zn-Fe LDH and Mg-Al LDH.

Zn-Fe LDH lost water molecules through three steps below 300 °C, and transformed to the amorphous phase. The recrystallization from the amorphous phase to ZnO, $ZnFe_2O_4$ and $Zn_3O(SO_4)_2$ occurred at approximately 450 °C. Furthermore, $Zn_3O(SO_4)_2$ decomposed to ZnO, $SO_2$ and $O_2$ above 700 °C. Zn-Fe LDH was found to be a more effective adsorbent. In particular, Zn-Fe LDH exhibited high selectivity for phosphate, chromate and selenate ions. The adsorption ability of Zn-Fe LDH for phosphate ions depends on the initial pH, and it increases with decreasing pH. It becomes clear that Zn-Fe LDH was stable over a wide range of pHs (pH = 2-12). Considering the simple synthesis, high anion adsorption capacities and pH stability of Zn-Fe LDH, this material has high potential for use as an effective adsorbent for water purification.

**Keywords**: Zn-Fe layered double hydroxide, Harmful anions adsorptions, Thermal behaviour.

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# APPLICABILITY OF AUSTRIAN CLAYS AS ADOBE CONSTRUCTION MATERIAL

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Loam was used as a traditional construction material for more than 10.000 years and nowadays the advantages of this material are appreciated again in many different ways (MINKE, 1995).The applications of loam reach from the preservation of ancient monuments and historical buildings, sealing compound up to the low energy housing - the so called passive house. Loam is a sustainable, renewable material that can be recycled and therefore harmonises with nature.

Loam, is a fine-grained sediment consisting of sand, silt and clay in similar portions. Clay as the binding agent with its typical characteristics like swelling and shrinking, the ability to regulate air humidity, as well as its typical plasticity properties, and the adsorption capacity give reason to find out more about this resource.

The objective of this project is to find out 1) if the mineralogical composition is correlated with physical parameters such as compression and tensile strength, fluid and shrinking limits; and 2) it is possible to deduce the physical properties from the mineralogical composition.

Particle size analysis, bulk and clay mineralogy, and pH measurements on the one side and typical geotechnical and physical examinations on the other side should point out that significant mineralogical patterns influence the physical and mechanical properties.

The results of the study show properties and skills of this renewable building material and also point out the sustainability of adobe construction.

**Keywords:** Adobe construction, Clay minerals, Loam.

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# IMPACT OF BITUMEN SURFACE CHEMISTRY ON BITUMEN RECOVERY FROM CLAY TAILINGS

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Water-based extraction of bitumen from surface-mined oil sands is often hampered by bitumen oxidation, as well as high clay content in the ore. During flotation, both of these factors result in the carryover of large quantities of clay minerals, which would normally report with the extraction tailings, to the bitumen froth. Mineral-bitumen interaction can also result in the loss of bitumen to the clay and mineral tailings streams. In general, bitumen recovered from tailings has a surfactant loading that makes recovery and re-introduction to bitumen process streams difficult. This study examines the relative influences of bitumen chemistry and clay minerals on tailings-bitumen recovery, as well as their roles in determining overall recovery in problem ores. Surface chemistry modifications to enable the processing of bitumen recovered from tailings streams in existing unit operations were evaluated.

Microscopic, spectroscopic, and diffraction techniques were used to evaluate the nature of the bitumen surface and associated clay minerals for several Athabasca oil sand ores and clay tailings. A bench-scale extraction protocol was developed to recover oxidized bitumen from clay tailings.

The extraction studies revealed that bitumen recovery from tailings is limited by the degree of bitumen oxidation rather than the high concentration of high-surface-area clay minerals in tailings. Bitumen oxidation concentrates surfactants on the surface and results in the formation of amoebic bitumen microstructures that trap minerals, reducing froth quality and increasing the loss of bitumen to tailings. Reducing the effects of oxidation by solubilizing naphthenic acids was found to inhibit the formation of mineral-trapping microstructures, thereby improving bitumen recovery and froth quality significantly.

**Keywords:** Bitumen, Clays, Microscopy.

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# FIELD EVALUATION OF LOCALLY PRODUCED COLLOIDAL-SILVER-IMPREGNATED CERAMIC FILTERS FOR POINT-OF-USE WATER PURIFICATION IN SAN MATEO IXTATÁN, GUATEMALA

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A recent study (Oyanedel-Craver and Smith, 2008) has demonstrated that colloidal-silver-impregnated ceramic filters (produced according to the manufacturing and design criteria of the non-governmental organization Potters for Peace) can effectively remove *E. coli* from water in laboratory tests. Herein, we extend this research to investigate the performance and social acceptance of ceramic filters in a controlled field study in San Mateo Ixtatán, Guatemala.

Ceramic filters were manufactured in the community with local labor and materials (clay, water, and sawdust) and then treated with colloidal silver (which acts as a disinfectant). In August 2007, 30 households received filters and minimal instruction in their use and maintenance. The heads of each household were surveyed to collect basic educational, socioeconomic, and health data. In June 2008 a second survey was conducted to assess the level of satisfaction of filter use. Household unfiltered and filtered water samples were collected three times – in August 2007, January 2008, and June 2008. Samples were tested for total coliform and *E. coli* bacteria using a membrane filtration/incubation method. After 10 months the filter effluents were also tested for colloidal silver leaching using a colorimetric method. For the three consecutive sampling events, respective percent removals of total coliform and *E. coli* bacteria were 97.68% and 99.99% (August 2007), 90.63% and 75.38% (January 2008), and 66.16% and 92.63% (June 2008). In January and June, the filtered water had a higher concentration of *E. coli* than the unfiltered water in six and five filters, respectively. This is likely caused by one or more of the following factors; 1) the unfiltered and filtered samples may have different starting concentrations of *E. coli* bacteria 2) potential flaws and/or variability in the manufacturing process, and 3) recontamination of filtered water due to improper handling. In June 2008, the average colloidal silver concentration in the filtered water was 0.02 mg/L, well below the USEPA standard of 0.1 mg/L.

At the end of ten months, 28 out of 30 families were still using the original filter. One family's filter broke at nine months and a second family chose to discontinue use. The overall response of those surveyed was positive; of the 30 households that received filters, 29 were satisfied with the technology. The most common benefit cited was improved health, specifically a reduction in both stomach pain and occurrence of diarrhea.

**Keywords:** Nanosilver, Pathogen, Disinfection.

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# ENVIRONMENTALLY FRIENDLY SLOW RELEASE FORMULATIONS OF ALACHLOR BASED ON CLAY-PHOSPHATIDYLCHOLINE

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A new clay-liposome complex was developed for reducing leaching of herbicides and contamination of groundwater. The liposomes were composed of the neutral and EPA approved phospholipid phosphatidylcholine (PC). Adsorption of PC liposomes on the clay mineral montmorillonite could exceed the cation exchange capacity of the clay, and was well simulated by the Langmuir equation. XRD results for 6 mM PC and 1.6 g/L clay (3 d incubation) yielded a basal spacing of 7.49 nm, which was interpreted as the formation of a supported planar bilayer on montmorillonite platelets. Fluorescence methods demonstrated structural changes which reflected adsorption of PC followed by loss of vesicle integrity as measured by the penetration of dithionite into the internal monolayer of fluorescently labeled liposomes, resulting in a decrease in fluorescence intensity to 18% of initial after 4 h. Energy transfer was demonstrated after 1h from labeled liposomes to montmorillonite labeled by an acceptor. The neutral herbicide alachlor adsorbed on the liposome-clay complex, yielding a formulation of up to 40% a.i., and 1.6-fold reduction in herbicide release in comparison to the commercial formulation. Hence, the PC-montmorillonite complex can form a basis for environmentally-friendly formulations of herbicides, which would yield reduced leaching.

**Keywords:** Clay-liposome complex, Slow release formulations, Herbicide, Leaching.

# ENVIRONMENTAL MATERIALS FOR PHOSPHORUS REMOVAL: ALLOPHANE AS AN EXAMPLE

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Environmental materials, either naturally occurring or manufactured ('man-made'), can 1) sense, detect and analyse pollutants; 2) reduce the amount of pollutants generated and released into the environment; 3) decrease the mobility, reactivity, bioavailability, and ecotoxicity of pollutants; 4) decompose or transform pollutants to non-toxic or less toxic compounds; 5) deliver chemicals by environmentally friendly means; 6) improve the quality of built environments; 7) increase energy efficiency; and 8) be derived from waste for beneficial use (Yuan, 2008a). In other words, environmental materials can function as adsorbents, filters, membranes, catalysts, antimicrobial materials, sensors, and carriers of chemicals, and contribute to pollution control, environmental remediation, and health protection.

Phosphorus (P) is a biocritical element. It would not be possible to feed the world population without the addition of the element as fertilisers to soil. When in excess, however, dissolved P leads to uncontrollable biological growth in water bodies and reduces water quality. Thus, decreasing P inputs from effluent, soil, and sediment to lakes and coast areas would minimise the chance of eutrophication, the cost-effective solutions to which are in increasing demands.

Here I report the use of allophone as an adsorbent of P. Allophane is a short-range-order clay mineral, abundant in New Zealand soils derived from volcanic ash (Theng and Yuan, 2008). The strong propensity of allophane for adsorbing P may be ascribed to its large surface area and to its (OH)Al(OH$_2$) groups capable of forming inner-sphere complex with phosphate. Allophane was added to meat-work effluent and simulated eutrophic water to remove P. It was also assessed, in a continuous flow incubation system, as a capping material to stop P release from eutrophic lake sediment. Results from these experiments will be presented. Being natural, abundant, inexpensive, and safe, allophane has the essential attributes of usable environmental materials (Yuan, 2008b) and thus offers a good potential for the development of an environmentally friendly method of sequestering P in wastewater and deactivating P in sediment.

**Keywords**: Allophone, Lake eutrophication, Effluent treatment.

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# HEALTH & ENVIRONMENT

## SESSION HE4
## *Characterization and Reactivity of Airborne Minerals and their Effects on Human Health*

# HEALTH AND EARTH –MEDICAL GEOLOGY BUILDING A SAFER ENVIRONMENT

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Emerging diseases commonly present the medical community with many difficult problems. In addition, emerging disciplines may offer the medical community new opportunities to address a range of health problems. One such emerging discipline is Medical Geology.[1-4] Medical Geology can be considered as a complement of environmental medicine dealing with the impacts of the natural geologic materials and processes (that is, the natural environment) on the incidence and spatial/temporal distributions of human (and other animal) diseases. As one of the selected topics to be highlighted during the International Year of Planet Earth, medical geology is aimed at improving interdisciplinary interactions among earth and public health scientists, providing the basis for innovative and exciting research that can lead to new discoveries and greater knowledge. Among the environmental health problems that medical scientists are working with the geosciences community are: exposure to toxic levels of trace elements such as arsenic, cadmium, mercury and uranium; trace element deficiencies; exposure to natural dusts and to radioactivity, and naturally occurring organic compounds in drinking water. Analytical characterization of naturally-occurring trace elements and toxic organic compounds in ground water is helping to explain patterns of diseases such as arseniasis, fluorosis, and Balkan Endemic Nephropathy – a condition leading to end-stage kidney failure. Satellites and geographic information systems are being used to monitor the movement of large dust clouds moving across oceans carrying toxic metals and pathogenic microbes that may significant health effects. Regionally, dust exposure can affect broad regions such as the dust stirred up by earthquakes in the arid regions of the southwestern U.S. and northern Mexico. This dust carries spores of a fungus (*coccidiomycosis immetus*) that cause Valley Fever, a potentially fatal respiratory condition. Although the consequences of this type of exposure are not fully understood, modern medical and environmental techniques offer promise of developing innovative solutions to prevent or minimize exposure to potentially deleterious natural environmental pollutants and processes. In this presentation, we provide an overview and examples of some of the health problems being addressed by medical geologists dealing with exposure to natural materials and environmental processes.

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# INHALED NON-FIBROUS PARTICLES IN LUNG SAMPLES

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Respirable particles from environmental or occupational air pollution are continuously inhaled and part of them is retained in the lungs over time. Accumulated particles may induce various respiratory diseases (pneumoconiosis, lung granulomatosis, alveolar proteinosis,..). Most of these diseases are dose related. Since it is often difficult to obtain a thorough exposure history from the patients, mineralogical analysis of the particles recovered from their lungs can be used to get individual estimates of previous exposures. Compared to the numerous studies about asbestos burden in lungs, systematic data about the non-fibrous mineral particles (NFPs) contained in lung samples (bronchoalveolar lavage fluids (BAL) or lung tissue (LT)) are currently scarce. This is perhaps due to the complexity and diversity of the analytical methods (light and electron microscopy, x-ray diffraction) required to analyse particles in the submicron range and to the lack of specific markers for routine analysis. Other obstacles are the variety of particles to be analysed and the existence of a background burden of NFPs in the lungs of everyone which may interfere with the particles directly related to the exposure or disease under investigation. Our experience with NFPs analysis will be summarized and compared to the data available from the literature. From one to over 20 different particle types can be detected in lung samples by analytical transmission electron microscopy. The most frequent are silica, silicates (including clay minerals), iron compounds and titanium oxide. Particle sizes are log normally distributed. Geometric mean diameter range from 0.21 to 1.13 µm. Considering the influence of particle type on particle size, the following gradation can be established; Ø metallic compounds < Ø non lamellar silicates (silica, feldspar, siliceous flyash,...) < Ø lamellar silicates (kaolinite, illite, mica, talc, chlorite). NFPs concentrations range from $X*10^4$ to $10^7$ P/ml in BAL and from $10^9$ to $10^{10}$ P/gm dry tissue in LT. Reference levels are obtained by analysing samples for individuals without particular dust exposures. An "abnormal" result can help to confirm the diagnosis of a suspected particle-induced lung disease. In the absence of detectable disease an abnormal mineralogical analysis result is in no way a proof of disease. Nevertheless, these individual situations need a follow up, since the probability of developing a pathological reaction to inhaled dusts increases with time. The absence of mineralogical abnormalities is an argument against particle-induced lung disease and further investigations are needed to obtain a diagnosis. By helping to the etiological diagnosis of a lung disease, these analyses may have clinical implications in case treatment is available and social benefit if disease can be compensated

**Keywords:** Lung diseases, Non-fibrous particles, Analytical electron microscopy.

# DISTRIBUTION OF HEAVY METALS IN EFFLORESCENT SALTS FROM MINE TAILINGS IN ARID ZONES: IMPACT IN RESIDENTIAL SOILS, NACOZARI, SONORA, MEXICO

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Metal content was measured in mine tailings, efflorescent salts, roadway dust and residential soils to investigate contamination derived from past mining activity in Nacozari, Sonora, Mexico. Climatic effects such as heavy wind and rainfall events can have great impact on the dispersion of metals in semi-arid areas, since soils are typically sparsely vegetated. Analyzed metals include: Ba, Ti, Mn, Cr, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Hg, Tl and Pb. Results show that metal(loid)s in the tailings are dispersed both downstream and downslope via two mechanisms, surface runoff and wind-dispersion of efflorescent salts. Dispersion resulted in elevated levels of metal(loid)s in nearby residential areas in patterns that were dependent on climatic parameters (wind direction, rainfall, etc.). The pattern of elevated concentrations of Cu and As found in residential soils indicates that dispersion of both their soluble and particulate forms is important. Further results suggest that the processes governing metal(loid) transfer from the tailings zone to residential soils are strongly influenced by the semi-arid climate in Nacozari. In this semi-arid region, there is little likelihood of metal transport to groundwater. Instead, transport occurred via surface runoff which impacted immediately adjacent areas most strongly. Perhaps more importantly, transport of fine efflorescent salts that are created at the tailings surface following evaporation during the short rainy seasons, occurs over longer distances via wind dispersion. These efflorescent salts are of concern because they can concentrate metal(loid)s, e.g., Cu, from the tailings at levels exceeding 200-fold.

Our results highlight the importance of seasonally dependent salt-formation and wind erosion in determining risk levels associated with potential inhalation or ingestion of airborne particulates originating from contaminated sites such as tailings impoundments. In low metal-content mine tailings located in arid and semi-arid environments, efflorescent salts could represent a human health risk and a challenge for plant establishment in mine tailings.

**Keywords:** Efflorescent salts, Heavy metals, Wind-dispersion.

# EFFECT OF ORGANIC LIGANDS ON THE ALTERATION OF AIRBORNE SMECTITE PARTICLES

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The mechanism of smectite (montmorillonite) degradation in synthetic lung fluids was investigated by adsorption and dissolution experiments to gain knowledge of the clearance mechanisms of inhaled particles in the human body. Lactate, citrate and glycine were used as proxies for organic acids and proteins in lung fluids.

Ligand adsorption on smectite was investigated as a function of the solution pH (adsorption edges, pH 2 and 9) at several ligand concentrations (0.15, 1.5 and 15 mM), using a smectite suspension of 5.8 g/L. After 24 h, the concentration of ligand was analysed in the solution. Lactate progressively adsorbs onto smectite between pH 9 and 7, remaining approximately constant below pH 7. Under alkaline conditions (pH>9) lactate does not interact with the smectite surface. Citrate adsorbs onto smectite at pH 4-8, with a maximum at pH 6-7. Below pH 4 it does not substantially interact with the smectite surface. Above pH 7, citrate adsorption decreases progressively. There is no clear evidence of glycine adsorption under similar conditions.

Dissolution rates of K-montmorillonite were measured in modified Gamble's solutions at pH 4 (macrophages) and 7.4 (interstitial fluids) at 37ºC in stirred flow-through reactors containing 0, 0.15, 1.5 and 15 mM ligand. The dissolution rates calculated from Si and Al concentration in the output solutions showed that lactate and glycine do not induce any relevant effect on montmorillonite dissolution rates at pH 4, irrespective of ligand concentration. At pH 7, dissolution rate is incongruent and Al hydroxides precipitate, due to the low capacity of lactate and glycine to form stable Al complexes. On the contrary, citrate enhances smectite dissolution between pH 4 and 7, ten times at 15 mM with respect to citrate free solutions. This effect is derived from the strong capacity of citrate to for Al complexes in solution.

We may conclude that the studied ligands contribute to the dissolution rate of montmorillonite in lung fluids by formation of soluble complexes with detached cations, according to a ligand-promoted mechanism. The specific effect of every ligand depends on the stability of the Al-ligand complexes.

**Keywords:** Montmorillonite, Dissolution, Lung fluids.

# MINERALOGY, BACTERIAL SPECIES DIVERSITY, AND BIOAVAILABLE TRACE-ELEMENT LOADING ON THE SILT/CLAY FRACTION OF SURFICIAL SANDS FROM IRAQ AND KUWAIT

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In arid environments, winds, storms, and other physical disturbances can suspend surficial sands, silts, and clays and subsequently transport these materials over distances from meters to hundreds of kilometers. This airborne material carries with it any organisms and inorganic or organic constituents that are associated with particle surfaces. Exposure to large burdens of airborne "dust", specifically silts and clays during mass transport events such as sand storms, has been linked to human health effects including respiratory problems and disease. Bacterial species richness and diversity on the readily-suspendible silt/clay fraction of surficial sands collected from Iraq and Kuwait in 2007 was quantified using length heterogeneity polymerase chain reaction (LH-PCR) on DNA extracts. Samples were also characterized geochemically and mineralogically using Energy-Dispersive X-ray Fluorescence (ED-XRF) and X-ray Diffraction (XRD). Lastly physiologically-based extractions were conducted and analyzed by High Resolution Inductively-Coupled Mass Spectrometry (HR-ICP-MS) to investigate the potential bioavailability of select trace elements associated with the silt-clay fraction. Results suggest clay content and mineralogy may be a primary factor influencing bacterial species richness and diversity and bioavailable trace element loading on the readily-suspendible silt/clay fraction of Iraq and Kuwait surficial sands. Understanding this linkage is important to address questions related to human health in Iraq, Kuwait, and other arid regions. As human population grows, the climate changes, and desertification increases, arid regions will become more important globally.

**Keywords:** Sands, Clay Mineralogy, Bacteria, Bioavailable Trace Elements.

# HEALTH & ENVIRONMENT

## SESSION HE5
## *Moisture Transport Through Clay*

# STRUCTURE AND DYNAMICS OF WATER IN CLAYS FROM MOLECULAR SIMULATIONS

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Water at the surface of clays determines the hydrodynamic properties of ows through the interlayer, interparticle and macroscopic porosities. Molecular simulations can provide information on water properties at the microscopic scale. The existence of preferential sites on the clay surface leads to specific hydrogen bonds patterns which influence the dynamics along and perpendicular to the clay surfaces.

In the interlayer spaces, the water diffusion coefficient along the surfaces in the monohydrated state is reduced by a factor of ten with respect to the bulk diffusion coefficient, and by a factor of three in the bihydrated state. These values are compared to QENS measurements on Na- and Cs-montmorillonites.

In microscopic pores, the surfaces (basal and clay edges) organize water over two to three molecular layers. The diffusion of water molecules along the surfaces is slowed down compared to the bulk case and depends on the counterion. The basal surface Hbonds formation and dissociation dynamics can be described by a simple kinetic model which suggests that formation is faster with the surface than in the bulk, while H-bond dissociation is slower. Further away from the surface, the structure of water and its diffusion coefficients parallel to the surfaces are similar to the bulk one. However, the influence of the surfaces on perpendicular diffusion appears to be longer-ranged and the sizes of the considered pores do not allow to recover the bulk value in that direction.

The study of exchanges between interlayers and micropores shows that water transfer from a pore to another is not activated, which justifies the averaging procedures used to interpret macroscopic tracer diffusion data in compacted, water-saturated bentonites.

# COMPACTED CLAY SAMPLES: A MULTI-SCALE DESCRIPTION OF POROSITY

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In the concept of deep geological repositories, compacted bentonites are planned worldwide as artificial clayey barriers between nuclear wastes and natural host rocks. Their porosity is the focus of numerous studies as it will be a key parameter controlling the potential migration of radionuclides. The evolution of porosity as a function of external conditions such as water activity is strongly linked to the complex hierarchical organization of solid assemblies.

Determining the distribution of pores under confined conditions at various hydration states would represent a major advance for predicting transport properties. To study the influence of water relative pressure in compacted and confined conditions, in situ analyses were carried out by neutron diffraction and small angle neutron scattering (SANS) (ILL, Grenoble, France). Such a combination allows exploring the association of clay layers from the interlamellar spacing levels to the submicronic fabric and can then provide a continuous description of the texture of dense samples on length scales ranging from a few Å to a few hundred of nanometers (Devineau et al., 2006).

In this presentation, the discussion will be focused on results obtained on compacted and dry samples of different clay nature (illite, kaolinite and montmorillonite). From the SANS curves, a pore size distribution was derived and compared which distribution obtained by nitrogen adsorption using the Barret-Joyner-Halenda method. The proper agreement between both distributions validates the approach used to interpret scattering curves (Bihannic et al. 2008). Additional results recorded on hydrated samples will also be presented, showing that for relative humidities higher than 80%, i.e. at the onset of osmotic swelling, a reduction of mesopores is evidenced.

**Keywords**: Porosity, Texture, SANS.

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# ENVIRONMENTAL APPLICATIONS OF SMECTITES AND ZEOLITES RELATED TO LAYER CHARGE AND CATION EXCHANGE CAPACITY

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Smectites and zeolites find important environmental applications, which are related to the exchangeable cations and the water molecules associated with these cations and their surfaces. In the case of smectites, characterization of layer charge is of economic, environmental and geologic importance, because it strongly affects swelling, cation exchange capacity (CEC), ion exchange selectivity and rheological properties. These properties are strongly associated with environmental applications. Smectites often are compositionally and structurally heterogeneous. This heterogeneity contributes significantly to layer charge heterogeneity, both in terms of charge location (tetrahedral versus octahedral charge) and charge magnitude (i.e., individual smectite 2:1 layers may differ in charge, with the total layer charge for a sample being an average of these different charges). There are low charge, intermediate charge and high charge smectite layers which display full, partial or lack of swelling respectively; the relative abundance of these layers determines the presence of low charge, intermediate charge or high charge smectites (Christidis et al., 2006). The relative proportion of layers with different layer charge may affect the behavior of smectites during weathering. The presence of high-charge layers accelerates the formation of mica (illite)-like layers during subsequent wetting and drying cycles in the presence of a potassium source, thus promoting illitization in soil profiles and in landfill liners which use bentonites containing high charge smectites as main impermeable barriers. High charge smectite layers display less swelling capacity compared to their low charge counterparts, thereby decreasing impermeability and increasing diffusion and/or transport of soil water molecules. Moreover with increasing layer charge the selectivity for ions with lower energy of hydration and of greater valence increases. This has significant implications in soil science and in nuclear or urban waste disposal. Zeolites also display significant CEC and find applications in nuclear waste disposal, although they are permeable allowing transport of water molecules. Irradiation of clinoptilolite by β- or γ-radiation does not affect CEC significantly but modifies selectivity for certain univalent cations ($Cs^+$ and $K^+$) and bivalent cations ($Sr^{2+}$, $Ca^{2+}$) over Na. These changes are due to modifications in exchangeable sites and in site occupancy after irradiation, as was indicated by Rietveld refinement (Moraetis et al., 2007).

**Keywords**: smectite, layer charge, clinoptilolite.

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# UNDERSTANDING THE BEHAVIOUR OF DEHYDRATED AND HYDRATED CLAYS USING LOW-FIELD NMR

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Low-field NMR is currently used in well logging to evaluate and locate potential oil and water bearing zones of petroleum reservoirs and can also be extended to other disciplines such as environmental research. Low-field NMR primarily deals with measuring spin-spin ($T_2$) relaxation. In reservoir or soil applications the variability of the $T_2$ relaxation time can be correlated to the viscosity of a fluid or to the size of the pores that surround it. Of interest is the NMR response of water or hydrocarbons in clays that exist in a reservoir or a soil. Imbedded clays and clay content alter the NMR response in a given formation. Analysis of NMR responses in a brine-saturated clay will provide a better understanding of the clay-brine interactions. Furthermore, methods for monitoring the potential for a clay to swell, could be used to prevent pore plugging. This paper evaluates the clay-brine NMR responses in the presence of different cations ($Na^+$, $Ca^{2+}$ and $Mg^{2+}$) and in two different conditions: dry and hydrated. Four types of clays are used: kaolinite, illite, calcium-montmorillonite and sodium-montmorillonite. In a first set of experiments, dry clay was exposed to various brine solutions in a primary imbibition invasion. In a second set of experiments the wetting process was repeated with hydrated clay in a secondary imbibition invasion. Experiments were performed in bench top NMR systems that resemble NMR logging tools. The use of low field NMR was found to be very helpful in evaluating the wetting history of clay-brine as both the water content in the clay. An observed cut-off $T_2$ of the whole spectra at 200ms, allowed for a separation between brine that is interacting with clay versus bulk brine, and yielded valuable information about brine imbibition in clay. The presented work has applications in understanding clay behaviour in reservoir rocks and also brine contamination of surface soils. Thus there are implications in both the logging industry and the environmental industry.

# SEPIOLITE CALCIUM INTERACTIONS IN DESICCANT CLAY PRODUCTION

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The aim of the present study is to determine the applicability of three different sepiolite samples obtained from Eskisehir region of Turkey in the production of desiccant clay. According to Japanese (JIS-Z-0701) and English (BS 3482-6) standards; effective sepiolite should uptake water at least 8 % of its weight at 20% RH. These value must be 20 % at 50 % RH and 30 % at 90 % RH. Therefore, the moisture adsorption capacity of sepiolites were modified by subjecting them to heat treatment at 200 ºC and different relative humidity (RH) values of 20 to 90 % as a function of time. The data obtained was explained on the basis of adsorption isotherms. The results indicate that sepiolites at 50% RH do not conform to the desiccant standards. Therefore, sepiolites were mixed with $CaCl_2$ known as effective desiccant. $CaCl_2$ is commonly used as desiccant particularly in container shipment. Sepiolite is occasionally used as a humidity controller because it has great humidity adsorption characteristics but it turns to liquid phase above 33% RH. On the contrary, sepiolite is a material with great water uptake capacity. Because of these unique characteristics of these materials, sepiolites/$CaCl_2$ mixture with the ratio of 1 to 10 % was evaluated for its potential. It is shown that sepiolite mixed with 5% $CaCl_2$ at 50% RH exceeds the required specifications from a desiccant of commercial quality.

**Keywords** : Sepiolite, CaCl, Desiccant.

# NMR RELAXOMETRY OF PARTIALLY SATURATED MODEL SOILS

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.Nuclear magnetic resonance (NMR) relaxometry is a convenient tool for the characterization of water in natural porous media. It can determine spin-lattice ($T_1$), or spin-spin ($T_2$) relaxation times, which are affected by pore sizes, pore shapes and paramagnetic impurities in the pore fluid or at the solid-liquid interface. In natural porous media relaxation is not monoexponential and the obtained relaxation curves are analysed by inverse Laplace transformation yielding distribution functions of $T_1$ and $T_2$ respectively(1,2). The latest development in relaxometry is the combination of $T_1$ and $T_2$ measurements: the resulting $T_1$–$T_2$ and $T_2$-$T_2$ correlation maps imply further information about dynamic processes like inter-pore fluid exchange (Fig. 2). A further development in NMR relaxometry in unsaturated porous media is the investigation of dependence of relaxivity on the main magnetic field by means of Fast Field Cycling (FFC). The slope and shape of the so-called dispersion curve depend on local dynamic processes at the solid – liquid interface and allow e.g. differentiation between 3D or 2D diffusional processes in pores. Fig.3 shows exemplarily the dispersion curves in medium sand and in natural clayey soil. The curve for sand is approximately linear as expected for 3D diffusion and that for the soil is bi-linear, characteristic for 2D diffusion in layered structures(1,3).

*Fig. 1: $T_2$ distribution functions of sand-5% kaolinite mixture at different water content*

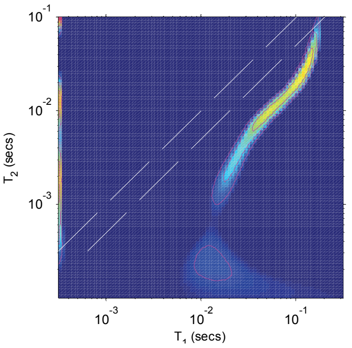

*Fig. 2: $T_2$-$T_1$ correlation of sandy loam*

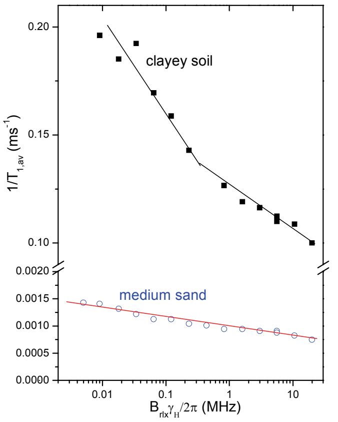

*Fig. 3: $T_1$ disperison curves*

**Keywords:** NMR relaxometry, Soil, Clay minerals.

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# ASSESSMENT OF THE VOLUME CHANGE BEHAVIOUR OF CLAY AGGREGATES BY ESEM OBSERVATIONS

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Expansive clay buffers in hazardous waste isolation fills experience cyclic drying and wetting paths during different stages of their design life. Clayey soils subjected to these processes undergo swelling and shrinkage deformations, giving rise to the accumulation of compression or expansion strains, which in the long term could result in a degradation of such barriers. The overall behaviour of expansive clays subjected to cyclic moisture variations has been recognized to depend on the response at microscopic level of single clay aggregates and the consequent soil structure rearrangement (Alonso et al. 1999). For this reason, quantitative prediction capability relies on the possibility to describe the volumetric change response of expansive soils both at macroscopic and microscopic scales. While evidence has been collected for a long time on the macroscopic behaviour, direct observations at the microscopic scale is still limited. To this regard, environmental scanning electron microscopy (ESEM) is considered one of the newer and most promising techniques for studying in a quantitative way the behavioural features of clay aggregates under different hydraulic paths.

The study presents ESEM observations on a variety of clays. The research was specifically focussed on the assessment of the reversibility or irreversibility features of their volume change behaviour on wetting and drying paths. Microscopic scale observations were performed on isolated aggregates. Evolution of the volume change response was obtained processing photomicrographs taken under different controlled environmental conditions. The control of the relative humidity within the microscope chamber let to fix the water potential in the aggregates. Image segmentation was then applied in order to compute the aggregate deformation as a function of the applied potential. As a result, obtained deformations at microscopic scale were almost reversible at least in the lowest range of applied water potential. This result is considered relevant since it corroborates one of the main assumptions adopted in the formulation of constitutive models used to describe the overall behaviour of expansive clay systems. Irrecoverable deformations at macrostructural scale are then proved to depend on the coupling between the different structural levels.

**Keywords:** Clay aggregates, ESEM, Volumetric response.

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# UNAFFECTED MICROSCOPIC DYNAMICS OF MACROSCOPICALLY ARRESTED WATER IN DILUTE CLAY GELS

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Adequate clay minerals considerably affect the macroscopic mechanical behavior of water even at concentrations of a few percent. Thus when 2wt.% laponite clay mineral nanoparticles are added to water, the resulting colloidal suspension after some time takes on the semisolid characteristics of a jelly-like material at room temperature. This type of jelly-like material is usually denoted a hydrogel. Cold neutron time-of-flight spectroscopy data are in agreement with the assumption that notwithstanding this macroscopic change from liquid to semisolid, the mobility of the water molecules on inter- and intramolecular length scales remains largely unaffected. This observation is discussed in the context of the properties and the role of water in different more or less dilute ionic environments. The result contributes to the ongoing debate of the properties and role of water in living cells - where a similar absence of any atomic-scale change in the water mobility compared to bulk water has been observed [1] - in the context of the hypothesis that at the origin of life the first cells assembled in a hydrogel environment [2].

**Keywords:** Dilute laponite hydrogels, Water diffusion, Neutron spectroscopy.

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# WATER DYNAMICS IN COMPACTED CLAYS

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The molecular dynamics of interlayer water has been studied in vermiculite and smectite clays, using a combination of neutron scattering and computer simulation. Experimentally we have studied 1- and 2-layer hydrates of Na- and Ca-vermiculite and hydrates of Na- and Ca-smectite, from around 240K up to moderately elevated temperatures and pressures. Studies of water in high-charge synthetic micas are ongoing, and will be reported at the meeting if results are available. We find that for clay-layer spacings greater than those encountered in the 2-layer hydrates, the proton diffusion coefficients measured by neutron scattering rapidly approach those of bulk water. Only in the 1-layer hydrates is the proton mobility reduced by more than an order of magnitude. Molecular dynamics computer modelling has also been used to study water in clay hydrates. The calculations show similar trends to those obtained by experiments, but with a tendency to overestimate the effects of confinement on the water diffusion. The origins of such discrepancies between experimental and computational methods will be discussed. In addition, we will describe the possibilities for using neutron imaging to monitor water and fluid transport in real compacted clay shales, and the opportunities to use neutron spectroscopy at elevated temperatures and pressures.

**Keywords:** Water, Diffusion, Clays.

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# NUCLEAR MAGNETIC RESONANCE METHODS TO STUDY IN SUBSURFACE ENVIRONMENTS

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Nuclear Magnetic Resonance (NMR) is a powerful technique to study subsurface processes in a non-invasive manner. In geosciences four different methods which are all based on NMR are presently being applied: i) NMR spectroscopy for structure determination of chemicals, organic matter and to analyse binding mechanisms, ii) Magnetic resonance sounding for aquifer characterization, iii) NMR Relaxometry/Diffusimetry for pore space exploration, and iv) NMR imaging (MRI) for visualization of subsurface structures (e.g. plant roots, preferential flow channels) and water dynamics in soils, sediments and rocks. This keynote talk will focus on points iii) and iv).

Basically, NMR is the reaction of spin bearing nuclei (mostly $^1H_2O$) of matter placed in an external magnetic field on pulses of electromagnetic radiation and magnetic field gradients. NMR Relaxometry uses the analysis of relaxation curves after precedent excitation. In water filled porous material the temporal development of these curves are controlled by pore size distribution, water saturation and chemical composition of the solid-liquid interfaces. Examples will be given that illustrate the application of these methods in characterizing pore space structure of sands, sand-clay mixtures as well as natural soils. This information can be used to derive pore size distribution, connectivity and hydraulic properties of porous materials.

Nuclear magnetic resonance imaging (MRI) has been developed during the past decades mainly for medical diagnostics, but since about 10 years also dedicated scanners for soil and plant research are available. The method enables non-invasive visualization of root systems, water content changes in soils, and diffusional processes in porous media. Examples will be given that deal with water uptake processes in maize and ricinus plants, where we could show that at low water contents the root water uptake is not fully compensated by supply from the surrounding soil matrix. We will discuss the potential of i) extending MRI to image water dynamics in natural soil cores, ii) linking MRI-information with a fully coupled 3D root-soil water model (RSWMS), and iii) in applying NMR logging tools at the lysimeter and field scale.

# HEALTH & ENVIRONMENT

## SESSION HE7

## *Speciation of Trace Elements in Soils and Sediments*

# ACTINIDE SPECIATION USING SYNCHROTRON TECHNIQUES

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One of the key concerns in the safe disposal of high level nuclear waste is the possibility for radionuclides to leach out of a waste form, breach the repositories multi-barrier system and enter the surrounding environment. Predicting or ultimately controlling or prohibiting transport of released radionuclides through the environment requires a detailed understanding factors determinant in their transport.
Radionuclide speciation and interaction with ground/pore water and with minerals comprising rocks of proposed host geological formations is requisite to performance assessment of nuclear repositories. Synchrotron-based speciation techniques have proven to be valuable speciation tools. Results form such studies provide fundamental molecular scale information of processes determinant in the behaviour of radionuclides released into the environment, their transport properties (mobilization/immobilization), reactivity, bio-availability and, hence, potential risk.
In this presentation both experimental aspects of synchrotron-based X-ray spectroscopic techniques and application examples of radionuclide speciation are presented. Examples conveying the information content of sophisticated spatially resolved X-ray spectro-microscopy techniques in both the hard and soft X-ray regime (combined confocal mode µ-XRF / µ-XAFS and STXM, respectively) will be presented. In addition, results from molecular radionuclide speciation studies at the water/mineral interface using incident X-rays at a grazing angle of incidence (GIXAFS) to provide surface selectivity will be shown.
Such techniques are important in tackling the complex challenge of environmental radionuclide speciation.

**Keywords:** Radionuclide speciation, Actinides, Synchrotron.

# CHEMICAL SPECIATION AND BIOAVAILABILITY OF TRACE ELEMENTS IN SOILS

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The term trace elements (TE) includes essential (e.g., Cu, Mn, Se, Zn, Co) and nonessential (e.g., Hg, Cd, Pb) elements. The elements essential for plants and animals are required in low concentrations and are termed micronutrients, but at high concentrations they may be toxic for plants, animals, and humans. TE are persistent contaminants in the soil environment. Changes in the environmental conditions, whether natural or anthropogenic, can strongly influence the behaviour of both essential and toxic elements by altering the form in which they occur. Some of the most important factors controlling element behaviour include pH, redox potential, sorption–desorption reactions, as well as chemical complexation with inorganic and organic ligands.

The simple determination of TE total or "pseudototal" content in soil might minimize the risks for biota and human health, assuming that pollutants transferring to water resources or biota are simply correlated with contamination level. In contrast, relevant paradigms in environmental monitoring, risk assessment and remediation feasibility are the TE mobility and bioavailability to microorganisms, plants, animals and humans. For a correct assessment of risk/toxicity (according to TE content and availability) of a polluted soil and to predict its reduction after application of remediation techniques it is crucial to establish the speciation, mobility, and biogeochemistry of the contaminants. In this sense, a requirement exists for analytical methods and strategies that provide information on the dynamics and behaviour of TE in soil.

Speciation science seeks to characterise the various forms in which TE occur or, at least, the main metal pools present in soil. It can be achieved using either direct, mainly non-destructive, or indirect analytical methods. This note provides a review of the single and sequential chemical extraction procedures that have been more widely applied to determine the plant bioavailability of TE from contaminated soil and their presumed geochemical forms. Examples of complementary use of chemical and instrumental techniques and applications of TE speciation for risk and remediation assessment are illustrated.

**Keywords**: Soil contamination, Bioavailability, Chemical extractions.

# INTERACTION OF SE WITH BOOM CLAY: XAS SOLID PHASE SPECIATION

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The Boom Clay formation mainly consists of mixed clay minerals (illite, interstratified illite-smectite), pyrite and immobile and dissolved natural organic matter. Within the geological repository concept, the Boom clay formation itself is considered the primary barrier against radionuclide migration. It provides good sorption capacities, very low permeability, and chemically reducing conditions due to the presence of pyrite ($FeS_2$) Since the mobility and consequently also the dose contribution is highly related to the speciation of selenium, the knowledge on its behaviour in the far field of the Boom Clay formation is very important for the safety case of the future Belgian high level waste disposal program.

In all previous studies, the interpretation of the behaviour of Se in Boom Clay conditions has always been based on circumstantial evidence such as solubility measurements or comparison with the spectroscopically identified speciation of Se in model systems [1-3]. Since pyrite ($FeS_2$) is one of the main minerals governing the redox conditions of the Boom Clay solid phases, it is expected that selenite will be reduced to $Se^0$ in the Boom Clay system, thereby effectively limiting the solution concentration to the solubility of $Se^0$, provided that there is no interaction with the mobile Boom Clay organic matter.

Selenite was equilibrated with Boom Clay for 1 month, before phase separation into 4 size fractions (clay-rich, pyrite-rich, organic matter-rich, supernatant) was achieved using centrifugation. For the first time the solid phase reaction products for the interaction of selenite with the Boom Clay solid phase have been spectroscopically identified. Based on the XANES/EXAFS analysis, selenite is reduced to $Se^0$ on all solid phase size fractions of the Boom Clay, confirming the reduction of selenite to metallic selenium in the Boom Clay system. Despite of the low equilibrium concentration in the supernatant solution ($5x10^{-6}$M of Se) XANES measurements were possible and unexpectedly indicated the presence of a selenide phase (FeSe or an organic selenide), although $Se^0$ was observed on the respective solid phase fractions.

**Keywords**: EXAFS/XANES, Selenium, Solid phase speciation.

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# MERCURY SPECIATION IN THE ENVIRONMENT AFFECTED BY INDUSTRIAL POLLUTION: DETERMINATION AND MODELLING

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Mercury concentrations have increased in the world as result of industrial activities. It has been published that mercury emissions are mostly due to coal burning power stations, chlor-alkali facilities, minig and other industrial processes.

Mercury is present in the environment in different molecular forms with specific biogeochemical transformation and ecotoxicity. Inorganic $Hg^{2+}$ is the main form in water and sediment samples. Special attention is given to transformations which lead to the in situ production of methylmercury. Concentration levels of organomercury species is very low (usualy ng $L^{-1}$) in environmental aquatic environments but the toxic effect of these compounds can be significant due to their tendency for bioaccumulation and biomagnification in the food chain.

The determination of the total concentration of mercury is not sufficient to understand its fate in the environment. The development of a sensitive, reliable, simple, and cost effective procedure for speciation analysis of mercury in different environmental compartments is currently one of the principal research challenges in environmental analytical chemistry.

The objectives of the present study were to develop and optimise analytical procedures for mercury speciation analysis and their applications for analysis of water, sediment profiles, soils, plants, fish and human hair in the regions affected by environmental pollution due to reprocessing of old gold tailings damps and chlor-alkali factory. The study included collection of ancillary data (pH, redox potential) which are critically important for mercury monitoring program.

The development of predictive models based on thermodynamic solution equilibria including mercury tranformations, transport, fate and biological uptake are presented.

**Keywords**: Mercury, Speciation, Modelling.

# MOBILIZATION AND FATE OF HEAVY METALS IN RED MEDITERRANEAN SOILS POLLUTED BY MINING ACTIVITIES

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A study on the natural mobility, fate and, consequently, the risk posed by heavy metals (Pb, Cd, Cu and Zn) in polycyclic soils with argilic horizons in semi-aridic conditions (South-East of Spain) is presented. The study area has geomorphological, edaphological and climatic characteristics similar to other mining areas in the Mediterranean area, with a scant degraded vegetation. The soils studied (calcic Luvisols and luvic Calcisols) are dedicated to the cultivation of citrus trees. The soils are in a slight slope (0.6%) in the neighbourhood of an old mining site and so affected by heavy metals contamination due to physical and physico-chemical transport of materials. Although the annual pluviometry is low, torrential rainfalls occur sometimes, extensive amounts of both soluble materials and particulate being supplied to the soils.

The mobility of both solid particles and soluble heavy metals compounds from the emission source and the argilic horizon is studied. Selective extractants (DTPA, sodium dithionite plus sodium citrate (M-J),nitric acid and sodium hydrogencarbonate) were used, the levels of heavy metals being determined in each fraction and in the raw soils by means of atomic absorption spectrometry using electrothermal (ETAAS) or flame (FAAS) atomization. X-ray diffraction (XRD) and scanning electron microscopy coupled to energy-dispersive spectrometry (SEM-EDS) were applied to the characterization of both raw samples and the residues remaining after each extraction, thus providing additional information about the sediment phases carrying the metals studied. On the hand, studies on the bioavailability of the metals assessed by means of in-vitro digestion experiments were carried out.

The processes governing the heavy metals transfer are strongly influenced by the semi-aridic climate, the presence of a high proportion of carbonates and the occasional but torrential rainfalls which, favoured by the Bt horizon impermeability, result in the transport of heavy metals from the upper zone of the hill to the surrounding agricultural soils. The gullies play an important role for the immobilization processes, their high carbonate contents providing a first barrier for metals mobility.

**Keywords:** Red Mediterranean soils, Heavy metals, Risk assessment.

# A XAS STUDY OF ARSENIC SPECIATION IN WASTE MATERIALS FROM LODE GOLD DEPOSITS

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Gold production at two historic mine camps (Nova Scotia and British Columbia) have resulted in the production of tailings and other waste products with elevated concentrations of As and Hg. Their distribution in the receiving environment has been documented as part of a larger study examining the processes that control their fate and transport. Results will be used to characterize the environmental signature of these and other similar mesothermal gold mineralizations to build geoenvironmental ore deposit models and support on-going environmental management initiatives aimed at reducing risks to human and ecosystem health.

Both mine camps processed Au-bearing ore using Hg-amalgamation and/or cyanidation during the late 19th and early to mid 20th centuries. Exploration and production continue today sporadically. Gold occurs in veins and is associated with a host of sulphide minerals including arsenopyrite, galena, sphalerite, chalcopyrite, pyrrhotite, and stibnite (B.C. camp only). Gangue minerals include mainly quartz and carbonate minerals (calcite, dolomite, and ankerite at NS mines) with subordinate feldspar, mica and chlorite. Synchrotron X-ray absorption spectroscopy (XAS) was used to investigate the As speciation in a variety of bulk samples including tailings, sediments, sludges and precipitates. Fluorescence experiments using Lytle and single element Vortex Si-drift detectors were carried out on the Hard X-ray Micro-Analysis (HXMA) beamline at the Canadian Light Source (CLS), University of Saskatchewan. Several spectra (3-10) were collected and averaged for each of the 10 reference minerals and compounds and 33 samples. The As K-edge X-ray absorption near-edge structure (XANES) spectra were used to characterize speciation of As within the tailings. Results on tailings from N.S. indicate the presence of scorodite, and adsorbed $As^{V}$. Sediment samples from B. C. indicate that in an active drift $As^{V}$ sorbed to amorphous Fe-oxides dominates, whereas in another (inactive) drift, $As^{-I}$, $As^{III}$ and $As^{V}$ occur. In a sediment sample from a settling pond near the second drift, $As^{-I} >> As^{V}$ whereas in amorphous Fe-oxide samples, near the portal, $As^{V} >> As^{-I}$. In a sample characterized by a surface biofilm and Fe-oxides, $As^{III}$ was found. The oxidative dissolution of sulphide minerals and As-bearing phases like arsenopyrite from exposed surfaces in both these drifts results in an increased solubility for As and Fe with subsequent precipitation of amorphous Fe-oxides enriched with oxidized As species but the presence of organics may inhibit the complete As oxidation reaction.

**Keywords:** Arsenic speciation, XANES, Mesothermal gold deposits.

# ASSESSMENT OF THE ENVIRONMENTAL EFFECT CAUSED BY HEAVY METALS IN SOILS AFFECTED BY OLD MINING ACTIVITIES

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The nature of the materials present in mining sites (granulometry, chemical and mineralogical composition) is a consequence of the circumstances that have prevailed at the site and which have conditioned the processes of alteration caused by climatic agents. In sulphide outcrops we find the so-called zones of supergenic alteration, oxidation zones or gossan, in many of which rich metallic deposits occur . In addition, when the surface materials are the result of processes associated with the metallurgic industry, their reactivity in the face of supergenic alteration processes is much greater and the whole process of metal mobilisation is affected. There are several former mining sites in SE Spain, the Sierra Minera of Cartagena (Murcia) being a good example. These sites were exploited since antiquity (Phoenician, Carthagenian and Roman remains have been found) and, as a consequence, surrounding soils have been affected, the levels of metals being high.

A study on metal speciation (Zn, Pb, Cd and As) in soils placed in the neighbouring of one of these sites (surroundings of Portman Bay) was carried out. A three-step sequential extraction procedure, modified from the BCR method, as well as selective extractions ($H_2O$, 0.1 N $HNO_3$, citrate-dithionite and 1M $NH_4OAc$ after $H_2O_2$ attack) were applied to selected samples in order to evaluate the potential mobility of fixed metals. Acid volatile sulphides (AVS) and simultaneously extracted metals were also determined. X-ray diffraction (XRD) and scanning electron microscopy coupled to energy-dispersive spectrometry (SEM-EDS) were applied to the characterization of both raw samples and the residues remaining after each extraction, thus providing additional information about the sediment phases carrying the metals studied. Metals associated with sediments showed different behaviour depending on the mineralogical phase they were bound to. Zn and Cd were the most labile metals, while Pb and As showed a lower mobility. The fraction of metals associated with jarosites presented a high stability under different physicochemical conditions, while metals associated with mineralogical phases that are undergoing supergenic alteration processes presented a high mobility. The results obtained may be useful to assess both the short and the long-term environmental impact of such disposal activities as well as may support decisions for a future recovery of the zone.

**Keywords:** BCR sequential extraction procedure, Supergenic alteration, Risk assessment.

# CHANGES IN CHEMICAL FORMS OF LEAD IN TEMPERATE AND SEMIARID SOILS

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Sequential extraction has been used as a suitable method for identification of chemical forms of trace elements and their plant availability. Surface soils were sampled from Guilan and Hamadan provinces in north and northwest of Iran with temperate and semiarid climates. The chemical forms of Pb in the $Pb(NO_3)_2$ treated (400 $\mu$g Pb $g^{-1}$) soils have been studied in solid state incubation (FC) at 27 $^{o}$C. Separate batches were taken after 0.16, 0.33, 1, 2, 5, 24, 48, 168, 336, 720, and 2160 h for extraction with DTPA (Diethylene triamine pentaacetic acid) (Lindsay and Norvell 1978). After 20 minutes and 3600 hours a sequential extraction scheme was also used to fractionate Pb of incubated samples into soluble-exchangeable (Sol-Ex), carbonates associated (Car), organic matter associated (OCd), Mn oxide associated (MnOx), Fe oxide associated (AFeOx), and residual (Res) forms (Tessier et al. 1979). Temperate soil samples had higher clay content, cation exchange capacity (CEC), dichromate (oxidable) organic carbon (OC), total Kjeldahl-nitrogen (TN), biological activity, amorphous and crystalline Fe and Al, but semiarid soil samples had higher sand content, pH, equivalent calcium carbonate (ECC), available P and K. The availability of added Pb differed widely among soils after incubation, and DTPA-extractable Pb decreased markedly with time of soil-Pb contact. DTPA-extractable Pb of temperate soils was considerably lower than that of semiarid soils after Pb addition. Soil lead fractionation revealed that in both groups of soils Pb largely changed to exchangeable, carbonates associated and organic associated forms after 20 minutes. The chemical forms of Pb differed widely among soils after 3600 hours incubation. The added Pb largely changed to residual and carbonates associated forms in semiarid soils and to residual, Mn oxide associated and organic matter associated forms in Gilan soils after 3600 h.

**Keywords**: Sequential extraction; DTPA-extractable Pb; Temperate and semiarid soils.

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# MERCURY DISTRIBUTION AND SPECIATION IN THE COLLOIDAL FRACTION OF SOILS CONTAMINATED BY INDUSTRIAL ACTIVITIES: A CASE STUDY IN THE SOUTH OF ITALY

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Mercury (Hg) is scientifically demonstrated and politically acknowledged as a global pollutant. It is found in the environment mainly because of anthropic activities. The chemical speciation of Hg, also including the determination of the size of the Hg-bearing particles, is of great relevance to better assess the environmental fate and toxicity of this dangerous pollutant. In addition, soil colloidal particles (either organic or inorganic) can be potentially mobilised, thus diffusing into other environmental compartments or endangering the health of living organisms and human beings.In the present study, the distribution and speciation of Hg in the colloidal fraction of soil samples collected in an industrial area located in the South of Italy (Ferrandina, *Val Basento*, Basilicata) and polluted by the dumping of Hg-containing wastes from a chlor-alkali plant, was investigated. The total amount of Hg in the soil samples ranged from 1 to 250 μg/g. However, most of this Hg was found concentrated, up to 10 times, in the clay fraction (<2 μm). Therefore, a detailed Hg distribution in the soil colloidal fraction was studied by using SdFFF-MH-FI-ETAAS (Sedimentation Flow Field Fractionation coupled off-line to a Mercury Hydride-Flow Injection-ElectroThermal Atomic Absorption Spectroscopy), to identify the most relevant Hg-bearing fractions. SdFFF is an established method for the high resolution, mass based separation and sizing of small particles in the 0.05-1 μm size range. From the obtained results, it emerged that most of Hg is concentrated in one main fraction containing particles with a size in the order of few hundreds of nanometers (400-700 nm). This fraction was then collected and analysed by using synchrotron Ultradilute XAFS (X-ray Absorption Fine Structure) spectroscopy, in order to gain a detailed Hg speciation. Changes in Hg-speciation going from the 2 mm soil fraction down to the colloidal particles were also evaluated.

The results produced suggest that, despite the presence of scarcely soluble Hg-chemical forms, particular attention should be paid to the submicrometer-sized soil particles that can potentially turn into a serious danger for other environmental compartments as well as for humans, not only for the higher mobility of the colloidal particles, but also for the changing speciation moving toward smaller particle sizes.

**Keywords**: Mercury speciation, Soil colloids, Synchrotron.

# CHARACTERISATION OF CYANIDE IN GOLD-MINE TAILINGS OF THE WITWATERSRAND, SOUTH AFRICA

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The use of cyanide in gold extraction is of concern as, in South Africa, this pollutant is discharged with the effluent and tailings based on the assumption it will decompose within a relatively short period of time. The distribution and fate of cyanide in the environment upon release from the tailings dumps depends on its physical-chemical speciation. This study describes the characterisation of cyanide in the superficial deposits of a re-processed gold tailings dump, and implications for its potential release and redistribution. Sampling was done in 2006 and 2007 to assess the impact of tailings acidification on cyanide release over that period. Elevated concentrations of total cyanide ($CN_T$) and weak acid dissociable cyanide ($CN_{WAD}$) were obtained for 2006. The concentrations of free cyanide ($CN_{free}$), cyanates ($CNO^-$) and thiocyanates ($SCN^-$) were higher for 2007 than 2006, and conversely the concentrations of metal-cyanide complexes, namely $Cu(CN)_3^{2-}$ (up to 35 $mgkg^{-1}$), $Fe(CN)_6^{4-}$ (more than 80 $mgkg^{-1}$) and $Ni(CN)_4^{2-}$ (up to 30 $mgkg^{-1}$) were higher in 2006 compared to 2007. Decreases of 25% for $Cu(CN)_3^{2-}$; >30% for $Fe(CN)_6^{4-}$; and 40% for $Ni(CN)_4^{2-}$ were observed in some cases between the sampling periods. These findings indicate that metal cyanide species in the tailings had degraded as a result, primarily, of decrease in pH. The released cyanide is either volatilised as HCN or transported in solution with the contamination plume.

# HEALTH & ENVIRONMENT

## SESSION HE8

## *Stability of Clay Minerals in Geological Radioactive Waste Disposals*

# STABILITY OF CLAY MINERALS IN GEOLOGICAL RADIOACTIVE WASTE DISPOSALS
# FROM DATA ACQUISITION TO MODELLING

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The stability of clay minerals in geological radioactive waste disposals is a key issue in order to assess the safety of the future disposal. Clay minerals will be used for the engineered barriers and can constitute the host formation. The modelling of the long term evolution of the disposal needs 4 majors steps that are (1) a accurate description of the materials (barriers, host rocks), (2) the development of databases (thermodynamic and kinetic), (3) the identification of the chemical pathways (experiments and natural analogues), (4) Transport-Chemistry Modelling.

In the framework of the ANDRA/BRGM partnership, it has been possible to develop a complete methodology allowing robust modelling.

Step (1): The Callovian-Oxfordian formation has been characterized by high resolution mineralogy using also isotopic tolls. In addition, the data acquisition (anion leaching, cation exchange, and $pCO_2$) has furnished the elements used in a numerical modelling of the clay/rock interactions including the dissolved gas (Gaucher et al., submitted). Our calculations show a very stable chemistry and a very strong buffer capacity of the clay formation at the regional scale.

Step (2): New data obtained by calorimetry and aqueous solution methods have completed thermodynamic database for clay minerals (Gailhanou et al., 2007). A complete revision of the ion exchange selectivity coefficients for illite and smectite has also been conducted.

Step (3): Identification of the chemical pathways has been made for the interaction of clays with concrete or iron source, using experiments and analogues.

Step (4): Transport-chemistry codes are the ideal tools to test the interaction of the different materials in contact in the disposal (Marty et al., 2009). They demand the integration of the accurate description of the geochemical systems and a large list of minerals that are susceptible to precipitate in the foreseen conditions in order to avoid forcing the calculation to a unique solution.

**Keywords:** Clay stability, Disposal, Thermodynamic, Modelling.

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# RADIATION EFFECTS ON CLAY MINERAL PROPERTIES: A REVIEW

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The influence of radiation on clay mineral properties remains relatively poorly documented, despite its importance for the safety assessment of high level nuclear waste repositories (HLNWR) where clays are components of the engineered barrier or the host rock in many countries. Since more than 30 years, various radiation-induced defects have been observed in kaolinite, dickite, montmorillonite and illite. In kaolinite, the defects stable at the scale of geological periods have been used for geochemical applications or dating. Nevertheless, the potential influence of these defects on clay properties has been only scarcely demonstrated.

Ballistic effects of heavy ions (alpha recoil nuclei) are able to amorphize the structure of clay mineral. This was shown for smectite either irradiated with ion beam or doped with alpha emitters, leading to consistent amorphization doses. Amorphization of smectite from the engineered barrier would occur after 1000 yrs of exposure arising from waste leakage, that is to say a short time when compared to the timelife of a HLNWR. Besides, amorphization by ionizing radiation in a HLNWR is unlikely because required dose is unrealistically too high. Consequences of amorphization on physico-chemical properties such as swelling, CEC, are potentially very important but have not yet been described for clay minerals. Nevertheless, kinetics of dissolution has been shown to be significantly enhanced after radiation-induced amorphization. Besides, ionizing radiations can reduce structural $Fe^{3+}$ in montmorillonite and may thus potentially modify its layer charge and CEC. The influence of irradiation on physico-chemical properties such as CEC is revealed only at high irradiation doses, larger than several MGy, and remains relatively limited. Nevertheless, contradictory results still exist about the effect of irradiation on redox and surface reactivity.

These parameters, together with their consequences on properties, obtained on model specimen used in laboratory or test experiments, must be considered in the performance assessment of the engineered barrier of a nuclear waste disposal.

**Keywords:** Clay, Irradiation, Property.

# BENTONITE REACTION IN NATURAL HYPERALKALINE GROUNDWATERS: EXAMPLES FROM THE PHILIPINNES

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Bentonite is one of the key components of the engineered barrier system in the disposal concepts developed for many types of radioactive and chemo-toxic wastes. The choice of bentonite results primarily from its sorption, plasticity and swelling capacities that have the potential to retard key radionuclides. Unfortunately, it is unstable at high pH condition which is a potential problem in its use as an engineered clay barrier for current repository designs. Groundwater interaction with standard OPC (Ordinary Portland Cement) produces pH>13 alkaline leachate.

Utilization of alternative low-alkali cements can reduce the alkaline leachate to pH 10-11. It is hoped that this lower pH will reduce bentonite degradation, and is currently being tested in the laboratory. The very slow reaction rates however require data from long-term experiments. Such information can be deduced with the so-called natural analogue approach (see Miller et al., 2000, for details).

Here, details of a new study of long-term bentonite reaction in the natural hyperalkaline groundwaters of the Zambales ophiolite in the Philipinnes are presented. Widespread active serpentinisation, resulting in hyperalkaline springs at several locations, is ongoing in the ophiolite. Groundwater pH values up to 11.1 have now been measured, falling into the range typical of low-alkali cements that are presently being developed for use in waste disposal. In addition, bentonite has been analysed from several sites which show clear evidence of reaction of the clay in the hyperalkaline groundwaters and these data will be presented here for the first time and, where possible, comparison with appropriate short-term laboratory data will be made. In addition, the relevance of the data to waste repository designs and long-term performance of the engineered barriers will be directly addressed.

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# EFFECT OF AQUEOUS ALUMINIUM AND SILICA CONCENTRATIONS ON SMECTITE DISSOLUTION KINETICS AT HYPERALKALINE CONDITIONS

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Steady-state dissolution rates of smectite were determined as function of aqueous Al and Si concentrations using a stirred-flow-through reactor at 70°C in 0.3M-NaOH solution to obtain the reliable dissolution rates of smectite at hyperalkaline condition and to formulate the effect of deviation from equilibrium on smectite dissolution rate. In the flow-through dissolution experiments, high Si and Al concentrations were observed at the initial stage. The rise in Si and Al concentrations steadily decreased until the steady state condition was achieved and no secondary formation of minerals were detected by Xray-diffraction analysis in any experiments. However, in one of the experiments with high dissolved Si or Al concentration, less Si or Al concentration was detected compared to input solutions. In thermodynamic calculation, analcime formation was suggested in those conditions. This probably indicates polymerization of monomer silica or formation of some secondary precipitates with X-ray amorphous. Hence, in such conditions, the dissolution rates not be calculated based from the dissolved Si or Al concentrations of the output solutions but were obtained from *ex situ* AFM observations.

Results of the flow-through dissolution experiments and ex situ AFM observations suggest that the dissolved Si and Al concentrations in the solutions appear to be retarding the dissolution rate of smectite. Namely, the dissolution rate of smectite decreases as a function of the Si and Al concentration. The decrease of smectite dissolution rates a function of the Si and Al concentrations is however explained both by the effect of deviation from equilibrium on dissolution rate and by Si and Al inhibitions. If we assume the decrease is attributed by the effect of deviation from equilibrium (ΔGr effect) on dissolution rate, the dissolution rate of smectite can be expressed in a non-linear function of the Gibbs free energy. This non-liner relationship is nearly same as that obtained by Cama et al. (2000). However, the ΔGr effect of the obtained non-linear relationship was much stronger than that obtained at moderately alkaline condition. This relationship cannot be completely explained by transition state theory. Moreover, the smectite dissolution was retarded and deviated based farther from equilibrium at hyperalkaline condition compared to moderately alkaline condition.

**Keywords**: Dissolution, Hyperalkaline, Smectite.

# SWELLING, DISSOLUTION, AND SEDIMENTATION OF BENTONITE CLAY IN WATER: NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AND IMAGING STUDIES

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Compacted bentonite clay is currently attracting attention as a promising "self-sealing" buffer material to build in-ground barriers for the encapsulation of radioactive waste. It is expected to fill up the space between waste canister and surrounding ground by swelling and thus delay flow and migration from the host rock to the canister. Evaluation and understanding of the swelling properties of pre-compacted bentonite are of uttermost importance for designing such buffers.

The major goal of our studies was to provide, in a non-invasive manner, a quantitative measure of bentonite distribution in extended samples during different physical processes such as swelling, dissolution, and sedimentation on the time scale from minutes to years. The primary variables were clay composition and water ionic strength. Both natural montmorillonites and purified and ion-exchanged montmorillonite clays were studied. Magnetic resonance imaging and nuclear magnetic resonance spectroscopy were adapted and used as main experimental techniques. With this approach, clay particle distributions in water in the concentration range over five orders of magnitude and with sub-millimetre spatial resolution were obtained (Dvinskikh 2009). Samples with swelling in one (vertical tube) or two (slit) dimensions were investigated. The distribution and displacement within the bentonite systems of foreign particles, either natural ones (sand or quartz) or artificially admixed model particles of controlled size were also studied. Diffusion experiments were performed with the aim of characterizing the state of colloids that form after/during clay dissolution.

**Keywords:** Bentonite clay, Swelling, Sedimentation.

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# ALTERATION OF COMPACTED BENTONITE BY DIFFUSION OF HIGHLY ALKALINE SOLUTIONS

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Compliance ance of concrete – bentonite barriers is a key issue in the performance assessment of long-term underground storage of radioactive waste. The reaction of synthetic alkaline solutions (K-Na-OH and Ca-$(OH)_2$) interacting by diffusion with a Mg-saturated compacted FEBEX-bentonite column of 2.1 cm thickness was investigated through closed-system experiments at 60-90 ºC from 6 to 18 months. The first few millimeters near the surface were grated to resolve mineralogical changes at mm resolution determined by XRD, SEM, BET and the analysis of exchangeable cations.

Alkaline cations diffused beyond the mineralogical alteration zone (2 – 2.5 mm), and were exchanged by $Mg^{+2}$ in the interlayer region of montmorillonite, but no K-silicates were formed. The presence of minor zeolites in the alteration assemblage was only detected by XRD on samples treated with ethylene-glycol. A cemented rim mixed with poorly ordered clay materials, mainly brucite, a chlorite-like phase and Mg-smectite was found at the interface. At 90 ºC, chlorite-like phases dominated and alkaline cation diffusion was significantly limited in comparison with 60 ºC. Montmorillonite was partially dissolved and a part of it remained shielded by the newly-formed cementation crusts. Cation diffusion through the interlayer of montmorillonite is inferred to be the dominant transport pathway in compacted bentonite equilibrated with external high pH solutions. The high pH front diffused at a much slower rate due to buffering of mineral reactions.

When $Ca(OH)_2$ solution diffused through bentonite, the exchange of Mg and migration of Ca was very restricted. A sub-mm Mg-silicate cemented rim was observed after 18 months.

**Keywords:** Bentonite alteration, Alkaline plume; Reactive transport.

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# OCCURRANCES OF IRON-BENTONITE INTERACTION FOUND IN BENTONITE DEPOSITES

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It is proposed that high-level nuclear wastes (HLW) will be disposed in underground repositories, where steel overpack containing HLW is surrounded by the bentonite-sand buffer. Steel components are unstable under the disposal environment. They will corrode and react with the adjacent clay materials. The interaction may affect the properties of the clay. The effects of interaction on the stability of clay materials have received much attention. Some laboratory experiments and geochemical modeling in regard to the iron-clay interaction have been performed (Lantenois et al. 2005, Wilson et al. 2006ab, Perronnet et al. 2008). In order to support the plausible prediction of long-term iron-bentonite interaction, the natural analogue studies for iron-bentonite interaction have been desired.

The ideal situations for the natural analogue of the iron-bentonite interaction are the occurrences for the long-term interaction of bentonite with native iron under reducing environments. However it is quite rare in nature. On the other hand, it is not improbable to find the iron accumulations in bentonite deposits. These occurrences may indicate the interaction of bentonite with iron-rich fluid if the accumulations occurred by the reaction after bentonite formation. If the accumulations were occurred by other processes like a simultaneous formation with bentonite, the surrounding part of bentonite must be suffered by long-term interaction with iron accumulations. The occurrences of the iron accumulations in bentonite were found in Kawasaki bentonite deposit at Miyagi Prefecture, Japan and Kuroishi bentonite deposite in Aomori Prefecture, Japan. The purpose of the present study is to reveal the mineralogical changes of bentonite interacted with iron and to estimate the physical and chemical conditions of the bentonite alterations.

**Keywords**: Iron-Bentonite Interaction, Natural Analogue, Bentonite deposits.

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# CRYO-STABILIZED PORE STRUCTURE OF BENTONITE AND OPALINUS CLAY

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Clay rich materials play an important role in nuclear waste repositories either as back fill materials in engineered barrier systems or as host rocks. In this study we investigate opalinus clay as a potential host rock and compacted bentonite as a major component of the barrier system.

For the long term prediction of nuclear waste repositories, it is of major interest to understand the relationship between the pore structure in the clay rich materials and the corresponding transport properties of dissolved radionuclides. Unfortunately, characterization of the multi-scale pore structure in hydrated bentonite and in natural opalinus clay is a difficult task. Because of the swelling clays, the microstructure is strongly changing with variable moisture contents. Therefore, it is difficult to prepare bentonite and opalinus samples with defined water contents for subsequent microstructure analysis by means of electron microscopy.

In this article, we present state of the art cryo-preparation techniques including high pressure freezing and low temperature freeze substitution, which enable the stabilization of the pore structure in bentonite and opalinus samples which contain significant amounts of swelling clays. Microscopic analyses of the cryo-stabilized clay samples are then performed with conventional SEM, with cryo-SEM, with FIB-nanotomography and with TEM. From the resulting 2D- and 3D-images, so-called "continuous pore size distributions" are calculated and the 3D-connectivities of the mesopores are documented. It is demonstrated that reliable quantitative 3D-characterization can be achieved from the pore structures in bentonite and in opalinus rocks when high resolution 3D-imaging by TEM- and FIB-nanotomography is combined with modern cryo-preparation techniques (i.e. high pressure freezing).

**Keywords:** 3D-pore structure, Swelling clay, Cryo-microscopy.

# STABILITY OF BENTONITES IN GEOTECHNICAL BARRIERS FOR HLRW REPOSITORIES

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Currently many clay scientists are involved in the investigation of the suitability of bentonites as barrier for high level radioactive waste (HLRW) repositories. The desired bentonite properties are mainly high swelling pressure and active surface sites potentially retaining some of the radionuclides. The present paper attempts to summarize the current knowledge about the stability of bentonites under the conditions expected in a HLRW repository. Bentonites have to be stable (retain their swelling capacity) in contact with highly saline solutions (e.g. formation water in granites), highly alkaline Ca dominated solutions (cement pore water), and in contact with corroding metals (e.g. iron). The formation of non-swelling (or irreversibly collapsed) layers, regardless if it actually can be termed illitization, represents one of the key problems because the geotechnical buffer would loose swelling capacity (potential to seal cracks) and the porosity would increase which in turn increases the hydraulic conductivity. Particular focus, therefore, is on the identification of processes which can lead to the formation of non-swelling layers.

Own investigations proved the montmorillonite stability in highly concentrated NaCl solutions at 60°C. Literature data, however, suggest that hydrothermal conditions (> 100°C) can lead to irreversible mineral alterations. Expectedly, the presence of $K^+$, on the other hand, led to the formation of non-swelling layers and a decrease of the CEC even at 60°C after 5 months (10 % decrease, average value of 36 different bentonites). In summary there is not much doubt that $K^+$ can affect the barrier properties, particularly if wet and dry conditions alternate (which is known to facilitate illitization). Owing to their high pH cement pore waters congruently dissolve montmorillonite and precipitate zeolites (amongst others). This reaction is only limited by the amount of available cement pore water which fortunately is expected to be limited at the cement – bentonite interface. Under the reducing conditions expected in a HLRW repository ferrous iron is released at the montmorillonite – iron interface and diffuses into the bentonite. This in turn increases the iron content and after reaching a critical amount changes the thermodynamic stability of the mineral constituents. Different experimental studies proved the formation of 7 Å or 14 Å iron rich phyllosilicates (either serpentines or chlorites) and different mechanisms are proposed explaining the process of mineral alteration. In the present paper an alternative mechanism is proposed.

All relevant processes which might occur have to be understood well in order to enable reliable modelling which in turn is used for the long term safety assessment of a geotechnical barrier. In this respect it is essential to conduct real scale long term tests in order to be able to compare the results obtained by the current models with the processes which actually take place. Due to the comparably long heating period the LOT test setup by SKB is one of the most interesting real scale tests. Results obtained so far are presented in the present paper as well.

# FE(0)-CLAYS INTERACTIONS AT 90°C UNDER ANOXIC CONDITIONS: A COMPARATIVE STUDY BETWEEN CLAY FRACTION OF CALLOVO-OXFORDIAN AND OTHER PURIFIED CLAYS

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In the context of the geological disposal of high-level radioactive waste it is of prime importance to understand the interactions between the saturated clay formation and steel containers. This can be achieved through an in-depth analysis of iron-clay interactions. Previous studies on the subject investigated the influence of solid/liquid ratio, iron/clay ratio, temperature and reaction time [Guillaume (2002), Lantenois (2003), Perronnet (2004)]. The aim of the present study is to understand in more detail the role of the nature of the clay on the mechanisms of interaction between iron metal and clay particles by combining chemical analyses, X-ray diffraction, infrared spectroscopy and scanning and transmission electron microscopy.

In a first step, the Callovo-Oxfordian argillite from the ANDRA underground laboratory was purified to extract the clay fraction (illite, illite-smectite, chlorite and kaolinite). Batch experiments were carried out in anoxic conditions at 90°C in the presence of background electrolyte (NaCl 0.02 M/L, $CaCl_2$ 0.04 M/L) for durations of one, three or nine months in the presence of metallic iron. Experiments in absence of iron were used as control. The Iron/clay ratio was fixed at 1/3 with a solid/liquid ratio of 1/20.

In order to get some insight about the relationships between interaction mechanisms at the molecular scale and crystallographic properties (particle size, TO or TOT layers, amount of edge faces…), the above mentioned experiments were also carried out in parallel on other purified clays : two smectites (Georgia bentonite and SWy2 from the Clay Minerals Society), one illite (illite du Puy) and one kaolinite (KGa2, from the Clay Minerals society).

**Keywords:** Clays, Iron, Anoxic interaction.

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# EFFECT OF COMPACTION ON DISSOLUTION RATE OF SMECTITE UNDER HYPERALKALINE CONDITION

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Bentonite-cement fluid interaction has been a key research issue in performance assessment of radioactive waste disposal. It has therefore been investigated on dissolution rate of smectite (main constituent mineral of bentonite) under such hyperalkaline condition. Generally, the dissolution rate has been obtained from batch and flow-through experiments under the conditions with high fluid/solid weight ratios. These previous studies have provided a contribution to kinetical model of smectite dissolution. Especially, some of them showed some equations explaining the effect of factors such as pH of reactive fluid, temperature, deviation from equilibrium on smectite dissolution rate. However, the experimental conditions in such studies were completely different from the conditions in actual radioactive waste disposal system. For quantitative understanding, dissolution experiments for the compacted bentonite have also conducted. These studies showed that the dissolution rate for compacted bentonite was different from that obtained from batch and flow-through experiments. However, the difference has not been understood in details.

In this context, the dissolution experiments for the compacted smectite with different dry densities were performed to understand the effect of compaction on dissolution rate of smectite under hyperalkaline condition.

From the experimental results, it is clearly showed that the more compacted smectite has the less dissolution rate. However, there are no obvious changes in coefficient of permeability of the compacted smectite with different dry densities during the experiments. According to the results of caesium adsorption test, variable charge density was decreased with increasing of dry density. This decreasing indicates that apparent and active edge surface area was decreased because the variable charge density generated from the edge surface. According to the previous studies such as Yokoyama et al. (2005), smectite particles are predominantly dissolved from the edge of the particle. Therefore, the difference of dissolution rate in the compacted samples was probably due to the extent of exposed reactive surface area. However, the difference in dissolution rate between lower and higher compacted smectites can not be fully explained by considering of the decreasing in the reactive surface area. According to the results of reactive transport modeling, $\Delta Gr$ effect obtained by Sato et al. (2007) should be took into account for filling the gap in dissolution rate.

**Keywords:** Dissolution, Hyperalkaline, Smectite.

# LONG-TERM STABILITY OF THE BENTONITE BARRIER: HOW MUCH DO WE NEED TO KNOW?

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In many countries, multiple barrier systems have been adopted as the fundamental strategy to assure long-term safety of geological disposal of radioactive wastes. Within such systems, a bentonite buffer is often incorporated as the primary safety barrier. However bentonite is not thermodynamically stable under strongly alkaline conditions, such as may arise from cementitious materials introduced into the repository, principally to ensure operational safety. Hence, to demonstrate long-term safety from any multiple barrier system which includes both clay and cementitious materials, it is critically important to demonstrate clay stability for sufficiently long times; for example, on the basis of simple mass balance, slow dissolution kinetics, restricted mass transport, etc.

Alteration of clay minerals in contact with cement involves a variety of reactions such as dissolution, precipitation and ion exchange which, coupled with transport of solutes, form a highly nonlinear coupled system containing positive and/or negative feedback loops. Our understanding of such systems, based on observations of short-term experiments and analogous natural systems, is inevitably limited. Indeed, there remain uncertainties at both the conceptual level, due to the range of possible alteration scenarios for the complete engineered barrier system, as well as errors associated with key input parameters, such as reaction rates. These uncertainties make it extremely difficult to prove long-term stability of bentonite in a rigorous manner and the associated R&D programme could lead to an endless chain of experiments and modelling.

An innovative way to formulate this problem is to regard this task in terms of argumentation rather than scientific proof. This allows us to set the more practical goal of constructing a convincing case, together with defence backed up by multiple lines of reasoning against all potential criticisms. In this talk we will provide an overview of the processes influencing the stability of bentonite and summarise relevant knowledge and supporting evidence, highlighting where key uncertainties lie. We will then draw an argumentation diagram based on this overview and make clear where we already have a convincing arguments and where “threats”, i.e., counter-arguments without acceptable defence, exist. Then we will try to answer the question “How much do we need to know?” by defining a set of practical goals and by identifying any gaps in the chain of argumentation that need to be filled by future R&D.

**Keywords:** Radioactive waste management, Bentonite, Argumentation.

# A 15 YEARS *IN SITU* ALKALINE PROPAGATION INTO THE TOURNEMIRE ARGILLITE

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The migration of an alkaline plume in argillaceous media in contact with cement and its consequences on the containment properties of these clay barriers is an important issue regarding to the safety of a potential repository of high-level radioactive wastes in deep geological formations in France. A borehole sealed by concrete at the IRSN's Experimental Platform in Tournemire offers the possibility of studying transformations undergone by argillite in contact with cement in an "in situ" context for 15 years. Preliminary mineralogical and reactive transport modeling studies of the overcored samples (De Windt *et al.*, 2008) highlighted several fronts of mineralogical perturbations within the argillite matrix (so-called P1) and along inframilllimetric decompression fissures perpendicular to the cement contact (so-called P3). The present work focuses on further characterisations of these samples. Analytical methods have consisted in petrophysical and microstructural measurements (autoradiography, X-ray microtomography methods), petrography and mineralogy analyses (XRD, SEM, TEM, ICP-MS) and isotopic Sr, C and O measurements. Nearly same mineralogical phases were observed for P1 and P3 with the following minerals occuring in the first cm: (1) ettringite, gypsum and small amounts of calcite, (2) CSH and CASH associated to calcite, (3) CASH and celestine. After this centimetric zone, P3 displayed a gradient of calcite crystallization. For both P1 and P3, the last front showed K-Feldpars overgrowths, calcite and gypsum precipitation. The Sr and C isotopic properties of the newly formed carbonates pointed out the propagation of an alkaline fluid. Far from the concrete (2.5 to 3 cm), homogeneous $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ isotopic ratio were measured in the argillites. Going towards the concrete zone (0 to 2.5 cm to the concrete interface) these data changed and tended to reach ratios measured in the cementitious carbonates, suggesting an alkaline fluid / argillite interaction. Overall porosity measured in the cement increases from the core to the rim, and decreases in the argillite in the P1 disturbed zone. Ongoing work with X-ray microtomography and autoradiography will enable to visualize textural changes and to quantify the porosity evolution.

**Keywords**: Argillite, Cement, Alkaline plume.

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# HEALTH & ENVIRONMENT

## SESSION HE9

## *The Interaction of $CO_2$ with Clay Minerals*

# CARBON DIOXIDE SEQUESTRATION IN OIL SANDS CLAY SLURRIES

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The carbon dioxide footprint associated with the development of the Canadian oil sands resource has recently become the source of some controversy. Although the extraction of this resource is somewhat more energy intensive than the world's ever decreasing light, sweet, primary oil resources, a major source of the GHG impact for oil sands is in the introduction of hydrogen in order to create Athabasca light sweet crude from the original bitumen. This hydrogen is typically created by steam reforming of methane, the by-product of which is a relatively (>90%) pure carbon dioxide stream.

The clay slurries associated with the surface mining of oil sands can be reclaimed to a dry landscape by a variety of methods, all of which require some chemical intervention to modify the settling behaviour of the clays. A commercially developed process for the reclamation of the clay slurry tailings is the consolidated or non-segregating tailings process. A variety of process aids can be used to implement the consolidated tailings process, including carbon dioxide.

Discussion of the fate of this carbon dioxide process additive takes the same form as other sequestration processes, with a portion physically sequestered, a portion ionically sequestered, and a portion sequestered as a carbonate mineral. In contrast to deep well injection processes, the major sequestration mechanisms when carbon dioxide is used for oil sands clays are ionic and mineral sequestration. Aside from carbon dioxide sequestration in the consolidated tailings process, addition to the whole tailings stream also results in some sequestration along with a more rapidly consolidating clay tailings.

This paper will discuss the chemistry of the clay minerals and carbon dioxide interaction and the potential for reducing the oil sands carbon dioxide footprint via sequestration in a variety of oil sands tailings streams. Results from pilot studies and preparation for an upcoming commercialization will also be discussed.

**Keywords**: Carbon, Sequestration, Oilsands.

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# CARBON DIOXIDE RETENTION OVER CLAY-DENDRIMER MATERIALS

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Capture of carbon dioxide from major emission sources is a key-step in reducing greenhouse gases. The use of liquid amines as adsorbents gave unsatisfactory performances due to amine leakage and thermal oxidation during $CO_2$ desorption. To prevent from these shortcomings, amine immobilization over solid supports turns out to be a more convenient route [1-3] but large-scale processes still require high amounts of amines.[4] Clay-based nanocomposite materials for adsorption of $CO_2$ were obtained through intercalation of montmorillonite-rich clay (Mt) with mono- and di-butylamine, dioctylamine, pentaérythritol, bisphénol-A, and a series of polyol dendrimers (H-20- H-30 and H-40, from Boltorn Co). These three bulky hyperbranched polyester dendrimers deriving from 2,2-bis (hydroxymethyl) propionic acid have average numbers of terminal OH groups of 16, 30 et 40, respectively. The reversible $CO_2$ adsorption-desorption equilibrium is discussed in terms of acid-base interactions between the organoclay surface and $CO_2$ molecules
The effect of the exchangeable cation and the number of OH groups grafted on the dendrimeric moiety was investigated. Characterization through X-rays diffraction and scanning electronic microscopy reveal that divalent cations exert strong sandwiching effect on the clay lamellae that prevent from clay intercalation. Higher exfoliation obtained by ion-exchange with sodium followed by intercalation by H-20 and H-40 polyol dendrimers gave the highest surface areas and carbon dioxide retention capacity. Thermal programmed desorption analyses (TPD) show that even with weak interactions towards $CO_2$, used as the probe gas, polyol organoclays display optimal base properties that allow adsorption of maximum amounts of carbon dioxide, with easy consecutive gas desorption upon slight heating.[5] The results obtained herein open new opportunities in obtaining microporous materials, able to reversibly retain gaseous pollutants. The adsorbed gases can easily be released through thermal desorption under moderate heating, around the ambient temperature, or more conveniently under low pressure.

**Keywords:** Montmorillonite, Acid-base interactions, Dendrimers.

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# REACTIVITY OF SMECTITE AND MIXED-LAYER ILLITE/SMECTITE IN $CO_2$ GEOLOGICAL STORAGE

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The capture and geological storage of $CO_2$ in deep saline aquifers, depleted oil and gas fields and coal seams appears to be one of the main solutions to reduce greenhouse gases release to the atmosphere. Clay minerals play an important role in the sealing and confinement functions of the cap-rock formations with respect to $CO_2$. They reduce porosity, permeability and reactivity, and thus limit the vertical fluid migration for the long-term $CO_2$ storage performance and safety.

This study presents experimental and modeling results regarding the geochemical reactivity of two clay minerals: Na-Montmorillonite SWy-1 smectite MX80 (Wyoming – USA) and a Na-mixed-layer illite/smectite obtained directly by extraction from the Chinle clayey cap-rock sample (Utah – USA). A series of experiments were designed to distinguish the net effect of $pCO_2$ versus that of pH and aqueous carbonated species.

For all the experiments, a simplified NaCl 0.1M solution at a constant temperature of 80°C was used in order to facilitate the interpretation of the results in terms of geochemical reactivity and to represent the ionic strength and the temperature in saline aquifers. Then, the solution was maintained at pH 4, 5 and 7.5 to assess the clay material reactivity in acidic conditions. A series of experiments were performed at pH 8.5 with a [NaCl 0.1M; $NaHCO_3$ 0.05M] solution to assess the influence of aqueous carbonated species on clay samples reactivity. The solution and solid phases were sampled after 1, 30, 60 and 90-day experiment in the Teflon cells. Finally, the two samples are reacted in a Titanium pressurized cell where the saline solution is maintained at 80°C and 30 bars of $pCO_2$. In-situ measurements of pH were performed during 40-day experiments.

It is observed that the direct effect of $CO_2$ on clay minerals is small. As a result, the major parameter governing the dissolution of clay minerals is the pH of the interstitial solutions getting in contact with the clayey caprock. In addition, major mineralogical transformations appeared after 90-day experiments in acidic conditions where illitization is observed for smectite and mixed-layer illite/smectite. For each experiment, the results were inferred from ICP-AES analysis performed on solution to determine Si, Ca, Mg, K, Na, Al evolution and XRD and TEM characterization performed on clay minerals to conclude on the structural modifications.

**Keywords**: Smectite, Mixed-layer illite/smectite, $CO_2$, Experiments, pH, Illitization.

# $CO_2$ SEQUESTRATION ON CERAMIC BUILDING MATERIALS

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Carbon dioxide capture and storage (CCS), is one of the options for reducing atmospheric emissions of $CO_2$ from human activities. The aim of this research is to assess the possibilities of $CO_2$ sequestration on ceramic building materials, in order to propose the injection of $CO_2$ in construction ceramic wastes used for mining reclamation.

Raw materials with suitable composition to prepare porous red wall tiles and porous light-weight bricks wall tiles were heating between 800ºC and 900ºC. The reactivity of those heating bodies with $CO_2$ was followed *in situ* using an X-Ray Diffractometer equipped with a temperature chamber. The reaction products were evaluated in function of relative humidity and reaction temperature for a constant pressure of $CO_2$. The mineralogical composition of these products was quantified using a Rietveld procedure (TOPAS).

Calcite was the main product formed in any experimental condition. Those formulations heating at 850ºC presented a higher reactivity than the others, because of the mineralogical composition of the starting materials. The amount of calcite increased until five times the original amount in function of the experimental conditions.

**Keywords**: $CO_2$ sequestration, ceramic materials, carbonation.

# CHARACTERIZATION OF CARBON STORAGE RESERVOIRS

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Clay-rich cap rocks provide one component of a reservoir seal. Other components include faults, unconformities, and facies changes. Seals classify as leaky, rate, capillary, and true pressure seal. The type of seal changes over space and time. The type of seal and its long-term integrity affect the storage of $CO_2$ in a subsurface reservoir. A study of a petroleum field in the Gulf of Mexico examined the integrity of reservoir seals and proposed guidelines and methods of computational modelling.

This presentation limits consideration to (1) effects of observational scale on computational algorithms, (2) role of permeability in $CO_2$ storage requirements, and (3) geological, physicochemical, and mathematical characterization of potential storage reservoirs.

Subsurface reservoirs typically exhibit a high degree of heterogeneity and anisotropy. The nature of those differences change with scale. Grain boundaries and pore spaces predominate at the microscopic scale. Faults, folds, and formational contacts assume importance when taking a larger view. Features at several scales affect spatial distributions of porosity, permeability, pressure, temperature, and hydrocarbons in the Gulf of Mexico. Statistical techniques identified appropriate observational scales and predictive models developed to accommodate the effects.

Permeability alters the fate of $CO_2$ injected into a reservoir. It influences injection rates, velocities of transmission, degree of penetration into reservoir and boundary rocks, and escape from the reservoir. That modifies the extent and rates of chemical reactions in which it might participate. Heterogeneity and anisotropy affect values of permeability and are accommodated in predictive models for the Gulf of Mexico field.

Chemical characterization of a potential storage reservoir requires knowledge of compositions of reservoir and boundary rocks and fluids. Competing reactions may reduce the supply of potential reactants. E.g., Ca may exchange with Na adsorbed on clay minerals in preference to forming carbonates. Values of pressure and temperature require accurate prediction for estimating thermodynamic properties.

**Keywords:** Carbon storage, Reservoir seals, Computational models.

# HEALTH & ENVIRONMENT

## SESSION HE10

## *Interactions between Clays and Inorganic and Organic Pollutants*

# SORPTION OF PHENANTHRENE AND PYRENE ON SMECTITE AS AFFECTED BY THE PRESENCE OF IRON AND ITS IMPLICATIONS ON BIOAVAILABILITY

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The adsorption of hydrophobic organic contaminants has traditionally been associated with the organic components of soils and sediments, but nowadays the knowledge of the contribution of the mineral components, mainly clay minerals, is being developed. The large interlayer surface of smectites and its dual hydrophobic/hydrophilic character, which in turn depends on the nature of the interlayer exchange cations, make them the most potential mineral adsorbent in soil, sediment or subsurface material, particularly in those of low organic carbon content. The objective of this work was to evaluate the effect of the presence of Ca(II) and Fe(III) ions, either in solution or as interlayer exchange cations, on the adsorption of the polycyclic aromatic hydrocarbons (PAHs) phenanthrene and pyrene by smectite (SWy), and its implications on bioavailability. Results show a large enhancement of adsorption of the PAHs on smectite (Ca-SWy) by the presence of Fe(III) in phenanthrene or pyrene solutions (as culture medium) and also with Fe(III) as interlayer exchange cation (Fe-SWy). Accordingly, the desorption of phenanthrene and pyrene from smectite showed greater irreversibility when Fe(III) was present as interlayer cation and also in solution. X-ray diffraction and IR spectroscopy revealed that phenanthrene molecules are adsorbed mainly in the interlayer space of those smectites, possibly through i) $\prod \rightarrow d$ interactions between the aromatic rings of the PAH and Fe(III) center and ii) hydrophobic interactions with the basal siloxane surface. Mineralization of phenanthrene and pyrene from their complexes obtained on the different smectites studied confirmed that the strong interlayer adsorption observed when Fe(III) is present both as interlayer cation and in the medium limits largely the bioavailability of the PAHs, which could be relevant in the design of soil remediation techniques.

**Keywords:** Bioavailability, Polycyclic Aromatic Hydrocarbons, Organic-Clay Intercations, Smectites, Sorption.

# COMPETITIVE ADSORPTION OF CU(II) AND CR(III) ON BENTONITE

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Heavy metals present in wastewaters from mining and metal finishing operations are very toxic pollutants. One of the most efficient methods of removing metals from water solutions is adsorption. Due to the availability of the clays and their high cation exchange capacity, adsorption of heavy metals on clays is very promising and potential method for removing metals from wastewater. Several works have been reported on the individual adsorption of different heavy metals on bentonite, vermiculite, sepiolite, palygorskite, kaolinite, illite, and perlite. However, no work has been reported on the competitive adsorption of heavy metals on clays. The effects of pH, temperature, nature of metal, nature of clay and interactions between the metal ion and the surface of clay on the adsorption capacity have been studied extensively. The competitive adsorption equilibrium data of Cu(II) and Cr(III) on bentonite at pH=3 and T=25°C were obtained in a batch adsorber. The pH of the solution was kept constant during the adsorption experiment by adding either 0.01 N NaOH or 0.01 N $HNO_3$. The Langmuir isotherm fitted the individual adsorption equilibrium data of Cr(III) and the Freundlich isotherm fitted the individual adsorption data of Cu(II). Comparing these individual isotherms it can be noted that the capacity of bentonite for adsorbing Cr(III) is 2.7 times greater than that for Cu(II). In other words, bentonite exhibits a higher selectivity for Cr(III) than for Cu(II). The multicomponent isotherm models of non-modified competitive Langmuir, modified competitive Langmuir, Sheindorf-Rebuhn-Sheintuch (SRS), non-modified competitive Redlich-Peterson and modified competitive Redlich-Peterson were used to fit the experimental competitive adsorption data of Cu(II) and Cr(III). The isotherm parameters were evaluated by minimizing the Marquardt's percentage standard deviation (MPSD) using an optimization algorithm. The isotherm best fitting the experimental data was assumed to be that having the lowest MPSD. The SRS model was the isotherm best fitting the experimental data and this isotherm fitted reasonably well the experimental data. The competitive adsorption data revealed that the capacity of bentonite for adsorbing Cr(III) was not affected by the presence of Cu(II) whereas the capacity of bentonite for adsorbing Cu(II) was drastically reduced about 7 times by the presence of Cr(III). This result indicates that the competing ions can play a very important role in the adsorption capacity of clays in multicomponent metal ions systems.

**Keywords:** Adsorption, Competitive, Bentonite.

# INTERACTION OF SE(VI) AND SE(IV) WITH ILLITE: EXPERIMENT AND MODELING

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A comprehensive study was undertaken to describe the adsorption of $SeO_3^{2-}$ and $SeO_4^{2-}$ on conditioned Na-illite. Illite du Puy was chosen as a model clay mineral to simulate the interaction of Se and other radionuclides with more complex geological formations studied as potential host rocks for the geological disposal of high level radioactive waste [e.g.: Boom Clay (Belgium), Callovo-Oxfordian Clay (France), Opalinus Clay (Switzerland)].

Short term Se(VI) adsorption (<7 days), was measured in the pH range 3.0- 10.0. and was found to be negligeable beyond pH 4 and to be low ( Kd~ 0.50 L/Kg) below pH 4. Consequently , no surface complexation modeling was attempted.

Short term Se(IV) adsorption (<7 days) was studied by measuring adsorption edges (adsorption versus pH for of a constant dose of Se(IV) ranging from $10^{-8}$ to $10^{-5}$ M) and adsorption isotherms (varying Se(IV) concentrations at different ionic strengths and at constant pH of 4.0 and 6.0). The sorption of selenite as a function of pH showed a so-called “sorption edge” typical for anion sorption on oxides and corresponding to a ligand exchange mechanism. Adsorption was maximal ($\log K_D \approx 1.5\text{-}2.0$) in the neutral-to-acid pH range and decreased sharply from pH 6.0 to pH 8.5. The sorption isotherms at pH 4 were fairly linear and independent of the electrolyte concentration, a feature which is typically observed for an inner-sphere sorption mechanism.

Surface complexation modeling based on the Site Protolysis model with No Electrostatic interaction (SPNE model of Bradbury and Baeyens (1997) could adequately describe the selenite adsorption by the sorption of $HSeO_3^-$ and $H_2SeO_3$ on both positively charged weak basic (╟$S_{wb}OH_2^+$) and positively charged weak acid (╟$S_{wa}OH_2^+$) surface sites. [$\log k_{wb}(HSeO_3^-) = 2.9$; $\log k_{wb}(H_2SeO_3) = 3.10$; $\log k_{wa}(HSeO_3^-) = 2.35$; $\log k_{wa}(H_2SeO_3) = 3.10$]

**Keywords**: Selenium, Illite, Surface complexation modelling.

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# PICLORAM ADSORPTION ON PILLARED CLAY

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Picloram acid, 4-amino-3,5,6-trichloropicolinic acid, is a herbicide commonly used in agriculture in Argentina and Brazil. A significant amount of applied pesticide can reach soil and groundwater and / or surface water bodies through the drainage and/or lixiviation processes due to different application methods and environmental conditions. Pillared clays (PILCS) are interesting material to be used as catalysts and adsorbents, due to its multi-charged centers, large area, high interlayer space and thermal stability. PILCS synthesized with oxide pillars of Cr, Zr, Al, Ti, and Fe have been used in studies of adsorption of organic compounds as well as toxic metals such as As, Cd, Cr, Co, Cu. Adsorption of Picloram on iron oxides PILCS could be the basis for the development of adsorbent materials for the remediation of polluted environments and to design materials for controlled release of herbicides.

Fe Oxide Pillared Clays (Fe-PILCS) were synthesized from the montmorillonite clay (Wyo, USA) and Fe(NO3)3 as was previously reported (Belkhadem et al, 2008; Cañizares et al, 1999). PILCS were characterized by XRD, elemental analysis, DTA, TGA and by N2 adsorption (BET). Adsorption studies on Fe-picloram PILCS were made after 48hs equilibration of PILCS with an aqueous solution of Picloram at known concentration, pH and ionic strength were kept constant during the whole experiment. Picloram-Fe-PILCS were characterized using the same techniques as for PILCS. The adsorption results were compared with those obtained previously for the picloram adsorption on un-modified Wyo (Marco Brown et al, 2008).

Surface area and interlayer space of Fe-PILCS were bigger than Wyo. An analysis of the adsorption isotherms of picloram on the Fe-PILCS showed that picloram adsorption increases with decreasing pH. The adsorption of picloram was over 90% at pH=3, this value is much higher than the adsorption on Wyo over similar conditions, 20%. However, at pH 7 adsorption on Fe-PILCS was lower than these obtained on Wyo. Picloram adsorption on Fe-PILCS is heavily greater to pHs below 7 showing a significant increase in the efficiency of the process which makes them susceptible to be used for dosing or remediation of pesticides.

**Keywords:** Picloram, Pillared clay, Herbicides.

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# CLAYEY MATERIALS AS ADSORBENTS FOR A SUSTAINABLE APPLICATION

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Thanks to the development of the science and the technology of the nourishment in the last 50 years, there have revealed itself several new substances that can fulfill beneficial functions in the food, and these substances, named food additives, are today within reach of all. The food additives recover a very important role in the complex nourishing supply. The additives fulfill several useful functions in the food, which often we give for sat. Nevertheless the widespread use of food additives in the food production also influences the public health. The food industries, which are very important for the economy, spill residues proved from its activity that they have to be controlled to evaluate the environmental impact and to offer the necessary information about the quantitative evaluation of the chemical risk of the use of food additives for the public health.

Among the strategies used at present to preserve the quality of the water and this way to diminish the environmental risk that supposes the chemical pollution, stands out the use of adsorbents of under cost, already they are natural or modified, to immobilize these compounds and to avoid the pollution of the water with the consequent reduction of environmental and economic costs. Regarding innocuous and low cost materials, it is necessary to mention clays and clay minerals, which colloidal properties, facility of generating structural modifications, abundance in the nature and low cost make them very adapted for the adsorption of chemical pollutants. The clayey materials have given place to numerous applications in the field of the public health (1, 2) and its efficiency having being demonstrated as natural or modified adsorbents of all kinds of pollutants (3). We have studied the adsorption of several food additives by natural or thermally modified clays, searching their interaction mechanisms and the possible recycling of these materials for environmental purposes and prevention of the public health.

**Key words**: Clayey materials, Adsorption, Recycling.

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# MECHANOCHEMICAL INTERACTIONS OF CLAY MINERALS WITH ORGANIC POLLUTANTS: A SUITABLE APPROACH TO SOIL REMEDIATION

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Owing to their surface properties, clay minerals are often used in a large number of industrial applications in which mechanochemical treatments play a fundamental role. Strong milling treatments gradually reduces crystallinity in the study clay minerals by causing diffusion of atoms (mainly protons, “prototropy”), delamination, and layer breakdown, therefore affecting the surface and colloid properties clay minerals and causing the increase of their catalytic activities (Yariv and Lapides, 2000). In the present study were investigated - by means of X-ray diffraction, spectroscopic methods (IR and solid-state NMR), and thermo-gravimetric analysis (TG-DTA) - the mechanochemical reactions of dioctahedral smectites (BentoliteH), trioctahedral smectites (LaponiteRD), and well crystallized kaolinite (Kga-1b) with organic molecules (phenols) as representative of pollutants with enhanced polarity: cathecol (CAT) and pentachlorophenol (PCP). Pollutant removal efficiency of clay minerals was evaluated by chromatographic analysis (HPLC-DAD). Prolonged high energy grinding in planetary zirconium ball mill likely promotes intense sequestration of PCP and CAT by trioctahedral and dioctahedral smectites and kaolinite with respect to the simple contact between sorbants and pollutants. Mechanochemical interaction of PCP molecules with the trioctahedral smectite Laponite is weak, mainly occurs on the external surfaces, and does not involve the OH-phenolic group or any complexation of the interlayer cation ($Na^+$). Such interaction only causes amorphization of Laponite by formation of a double films of PCP molecules adsorbed on the external clay mineral surfaces. On the contrary, the dioctahedral smectite Bentolite exhibits strong mechanochemical interactions with PCP molecules via the phenolic group. Prototropy, induced in Bentolite surfaces by milling, is responsible for the PCP molecule perturbation and the enhanced capability of Bentolite surface to promote formation of intermediate products via OH groups. Mechanochemical interactions of CAT with both smectites mainly occur in the interlayers. For the dioctahedral smectite they are stronger than for the trioctahedral one, and likely involve inner-sphere complexation of Bentolite interlayer cation ($Na^+$) by CAT phenolic groups. Mechanochemical interactions of both pollutants with kaolinite mainly occurs via adsorption on external clay mineral surfaces through the phenolic group and, in the case of PCP, do not involve the chlorine atoms of the ring.

**Keywords:** Clay minerals, Organic pollutants, Mechanochemistry.

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# DEGRADATION OF ORGANOCHLORINE COMPOUNDS BY HYDROPHOBIC VERMICULITE AMENDED WITH ZERO IRON PARTICLES

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In recent years due the intense use of oil-compounds several technologies have been proposed and even used for the decontamination of affected areas by accidental spills with oil derivatives. The most concern pollutants are organochlorine compounds because of its low solubility in water and toxicity, characterizing as recalcitrant compounds in the environment. However, there are some alternatives that may increase the degradation of these compounds, such as the use of modified clays. The hydrophobic modified clays can be obtained by the replacement of mono valent cations naturally present on the surface of clay by hydrophobic cations, such as hexadecyltrimethylammonium. The replacement creates an environment capable of accommodating hydrophobic substances poor water soluble. Also, in the hydrophobic layer we tested nano particles of zero iron valent incorporated in the hydrophobic layer of clays. Such incorporation of zero iron allows the degradation of organochlorine compounds by reducing with iron. In this study we evaluated the use of hydrophobic vermiculite with zero iron incorporated for chemical reducing of ethylene tetrachloride adsorbed on the surface vermiculite.

The experiments were conducted in columns filled with sand and hydrophobic modified vermiculite in different proportions (2, 5, 10, 25 and 50%) containing zero iron particles (fixed amount). The columns had 30 cm length and 1.5 cm of internal diameter. Volumes of aqueous solution containing ethylene tetrachloride were passed through the column. The products of degradation were followed by gas chromatography (ethylene trichloride, cis and trans-dichloroethylene) according the methodology described by Bowman et al. (1999).

The results showed that the amount adsorbed increase with higher proportions of modified vermiculite, approximately 80 mg.g$^{-1}$ (Froehner et al. 2008). Sorption/retardation media reaction had high retention rates and large capacities. Also the degradation rates were high, increasing with the high proportions of modified clay, in another words, increase in proportion of zero iron amount available for redox reaction. Definitely, degradation media can provide ultimate contaminant control as content barriers.

**Keywords:** Organochlorides, Organo clays, Zero iron particles, Content barriers, Contaminated areas.

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# FORCE MEASUREMENTS ON CLEAN AND HYDROCARBON CONTAMINATED CLAYS

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The material used for this study was a colloidal fraction separated from natural clay samples chosen to constitute a smectite and kaolinite mixture [1]. One of the samples was contaminated *in situ* by diesel oil. Results of force measurements were compared with the control, not contaminated sample. Force measurements were performed in demineralised water and KCl salt solutions of 0.01M and 0.1M concentration, using AFM Digital Instrument, Santa Barbara, according to procedure described in [2]. The initial experiments described here have produced clear qualitative information about the interaction between clay particles in the mixture of clay minerals.

The control clay sample. The curves recorded on surfaces separation on approach and retrieval of colloidal probe from clay surface showed that only repulsion forces have been recorded. No adhesion was observed, i.e. clay platelets attached to each other neither in water nor in electrolytes. On the average, force curves on retrieval are similar to those on approach. This is typical picture of hydrophilic interaction where electrostatic repulsion of electric double layer prevails.

The contaminated clay sample. The presence of strong adhesion on approach and in particular on the retrieval curves in hydrocarbon contaminated clay sample was recorded. This might be a result of hydrocarbon chains presence on the clay surfaces, which might inhibit micro-bubbles attachment to hydrophobic clay surfaces. The curves recorded show a typical hydrophobic type of interaction.

The described hydrophobic interaction in diesel oil contaminated sample may explain the structural differences between this and the control sample studied in SEM [1]. Electrostatic interaction measured in the control clay shows short distance interactions in comparison to the long distance hydrophobic interaction measured in contaminated clay sample. Because of this the pores diameter observed in contaminated sample was much larger than in the control clay.

**Keywords:** Clays, Microstructure, Force measurements.

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# SELENIUM SPECIES RETENTION ONTO CLAY MINERALS

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In the context of nuclear waste management, long-term safety assessments have shown that selenium-79, released from the solid waste matrix, could be one of the major isotopes contributing to the global radioactivity potentially reaching the biosphere. Selenium has a quite complex speciation, with four main oxidation states, depending on both the pH and the redox potential of the surrounding environment. Sorption onto minerals can strongly affect the availability and the mobility of selenium. It is thus of great importance to be able to characterize both at a macroscopic and a microscopic level the different processes (retention, reduction, surface precipitation, …) that can potentially take place.

Regarding the multi-barrier concept considered for deep underground storage of high level and long-lived radionuclides, clays are candidates as host rock as well as backfill materials. The main phases constituting clay rocks are minerals such as montmorillonite, bentonite, or illite, but also other compounds like iron oxides, titanium oxide, pyrite, calcite and organic matter. It has already been shown that the first two can sorb and reduce selenium (VI) and selenium (IV) [1-2].

Thus, sorption experiments of selenium (VI), selenium (IV), elemental selenium and selenium (-II) onto kaolinite, montmorillonite, bentonite and illite have been performed. Kaolinite has also been studied since it is an abundant and well crystallized clay mineral in soils. Elemental selenium and selenide ions have been synthesized by bulk electrolysis according to Liu et al. (2008) [3]. All the experiments have been performed under anoxic conditions in a glove box under $N_2$ atmosphere ($O_2 < 2$ ppm). Selenium speciation in solution has been checked and investigated using Hydride Generation-Atomic Absorption Spectroscopy, IR, NMR $^{77}$Se and UV-vis measurements. The oxidation state of the selenium species once sorbed onto the clay surfaces have been evidenced using Raman, XPS, XRD and EXAFS.

**Keywords:** Selenium, Clays, Retention.

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# DIFFUSION OF ORGANIC POLLUTANTS THROUGH GCLs

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Compared to the United-States where mainly Wyoming natural sodium bentonite is used, Europe is facing a variety of GCLs containing natural sodium bentonites, natural calcium bentonites and sodium-activated calcium bentonites. Furthermore the manufacturing process of GCLs varies from manufacturer to manufacturer in terms of geotextiles used, bentonite used and mode of assembly of the GCL (needlepunched or stitched for example). The question then arises of the performance of landfill composite bottom liners depending on the nature of the GCL. An adequate modelling of contaminant advective-diffusive flow through GCLs requires the quantification of sorption parameters of the geotextile and bentonite components of those materials for a variety of contaminants contained in leachate, as well as the quantification of diffusion coefficients.

Purchasing the determination of the sorption on various constitutive geotextiles from GCLs (Ganne et al. 2008), the aim of this paper will be to present the experimental results obtained regarding diffusion through GCLs of 5 volatile organic compounds (VOCs), namely dichloromethane, 1.2 dichloroethane, trichloroethylene, benzene and toluene. Indeed these pollutants seem to be potentially dangerous substances for human health according to their amount found in leachate and their Toxicology Reference Value (TRV). Diffusion test took place in a glass cell; GCL split the diffusion cell into two 1.6l waterproof tanks called respectively source and receptor reservoirs. 2 GCLs from two different manufacturers were selected for this study. GCLs were hydrated by deionised water during 2 weeks then a known initial concentration of VOCs was introduced into the source reservoir. Samples in each tank were collected three times per week then analysed by head space – gas chromatography – mass detector. The tests run for 3 weeks. Results show a pronounced diminishing of the pollutant concentration in the source reservoir during the 20 first days followed by a stabilisation. In the receptor chamber, the VOCs concentrations increased progressively. Pollute v6 (Rowe and Booker, 2005) was used to determine the VOC GCL diffusion coefficient.

**Keywords:** Adsorption, Volatile Organic Compounds, Geosynthetic Clay Liners.

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# PREPARATION OF ORGANOVERMICULITES AND THEIR CHARACTERIZATION FOR USAGE IN WASTE WATER AND AIR TREATMENT

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Organoclays have been studied in a range of research works. They can be used in many branches, e.g. potential sorbents for removal of organic pollutants from contaminated water, air or soil. In contrast to activated carbon they have got special sorptive characteristic and they are effective sorbents especially for highly polluted matrices. Smectites, such as montmorillonite or bentonite, are usually used for the preparation of organoclays. In our study we used for organic modification other phyllosilicate – vermiculite from Czech locality of Letovice (CEC 144 cmol(+).kg$^{-1}$). Purpose of this study was to observe sorptive characteristics of vermiculite modified with hexadecyltrimethylammonium and hexadecylpyridinium cations on three levels and testing of the sorptive efficiency on naphthalene from polluted air and water. The quantity of organic cations in interlayer space of modified vermiculite has seemed to be an important parameter for organovermiculite preparation and its usability in pollution removal. The changes in organovermiculite structure after an exposure to different ambient conditions and an influence of organovermiculite particle size on the sorptive process. For characterization of organovermiculites we have used XRD, IR and TOC analysis. Sorption of naphthalene was tested with purge and trap method in connection with gas chromatography with mass spectrometry.

**Keywords:**Organovermiculite,Hexadecylpyridinium, Hexadecyltrimethylammonium.

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# MODIFICATION OF ORAGOCLAY WITH A PHOTOSENSITIZER OF METAL PHTHALOCYANINE FOR WATER TREATMENT

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Direct utilization of sun light and molecular oxygen for degradation and mineralization of toxic pollutants is the mostly attractive, economic and green technology. Up to date, the photocatalysis by $TiO_2$ seems to be the best one among several advanced oxidation processes for water treatment. However, the system only absorbs about 5 % of solar radiation, and the quantum yield is also low partially due to weak affinity of $TiO_2$ toward most of the organic pollutants in water.

Natural clays pillared by a quaternary ammonium cation are known to be a good sorbent for removal of organic pollutants from water. This is simply because the intercalated surfactants create a hydrophobic zone into which target substrates can easily enter through a partition pathway or other specific mechanisms. However, such organoclays after uptake of organic pollutants are hardly regenerated without damage or change of their original structure and properties. Therefore, a simple and economic method to only remove the sorbed pollutants in the interlayers is needed.

We have recently engaged in the development of such “green” organoclay. It is known that metal complex of phthalocyanine (MPc) can generate singlet oxygen under visible light, via energy transfer from the electronically excited state of MPc to the triplet state of molecular oxygen at ambient temperature. Singlet oxygen is reactive to phenolic compounds, but it hardly reacts with saturated hydrocarbons, such as alkyl surfactants often used in organoclay.

In this Talk, we will present results of MPc immobilization on the external surface or in the internal pores of cationic and anionic clays previously pillared with alkyl ammonium cation. The composite materials are not only good sorbents for uptake of phenolic compounds and organic sulfides from water, but also efficient photocatalysts for degradation of the sorbed pollutants. Such “green” organoclay can be repeatedly used without significant loss in both sorption capacity and photosentization ability. The results will be also compared with those from immobilized MPc on an ionic resin and on $TiO_2$.

This work is supported by NSFC (20525724) and 973 program (2009CB825300).

**Keywords**: Clay, Phthalocyanine, Sensitization.

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# MINERALOGY & CRYSTALLOGRAPHY

## MC1 • CLAY MINERALS IN EXTRATERRESTRIAL ENVIRONMENTS

## MC2 • CLAY SYNTHESIS

## MC3 • CRYSTAL CHEMISTRY AND STRUCTURE OF CLAYS

## MC4 • LAYERED DOUBLE HYDROXIDES

## MC5 • SERPENTINES AS HOT CLAYS

## MC6 • SIMULATION AND THEORY OF CLAY MINERALS AND INTERFACES

## MC7 • STRUCTURAL CHARACTERIZATION OF LAMELLAR COMPOUNDS

## MC8 • MODELING DIFFRACTION EFFECTS FROM LAYERED SYSTEMS AND NANOMATERIALS

# MINERALOGY & CRYSTALLOGRAPHY

## SESSION MC1

## *Clay Minerals in Extraterrestrial Environments*

# EXTRACTING AQUEOUS CHEMISTRY FROM CLAY-BEARING ASSEMBLAGES FORMED ON ANCIENT MARS

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Liquid water undoubtedly left its mineralogical mark on the earliest martian surface. Hydrated silicates (including clays), sulfates, (hydr)oxides and, most recently, carbonates, occur in exposures of Noachian and Hesperian age (~4.2-3.5 Ga; Ga: billion years) and they reflect spatial and temporal variation in acidity, volatile content and redox state. Unraveling this complex chemical evolution of the earliest martian surface is one of the highest priorities in solar system exploration.

Clay minerals are uniquely positioned to better define the habitability of the ancient Martian surface not only in chemical terms, but also by constraining the duration of aqueous episodes on Mars. Here, I will discuss chemical weathering and secondary mineral formation on ancient Mars, focusing on the premise that, in clay-forming systems, the bulk aqueous fluid is the interface between micro-scale processes and climate. Building from our current (but limited) understanding of igneous lithology and possible pH, $pO_2$, $pCO_2$, temperature and hydrologic conditions on ancient Mars, aqueous alteration assemblages on Mars can be tied to more specific chemistry, which paints a more detailed picture of both the chemistry of ancient water and its duration at the martian surface.

I will discuss ongoing research devoted to: (1) the targeted synthesis of clay minerals from basaltic-weathering derived fluid chemistry, (2) the formation of clay mineral assemblages from long-term basaltic weathering experiments, and (3) relating the properties of the bulk aqueous fluid to the alteration assemblage using a kinetic and thermodynamic framework. This approach has the advantage of highlighting the differences between the formation of clay minerals under controlled synthesis conditions and from the chemical weathering of individual mafic minerals and basaltic rocks.

More specifically, the discussion will be focused on: (1) how Fe-bearing clays may constrain the evolution of paleo-redox conditions on Mars, (2) relating pH, clay mineral formation and carbonate mineral stability on Mars, and (3) the effect of cation concentrations (e.g., Mg, Al, $SiO_2(aq)$) on the formation of various clay minerals (including aluminous smectites, vermiculite and saponite) from both synthesis and weathering experiments. Finally, a summary of mineralogical constraints on the habitability of ancient mars will be discussed, with emphasis on the most important factors that may have influenced the chances for life on Mars.

# THE OUT-GASSING OF A BASALT FLOW AS A SOURCE OF MARTIAN PHYLLOSILICATES

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Geomorphological observations of Mars surface and mineral detection, in particular hydrated sulphates, militate for the idea that liquid water have existed on Mars surface, even if physical conditions forbid its presence today. Beside the sulphate formation which requires particular chemical conditions, clay minerals are of particular interest because they are the first by-product of aqueous alteration of silicate rocks. Martian clays have been directly observed as iddingsite in SNC Martian meteorites (Leshin & Vicenzi, 2006), and Fe-Mg clays were spectroscopically detected on the surface of Mars by OMEGA (Poulet *et al.*, 2005).

Basically, clays are produced on the Earth by two contrasted mechanisms: bio-mediated alteration of silicate bedrocks by pedogenetic processes or hydrothermal abiotic thermoactivated alteration. The former being speculative in the Mars context, we focused on hydrothermal processes that could happen on Mars and affect volumes of rocks sufficiently important to be detected by remote sensing techniques. We tested the assumption of Fe-Mg clays formation during magma degassing by analysing terrestrial analogues in the Parana flood basalt province (Brazil). The petrographical and mineralogical characteristics of clay deposits in the prismatic joints of a lava flow (Gonçalves *et al.*, 1990) are interpreted here using quantitative chemical and thermodynamical models simulating the basalt interaction with $Cl_2$ rich volatiles. We reproduced an early acidic and oxidizing alteration of the lava flow by out-degassing of $H_2O$-$Cl_2$ fluids with disproportionation reactions, followed by a later more conventional alteration by neutral or alkaline evolved hydrothermal solutions. The above alteration model is supported by the mineralogical observations that clearly evidence two different reaction sequences, within the basalt columns or within the inter-columnar joints. The degassing pathways, by contrast with local hydrothermal systems, can affect large areas (several tens of square kilometres) as it is the case in Mars sites described by Poulet et al. (2005).

**Keywords**: Phyllosilicates, Out-gassing, Mars.

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# DISTRIBUTION AND VARIABILITY OF PHYLLOSILICATES ON MARS OBSERVED BY MRO/CRISM

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Recent analysis using the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on MRO has enabled identification and characterization of abundant and varied phyllosilicates across the planet (Mustard et al., 2008). One region with ample phyllosilicate outcrops is the Noachian-aged upland terrains near the ancient outflow channel Mawrth Vallis; a common phyllosilicate stratigraphy is observed here with nontronite at the bottom, covered by a ferrous phase, then hydrated silica, montmorillonite and kaolinite (Bishop et al., 2008). A similar clay profile is observed in smaller outcrops across a region up to $10^6$ km$^2$ (Noe Dobrea *et al.*, 2008). Nili Fossae is located west of the large Isidis Basin and contains large outcrops of multiple phyllosilicate minerals (Mustard et al., 2008) and also carbonates (Ehlmann et al., 2008). Phyllosilicates were identified previously at these sites via analyses of the Mars Express/OMEGA images (Bibring et al., 2005; Poulet et al., 2005). Smaller phyllosilicate outcrops also occur throughout the planet where they are exposed in ancient rocks, often associated with craters (e.g. Bishop *et al.*, 2007; Buczkowski *et al.*, 2008; Marzo *et al.*, 2008). We will present the types, distribution, and environments of phyllosilicates detected on Mars by CRISM.

**Keywords:** Mars, Phyllosilicates, CRISM.

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# CHEMIN: *IN SITU* X-RAY DIFFRACTION ANALYSES OF MARTIAN PHYLLOSILICATES ON MSL '11

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Observations from the OMEGA imaging spectrometer aboard Mars Express and CRISM on Mars Reconnaisance Orbiter have revealed a rich diversity of clay mineralogy on Mars, including nontronite, kaolins, chlorites and serpentine minerals [1-6]. Although orbiters and rovers have provided tantalizing clues regarding alteration mineralogy on the martian surface, the traditional method for analyzing mineralogy is X-ray Diffraction (XRD). The CheMin mineralogical instrument on Mars Science Laboratory (MSL '11) [7] will return quantitative XRD data from scooped soil samples and drilled rock powders collected from the Mars surface.

CheMin has a Minimum Detection Limit (MDL) of <3% by mass, an accuracy of better than 15% and a precision of better than 10% for phases present in concentrations >4X MDL (12%). CheMin utilizes a Co X-ray tube so that absorption in iron-rich samples is minimized. The resolution of the diffraction patterns is 0.30° $2\theta$, and the angular measurement range is 4-55° $2\theta$.

With this performance, CheMin can identify and distinguish a number of clay minerals. For example, discrimination between 1:1 phyllosilicates (such as the kaolin minerals), with repeat distances of ~7Å, and smectites (e.g., montmorillonite, nontronite, saponite), with repeat distances from 10-15Å, is straightforward. Study of clay mineralogy *in situ* on Mars will begin with the arrival of CheMin on MSL in 2012. Potential landing sites include Mawrth Vallis, Southern Meridiani, Holden Crater, Miyamoto Crater, Eberswalde Crater, and Gale Crater. All sites have evidence of sedimentary processes along with spectral signatures of smectites and, in many cases, kaolinite. Wherever MSL lands, clay mineralogy will be a critical component of determining hydrogeologic history and habitability.

**Keywords:** Mars phyllosilicates, robotic XRD, Mars Science Laboratory.

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# ORGANICS-BEARING PHYLLOSILICATES UNDER HYPERACIDIC AND OXIDIZING CONDITIONS: PRESERVATION POTENTIAL AND APPLICATION TO MARS

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Phyllosilicates have been identified on the surface of Mars by the OMEGA-Mars/Express [e.g., 1], the Mars Reconnaissance Orbiter (MRO) instruments, i.e., HiRISE and CRISM, as well as inferred from the Spirit rover observations in Gusev Crater [2]. Furthermore, near surface, or even deeper buried deposits of phyllosilicates could also exist. If such deposits could be stable over time, and organics of biological origin were once produced on Mars, they could represent the best candidate for preservation of organic biosignatures. The preservation potential in phyllosilicate deposits is plausibly higher than that of ancient wetlands/ hematite sites (e.g., Meridiani Planum) where organics are unlikely to be preserved [3,4,5].

A better understanding of the stability and preservation potential of phyllosilicates under hyperacidic conditions, and in association with hematite-rich materials, can be achieved by studying analog sites. Outcomes can provide critical information in support of landing site selection for the Mars Science Laboratory and other future missions, e.g., the ESA Pasteur ExoMars.

We present evidences for high preservation potential of organics in nearsurface, ~3.5-4.0 m-depth, robotically accessed phyllosilicate-rich zones (47-74wt.%) at stratigraphic contact with oxidizing rocks units of the Rio Tinto (RT) region [5] within the upper sequence of a hyperacidic rock-drainage-system [e.g., 6].

The preservation potential of clay minerals is well known in a variety of Earth environments. However, the RT near surface represents the first known example where phyllosilicate-rich zones can preserve up to 10-time higher amount of organics ($C_{org}$: 0.23 wt.%) than the embedding hematite/goethite-rich rocks ($C_{org}$: ~0.05 wt.%). In this low pH, highly oxidizing (aqueous) environment [e.g., 3] even the continuous supply of modern soil organic matter from surface is poorly preserved, i.e., SOM suddenly drops from ~3-11wt.% to <0.05 wt.% [5].

**Keywords:** phyllosilicates, organics, Mars.

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# PEDOGENESIS ON THE RED PLANET? EVIDENCE FOR POSSIBLE ALTERATION HORIZONS ON MARS

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An impressive diversity of phyllosilicates has been identified in the martian highlands, with Fe/Mg-rich phyllosilicates being the most prevalent (e.g., Mustard et al., 2008 and references therein). When observed, aluminum-rich phyllosilicates (i.e., Al-rich smectite and kaolin group minerals) are found overlying Fe/Mg-rich smectites (e.g., Bishop et al., 2008; Noe Dobrea et al., 2008, 2009; Ehlmann et al., 2008). This type of sequence is observed at multiple locations across the martian highlands, suggesting that results from regional- or global-scale geologic processes. We suggest that the leaching of near-surface basaltic materials by pedogenic or acidic-leaching processes may have formed these sequences.

On Earth, kaolin group minerals can form by a variety of processes, but the generation of widespread, stratified kaolin deposits is most commonly associated with regions where intense rainfall or leaching is available. In such settings, there is a well-understood paragenesis from primary igneous minerals, to immature smectite clays, to kaolin group minerals. In less water-rich environments, kaolin group minerals may form by acidic conditions provided by volcanic condensates in contact with groundwater. As a case example, Mg-rich phyllosilicates are exposed in escarpments in m-scale layers over a topographic range of over 1000-m in Eridania Basin. Kaolinite-like phases are found draped over these exposures, typically as part of the rock mass or in fractures, indicating different degrees of alteration. The draping nature of the kaolin-rich material at multiple locations over the martian surface is inconsistent with hypotheses involving lacustrine or volcanic origins for the formation of the observed sequence (e.g., McKeown et al., 2009 and references therein), but consistent with extensive leaching of the kaolin-rich layers, possibly by acidic solutions.

**Keywords:** Mars, Kaolinite, Alteration.

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# EVIDENCE FOR LOW-GRADE METAMORPHISM/DIAGENESIS ON MARS FROM PHYLLOSILICATE MINERAL ASSEMBLAGES

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The enhanced spatial and spectral resolution provided by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) on the Mars Reconnaissance Orbiter (MRO) has led to the discovery of a great diversity of hydrated silicate minerals on the Mars surface, particularly in the ancient, cratered crust comprising the Southern Highlands. Recently discovered minerals found in and around impact craters include chlorite, prehnite, kaolinite, potassium mica (illite or muscovite), the sodium zeolite analcime, and opaline silica [Mustard et al., 2008; Ehlmann et al., 2009]. These minerals are not distributed homogeneously. Rather, west of the Isidis basin near Nili Fossae, 25-50 km craters host significant deposits of hydrated minerals which comprise distinctive mineralogic assemblages: (1) chlorite-prehnite-silica, (2) chlorite-prehnite-K mica, (3) Fe/Mg smectite-chlorite-analcime-silica. These assemblages contrast with prevalence of Fe/Mg smectites in most phyllosilicate-bearing terrains on Mars. We propose that these varied assemblages result from distinct conditions—temperature, water-rock ratio, fluid composition, and starting materials—in subsurface diagenetic or low grade metamorphic/hydrothermal systems. Of the minerals found to date, prehnite has been found in several locations on Mars [Clark et al., 2008] and provides the clearest evidence for subsurface, low grade metamorphic activity, since it forms only under highly restricted conditions: $T = 200\text{-}350^{\circ}C$, $P < 3$ kbar, and low $pCO_2$ [Schiffman and Day, 1999]. Multiple mechanisms (some at elevated temperature, others not) exist for forming the other individual minerals. However, for the characteristic assemblages observed, we suggest that from basaltic starting materials, the probable formation mechanisms are, for (2), transformation of trioctahedral smectites to chlorite and dioctahedral smectites to illite during diagenesis, and for (3), low temperature (<200 C) hydrothermal circulation of fluids in basalt.

**Keywords**: Mars, Phyllosilicates, Hydrothermal alteration.

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# ADSORPTION STUDIES ON THE CHONDRITE ORGUEIL METEORITE

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The sorption properties of extraterrestrial minerals have been studied on a sample of the meteorite Orgueil (CI chondrite group) which landed near Orgueil in southern France on May 14, 1864. This chondrite was subject of many scientific studies in the past including some recent biologically oriented speculations. The present paper, however, focuses on a physicochemical characterization and especially on the water sorption properties (of a small amount) of Orgueil provided by the “Museum für Naturkunde” (Humboldt-Universität zu Berlin, Germany). The study has to be seen also in the light of the origin of water on Earth and other terrestrial planets, as it has been controversially discussed in the last years.

The Orgueil meteorite has been examined by scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX), X-ray powder diffraction (XRD), thermogravimetry connected with mass spectrometry (TG/MS), differential scanning calorimetry (DSC) as well as by gravimetric and volumetric isotherm measurements using $H_2O$, n-heptane, $CO_2$ and $N_2$ as probe molecules.

From SEM, EDX and XRD can be concluded that our part of Orgueil is a complex mixture of (at least partially) crystalline components composed of S, O, Si, Fe, Ca, Ni, Mg, C, Al which are hardly to be identified as a certain mineral. Results of the combined SEM and EDX study might point to the presents of gypsum. The thermogravimetric investigations show a total mass loss of about 25 wt% from 300 to 1370 K. According to MS this mass loss is $H_2O$/OH beside $CO_2$, SO- and C-components (for T>700 K). Even in the temperature range of 750-950 K $H_2O$/OH dehydrate/dehydroxylate from the sample suggesting the presence of strong hydrates.

The sorption experiments based on $H_2O$, $N_2$, $CO_2$ and n-heptane show results comparable with clay minerals or sulphates from Earth. The specific surface area of the Orgueil mineral mixture amounts to 30 $m^2/g$ (BET, using $N_2$ and n-heptane as probe). The formal application of the BET equation on the water isotherms results in an “apparent” value of 166 $m^2/g$ giving evidence of the formation of (reversible) hydrates in the bulk phase of the minerals such as in sulphates or adsorption in the interlayer spaces of smectites. The heat of desorption of $H_2O$ between 300 and 570 K amounts to 50-90 kJ/mol values typically found for water-bearing minerals on Earth. Some of the (strong) hydrates might be stable in open space also during formation of the planets in the early phase.

**Keywords:** CI Meteorite, Water adsorption, Orgueil.

# STRATIGRAPHY OF THE CLAY-UNIT OF THE MAWRTH VALLIS REGION, MARS

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OMEGA/Mars Express has discovered large outcrops rich in phyllosilicates in the region of the outflow channel Mawrth Vallis, Mars, around 20°W, 25°N [Poulet et al., 2005], through the detection of absorption bands at 1.4 and 1.9 µm, and at 2.2 or 2.3 µm. Comparison with laboratory spectra reveals similarities with clay minerals such as Al-OH smectites and Mg- or Fe-OH smectites [Loizeau et al., 2007]. Moreover the abundances of clay minerals in this region are the highest detected on Mars, reaching more than 65% in volume in some outcrops [Poulet et al., 2008], and showing a large diversity of alteration [Bishop et al., 2008].

Those hydrated minerals are located exclusively on strongly eroded bright and finely layered outcrops, exhumed from the Noachian plateaus, and cut by the outflow channel Mawrth Vallis. Those outcrops are the exhumed parts of a large phyllosilicate-rich unit, more than 150 m in depth and extending over more than 300 km x 400 km [Loizeau et al., 2007].

In the context of landing sites selection for the future rover missions, it is highly important to elect the most scientifically relevant sites through the diversity of the exhumed terrains.

The use of HRSC/Mars Express color imagery and Digital Terrain Models (DTM) provides helpful information to understand the geometry and stratigraphy of the phyllosilicate-rich unit.

We observe a paleo-surface on top of which the layered unit was deposited and later impacted and eroded, enabling today to see large sections of the unit through remote sensing. The link between the processes of deposition and alteration of the rocks is a fundamental issue concerning the presence of liquid water in the region.

**Keywords:** Extraterrestrial clays, Mars, Remote Sensing.

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# COMBINING VISIBLE/NEAR INFRARED AND THERMAL INFRARED REMOTE SENSING DATA TO ANALYZE MARTIAN CLAY MINERALS

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Most of what is known about clay minerals on Mars comes from visible/near infrared (λ •1-3 µm) remote sensing measurements. In recent years, two instruments have provided the strongest evidence for martian clay minerals: the Observatoire pour la Minéralogie, L'Eau, Les Glaces, et l'Activité (OMEGA) on board ESA's Mars Express mission, and the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) onboard NASA's Mars Reconnaissance Orbiter [1-2]. Evidence is building for the robust detection of a range of specific clay minerals discussed in other presentations [3]. The overall spectral shape of the deposits, the placement of particular absorption bands, and the structure of the absorptions all provide strong constraints on the possible minerals or mineraloids present. But, further constraint on the mineralogy and origin of these deposits is possible by combining near infrared measurements with thermal infrared datasets. Emissivity data from the Thermal Emission Spectrometer (TES) and Thermal Emission Imaging System (THEMIS) instruments place constraints on the physical state of the surfaces in which the clay minerals occur, the crystal chemistry of the clay minerals, the mineralogy of other phases associated with the clay minerals, and the abundance of various phases in these surfaces.

THEMIS and TES data show that the clay minerals often occur within surfaces that have moderate thermal inertia values, indicating that the clays occur within coarse-grained particulates and rock fragments. This supports the idea that the clays are components of local bedrock; they probably exist as clasts, cements, veinlets, and/or replacements of minerals or mesostatic phases in older rocks. TES data show that in many cases, the clay minerals are associated with plagioclase feldspar and pyroxene; from the TES perspective, many of the deposits have basaltic bulk composition. An exception to this is in the Mawrth Vallis area, where the largest exposure of clay minerals is seen with OMEGA data. Here, TES shows the clay deposits occur within silica-rich, possibly zeolite-bearing bedrock with low spectral contrast and no evidence for any primary mafic component. The Mawrth Vallis deposits may represent a more advanced stage of alteration than the others, or alteration of a different starting material such as indurated, layered dust deposits. Implications for different formation models of martian clay minerals will be discussed.

**Keywords:** Mars, Spectroscopy, Weathering.

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# SOURCES, SINKS, AND STABILITY OF CLAY MINERALS ON MARS

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High spatial and spectral resolution visible and near-infrared reflectance spectra have revealed the presence of diverse hydrated minerals on the Martian surface. Clay minerals, including smectites, chlorites, and kaolin group minerals, are the dominant alteration product in the heavily cratered ancient crust, suggesting liquid water and moderate pH conditions were prevalent on early Mars [1]. The majority of these clays are Fe/Mg varieties (e.g., nontronite, saponite, clinochlore). Al-bearing smectites are less common, consistent with alteration of the basaltic crust under low water-to-rock ratios for which Al is not removed from plagioclase [2]. Similarly, occurrences of illite are rare, likely due to the low abundance of K on Mars. Martian clays are presumably formed via alteration of basalt, although the relative contributions of surface weathering versus subsurface alteration (e.g., hydrothermal systems) are yet unknown.

Several of the clay deposits in the ancient highlands are found in clearly defined sedimentary sinks, often occurring as bedded sedimentary sequences in impact craters. The lowermost stratigraphic units in fan deposits in both Holden and Eberswalde crater contain Fe/Mg-rich clays that appear to source from the surrounding crater rim. In Eberswalde, these clays occur in the bottomsets of a delta, whereas they underlie alluvial fans in Holden crater. These deposits are intriguing in that they can be used to understand Martian clays in a 'source to sink' concept and contain rocks that record both time and changing environmental conditions in the earliest history of Mars. However, full alteration assemblages are often not detected in these deposits, even though smectite formation yields an excess of cations expected to produce complementary salts. Therefore, the composition and oxidation state of the early Martian atmosphere will remain ambiguous until the full alteration assemblages are identified in these ancient smectite-bearing terrains.

The apparent presence of >3 Ga clays on Mars also provides a unique opportunity to study long-term smectite stability over timescales not easily accessible in the terrestrial rock record. By minimizing time as a variable, clay transitions with depth on Mars record direct information about spatial distributions in fluids or local geothermal gradients. Future missions that help us to compare Martian clays to those found on Earth have the potential to vastly improve our knowledge of the fundamental factors that govern clay formation and stability.

**Keywords:** Mars, spectroscopy, smectite stability.

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# DIVERSITY OF MARTIAN PHYLLOSILICATE DEPOSITS FROM ORBITAL REMOTE SENSING

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The occurrences, types, and geologic settings of Martian aqueous minerals have been investigated by the orbital spectral mapping instruments TES, THEMIS, OMEGA, and CRISM, with increasingly higher spatial resolution. CRISM data are obtained typically at 20 m/pixel, accompanied by HiRISE imaging at 30 cm/pixel and CTX imaging at 6 m/pixel to provide complementary morphologic information. At least five different classes of Noachian-aged deposits containing phyllosilicates, each with a distinct combination of spectral signatures and morphological features, are recognized in these data sets. *Layered phyllosilicates*, which are most widespread surrounding Nili Fossae and Mawrth Vallis, occur over hundreds of kilometers spatial scale and exhibit a characteristic two-layer stratigraphy with Al-smectite overlying Fe/Mg-smectite. *Phyllosilicates in intra-crater fans* occur in the lower, horizontally stratified beds of some fans, and may have formed by erosion from the watershed and redeposition in a lacustrine environment. *Plains sediments* contain assemblages of clays and chlorides, and occur in topographically low areas of the southern highlands including crater floors and intercrater plains. *Deep phyllosilicates* exhibit diverse mineralogies and are exposed in crater walls, ejecta, and central peaks and in escarpments. They are massive or brecciated to layered, and outcrop in thousands of locations spread across the southern highlands. *Intra-crater clay-sulfate deposits* include kaolinite and hydrated sulfates that partially infill some highland craters. These five classes of deposits may represent depositional environments recording different phases of the history of water on Mars, and their future investigation promises significant new insights in Mars' hydrologic evolution.

**Keywords:** Mars, Noachian, Environments.

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# CHARACTER OF MARTIAN PHYLLOSILICATE-BEARING EARLY CRUST FROM ORBITAL REMOTE SENSING

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Remotely sensed data show that phyllosilicates are widely distributed in the oldest crust of Mars (Bibring et al., 2006), but composition of the protoliths altered to form the phyllosilicates and the conditions under which the minerals formed are key outstanding questions. Using high-resolution imaging and spectroscopic data from the Mars Reconnaissance Orbiter we find that in many regions the crust is a breccia consisting of blocks smaller than the image resolution of HiRISE (25 cm) to some several kilometers in size. There are unaltered blocks dominated by mafic minerals of olivine and pyroxene, as well as blocks dominated spectrally by phyllosilicate minerals that show evidence for sedimentary layering. The altered and unaltered lithologies may be in direct contact perhaps indicating alteration fronts. Typically the matrix is phyllosilicate-bearing. Changes in mineralogy with depth are examined in a survey of impact crater mineralogy in the ancient highlands focusing on rocks exposed on the walls, floors, and central peaks or peak rings. The impact craters range in size from a few kilometres to over 70 km, which sample approximately the top 7 km of crust. While a variety of minerals are detected in these settings, the overwhelming majority are Fe/Mg smectite clay and chlorite/prehnite. There clearly are regions that show the diversity and character of mineralogy expected in hydrothermal conditions (Ehlmann et al., 2009), as well as regions with intact compositional stratigraphy (e.g. Mawrth Valles). These areas however are uncommon and may reflect late stage alteration processes. Our observations suggest that the conditions of phyllosilicate formation for much of the crust strongly favored relatively low temperature and pressure, or subsequent processes changed higher temperature phases to the observed ones. The bulk of the upper 10 km of ancient crust is thus brecciated by impact processes with both altered and unaltered lithologies mixed on all scales, but a relatively low diversity of phyllosilicate minerals that do not systematically vary with depth.

**Keywords:** Mars, Mineralogy, Phyllosilicate, Environments.

[1] Bibring J-P. et al. (2006) The Mars History defined from the OMEGA/MEx spectra and inferred mineralogy, *Science,* v312, 400-404.
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# DELTAS AND PHYLLOSILICATES ON MARS: MRO-CRISM OBSERVATIONS

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Phyllosilicates are unambiguous proofs for the presence of water in every environment, being correlated to aqueous alteration of pristine minerals on Earth, Mars, and other celestial bodies (e.g. meteorites). On Mars the phyllosilicates were first identified with the help of Mars Express OMEGA data set, with most abundant occurrences in Mawrth Vallis region [1], and Nili Fosae [2].

Their presence is being constantly revealed in many other small areas on Mars, taking advantage of the high spatial resolution of CRISM spectrometer data set on MRO. We were able to identify new areas of occurrence for this class of minerals, choosing places where morphologies are consistent to water erosion, transport and deposition systems. On Mars such systems usually involve delta like deposition areas. Their presence call for specific water involvement in the studied areas with the possibility to validate the formational type itself, discrimination between delta like deposition and sapping being one of the goals for this study, with great importance for liquid water presence at surface.

We expand the list of the presence of the phyllosilicates in studied areas, revealing a good delta-phyllosilicate correlation: many of the targeted areas in a planned survey gave positive identification, strengthening the categorization as water derived morphologic and mineral units. The phyllosilicates so far, have been identified in similar settings in Holden, Eberswalde and Jezero craters [3] considered mostly to be allochtonous alteration result of sediments transported and deposited in water pounding depressions forming terraces that retreat upward stream.

We present two cases with distinct phyllosilicate occurrences: 1) An unnamed crater south of Nanedi Vallis 2° N 51' N, 51° 40' W presents a clear hydrated mineral band south of deltaic deposit onward flow direction. The hydrated minerals are present in the lower terrace in a band with a parallel trend to the advancing front, pointing to an allochtonous type of alteration, and 2) phyllosilicates present in a layer underneath the surface in an unnamed crater 9° 50' S, 96° 15' W pointing to sapping type of erosion, with possible hydrothermal water triggering of the collapse, with possible in-situ alteration type. The 1.37, 1.90 and 2.19 μm absorption spectral bands are characteristic for the first case consistent to kaolin class, whilst the second case is characterized by 1.4, 1.90 and 2.22 μm band absorptions. We could not spectrally match all spectral bands with end-members in available spectral libraries, unknown mixtures or new Martian environment stable minerals being probably responsible for some of the band absorptions reported here (e.g.1.37 μm).

**Keywords:** Mars, Phyllosilicates, Delta.

[1] J.-P. Bibring et al. (2006) Science, 312, 400-403. [2] Mustard et al. (2007) J.G.R. 112, 1-14. [3] Fassett, C. I et al. AGU, Fall Meeting 2007.

# DIVERSITY OF MINERALOGY AND OCCURENCES OF CLAY MINERALS ON MARS

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Minerals and their occurrences can tell us about the chemistry, pressure, and temperatures of past environments on the planetary surfaces, and the possible conditions for past habitability. Thanks to the observations by the visible/near-infrared imaging spectrometer ESA/OMEGA/Mars Express and NASA/CRISM/ Mars Reconnaissance Orbiter, a new vision is emerging for Mars to have possibly hosted environmental conditions favouring the presence of a key ingredient of potential astrobiological relevance. This epoch is identified by the presence of clay and hydrated minerals, which are generally contained in very ancient basement rocks (Poulet et al. 2008; Mustard et al. 2008). This talk will review the clay minerals and their diversity, and geologic environments on Mars and how they can constrain the past environment of Mars.

We will first emphasize the spectral diversity of each major class of phyllosilicates. While the Fe, Mg and Al-bearing smectites are the most common, kaolinite and chlorite are also potential spectral matches of some phyllosilicate-rich occurrences. New OMEGA and CRISM observations consistently indicate the presence of phyllosilicates in deposits that are in place, rocky units (outcrops, scarps and numerous crater ejecta and peaks) of ongoing erosion in very old terrains (dated to the Noachian period) scattered in both hemispheres. This strongly supports the following conclusions: (1) water-rock interactions at the surface likely occurred during the early Noachian; the formation may have continued into later periods but in this case, it occurred at depth; (2) the clay minerals are a bulk component rather than a soil surface coating, and the crust has been altered to depth; (3) the alteration processes occurred at the planetary scale; (4) the variations in modal mineralogy shows that the alteration and the lithology were different from place to place.

Some additional clay minerals are associated with sulfates, possibly indicating that the neutralization of the solutions that formed the sulfate-rich terrains could have occurred at least locally, or that the phyllosilicates have been remobilized since formation and are concentrated in global depocenters. Evidence of pumpellyite associated with clay minerals is observed in the central peaks of a few craters. This could suggest alteration resulting from metamorphism related to the impact that formed the crater. Some low albedo terrains also exhibit signature of clays, but the origin of these deposits is still under investigation.

**Keywords:** Mars, Spectroscopy, Smectites.

[1] References: Poulet F., et al. (2005), Phyllosilicates on Mars and implications for early martian climate, Nature 438, 623-627. Mustard J.F., et al. (2008). Hydrated silicate minerals on Mars observed by the Mars Reconnaissance Orbiter CRISM instrument, Nature 454, 305-309.

# MINERALOGY & CRYSTALLOGRAPHY

## SESSION MC2

## *Clay Synthesis*

# PREPARATION OF 2:1 COBALT CLAYS COMPOSED ON REGULAR HEXAGONAL PARTICLES AND OF 1:1 NICKEL CLAYS COMPOSED ON NANOTUBULAR PARTICLES

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The preparation of cobalt smectites consisting of regular hexagonal platelets, up to 300 nm in diameter, will be described. They were obtained by hydrothermal treatment at 250°C of reaction mixtures prepared by adding silicic acid to cobalt hydroxide suspensions. Selected area electron diffraction showed that some of these hexagonal platelets consisted of ordered coherent stacks of several clay layers, rather than the turbostratic stacking of layers usually found for natural smectites. It is postulated that the hexagonal cobalt hydroxide particles in the cobalt hydroxide suspensions served as templates for the condensation of the silica layers during the hydrothermal treatments. Examination of the powder isolated from these cobalt hydroxide suspensions showed they contained hexagonal particles of similar sizes to the clay platelets obtained after the hydrothermal treatments. Lowering the temperature used in the hydrothermal treatment produced less well-formed clay particles. Increasing the pressure during the hydrothermal treatment by adding argon to the autoclave did not affect the morphology of the clay particles.

The preparation of 1:1 nickel phyllosilicates composed of hollow, open ended, multiwall nanotubular particles, up to 200 nm in length will also be described. They were obtained by hydrothermal treatment of a mixture of nickel chloride, silicic acid and sodium hydroxide at relatively low temperature, 250°C, and pressure, 10 MPa. Previous reports on the preparation of tubular nickel phyllosilicate emphasized the need for high temperatures and pressures (ca. 400°C and 70 MPa), with lower temperature giving mostly small thin plate-like products. The tubular particles obtained also had larger outer diameters, 25 to 30 nm, and larger inner hollow cores, about 10 nm than nickel silicate nanotubes prepared at high temperatures and pressures. Preliminary results on the electrochemical responses of thin films of both types of clays will also be presented.

**Keywords:** Nickel Serpentine, Nickel silicate nanotubes, Cobalt smectites.

# INVESTIGATION ON CONTROLLABILITY OF METAL COORDINATION AND CRYSTALLINITY IN SYNTHETIC CATIONIC HECTORITE-LIKE SOLIDS

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Cationic clay minerals and related synthetic analogs are a class of layered compounds with particularly interesting and variable characteristics[1]. Through ion-exchange reactions, intercalation and exfoliation, layered compounds can be functionalized to yield ion-exchangers, porous pillared solids[2] and nanosheets[3], which are of great significance in the application of catalysis and separation. Besides natural minerals, these parent layered compounds synthesized hydrothermally are well-documented[4]. However, deep investigation on controllability of metal coordination and crystallinity in synthetic cationic clay-like solids have less been conducted so far. Yet these factors impact the structure, chemical reactivity and electronic properties of solids. Previously we have reported that hectorite-like solids can be synthesized in a hydrothermal system in which the crystallinity of synthetic hectorite-like solid can be enhanced with more Li substitution for octahedral Mg when the amount of lithium fluoride increases, leading to somewhat higher layer charge, and thus more exchangeable cations in the interlayers[5]. Here we show that layered hectorite-like solids were synthesized hydrothermally in the presence of organic surfactants, amine, or transition metal ions in reaction medium aiming at probing the controllability of metal coordination and crystallinity in synthetic solids. The samples were characterized by using FTIR, PXRD, FESEM, TGA/DTA, XPS and $N_2$ adsorption-desorption isotherms. The results show that with the addition of surfactant (either CTAB, DDA or CTAB+DDA) in the hydrothermal reaction medium, layered hectorite-like solid can be obtained with different structural characteristics. However, in the presence of two mixed surfactants of CTAB and DDA, DDA may hinder and reduce the degree of the intercalation of CTAB into interlayer. Furthermore, the existence of surfactants in the synthesis medium has an influence on the state of particle aggregation and thus leads to an effect on pore size distribution in synthesized solids. Acknowledgment. This work was supported by the NSF of China (No. 20773110; 20541002) and the NSF of Zhejiang Province of China (No. Y405064; Y407200; Y405025).

**Keywords:** Synthetic hectorite, Coordination, Crystallinity.

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# TEXTURAL AND HYDRATION PROPERTIES OF A SYNTHETIC MONTMORILLONITE COMPARED WITH THE NATURAL NA-SWY2 CLAY ANALOGUE

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Smectite, the main clay mineral in bentonites, is responsible for their low permeability, their high specific surface and their capacity to retain pollutants, properties of great importance in industrial applications. When looking at improvement of processes or at understanding the major mechanisms, it appears judicious to choose synthetic clays instead of natural reference clay samples, due to their homogeneity and their reproducibility. Whereas the dioctahedral smectites are predominant in soils and widely used in industry, these clays are rarely synthesized and used in systematic studies. The objective of this study is to synthesize a montmorillonite (Na-MMT), and to compare its textural and hydration properties to the natural Na-exchanged Wyoming montmorillonite (Na-SWy2).
Hydrothermal syntheses were carried out at 350°C and 120 MPa for 28 days, by using the gelling method of Hamilton (1968) (Lantenois et al., 2008). The chemical analyses using ICP-OES coupled with electron microprobe demonstrate that the obtained structural formulae is near from the theoretical one: $Na_{0.66}[Al_{3.34}Mg_{0.66}][Si_8]O_{20}(OH)_4.nH_2O$. Moreover, X-ray diffraction reveals that smectite is the only crystalline phase in the Na-MMT sample, with the mean position of the (06,33) band at 1.49 nm, confirming the presence of dioctahedral domains in the octahedral sheets. Na-MMT has a CEC value of 83 meq/100g and a specific surface area of 764 $m^2/g$, characteristic of swollen smectites. $N_2$ adsorption-desorption isotherms coupled with the t-plot method reveal a specific surface of 87 $m^2/g$ and also give the pore size distribution. In addition, low-pressure argon adsorption coupled with the Derivative Isotherm Method (Villiéras, 1992) provided information about adsorption energy distributions on basal and edge surfaces. Hydration properties were obtained at once by continuous water gravimetry and by X-ray diffraction along a water adsorption-desorption cycle. Percolation experiments using œdometer cells were carried out with water through compacted clay samples, in order to simulate subsurface waste landfill. Low hydraulic conductivities in the order of $10^{-12}$ m/s were obtained for Na-MMT and Na-SWy2.

**Keywords**: Hydrothermal synthesis, Adsorption isotherm, Oedometer cell.

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# SYNTHESES OF TRIOCTAHEDRAL PHYLLOSILICATES IN SODIUM SAPONITE –PHLOGOPITE SYSTEM

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Clay minerals have been used in various fields because of their unusual physical and chemical properties compared to other common inorganic materials. Expandable phyllosilicates have the affinity for organic materials through intercalation, ion exchange, adsorption and catalysis. Therefore expandable phyllosilicates have been known to act as hosts of intercalated compounds, as nanocomposites, and to function as catalysts for various organic reactions. However, most expandable phyllosilicates usually are aggregates of fine particles having low crystallinity. It is difficult to make them suitable for applications such as improving the functions of composite materials. The expandable phyllosilicates with a high degree of crystallinity and a large grain size have been demanded in fully understanding their essential properties. In the previous study, the highly crystalline trioctahedral Mg-smectite with a well-formed lath shape was synthesized under hydrothermal conditions[1]. Following this successful result, we investigated the effects of chemical composition on the crystallinity of trioctahedral phyllosilicates at hydrothermal conditions. Starting materials were quenched glasses with a stoichiometric dehydrated compositional join of Na-saponite and Na-phlopopite: $Na_xMg_6(Al_xSi_{8-x})O_{22}$, where x = 0.4 - 2. The mixtures of pulverized glass and water were sealed in Au-tube and treated hydrothermally at 300 - 800 °C and 100 MPa for 1 – 60 days. The obtained products were characterized by XRD, SEM, AFM, TEM, FT-IR and ICP methods. The results indicated that the formation of trioctahedral phyllosilicates was clearly dependent on synthetic temperature, duration and chemical composition. Above 500 °C, the high crystalline saponite, with layer charge was up to 1.2, was obtained. Vermiculite with high-crystallinity was also formed above 500 °C, with layer charge up to 2. No sodium phlogophite appeared in this study, which was consistent with the study in (K, Na)-phlogophite system[2].

**Keywords:** High-crystallinity, Saponite, Vermiculite.

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# SYNTHESIS OF ORGANOCLAYS USING NON-IONIC SURFACTANTS: EFFECT OF TIME, TEMPERATURE AND CONCENTRATION

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Research in materials sciences are driving attention to modifications of clay minerals, mainly montmorillonites, as one of the key topics in many research fields, including environmental (Zampori et al., 2008), rheological control agents, and cosmetics. The intercalation of different polymers inside the interlayer of montmorillonites allows for extension of the applications of organically modified clays to new fields, such as preparation of nanocomposites and drug delivery (Choy et al., 2008). Up to now, the majority of works dealing with organoclays have been addressed to study the interactions between clays and quaternary ammonium salts, and only few studies investigated the interactions between polymers and clays (Bertega de Paiva, 2008).

The objective of the present research was to investigate the intercalation of a polyethilene oxide (PEO) having a molecular weight of 1500 g/mol inside the interlayer of STx-1 montmorillonite. Three parameters were considered and varied: time (2, 4, 6 hours), temperature (ambient, 40, 50, 60, 70 °C) and initial concentration of PEO in solution (90 and 270 mM). A full microstructural characterization of the synthesized organoclays by XRD, FT-IR, and TG-DTA was performed. The quantification of PEO intercalated was estimated by COD (Chemical Oxygen Demand) analysis of the residual amount in solution.

The intercalation of PEO inside the interlayer was successful, as showed by XRD: the highest basal spacings ($d_{001}$) were equal to 15.7 Å for the sample prepared with 90 mM initial concentration, while they increased up to 18.2 Å for the 270 mM samples. Intercalation was confirmed by FT-IR, showing the typical C-H stretching bands in the spectra of the synthesized clays, and by TG-DTA. COD analyses highlighted that the amounts of PEO intercalated were equal to about 20% (with respect to the total initial concentration in solution) for all the 90 mM samples and to about 45% for the 270 mM samples. The role of temperature and time appeared to be unimportant for intercalating the polymer inside the interlayer of STx-1 montmorillonite.

**Keywords:** Organoclay, Polymer, Synthesis.

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# MINERALOGY & CRYSTALLOGRAPHY

## SESSION MC3

## *Crystal Chemistry and Structure of Clays*

# HP AND HT STRUCTURES OF SERPENTINE MINERALS

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By this review, the unfortunately few High Pressure (HP) and High Temperature (HT) structural and physical data for serpentine minerals are discussed. The rationale for the review lays in the important subjects related with the serpentine minerals stability; their effect over subducting slab behaviour, partial melting and magma generation; seismic events; crust-mantle geochemical coupling. For instance, antigorite, often disregarded as an alteration mineral with no petrological, geochemical or geological interest, received major attention after the piston-cylinder runs by Ulmer and Trommsdorff (1995). They emphasized three features: a) wide stability field (up to 720°C at 2 GPa); b) negative $dP/dT$ slope (i.e., breakdown of antigorite within the cold downgoing slab); c) huge water release (13 wt. %) at 150-200 km depth, with relevant implications on mantle geodynamics.

Strong anisotropic data are the rule (e.g., 1:3). Bulk compressibility values:

| | | | |
|---|---|---|---|
| Lizardite | HP-SCXRD | K = 57 GPa | Mellini & Zanazzi (1989) |
| | HP-XRPD | 68.9-71 | Hilairet et al. (2006) |
| | DFT | 61-87 | Auzende et al. (2006) |
| Chrysotile | HP-XRPD | 62.8-66.5 | Hilairet et al. (2006) |
| Antigorite | HP-XRPD | 62.0-67.2 | Hilairet et al. (2006) |
| | HP-SCXRD | 63.3 | Nestola et al.(in press) |

Thermal expansion values are available for lizardite only:

| | | | |
|---|---|---|---|
| LT-NPD | $\alpha_a = 0.95x10^{-5}$ | $\alpha_c = 1.38x10^{-5}$ | Gregorkiewitz et al. (1996) |
| HT-SCXRD | $\alpha_a = 0.37x10^{-5}$ | $\alpha_c = 0.70x10^{-5}$ | Guggenheim & Zhan (1998) |

Apparently similar values and common trends characterize the different serpentines. Values may differ depending on specimen, technique, P and T range. Closer details may reveal unexpected features. For instance, antigorite modifies its compressional mechanism close to 6 GPa, becoming softer with depth (Nestola et al., in press); the modified pattern may change phase equilibria. Hopefully, new adequate specimens may favour the obtainement of further data in the near future.

**Keywords:** Serpentine, Structure, Pressure, Temperature.

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# HALLOYSITE – ARE WE THERE YET?

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Halloysite and kaolinite have apparently identical aluminosilicate layers but different crystal morphologies and structures. The major compositional difference comes from water that is, or has formerly been, present in the interlayers of halloysite but not of kaolinite. As a result, halloysite particles generally have curled shapes. However, the origin of the interlayer water (IW) has remained a puzzle.
At the 9th ICC, S.W. Bailey proposed that halloysite has a higher layer charge than kaolinite and that the water of hydration of charge-balancing cations was responsible for the IW (Bailey, 1990). This is in spite of only equivocal evidence for a higher CEC for halloysites than for kaolinites. Bailey (1990) further proposed that the higher (negative) charge on the aluminosilicate layer in halloysite than in kaolinite originated from more Al in the tetrahedral layer. However, using $^{27}$Al-NMR, Newman et al. (1994) found that Al(IV) contents were similar in both halloysites and kaolinites. Furthermore, quasi-elastic neutron scattering (Bordallo et al., 2008) indicated that interlayer cations mobilised the IW in a smectite, but not in a halloysite, suggesting few, if any, cations in the interlayer of halloysites.
In Australian and New Zealand soils (Churchman and Gilkes, 1989; Churchman, 1990) halloysite tends to occur at depth, where water is more prevalent. Our work in Hong Kong (unpublished) showed that halloysite formed preferentially in saprolite in both granite and volcanic tuff when a lack of Mn and Fe oxides indicated prevailing wet conditions, while kaolinite was preferred when their occurrence indicated drying. The common association of halloysite with water suggests that Fe(II) in undried halloysites may raise layer charge to attract cations, with water, into the interlayer. We are measuring Fe(II) in undried samples of the mineral and plan to report these analyses, to help decide the origin of IW.

**Keywords:** Interlayer water, Layer charge, Ferrous iron.

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# MACROSCOPIC AND MICROSCOPIC (TEM-AEM, HRTEM) EVIDENCE OF SMECTITE KAOLINIZATION MECHANISM AND K-S STRUCTURE

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Previous evidence from chemistry, XRD, thermogravimetry (TG) and IR and NMR spectroscopy indicates that smectite kaolinization follows a mechanism of sequential removal of one of the tetrahedral sheets of smectite layers and subsequent chemical changes (references below). This results in a complex K-S structure where smectite layers contain “kaolinite-like patches or domains” that grow with progressive kaolinitization. When the patches are large enough, the layers collapse to ~7 Å. In the present study, we present a TEM-AEM and HRTEM study that provides further information.

Eight samples covering a range of K-S composition were studied. TEM showed irregular crystal morphology characteristic of smectite, with euhedral particles also present in a kaolinite-rich specimen. AEM chemical compositions are very disperse, but follow the pattern of Al→(Si+Mg) with the transformation. This dispersion of compositions within samples represents different degrees of transformation from particle to particle. In the sample with highest differences of compositions the tendency toward $Si_2Al_2Mg_0$ is evident. Compositions of the less evolved particles can be normalized to Ca-rich montmorillonites, with significant beidellitic and minor nontronitic substitutions. We compared microscopic (AEM) and macroscopic chemical analysis as well as d-spacing of the XRD 060 peak (proxy for octahedral composition) with percent kaolinite (%K) determined with TG. This shows that the chemical changes are accelerated at the intermediate %K values, which is reasonable as the corresponding structure must be the least stable in the K-S sequence. Frequently, HRTEM did not resolve individual layers but showed lattice fringes corresponding to layer superlattices. A model of possible layer series was created and we assessed the proportion of kaolinite and smectite layers. These proportions are in good agreement with those obtained from TG values. The present results support the model of smectite-to-kaolinite transformation that we proposed earlier.

**Keywords:** Kaolinite-Smectite, Electron Microscopy, Smectite-to-kaolinite Transformation mechanism.

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# ON THE CHEMICAL COMPOSITION OF SEPIOLITE

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Sepiolite has been largely studied, because it is a matter of a mineral having a huge number of industrial applications. However, the number of the chemical analyses is small and many of the chemical data reported in literature are the result of bulk analyses, and they can be affected by clay minerals and other associated minerals as impurities. In this work 22 samples of sepiolite and 4 in which sepiolite appears with palygorskite are studied from punctual analysis by AEM, with the aim to know the compositional limit for this mineral

Results obtained show that most sepiolites have minor substitutions, both tetrahedral and octahedral, in agreement with the general structural formula of the mineral ($Si_{12} O_{30} Mg_8 (OH)_4 4(OH_2) 8 H_2O$). The number of Si atoms ranges from 11.50 to 12.11 and the number of total octahedral cations ranges from 6.87 to 7.95. These values correspond to 0.6-14 % octahedral vacancies for sepiolite. Clearly, Mg is the main octahedral cation in sepiolite (4.88 - 7.92) and this mineral contains variable amounts of Al (0.01 - 1.24) and $Fe^{3+}$ (0.01 - 0.43). When comparing the results obtained for the studied samples with those in literature, a certain number of sepiolites show the same characteristic: lower content in Mg with respect to the ideal composition, due to the substitution by Al and/or $Fe^{3+}$. Recently García-Romero et al. (2007) have reported Al-rich sepiolite together with a very Mg-rich palygorskite in the Allou Kagne deposit (Senegal). Looking at the data, both from the literature and from AEM in this study, sepiolite can be classified into two groups: sepiolite and Al-sepiolite. A limit for these two groups can be established from the octahedral occupancy and Al-sepiolites are those that have more than 10% of octahedral positions vacant and more than 0.5 $Al^{VI}$ atoms.

It is remarkable that from the same chemical composition of the four main oxides ($SiO_2$, $Al_2O_3$, $Fe_2O_3$ and MgO) Al-sepiolite or sepiolite + palygorskite and even Mg-palygorskite have been described by García-Romero et al. (2004).

**Keywords**: Sepiolite, Al-sepiolite, Octahedral composition.

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# A NEW OCCURRENCE OF MASSIVE PALYGORSKITE FROM THE SESIA-LANZO ZONE, WESTERN ALPS

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An unusual occurrence of palygorskite, discovered near Montestrutto, lower Val d'Aosta, is reported. The mineral, with the appearance of "mountain leather", occurred in a quarry exploiting a quartz-jadeite-K-feldspar-phengite leucogneiss from the eclogite-facies Sesia-Lanzo zone. The monomineralic palygorskite veins, few mm thick and up to several m wide, were found as a filling of E-W trending vertical fractures during the exploitation of the leucogneiss.

The palygorskite was studied by Optical Microscopy (OM), XRPD, SEM-EDS, TGA-DTG and Micro-Raman Spectroscopy, and a full-structure refinement was carried out with the Rietveld method. At OM the mineral appears to consist of a matted felt of bundles about several hundreds μm long and a few μm thick, that at the SEM appear in turn to consist of long thin fibres, dozens of μm long but only fractions of μm thick.

Spot analyses of a number of fibres showed a remarkable homogeneity. The mean chemical composition, $(Mg_{2.18},Al_{1.71},Fe^{2+}_{0.14})Si_8[O_{19.91}(OH)_{2.12}\ (OH_2)_{3.97}]\cdot 3.71\ H_2O$, shows no tetrahedral Al and a zeolitic water content slightly lower than the ideal one, in agreement with TGA-DTA data.

As to the genetic conditions, because of the high crystallinity degree it is suggested that palygorskite formed at low-T° hydrothermal conditions, by interactions of a Mg-rich hydrous fluid derived from serpentinising ultramafics of the underlying Piemonte Zone and Al-rich continental rocks of the Sesia-Lanzo zone.

**Keywords:** palygorskite, zeolitic water, hydrothermal conditions.

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# DEEP OCEAN-FLOOR AND BORE-HOLE SIMULATIONS: EXAMPLES INVOLVING MONTMORILLONITE AND NONTRONITE

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One of the last scientific frontiers on earth is the deep-ocean floor and crust. Little is known about how geochemical processes or the ocean-floor biota affect clay, in large part because of the previous inability to simulate and study geochemical systems at ocean-floor conditions. Clays are especially difficult to study because they re-equilibrate rapidly when taken from ocean-floor to ambient conditions. Similarly, because little experimental information is available on deep bore-hole chemistry/mineralogy, salt-water/clay studies are applicable here as well.

A proto-type high-pressure environmental chamber (HPEC) is described for a transmission-mode, CCD-based X-ray diffractometer to study geochemical processes in real time at deep-ocean or bore-hole conditions. The HPEC has a capability for pressures to 1000 bars and temperatures from -20 $^{o}$C to 200 $^{o}$C. Clay samples (or any finely ground powder) in suspension in saline solutions (e.g., sea water or any liquid) in the chamber are pressurized by gas (e.g., He, $CH_4$, $CO_2$, $O_2$). The chamber incorporates a pump to circulate the suspension to allow the clay to remain illuminated in the X-ray beam and to allow continuous reactions between the solids, liquid, and the pressurizing gas. Furthermore, inert gases, e.g. He or Ar, may be mixed with the pressurizing gas to control fugacity of the gas components. Data-subtraction procedures are used to eliminate X-ray dispersion effects of the liquid, and chi-integration procedures result in a standard X-ray diffractogram.

Preliminary results indicate that layer-to-layer spacings of montmorillonite (SWy-2) expand at high pressure (to 500 bars, the maximum pressure studied). The pressure effect on the layer spacing of nontronite (NAu-2) is smaller. The effects of lowering temperature, increasing pressure, and lowering salt content on both smectite clays are consistent with an expansion of interlayer spacing.

**Keywords:** X-ray environmental chamber, Ocean floor, Smectite.

# SURFACE PHYSICS AND CHEMISTRY OF CLAYS

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The processes on a surface of clay minerals have an important scientific and practical value. A special case of such processes is sorption on the surface of clays. However much in this sphere remain vague. The basic difficulty in construction of theory of surface of clays is as follows: there is an asymmetry of coordination sphere of surface atoms, surface atoms cooperate with atoms of environment. Also the presence of significant disorder of surface phase should be mentioned. On the surface the interrelation of processes at electronic, atomic and molecular levels is realized. Availability of mineral surface to external influences opens wide scientific and technical opportunities of use of the surface phenomena, so the research of crystal-chemical and crystal-physical processes in near-surface area of clay minerals is important. Hydroxyl coat of clay minerals (structure, role in processes and phenomena) – it is a very important special direction of activity.

After long term researches of gas-clay mineral system in physical fields the author has obtained experimental and theoretical material contributing to the creation of the surface theory of clays. A part of the researches is dedicated to studying the mechanism of crystal-chemical and crystal-physical processes in near surface area of clay mineral systems, selectivity of the surface centers to interact with gas phase molecules and new adsorbophysical properties.

As a result of the researches, lead by the author, the methods of activation of surface of clays due to interaction of the surface centers with molecules of gas phase in physical fields have been established for the first time. It is established that photostimulated defect formation can reconstruct the surface of clay mineral systems, thus the oxygen of the gas phase becomes competitive in relation to mobile oxygen ions of the lattice at capturing energetically favorable positions. For the first time for clay mineral systems the mechanism and nature of surface non-compensated charge $Q_S$ is established. The influence of adsorbophysical fields on physical and chemical parameters of fine clay mineral systems is presented; it is caused by the connection of the adsorbed phase and volume at electronic, atomic and molecular levels.

Today micro- and nanodispersive mineral components of clays are engaged in technological schemes, therefore the research of their physical and chemical properties and modification has a decisive importance for developent of theory and practice of nanotechnologies.

**Keywords:** Clay minerals, Hydroxyl coat structure.

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# DETERMINATION OF THE KAOLINITE/HALLOYSITE RATIO IN KAOLINS USING XRD AND DTA-TG

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The kaolinite/halloysite ratio in different fractions (10-2μm, 2-0.2 μm and <0.2 μm) of seven kaolin samples from Ramon Fazouro deposit (Galicia, NW Spain), was calculated by X-Ray diffraction (XRD) and differential thermal and thermo-gravimetric analysis (DTA-TG).

Samples for XRD analysis were previously treated during 20 days in a 6.5 M potassium acetate solution (KAcO), and kaolinite/halloysite ratio was determinated by the variation of 10 Å and 7 Å peak areas ratio, before and after treatment (intercalation and deintercalation). This ratio was also calculated using the fitting procedure on the 002 reflection, applying a pseudovoight function by MacDiff Program. The kaolinite/halloysite evaluation by DTA-TG was based on the assumption that the kaolin thermal behaviour would depend on the presence of halloysite in the interval 50-120°C, and on the contribution of kaolinite plus halloysite in the endothermic effect around 550°C.

Results showed that kaolinite/halloysite ratio calculated after intercalation of KAcO agreed reasonably with that obtained by fitting of 002 signal ($\sigma_{n-1}$= 0.98) and with thermogravimetric data, specifically with speed of loss in mass ($\sigma_{n-1}$= 0.97). The major correlation values were obtained for <0.2μm fractions, and in general these values decreased with the increment of particle size.

**Keywords:** Kaolinite/halloysite ratio, XRD, DTA/TG.

# CRYSTAL STRUCTURE OF ILLITE

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Notwithstanding its geological importance, the exact crystallographic nature of illite is a matter of debate, in particular as far as the interlayer content is concerned. According to the IMA, the term illite should be used to designate interlayer-cation-deficient (< 0.85 a.f.u.) micas (Rieder *et al.,* 1998). Such a deficit could create the conditions for hosting of water, as $H_2O$ or, alternatively, as $H_3O^+$ (Hower and Mowatt, 1966). Following these authors, we present a combined study of illite standard IMt-2, using analytical transmission electron microscopy (AEM), thermogravimetry (TG) and Rietveld refinement of X-ray diffraction data.

Assuming all the water reported by Hower and Mowatt (1966), confirmed by our TG experiments, as $H_2O$ molecules, the AEM data would produce the formula

$$K_{0.70}\,(H_2O)_{0.42}\,(Al_{1.53}\,Fe_{0.25}\,Mg_{0.28})_{\Sigma=2.06}\,(Si_{3.44}\,Al_{0.56})\,O_{10}(OH)_2$$

Alternatively, assuming presence of $H_3O^+$ the formula becomes

$$K_{0.69}\,(H_3O)^+_{0.28}\,(Al_{1.47}\,Fe_{0.25}\,Mg_{0.28})_{\Sigma=1.99}\,(Si_{3.40}\,Al_{0.60})\,O_{10}(OH)_2$$

Whereas the first formula indicates a surplus of interlayer and octahedral species, the second one does not present any excess.

The X-ray data were refined down to a $R_{wp}$ factor of 11.35%, obtaining a composition consisting of illite-*1M* (29.1 wt. %), illite-$2M_1$ (58 wt. %) and quartz (12.9 wt. %). The two illite polytypes ( refined at $R_{Bragg}$ of 4.5 and 4.6 %, respectively) differ, being *1M* definitely more crystalline than $2M_1$. The obtained model is totally consistent with the chemical composition. In particular interlayer is fully occupied by the sum of K and $H_2O$ or $H_3O^+$. Attempts to introduce octahedral cations in excess over two were fruitless.

In conclusion

- the refined model seems to favour the latter formula, characterized by the presence of $H_3O^+$ ions;
- the illite structure strictly corresponds to a dioctahedral mica with a substitution of $H_3O^+$ for K.

**Keywords**: Illite, Composition, Structure, Rietveld.

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# REVISITING THE RULE OF CATION MASS-VALENCE SUM TO ASSIGNING OH- BANDS IN DIOCTAHEDRAL SMECTITES IN THE LIGHT OF NEW DATA FROM SYNTHETIC GA-SMECTITES

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One of the basic problems in the determination of the actual crystal structure of clay minerals is the reconstruction of the two-dimensional cation distribution patterns in terms of both short-range and long-range cation order. Whereas diffraction methods provide information on long-range cation order, various spectroscopic methods are sensitive to short range order in the cation distribution. One of the advantages of infrared spectroscopy over some other spectroscopic methods is that it can be used for samples of any chemical composition. Quantitative application of IR spectroscopy to the structural analysis of clay minerals and especially smectites, generally provides useful and accurate information. However, the assignment of the observed absorption bands is not always unambiguous and effort was made by some authors to rule up the empirical relationships between the wavenumbers of these OH bands and the local cationic configurations around the OH group. For dioctahedral micas Besson and Drits (1997) showed that for the same sum of valencies of the OH-sharing cation pair, an increase in the reduced mass of the cation pair will make decrease the resulting OH wavenumbers at which the stretching vibrations absorbs. This was verified for a representative set of natural dioctahedral smectites (Zviagina et al., 2004; Gates, 2005). Gates (2008) also applied the rule for predicting OH bending bands position. Because Ga has the same valence as Al and Fe(III), but a higher mass than these two cations, Ga- smectites were synthesized to study the effect of cations mass on OH vibrations wavenumbers more deeply. Both Al-Ga and Fe(III)-Ga smectitic chemical series were studied.

In the IR spectra of the synthesized smectites, the wavenumbers of the OH bands definitely do not follow the above trend indicating that even if this trend may be applied for some dioctahedral smectites, it cannot be established as a rule.

**Keywords**: OH vibrations, Synthetic smectite, Ga.

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# CONTINUUM PHASE IN SMECTITES: EXTENSION TO HYDROUS PHYLLOSILICATES

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In a previous paper[1], the particular physical properties of interlayer water in clay-water system was demonstrated on five smectites. To generalize this fact, ten smectites and eight other phyllosilicates types are studied. Each material is equilibrated over saturated saline solutions, which impose the relative humidity between 7 and 97 % RH. The water content and the bulk density of the assembly (mineral + water) are measured respectively by loss on drying at 105°C and by means of a helium pycnometer.

All the smectites show the same tendency: a water content which varies between 2 and 37 % accompanying by a decrease of the bulk density. The correction where a density of water must be greater than the liquid pure water, as demonstrated previously, is again needed to get a correct solid density of the smectite. According to the samples, the water density is measured between 1,10 and 1,31 g/cm$^3$. The non smectitic samples with a lesser water content (kaolinite, illite, allophone, argillite, halloysite) shows the same phenomenon, with a water density greater than 1,10. The water density of classically described as anhydrous materials studied (mica, talc and sand) cannot be estimated. By this procedure, the density of the skeleton is never directly reached, so the helium cannot penetrate the interlayer space, although the water can it.

The influence of the interlayer cation is also investigated on a smectite saturated. For $Li^+$, $Na^+$ and $K^+$, the solid density remain constant and the water density slightly increases. It is the same fact for $Mg^{2+}$ and $Ca^{2+}$. $Cs^+$ and $Sr^{2+}$ smectites shows a significant higher solid density than the mono- and di-valents ones.

So, the hydrated smectites, and by extent the hydrous phyllosilicates, must be considered by a continuum structure, where the interlayer water and the skeleton cannot be individualized in the 7-97% RH range.

**Keywords:** Smectite, Water density, Clay-water.

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# LAYER CHARGES OF ILLITE-SMECTITE AND IMPLICATIONS FOR WELL-LOGGING

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Chemical characterization of a set of pure mixed-layer illite-smectites from bentonites, including $NH_4^+$ contents (Środoń et al.), revealed a linear relationship between the fixed (FIX) and the exchangeable (EXCH) cations:
EXCH = – 0.43 × FIX + 0.41 - ($R^2$=0.98).
This relationship implies the stable layer charges of illite: $Q_i$=0.95 and smectite: $Q_s$=0.41. The evaluation of $Q_s$ was confirmed by the measurements of *CEC* and the measurements of total specific surface area (*TSSA*) from the EGME retention.
If illite-smectite controls *CEC* and *TSSA* of the rock (the rocks devoid of trioctahedral expandable clays, zeolites, opal A, or abundant organic matter) a known $Q_s$ can be used to estimate the rock *TSSA* from *CEC*:

$$TSSA = \frac{CEC \times 2.816}{Q_S}$$

and from *TSSA* the fraction of smectite in the rock ($f_s$) can be evaluated:

$$f_s = TSSA/TSSA_{smectite}$$

This approach was tested (Środoń) on over 100 core samples from the gas fields located in the Miocene sandstone-mudstone-shale formation of the Carpathian Foredeep, SE Poland. The rocks are characterized by a linear, extrapolating to zero relationship of EGME retention and *CEC*, indicative of stable $Q_s$=0.41. *TSSA* calculated from *CEC* and from EGME retention are identical within the experimental error and $f_s$ can be calculated from these data. If fraction of illite in the rock ($f_i$) is calculated from %$K_2O$, corrected for the $K_2O$ contained in K-feldspar, and assuming $Q_i$=0.95, $f_i + f_s$ comes close to % dioctahedral 2:1 minerals measured by XRD (QUANTA program).
Modelling of the chemical and mineralogical data for the Miocene rocks (BESTMIN program) revealed an excellent relationship between *CEC* and the macroscopic neutron absorption cross-section of the rock matrix ($\Sigma_{matrix}$), a parameter commonly measured by borehole geophysics. Thus in the sedimentary basin under study three rock parameters, essential for the rock electric and petrophysical properties: *CEC*, *TSSA* and $f_s$ can be evaluated quite precisely from one type of borehole measurement. It remains to be investigated to what extend this approach will apply to other basins.

**Keywords**: Illite-smectite, Layer charge, Well-logging.

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# COMPOSITION DEPENDENCE OF THE UNIT CELL DIMENSIONS OF PALYGORSKITE

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A recent AEM-NIR investigation of several palygorskites from different localities demonstrated that these samples can be described by the general formula $yMg_5 Si_8O_{20}(OH)_2 \cdot (1\text{-}y)[xMg_2Fe_2 \cdot (1\text{-}x)Mg_2Al_2]Si_8O_{20}(OH)_2$, where $x$ (the Fe-content of the dioctahedral component) and $y$ (the trioctahedral fraction) can be evaluated from the M1M2M2OH stretching overtone spectra active in the NIR (Chryssikos et al., 2009). Armed with a set of samples with very broadly varying octahedral composition ($0<x<0.7$ and $0<y<0.5$) we revisit and extend an earlier correlation between the octahedral composition of palygorskite and its unit cell dimensions (Suárez et al. 2007). The new data indicate that $d_{200}$ depends on $x$, $y$, and can be predicted via the relationship $d_{200}(\text{Å}) = 6.356 + 0.136\,x(1\text{-}y) + 0.308y$ ($R^2 = 0.96$, $\sigma = 0.012$ Å). A fully ferric dioctahedral palygorskite ($y$=0, $x$=1) is predicted to have $d_{200}$ = 6.49 Å, where a hypothetical fully trioctahedral magnesian palygorskite ($y$=1, $x$=0) extrapolates to 6.66 Å, i.e. very close to the $d_{200}$ spacing of Sepiolite.

In light of the above, we examine a number of combination and overtone bands (other than those due to the M1M2M2OH species) in the 2nd derivative NIR spectrum of palygorskite, and deduce the dependence of their position on octahedral composition and, hence, the $d_{200}$. $H_2O$ and surface SiOH features which depend exclusively on either $x$ or $y$ are identified. These results provide new and essential constraints on the possible ways trioctahedral and dioctahedral palygorskite ribbons combine to form palygorskite particles with a mixed dioctahedral-trioctahedral character.

**Keywords:** Palygorskite, Composition, Near-Infrared (NIR).

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# STRUCTURE AND PROPERTIES OF PALYGORSKITE WITH EXCESS AL

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Palygorskite is a 2:1 fibrous phyllosilicate with high compositional variability, mainly regarding the octahedral sheet. The ideal structural formula of palygorskite $Si_8O_{20}$ $M1M2_2M3_2$ $(OH)_2$ $(OH_2)_4$ $4H_2O$ allows 5 octahedral positions (p.h.u.c.). Most palygorskites are dioctahedral with the M1 position vacant and the M2, M3 positions occupied by Al and Mg, respectively. Mg-rich trioctahedral-rich palygorskites (García Romero et al 2004) and Fe-rich dioctahedral palygorskites (Gionis et al 2006) have been described.

In a wider study of palygorskites from various localities, we have found several samples that are richer in Al than the ideal dioctahedral composition. These samples were studied by HRXRD at the European Synchrotron Radiation Facility, by electron microscopy (both TEM and SEM) and by single particle microanalysis using AEM. Thermogravimetric analyses (DTA and TG), spectroscopic studies (NIR and ATR) and specific surface area measurements by $N_2$ adsorption-desorption were also performed.

These palygorskites are very pure, without impurities detectable by XRD. Their octahedral sheet has high content in octahedral Al, with $R3/R2 > 1$, $Si/Mg > 4$ and the total number of octahedral cations is less than 4 p.h.u.c. As such, they do not obey the structural formula of palygorskite. However, their morphology, size of fibre and textural relationships are similar to ordinary palygorskites. Thermal and spectroscopic studies reveal characteristic differences. Their specific surface area is lower than in other palygorskites. The experimental data suggest that these Al-rich palygorskites could be: 1- the result of natural acid leaching or 2- palygorskite with crystalline defects in the sense of intergrowths with wider dioctahedral ribbons.

**Keywords**: Palygorskite, Al-palygorskite, Octahedral composition.

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# CELADONITE VS. GLAUCONITE: ROOTS OF AND SOLUTIONS FOR THE MISUSE OF THE TERMS

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Celadonite and glauconite obtained their current mineralogical definition recently (IMA: Rieder *et al.,* 1998; also AIPEA: Guggenheim *et al.,* 2006). Although clear chemistry-based nomenclatures have been existing for three decades, the usage of the two names remained confusing. Some routinely applied protocols exist (IR: broad/sharp peaks; XRD: $d_{060}$) for the identification of and differentiation between celadonite and glauconite, but it is important to point out that they do not fit the currently valid nomenclature. We are to show the 200-year-long historical roots of that misfit, and suggest some simple ways to overcome this problem.

Celadonite (mostly basalt-related earthy bluish green material, chemically corresponding to the current definition of celadonite) had a practical application from the Antiquity as a green pigment. Glauconite (mostly sedimentary green grains, if mid- to dark green, chemically most cases fulfilling the current definition of glauconite) got into the focus of earth scientists (first geologists, then mineralogists) only at the beginning of the 19th century.

Creta viridis (Latin, „green chalk"), meaning a green pigment, is probably one of the earliest references to celadonite by Marcus Vitruvius Pollio (1st century B.C.). The most famous historical localities, Monte Baldo (near Verona, Italy) and the Troodos Massif (Cyprus), were still mined in the 20th century. Due to its continuous use, that „green earth" appears already in the earliest systems of mineralogy (*e.g.* Wallerius, 1750; Cronstedt, 1758). The term celadonite („Seladonites pictorum") was introduced by Glocker (1847).

Sedimentary green grains appeared first in geological descriptions as „green sands". Jameson (1816) mentions that green earth may tint sandstones green, so this might be the first mineralogical allusion to glauconite. The first chemical analyses of green grains are supposed to be those of Berthier (1820, 1821). The term glauconite („Glaukonit") was given by Keferstein (1828) to the green grains.

Even in classical mineral systematics (*e.g.* Dana, 1868, 1892), under the name glauconite, earthy and granular green materials were often handled together. Hintze (1897) proposed to separate the two species upon formation (celadonite of volcanic, glauconite of sedimentary origin). The idea was adopted by Doelter (1926), too.

New systematics (Bailey, 1980, 1986 and Rieder *et al.,* 1998) use solely crystal chemistry for classification. The latter, adapted for clays by Guggenheim *et al.* (2006), does not take into consideration the $^{IV}$Al substitution, directly related to the easily measurable IR and XRD features. We discuss both cases where the two approaches still can, or, respectively, cannot be applied simultaneously.

**Keywords:** Iron-micas, Mineral species Concept, Nomenclature.

# MINERALOGY & CRYSTALLOGRAPHY

## SESSION MC4

## *Layered Double Hydroxides*

# EFFECTS OF HYDROGEN BONDING ON THE PROPERTIES OF LAYERED DOUBLE HYDROXIDES INTERCALATED WITH ORGANIC ACIDS: MOLECULAR DYNAMICS COMPUTER SIMULATIONS

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Anion exchange capabilities of LDHs make them uniquely suitable for the creation of bio-inorganic nanocomposites, with amino acids and DNA fragments occuring as negatively charged species at most pHs. To better understand molecular-level structural, thermodynamic and kinetic aspects of their interactions with LDHs, we have performed MD computer simulations of glutamate($1^-$) and glutamate($2^-$) intercalated and adsorbed in Mg-Al LDH. The hydration and swelling of similar LDHs intercalated by smaller organic ions (formate, acetate, propionate, and citrate) were also simulated for comparison. The MD simulations (Kirkpatrick et al., 2005; Kumar et al., 2006, 2007) provide important insight into the interpretation NMR and X-ray diffraction data for the same systems (Reinholdt and Kirkpatrick, 2006; Li and Kirkpatrick, 2007). The organic species interact with the LDH layers principally via electrostatic and van der Waals forces, and the hydrated interlayer galleries are stabilized via the development of an integrated H-bonding network among the anions, water molecules, and OH-groups of the LDH surface. Deprotonated carboxyl groups are the primary strong H-bond acceptors, and for glutamate($2^-$), amino groups are additional H-bond acceptors from the LDH surface. The organic species preferably accept H-bonds from $H_2O$ molecules rather than from surface OH-groups due to structural restrictions on the development of tetrahedrally coordinated H-bonding environments for the $–COO^-$ groups at the surface.

**Keywords:** Hydrogen bonding, Molecular dynamics, Layered double hydroxides.

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# STABILITY AND TRANSFORMATION KINETICS OF 3R1 AND 3R2 POLYTYPES OF MG-AL LAYERED DOUBLE HYDROXIDES

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Hydrotalcites are stacks of magnesium and aluminum hydroxides layers with the interlayer water and anions compensating the charges. Hydrothermal synthesis of hydrotalcite from magnesium oxide and aluminum trihydroxide has been reported to produce two different polytypes, namely 3R1 and 3R2 polytype [Newman, 2002]. These polytypes have different layer stacking sequences, with a different interlayer spacing. Polytype 3R2 has a shorter interlayer distance and thus a more compact crystal structure. Since the difference in structure can potentially provide distinct performance characteristics of each polytype, it is of interest to determine the stability of both polytypes at different temperatures and their transformation accordingly.

Pure 3R1 and 3R2 polytype hydrotalcites were synthesized via hydrothermal synthesis of MgO and $Al(OH)_3$ at 90 °C and 170 °C. The hydrothermal stability of both materials in both forms was investigated. Directly after synthesis, the 3R1 polytype was hydrothermally treated at 100, 120, 140, and 170 °C, while the 3R2 polytype was treated at 50, 80, 100, and 120 °C for 72 hours. The composition of the material was monitored by analyzing the samples with p-XRD and. The shape of the crystal is observed with SEM. In addition, a slurry containing a mixture of 3R1 and 3R2 polytype was also hydrothermally treated at 120 °C.

This study showed that the transition temperature of 3R1 and 3R2 polytype is about 120 °C. Polytype 3R1 is the thermodynamically stable polytype below the transition temperature while polytype 3R2 is stable above this temperature. Hydrothermal treatments of the pure polytypes at their stable temperature range do not change their composition. The transformation kinetics from 3R1 to 3R2 above 120 °C increases with temperature, and is faster than the transformation from 3R2 to 3R1 below 120 °C. SEM pictures depicted different shapes of the 3R1 and 3R2 polytype crystals after transformation, so this transformation is solvent mediated. Solid phase transformation has indeed not been observed.

**Keywords:** Mg-Al LDH, Polytype transformation, Polytype stability.

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# MIXED METALS (Zn or Mg, Ni, Al) LAYERED DOUBLE HYDROXIDES AS PRECURSORS OF ETHANOL STEAM REFORMING CATALYSTS

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Recent papers have shown that the thermal decomposition of Cu/Zn/Al ternary layered double hydroxides (LDH), followed by Cu(II) reduction produces a mixture of oxides supporting copper clusters of nanometric size [1]. The materials have been found to be excellent catalysts for hydrogen production from oxidative steam reforming of methanol [2]. Following a similar strategy, well crystallized ternary LDH in carbonate form, containing Zn-Ni-Al or Mg-Ni-Al in different metal molar ratio, have been prepared with the urea method [3] in order to obtain precursors of active catalysts for the steam reforming of ethanol (SRE). The thermal treatment of the precursors at 700° C gives rise to high surface area mixed oxides which essentially retain the lamellar morphology of the precursors. However, the mixed oxides obtained from Zn-Ni-Al systems are poly-phasic (rock-salt NiO, wurzite ZnO, mixed spinel), whereas the mixed oxides obtained from Mg-Ni-Al systems are essentially mono-phasic, being mostly constituted by a rock salt NiO-MgO solid solutions. All the materials were characterized by ICP/OES, XRPD, TG-DTA, FT-IR and TEM analysis. The catalytic tests were carried out in a fix bed tubular quartz flow reactor connected to a gaschromatograph by feeding stoichiometric water to ethanol ratio ($H_2O/C_2H_5OH = 3$) sufficient to realize steam reforming and water gas shift (WGS) reaction. The data collected showed that Ni based hydrotalcites are active catalysts for the SRE as expected. Mixed oxides derived from Zn-Ni-Al and Mg-Ni-Al samples produces acetaldehyde as hydrogen containing by-product in addiction to $CH_4$ at 950 K in the outlet stream. Zn-Ni-Al catalysts have higher selectivity to methane (about 8%) than Mg-Ni-Al ones (about 3%). The yield to $H_2$ is similar (a little higher than 3.0) for both Zn-Ni-Al and Mg-Ni-Al catalysts.

**Keywords:** Layered Double Hydroxides, Mixed oxide Catalysts, Alkanol reforming.

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# NANOSIZED IRON OR TITANIUM OXIDES / LAYERED DOUBLE HYDROXIDES AS NANOSTRUCTURED ESSEMBLES

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Ensembles of different nanoarchitectures into which different components are able to join their features and organize themselves for giving rise to materials owning complex features are currently a subject of intense research interest [1]. Nanostructured assemblies of matrices of layered double hydroxides (LDHs) supported with nanoparticles of iron or titanium oxides have been obtained during the reconstruction process of the anionic clay, by manipulating its structural "memory effect". The morphology, composition and phase structure of as-prepared powders were characterized by X-ray diffraction (XRD), $N_2$ adsorption ($S_{BET,}V_p$), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The samples combine the characteristics induced by the nanoparticles of $Fe_2O_3$ or $TiO_2$ with the surface/textural functionality of the inorganic layered framework into one single material. In the straightforward synthesis route the reconstruction process of the clay, the formation of nanoparticles of metal oxides and their loading on the larger particles of the clay take place in one single step. The multifunctional capabilities of $Fe_2O_3$/LDH and $TiO_2$/LDH ensembles can be used to diversify the properties and applications of LDHs materials.

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**Keywords**: Nanostructured ensembles, Layered double hydroxides, Nanoparticles, Oxides.

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# EFFECT OF METAL BIBYRIDYL CATIONS ON THE ELECTROCHROMIC RESPONSES OF FILMS OF REDOX ACTIVE NICKEL-LAYERED DOUBLE HYDROXIDES

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The addition of $[Co(bpy)_3]^{2+}$ to the electrolyte greatly improved the reversibility of the colour changes observed in films of Ni-Al LDHs upon oxidation-reduction of nickel sites in the LDH layers. Sustained changes in relative transmittance between 95% in the reduced state and 75% in the oxidized state were obtained for films subjected to continuous potential scanning in pH 8 borate buffers containing 0.1 mM $[Co(bpy)_3]^{2+}$. This improvement in the electrochromic response is attributed to mediation of the reduction of oxidized nickel sites in the LDH layers by the cobalt cations. This allowed full reduction of all nickel sites in the films back to Ni(II) to occur by the end of each individual scan. In the absence of $[Co(bpy)_3]^{2+}$, the colour changes were not fully reversible and rapid darkening of the films was observed. Because the unaided electrochemical reduction of nickel in LDH films is very slow, oxidized nickel sites accumulated in the films with each scan. This was confirmed by increases in the average nickel valence in the films determined by iodometry, and by the appearance of reflections due to a Ni(III) oxyhydroxide phase in the XRD pattern of the films. This was not found when the cycling was done in presence $[Co(bpy)_3]^{2+}$. Mediation of the reduction of nickel in the Ni-Al LDH films by $[Co(bpy)_3]^{2+}$ was very efficient. The presence of 5 μM $[Co(bpy)_3]^{2+}$ was sufficient to cause a significant improvement of the bleaching process despite the fact that the cobalt cations were not adsorbed in the positively charged LDHs. Addition of $[Ru(bpy)_3]^{2+}$ to the mixture results in a further improvement in contrast. In presence of both $[Ru(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{2+}$ sustained transmittance changes between 35% and >90% were observed. Because the oxidation potential of $[Ru(bpy)_3]^{2+}$ is higher than that of Ni(II) in Ni-Al-LDH films, the ruthenium cation could mediate to oxidation of the Ni(II) sites in the LDH layers, resulting in an improved colouring reaction without adversely affecting on the bleaching reaction.

**Keywords:** Anodic electrochromism, Cyclic Voltammetry, UV-Visible Spectroscopy.

# MINERALOGY & CRYSTALLOGRAPHY

## SESSION MC5

## *Serpentines as Hot Clays*

*XIV International Clay Conference – Italy 2009*

# THE PHASE PETROLOGY OF SERPENTINITES

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Coexisting antigorite and olivine in prograde metamorphosed serpentinites vary systematically in their Fe/Mg ratios, such that a $K_D$ for $Fe^{2+}/Mg$ exchange equilibrium, $(Fe^{2+}/Mg_{Atg})/(Fe^{2+}/Mg_{Ol})$, of approximately 0.3 can be extracted. For example, in equilibrium with olivine $Fa_{9\text{-}10}$ the antigorite should contain 3.0 % of the $Fe^{2+}$ end-member. The corresponding end-member content of total iron in antigorite $X_{Fe}$, $\Sigma_{Fe}/(\Sigma_{Fe}+Mg)$ %, would be about 4.5%. The low $SiO_2$ and $O_2$ pore-fluid activities well known to attend retrograde serpentinization can be attributed to the chemical potentials respectively of components *fo* and *fa* in stable olivine at low temperatures. Thus, their difference, the $FeMg_{-1}$ exchange potential, can reasonably be expected to influence the $X_{Fe}$ of the product minerals. $X_{Fe}$ of 460 chemical analyses in the literature of lizardite in ophiolitic serpentinites shows an asymmetric frequency distribution, with an average at 0.058±0.030(1σ) and a modal peak at about 0.04. These data strongly suggest that the compositions of mesh and bastite lizardite in serpentinites are indeed governed by $Fe^{2+}/Mg$ exchange equilibrium with protolith olivine (and orthopyroxene). Because of the very low cation diffusion rates, progressive serpentinization involves bulk decomposition of the protolith minerals, and not a fractional evolution of mineral products and reactants according to a *T-X* phase-loop model. Mass-balance then requires the growth of an iron-rich mineral that is typically magnetite. The reaction involves hydration and hydrolysis, and hydrogen is evolved. The effectiveness of the $K_D$ control will decrease as olivine and orthopyroxene modally decline during serpentinization and they become progressively more armored. The $X_{Fe}$ of chrysotile in ophiolitic serpentinites (200 analyses) is more symmetric than lizardite, with an average of 0.034±0.018(1σ). The composition of chrysotile in veins thus appears to serve as an excellent monitor of the $FeMg_{-1}$ exchange potential of the pore fluid attending serpentinization. Mössbauer analysis has shown that chrysotile generally contains much less $Fe^{3+}$ than lizardite. Lizardite in mesh and many cases of bastite pseudomorphs accommodates $Fe^{3+}$ primarily as a cronstedtite component, $(Fe^{2+}{}_2Fe^{3+})(Fe^{3+}Si)O_5(OH)_4$. Thus it tends to contain slightly less Si than ideal lizardite, consistent with the presence of olivine and brucite. Some bastite lizardites have structural formulae with T/(T+M) cations > 0.4, signifying the presence of M-site vacancies. This would be appropriate for a secondary paragenesis that includes talc.

Hydrogen yield increases as modal brucite/serpentine ratios decline, that is, it is higher in metaharzburgite than metadunite. The uptake of $Fe^{3+}$ in lizardite can dramatically reduce the amount of magnetite that forms. The combination at 200-300°C temperatures of fast rates of hydrothermal alteration and slow rates of cation diffusion is optimal for the initial growth of metastable products at the reaction site with non-equilibrium Fe/Mg ratios.

**Keywords:** Serpentinite, Antigorite, Cronstedtite.

# SERPENTINIZATION AT OCEANIC HYDROTHERMAL SITES WITH EMPHASIS ON IRON INCORPORATION IN SERPENTINE

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Recent oceanographic expeditions revealed the existence of a new type of hydrothermal system, hosted in ultramafic basement rocks. Alteration of these ultramafic rocks during serpentinization reactions generates high amounts of $H_2$, $CH_4$ and supports novel biological communities along the Mid-Atlantic Ridge. The study of such environments can provide valuable information on natural processes for an efficient production of new energies like hydrogen. The reactions classically invoked propose iron oxidation (and iron oxide formation) as determinant in gas production; like e.g. the serpentinization of olivine:

$$\underset{\text{Olivine}}{6\,(Mg,Fe)_2SiO_4} + 8H_2O \rightarrow \underset{\text{Serpentine}}{3\,(Mg,Fe)_3(Si,Fe)_2O_5(OH)_4} + \underset{\text{Brucite}}{(Mg,Fe)(OH)_2} + \underset{\text{Magnetite}}{Fe_3O_4} + H_2$$

$$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O \quad \text{+/- others hydrocarbons}$$

The amount of hydrogen and hydrocarbons formed abiotically is thus directly linked to the amount and state of iron incorporated into product minerals (mainly serpentine) after being released from Fe-primary minerals during hydrothermal alteration.

We investigate these aspects on serpentinite samples collected at various hydrothermal sites of the Mid-Atlantic Ridge during the recent “Serpentine” and “MoMARDREAM” cruises. Textural, geochemical and microstructural studies have been realized to unravel the different stages of alteration history and identify the similarities and/or differences between the sites. In addition, micro-XANES analyses at the Fe *K*-edge were performed with the ID24 beamline of the ESRF to derive redox and speciation of iron in the various serpentines involved at the different stages. This allows discussing on the variability of iron state, content and distribution in serpentines with both the microstructure and the degree of alteration for different locations. This is a first fundamental step toward the identification of potential markers for gas production evolution and hydrothermal system dynamics and variability.

**Keywords:** Serpentinization, Mid-Atlantic ridge, Iron.

# THEORETICAL INSIGHTS IN THE INFRARED SPECTRUM OF SERPENTINE MINERALS

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Infrared (IR) spectroscopy is often used to investigate the finely divided minerals occurring in alteration environments, such as serpentine minerals. However, the straightforward interpretation of their IR spectra in terms of vibrational modes of the crystal structure is often difficult. The first-principles calculation of vibrational spectra thus represents an ideal tool to establish unambiguous relations between the IR spectrum and the microscopic structure of serpentine minerals. This is done by computing the phonon vibrational modes, and related oscillator strengths, using the density functional perturbation theory. It is then possible to improve the comparison between theory and experiment by combining the first-principles calculation of crystal properties with an electrostatic model of IR light absorption, which takes into account experimental and sample-dependent parameters. This approach applied to lizardite leads to an unambigous interpretation of the main absorption bands (Balan et al., 2002a).

An additional complexity of powder spectra stems from the influence of the shape of particles on the infrared spectra. Concerning this aspect, lizardite and chrysotile, whose particles display platy and nanotubular morphologies, respectively, are particularly interesting. Our theoretical investigations show that the peculiar electrostatic properties of the nanotubes lead to unexpected additional vibrational bands in the IR spectrum of chrysotile, compared with that of lizardite (Balan et al., 2002b). This shape-effect explains the some of the differences recognized a long time ago in the infrared spectrum of serpentine polymorphs (Yariv & Heller-Kallai, 1975).

**Keywords:** Infrared spectroscopy, ab initio, OH.

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# POLYHEDRAL SERPENTINE: A SPHERICAL ANALOGUE OF POLYGONAL SERPENTINE

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Serpentine spheres up to 1mm diameter, from hydrothermal veins in Cornwall, UK, are shown to consist of tapering hexagonal prisms of lizardite-1T. The prisms are organized radially in sets of paired 15-fold rings at +/- 60° to each other, such that the angle between [0001] of adjacent lizardite prisms is always close to 24°. This arrangement produces a surface tessellation that can be modelled on the buckminsterfullerene geometry, modified by adding face-centering points to each hexagon and pentagon. Thus modified, a 'face-centred buckyball' contains parallel pairs of 15-fold surface rings, offset azimuthally by 12° that together form 30-fold 'zig-zag' rings. A complete lizardite polyhedron therefore contains a crystallographically-controlled ordered arrangement of 92 single crystals. Cross sections (close to an equatorial plane) though these polyhedral spheres resemble cross sections of polygonal serpentine, with 15 sectors at 24°, though about 2000 times larger. When sectioned very close to an equatorial plane a 30-sectored arrangement becomes obvious. Clearly a 15-fold nucleation process is established early in the formation of the spheres and is almost certainly related to the 15-fold arrangement of the radial in-register H-bonding directions controlled by the 5-fold symmetry possessed by chrysotile (Cressey & Whittaker, 1993). For the commonly-observed polygonal serpentine, only one curvature direction develops producing a fibre with its axis parallel to *a*. However, if this fibre direction did not grow to any significant degree, a 15-sectored disc rather than a fibre could develop curvature directions at +/- 60° to the initial circumferential *b* direction outwards from the 15 positions where the H-bonding is set in register. This would potentially generate new sets of 15-node rings. Repetition of this process at each node will eventually produce a 'FC-buckyball' sphere, when lizardite prisms nucleate in the pentagon-centre positions at 24° from the structure of one near-neighbour node position in an already-established 15-node ring. Polygonal serpentine formation may therefore represent an early and massive increase in growth preferentially along one of the *a* axes of a sectored nucleus disc that would otherwise have developed into a polyhedral sphere. Similarly, it may follow that 30-sectored polygonal serpentine originates when fast growth along one *a* axis coalesces a parallel pair of 15-sectored discs offset azimuthally by 12° in an early, part-formed sphere. 15- and 30-sector polygonal fibres often occur together, and sometimes fibres are composite, part-15 and part-30 in character, providing further evidence for the coalescing of a primary part-spherical nucleus state.

**Keywords:** Serpentine, Lizardite, Polyhedral serpentine, Polygonal serpentine.

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# KINETICS OF CHRYSOTILE AND LIZARDITE DEHYDRATION

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Lizardite and chrysotile are two TO-phyllosilicate polymorphs belonging to the serpentine group minerals. Whereas the TO-layers are flat in lizardite, they are bent to cylinders in chrysotile, resulting in a nanotube morphology. Because of the cylindrical structure, chrysotile has only rotational, but no radial symmetry. The structure changes continuously with radius, and so do also the physical properties such as the (metastable) breakdown temperature. The outermost layers breakdown at temperatures between 450° and 500°C, whereas the innermost cylinders dehydrate at temperatures well above 600°C. (Metraux & Grobéty, 2002, Cattaneo et al., 2003). The goal of the investigation was to study the influence of the non-translational symmetry of chrysotile on dehydration kinetics, using the breakdown rate of lizardite as reference. High temperature x-ray diffraction is ideally suited to study the progress of dehydration reactions. Because the first products of chrysotile and lizardite dehydration are amorphous, the reaction rate can only be monitored through the intensity reduction of the reflections of the reactant phases. The dehydration kinetics of chrysotile, compared to lizardite, showed indeed exotic behavior. The data were treated both with the "Time to a given fraction" (TGF) method as well as with the conventional Avrami method. The activation energy, determined by the TGF method, at a given temperature between 550 and 700°C increased as function of reaction progress from values around 200kJ mol$^{-1}$ for a fraction transformed $f_t$ of 10%t o values as high as 600kJ mol$^{-1}$for $f_T$ of 60%. For higher values of $f_t$ , the activation energy drops back to 200kJ mol$^{-1}$. The order of reaction determined by the Avrami method showed also a linear increase from n=0.35 at 550°C to n=0.6 at 650°C The results were interpreted with a transport limited kinetic model that takes into account the non-translational structure of chrysotile.

**Keywords**: Chrysotile, Lizardite, Dehydration kinetics.

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# MINERALOGY & CRYSTALLOGRAPHY

## SESSION MC6

## *Simulation and Theory of Clay Minerals and Interfaces*

# MODELLING OF SILICATE AND ALUMINOSILICATE MATERIALS

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Computer simulation methods have had a major impact on our understanding of complex materials at the atomic level and the impact has nowhere been greater than in the study of silicate and aluminosilicate materials [1]. This lecture will give a general survey of field, describing both the application of interatomic-potential based and electronic structure methods. Modelling of structure properties and reactivities will be reviewed; and we will describe application to dense silicate and to both layer and framework structured systems. Future developments in the field will also be discussed.

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# CLAY MINERALS AS MATRIX FOR FUNCTIONAL NANOSTRUCTURES; MODELING AND EXPERIMENT

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Intercalation is the widely used method for structure modification of clays in order to prepare functional nanostructures usable as sorbents, catalysts, photocatalysts, drug carriers etc. Investigating the structure-properties relationship of intercalated clays we found that the surface and interlayer structure of guest molecules are different and these differences cause the inhomogenity in optical properties [1]. For many practical applications like: catalysis, photocatalysis, tunable laser dyes etc… the guest structure on the clay surfaces plays the crucial role. For this reason we focused our attention in recent years to the technology of surface modification, i.e. the nanoparticles of Ag, $TiO_2$, CdS etc. anchored on the clay surfaces [2]. Molecular modeling using empirical force field combined with experiment has been used in order to investigate the structure and structure related properties of clays modified by intercalation and surface modification. Modeling was performed in *Materials Studio* modeling environment and the key experiments supporting modeling are: X-ray powder diffraction, IR spectroscopy and electron microscopy (HRTEM) [2,3,4]. Clays with various layer charge and structure have been used as host matrices (montmorillonite, vermiculite, kaolinite). As a guest species we used organic cations, polar organic molecules, organometalic complexes and nanoparticles of metals, metal oxides and metal sulfides. Results of our investigation showed the strong effect of layer charge on the structure and properties of intercalated and surface-modified clays, whereas not only the magnitude of layer charge, but also the charge distribution is important factor for the interlayer and surface structure of the guest species and stability of the nanocomposites nanoparticle-clay. Molecular modeling revealed the preferred orientation of crystalline nanoparticles grown on the clay surface and the preferred orientation of the clay substrate for various types of clays and nanoparticles ($SiO_2$ basal plane, Al/Si faced edges of the clay particle have been tested). The optimum size of single crystalline nanoparticle obtained from modeling was in good agreement with the HRTEM observations.

**Keywords:** Modified clays, Modelling, Nanoparticles.

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# AB INITIO MD SIMULATION OF CLAY MINERALS

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The crystal chemistry and surface reactivity of phyllosilicate minerals is a key issue for modelling of the ion mobility and retardation in clayish rocks. Retention of ions in clay sediments occurs either by the mechanism of cation exchange in the smectite inter-layers or by pH dependent sorption on the edges of clay pallets. The ion selectivity in the cation exchange process is a trade between the energy and dynamics of ion hydration shell in the aqueous solution, and the extent of the isomorphic substitutions in the tetrahedral and octahedral layers of clay particles. The sorption on the edges of clay stacks depends on the proton affinities of the dangling oxygen sites and its surface density.

Ab initio simulations provide a unique insight into structure and reactivity of mineral surfaces on the atomistic scale. In contrast to the classical simulations using empirical force field parameters, the quantum mechanical calculations successfully describe interfacial reactions involving creation and breaking of chemical bonds. Recently, the structure and stability of pyrophyllite edges was modelled based on the density functional theory. Calculations of pyrophyllite surface energies enabled to access the energetically favourable structure of the edges and to estimate the capacity of the edge sorption sites (Bickmore 2003, Churakov 2006). Molecular dynamics simulations of the pyrophyllite-water interfaces revealed the dynamics of water molecules at the clay surface and the mechanism of the proton exchange between the reactive surface sites (Churakov 2007).

In the presentation I will give an overview of the density functional theory based applications to the reactivity of clay-water interfaces. Particular attention will be paid to the approximation used in the ab initio simulations and its consequences for the interpretation of the results. The limitations and challenges of the ab initio techniques will be discussed.

**Keywords:** Ab initio simulations, Reactivity of clay edges, Clay-water interface.

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# AB INITIO QUANTUM MECHANICAL SIMULATION OF SYSTEMS WITH HELICAL SYMMETRY: CARBON AND CHRYSOTILE NANOTUBES

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The helical symmetry of nanotubes, which can have more symmetry operators than cubic crystals, was exploited in a generalisation of the symmetry treatment as implemented in the CRYSTAL code. The computational cost of large basis set calculations of nanotubes dramatically decreases.[1] The exploitation of the helical symmetry allows to simulate very large size systems, for which *ab initio* calculations would not be affordable otherwise . Symmetry features of nanotubes are well-known and were described in a few papers.[2] To the authors' knowledge, this is the first complete, tested and documented implementation in a general computer code.
The modified CRYSTAL code was used for the study (structure, stability, band gap) of a set of carbon nanotubes at different DFT levels (LDA, GGA, hybrids) with Gaussian type basis sets of increasing complexity (from STO-3G to 6-1111(2d1f)), and the results compared with the available experiments and other simulations.[1,3]
A preliminary quantum mechanical *ab initio* analysis of the structure and stability of chrysotile[4] nanotubes ($Mg_3Si_2O_5(OH)_4$, phyllosilicate cylindrically wrapped that can contain thousands of atoms in the unit cell) was performed for the first time with the CRYSTAL code (DFT, different Gaussian type basis sets), concerning the relationship between the structure (*i.e.* radius of the tube and rolling direction in the flat layer) and the electronic stability.[5]

**Keywords**: Helical symmetry, Carbon nanotubes, Chrysotile.

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# OPTIMIZATION OF BRAZILIAN KAOLIN PROCESSING USING KUBELKA-MUNK THEORY

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The economic value of kaolin is directly associated with its optical properties (brightness, opacity, etc.) and in many cases these properties, especially the brightness, are used as a quality control parameter during its process.

The industries have a tendency to use kaolin brightness as a “grade” and the problem is that, unlike metallic ores, two ores with the same brightness passing through the same process may not achieve the same brightness at the end of the process. This occurs because each impurity has its own “coloring power” and its own behavior in each step of the process.

In this work we try to develop a tool to determine the concentration of each impurity of Rio Capim kaolins (essentially hematite, goethite and anatase) using their measured reflectance spectra in the visible region and the Kubelka-Munk theory, which is based on the sample´s absorption and scattering power. Through this technique it was discovered that anatase is the most harmful mineral in the system, and the next step is to establish a safe limit to its concentration and the other minerals, aiming to facilitate kaolin processing and mine planning.

**Keywords:** Kaolin, Brightness, Process control.

# VIBRATIONAL ANALYSIS OF CLAY MINERALS USING QUANTUM AND CLASSICAL SIMULATIONS

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While quantum mechanical methods provide an accurate theoretical description of a chemical system, their use on clay minerals has been limited due to the large number of atoms required in the calculations. Classical simulations are required when large system sizes or long simulation times ($<$ 1 ns) are required to describe phenomena such as solute adsorption, hybrid organic-clay interactions, and mechanical properties. Both quantum and classical methods can both be used for some molecular properties, and this combination provides a means to use higher level quantum results to develop and validate classical force fields. We have used vibrational power spectra from ab initio molecular dynamics (AIMD) simulations in the development of accurate intramolecular energy expressions for classical force fields. Our specific interest is a more realistic classical description of the O-H bond stretch energy for layer hydroxyl groups and eventually edge hydroxyl groups. Most clay (and water) force fields use a simple harmonic expression for O-H bond stretch, but our simulated power spectra in the O-H stretch region show that a Morse potential is able to predict shifts in this frequency depending on the morphology and charge of the clay mineral.

**Keywords:** Ab initio molecular dynamics, Simulation, Vibration, Hydroxyl.

# INVESTIGATING ORGANIC – CLAY INTERACTIONS TO UNDERSTAND THE PAST AND SHAPE THE FUTURE

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The interaction between organic matter and layered minerals has played a role in shaping the past and the present of human life on Earth, and will continue to in future. We describe a range of computational and experimental studies to understand the way that minerals and organic matter interact. The latest results from biofuel catalysis, clay-polymer composites, and prebiotic chemistry will be presented. The early Earth was a hostile place for biochemistry with volcanic activity, a reducing atmosphere and UV radiation favouring degradation rather than synthesis. In the Archean oceans, small molecules would have spewed out of hydrothermal vent systems, however without means of concentrating the organic molecules, the resulting dilute solution would not have allowed reactions to occur. We have used simulations to illustrate how clay minerals are able to both concentrate and react organic molecules and protect larger molecules.[1,2] Current work examines amino acid uptake, and any chiral selectivity, in layered double hydroxide mineral systems. As first life evolved, countless of simple organisms died and were buried under sediments where, over millennia, organic-mineral interactions converted the material to fossil fuels essential to mankind's industrial development. Early oil industries were extremely dirty, but in modern times oil exploration has become cleaner, however legislation has also tightened. When drilling for oil, a technical fluid is used, which has to fill several roles including stabilizing clay shales against swelling. Water-soluble oligomer inhibitors are used to control swelling; a fundamental understanding of the clay-swelling inhibitor interaction is needed. We use computer simulations, and experiments, to understand the subtle interplay between different functional groups, clay types and hydration state[3.] Through the 20th Century mankind's need for lightweight materials evolved rapidly. The latest generation of high performance composite materials, based on clay fillers entrained in polymers, present significant challenges to the materials scientist as many of the enhanced properties occur in the nanometer domain. We have made use of computational grids to run simulations at an unprecedented scale –millions of atoms – of clay platelets. These simulations have shown the emergence of thermal undulations, enabling the calculation of materials properties of both the whole system, and the clay platelets which are only a few nanometers thick.

**Keywords:** Origin of life; Oilfield research; Nanocomposites.

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# ACCURATE ATOMISTIC SIMULATION OF LAYERED SILICATES AND THEIR INTERFACES

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Atomistic force field models for the clay minerals mica, montmorillonite, and pyrophyllite are presented. Computed surface and interface energies are in quantitative (~5%) agreement with experiment which improves earlier models (including CLAYFF) with 50−500% discrepancies relative to experiment. The significance of a physically justified distribution of atomic charges is highlighted, as well as the assignment of van-der-Waals parameters. The models are also unique in taking the distribution and charge balance of Si->Al and Al->Mg charge defects quantitatively into account, consistent with solid state Si NMR data. The accurate simulation of ion exchange reactions, surfactant binding constants, and interfacial dynamics will be exemplified (i) for the binding of two dodecapeptides to montmorillonite in aqueous solution which were experimentally identified from a library of 109 phages, (ii) for the self-assembly of various alkylammonium surfactants on montmorillonite and mica surfaces as a function of chain length, head group chemistry (primary vs quaternary), and CEC of the clay mineral.

For the peptides, concentration-dependent binding energies, chain conformations (Ramachandran plots), and NMR data have been computed which agree with experimental data and suggest a molecular-level representation of the binding processes. Simulation results for the ammonium surfactants on clay mineral surfaces explain the structure of the organic interlayer, the interfacial mobility of surfactants, and thermal phase transitions on the clay mineral surface, including XRD, NEXAFS, IR, NMR, and DSC data. The results of the molecular dynamics simulation provide first insight into the integration of clay minerals in biological matrices and into control of exfoliation processes in polymer-clay nanocomposites by interface design.

**Keywords:** Force Fields, Molecular Dynamics, Inorganic-organic interfaces.

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# COARSE-GRAINING STRATEGY TO STUDY THE SALT EXCLUSION IN MONTMORILLONITE CLAYS

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We study the exclusion of salt from a lamellar Montmorillonite clay (Donnan effect), using a coarse-grained approach. The porous medium is in contact with a reservoir which contains an electrolyte solution. We develop a specific coarse-graining strategy to investigate the properties of this system. Molecular simulations are used to calibrate a mesoscopic model of the clay micropore in equilibrium with a reservoir. Brownian Dynamics simulations are then used to predict the structure of ions in the pore and the amount of NaCl salt entering the pore as a function of the pore size (the distance L between clay surfaces) and of the electrolyte concentration in the reservoir. These results are also compared to the predictions of a Density Functional Theory which takes into account the excluded volumes of ions. We show that the calibration of the mesoscopic model is a key point and has a strong influence on the result. We observe that the salt exclusion increases when $\kappa L$ decreases (where $\kappa$ is the inverse of the Debye length) and that this effect is modulated by the correlations between ions. Two different regimes are revealed. At low concentration in the reservoir, we observe a regime controlled by electrostatics: The Coulomb attraction between ions increases the amount of salt in the interlayer space. On the opposite, at high concentration in the reservoir, the excluded volume effect dominates.

**Keywords:** Coarse-graining procedure, Hydrated clay, Donnan effect.

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# MULTI-SCALE STRUCTURE AND DYNAMICS OF WATER AT MINERAL SURFACES: MD SIMULATIONS AND EXPERIMENTAL STUDIES

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Molecular scale knowledge of the thermodynamic, structural, and transport properties of water confined by surfaces and nanopores of clays and clay-related materials is crucial for quantitative understanding and prediction of many geochemical, environmental, and technological processes. Experimental nanoscale studies of such systems are not always feasible, and their results often require considerable interpretation in the efforts to extract surface-specific and confinement-specific quantitative information from the measurements. Computational molecular modeling significantly complements such efforts by providing invaluable atomic scale background understanding of the specific effects of mineral substrate structure and composition on the structure, dynamics and reactivity of interfacial and nano-confined aqueous phase. Individual water molecules simultaneously participate in several dynamic processes characterized by significantly different, but equally important time- and length- scales, which can be effectively probed by computer simulations, even in a single MD run.

On a relatively short time scale (~1-100 ps), the interfacial $H_2O$ dynamics is dominated by the molecular librational and re-orientational motions. The librations (hindered rotations) of surface hydroxyls also occur on this time scale. These motions are responsible for the reformation and breaking of individual H-bonds, and the strength of these bonds can be directly correlated with the frequencies of intra-molecular O–H vibrations at an even shorter sub-picosecond time scale. MD simulations combined with comprehensive inelastic and quasielastic neutron scattering measurements for hydrocalumite helped to capture important details of the librational dynamics of nano-confined water and the effects of $H_2O$ orientational ordering above and below the interlayer order-disorder phase transition.

The diffusional processes related to reformation of the entire interfacial and interlayer H-bonding network, the processes of surface adsorption of water and ions are characterized by much longer time scales (~0.1-10 ns). These slow diffusional motions can be quantified using van Hove self-correlation functions, $G_S(r,t)$. The MD results clearly show a distinct characteristic time and length ($\tau \sim 0.8$ ns; $l \sim 0.6$ nm) for the hopping diffusion of water molecules at the surface of tobermorite, in excellent agreement with $^1$H NMR field cycling relaxometry results for surface-associated water in this material. Similar hopping diffusional dynamics is almost an order of magnitude faster at the ideal (001) surface of quartz, but can be, in fact, significantly slowed down by the atomic-scale roughness of the real mineral surface.

**Keywords:** Molecular simulations, Aqueous interfaces, Surface diffusion.

# MONTE CARLO SIMULATION OF QUARTERNARY ALKYL AMMONIUM SURFACTANT ADSORPTION ON MUSCOVITE MICA

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Organically modified clay minerals play an important role in many industrial processes and various environmental engineering applications like nuclear waste repositories or sewage treatment since they are able to sorb both anionic and cationic contaminants. Currently applied experimental methods provide only partial information on the structure of the aggregates adsorbed to mineral surfaces.

Simulations using Monte Carlo Methods are performed to acquire detailed knowledge of the structure of the interface between the cleaved muscovite mica surface and aqueous alkyl ammonium chloride solution at ambient conditions. The interactions between atoms and molecules in the mica-surfactant-chloride-water-system are described using the OPLS-AA force field.

In a first series the adsorption of cetyltrimethylammonium chloride ($C_{16}TAC$) is modelled. The amount of $C_{16}TAC$ ranges from 0.25 to 2 molecules per unit cell area of mica. For each concentration two different initial arrangements are considered: “monolayer” with all headgroups of $C_{16}TA^+$ directed towards the mica surface and “bilayer” with half of the $C_{16}TA^+$ ions rotated by 180 degrees. The obtained results are compared to those of a similar study using cetylpyridinium chloride. In a second series the effect of chain length is considered. For this purpose simulations with $C_{12}TAC$ and $C_8TAC$ are carried out.

**Keywords:** Mica-water interface, Surfactant adsorption, Monte Carlo simulations.

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# DISTRIBUTION OF MG$^{2+}$, CA$^{2+}$, SR$^{2+}$ AND BA$^{2+}$ AT THE MICA–WATER INTERFACE: A MONTE CARLO STUDY

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Muscovite mica is a clay mineral with a basal surface structure very similar to that of illite and montmorillonite, which are two other clay minerals of high importance in various environmental and industrial applications. In contrast to the latter two minerals, however, muscovite has cleavage properties, which make it an excellent model system for studying phenomena occurring at solid-liquid interface in general and for investigating colloid properties of clays in particular.

Monte Carlo simulations of the interface between the cleaved surface of muscovite mica and aqueous solution containing $Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$ or $Ba^{2+}$ at varying concentrations as well as $H_3O^+$ ions compensating negative charge of muscovite at ambient conditions have been carried out. A detailed molecular-scale data on the structure of adsorbed water, equilibrium positions of the adsorbed alkali-earth ions as well as on the structure and type of their adsorption complexes at the muscovite-water interface have been obtained.

The simulated data have been compared with results of X-ray reflectivity studies [Fenter et al., 2006; Schlegel et al., 2006] as well as of the preceding simulation studies [Meleshyn, 2008a; Meleshyn, 2008b] of muscovite-water interface. In particular, the calculated equilibrium atomic density profiles have been used to estimate electron density profiles and integrated electron densities available from the X-ray reflectivity studies. On the basis of this comparison, conclusions about the adsorption structure and the relation beteen surface concentrations of adsorbed alkali-earth ions and their bulk solution concentrations as applied in the above experimental studies have been made.

**Keywords:** Mica-water Interface, Alkali-earth ions, Adsorption, Monte Carlo simulations.

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# DETERMINATION OF THE LIMITING STEP IN THE DEHYDROXYLATION-REHYDROXYLATION REACTIONS IN PYROPHYLLITE BY AB-INITIO MOLECULAR DYNAMIC SIMULATIONS

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High temperature transformations of dioctahedral 2:1 phyllosilicates are well known and it is still of great interest due to their importance in geosciences and technological processing of ceramics and material design. However, there is a lack of knowledge at atomistic and nanoscale level of the mechanism of this process. The dehydroxylation of pyrophyllite involves the reaction of OH groups and elimination of water molecules throughout two possible mechanisms: one evolving the bridging hydroxyl groups of an octahedral pair (on-site mechanism), and cross mechanism where two hydroxyl groups react across the dioctahedral vacancy. However, there are some discrepancies about both proposed mechanisms and the limiting steps of this reaction. Therefore, a deeper insight about the mechanism and structural rearrangements at high temperature are necessary for a better optimization of the phyllosilicates applications.

We apply quantum mechanical Car-Parrinello molecular dynamics simulations based on Density Functional Theory and the Metadynamics algorithm for simulating these reactions. Different reaction paths and the critical points of the FES are found for both possible mechanisms, reproducing the activation energy (Ea) found experimentally (60 kcal/mol) [1]. The water loss mechanism is not concerted but it is performed in at least two steps with intermediates. Besides, the apical tetrahedral oxygens are also implicated in the dehydroxylation mechanism forming intermediate silanol groups detected experimentally. For all mechanisms, the limiting step is the formation of water molecule, although it is trapped in the ditrigonal cavity and, during its release along the interlayer space (Ea = 17 kcal/mol), it reacts with other residual oxygens producing successive rehydroxylation-dehydroxylation processes justifying the wide temperature range needed in this reaction.

**Keywords**: Pyrophyllite, Dehydroxylation, Molecular-Dynamics.

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# MESOSOPIC MODELLING OF IONIC DISPERSION AND DIFFUSION IN CLAYS

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Understanding the diffusion of charged species through clays is a crucial point in assessing their use as barriers for the confinement of toxic and radioactive waste. Experimentally, it has been observed that the effective diffusion coefficient $D_e$ of tracers depends on their charge, with anions being "slower" and cations "faster" than neural tracers. This observation is related to the negative charge of the clay particles: In addition to the Donnan effect (leading to an excess of cations and the exclusion of anions from the pores of the material), one often invokes the fact that species of different charges follow different pathways through the porosity. In this communication, we will address this issue using simulations of ionic transport in the interparticle pores between clay particles (not the interlayer nanopores).

The size of interparticle pores (10-1000 nanometers) makes the simulation of solvent and ionic flow in such pores out of reach of molecular simulation. At this scale, it is more efficient to use mesoscopic models based on a continuous description of the fluid. We will introduce a lattice-based method to simulate the evolution of ionic solutions under the combined effect of advection, diffusion and migration (effect of the local or applied electric field). This algorithm can be seen as an efficient solver for the coupled Navier-Stokes and Nernst-Planck equations. In addition, it gives access to the Velocity Auto-Correlation Function of charged tracers, from which we compute their Time-dependent diffusion coefficient D(t).

By analyzing the influence of the tracer charge and of the salt concentration on D(t), we show how the effective diffusion coefficient (the long-time limit of D(t)) is related to the pathways of charged tracers through the mesopores. The negative charge of clays surfaces results in electrostatic bottlenecks hindering the diffusion of anions and in preferential pathways near the surface for cations. This pore-scale analysis provides a better understanding of macroscopic experimental observations.

**Keywords:** Lattice Boltzmann, Electrokinetics, Time-dependent diffusion coefficient.

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# DETERMINATION OF THE HYDRATION ENERGY IN SWELLING COMBINING ELECTROSTATIC CALCULATIONS AND EXPERIMENTS

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Clays have an important play for most industrial applications because of adsorption properties for ions or water molecules. In the case of nuclear waste storage, clay show interesting properties for confinement: swelling and cation retention. In our study, we propose to study the hydration properties for montmorillonites.

To understand the reactivity of swelling clays during hydration, it is important to be able to understand the different steps of the hydration process. Most experiments allow determining hydration sequence, but few energies values are directly accessible.

Using immersion data, we propose to determine values for hydration energies for cations and surfaces according to values of immersion data and swelling energies determined from electrostatic considerations and Hamacker constant (Van der Waals contribution). The surface energy for a lamellar solid at the dry state is defined by the splitting energy of clay layers. Electrostatic calculations, based on the determination of partial charges by equalization of electronegativities are used to evaluate surface energy values for each type of clays (kaolinite, serpentine, talc, montmorillonites saturated with alkaline cations, chlorites). We obtain an evolution of the surface energy as a function of the structure complexity and as a function of the charge. The comparison between immersion data and prediction for immersion values illustrates the role of the hydration energy of cation. These values are the starting point for (i) the determination of hydration energies for cations and surfaces in swelling clays and (ii) the determination of the reactivity sites in the montmorillonite. Our study is limited to alkaline cations[1].

Experimental data obtained on the MX-80 samples using thermal analysis and electrical conductivity are in good agreement with our theoretical values[2].

**Keywords:** Hydration Energies, Montmorillonites, Electrostatic calculations.

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# LARGE-SCALE MOLECULAR DYNAMICS REVEALS NOVEL PROPERTIES OF LAYERED NANOMATERIALS

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Large-scale atomistic simulations, which we define as containing more than 100 000 atoms, are becoming more commonplace as computational resources increase and efficient classical molecular dynamics algorithms are developed. Using this new technology, combined with unprecedented resources through geographically diverse computational grids (the US TeraGrid, the UK National Grid Service and EU DIESA grid) we have simulated several montmorillonite clay systems containing up to approximately ten million atoms. At such sizes, the dimensions approach those of a realistic clay platelet. This considerably extends the spatial dimensions of microscopic simulation into a domain normally encountered in mesoscopic simulation. The simulations exhibit emergent behaviour with increasing size, manifesting collective thermal motion of clay sheet atoms over lengths greater than 150 Å. This motion produces low-amplitude, long-wavelength undulations of the clay sheets, implicitly inhibited by the small system sizes normally encountered in atomistic simulation. The thermal bending fluctuations allow us to calculate material properties, which are hard to obtain experimentally due to the small size of clay platelets. Similarly, we have investigated the thermal bending undulations of layered double hydroxide (LDH) sheets, intercalated with chloride ions, various organic polymers and DNA.

Using large scale molecular dynamics, we have investigated the effects of montmorillonite clay filler on poly(ethylene) glycol in the formation of clay-polymer nanocomposites. The simulations allow us to determine the difference between polymer adsorbed on the surface of the clay and that more remote from it. All polymers arrange themselves in layers parallel to the surface, each layer being approximately 4 ˚ thick. We find the polymer conformation of the innermost layer is distinct, due to complexation with the counterions found near the charged clay surface. We perform non-equilibrium molecular dynamics simulations by imposing a strain on the model and analysing the stress response. By partitioning the stress response into clay and different polymer layers, we find that the inner-most polymer layer has a much higher Young's modulus than the remaining layers in the direction of the polymer chains. From these large-scale molecular dynamics simulations, we have constructed preliminary coarse-grained MD simulations of a stack of clay sheets immersed in polymer, which allows 1-2 orders of magnitude increase in simulation time and size for the same computational cost, putting the simulations firmly in the mesoscopic regime.

# MATHEMATICAL CLASSIFICATION AND GRADING OF CLAY MINERALS

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Mathematical methods are illustrated for classifying clay minerals and deriving their ‘quality’ or grade from composition data. Using a statistically derived computational procedure, classification scores are obtained from the values of total layer charge, K content, octahedral Al and Mg, tetrahedral and octahedral charge. The computation identifies if a mineral is a clay mica, smectite or vermiculite. Then another set of equations identifies the mineral as illite, glauconite, celadonite, montmorillonite, beidellite, nontronite or saponite. Quantification of the differences between minerals of the same sub-group is possible from a fuzzy mathematical relation. Clay minerals can, thus, be graded. For example the ‘montmorillonite-ness’ of a montmorillonite is obtained on a scale of 0 to 1. The degree of ‘resemblances’ between minerals can also be derived. Thus a quantitative measure of the ‘illite-ness’ of a beidellite can be obtained. The method also helps to quantify the extent of transformation of one mineral to another.

**Keywords:** Classification, Grading, Clays.

# AB-INITIO AND DENSITY FUNCTIONAL THEORY STUDIES OF HYDRATED SELENITE CLUSTERS

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Due to their ability to inhibit the migration of both cationic and anionic contaminants, there exists substantial interest in organically modified clay minerals as a potential geo-engineered bareer in nuclear waste repositories. Such systems could substantially slow down the entrance into the biosphere of long-lived dose-relevant radionuclides like e.g. $^{79}$Se, which exists mainly in anionic form in aqueous solutions.
In order to enable eventual classical Monte Carlo studies of the sorption of selenite $^{79}SeO_3^{2-}$ from aqueous solution on organically modified clay minerals using a locally developed code [Meleshyn A. and Bunnenberg C., 2007] [Meleshyn A., 2008], quantum chemical calculations of the hydration shell of selenite have been conducted.
The structures of the molecular anion selenite as well as hydrated selenite clusters $SeO_3^{2-}(H_2O)_n$, $n = 1 - 6$, have been obtained using density functional theory (DFT) employing the common hybrid density functional B3LYP along with diffuse basis sets of up to triple zeta quality. Solvation energies have been studied using both second order Moller-Plesset perturbation theory as well as DFT methods.
The interaction of the $SeO_3^{2-}$-ion with the water molecules of the $SeO_3^{2-}(H_2O)_6$ cluster has been parametrized at a post-Hartree Fock level in order to extract force field parameters for intermolecular interactions, i.e. Coulomb- and van der Waals-forces, to be used for Monte Carlo calculations.

**Keywords**: Hydrated selenite clusters, Quantum chemical calculations, Interaction parametrization.

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# MINERALOGY & CRYSTALLOGRAPHY

## SESSION MC7

## *Structural Characterization of Lamellar Compounds*

# VISUALIZATION OF STACKING DISORDER IN KAOLINITE BY HRTEM

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Kaolinite, $Al_2Si_2O_5(OH)_4$, has been widely investigated because of its geological and industrial importance. Especially, the nature and degree of stacking disorder in kaolinite has been the subject of sustained interest. A number of quantitative models have been proposed to describe stacking disorder in kaolinite. At present, kaolinite stacking disorder is attributed primarily to two types of faults that include (1) disorder by alternative directions, $\boldsymbol{t}_1$ (approximately $-\boldsymbol{a}/3$) and $\boldsymbol{t}_2$ ($-\mathbf{a}/3 + \boldsymbol{b}/3$,) for layer shift between adjacent layers, and (2) the displacement of the vacant octahedral site in the dioctahedral 1:1 layer. XRD analyses by Plançon et al. (1989) suggested that the first type is dominant in many kaolinite specimens. Kogure & Inoue (2005) succeeded to identify the stacking disorder directly from high-resolution transmission electron microscopy (HRTEM) of kaolinite, overcoming the difficulty to record the HRTEM images due to rapid radiation damage. They investigated kaolinite of diagenetic origin and concluded that all structure defects were related to $\mathbf{t}_1$ and $\mathbf{t}_2$ interlayer shifts, in accordance with the conclusions of Plançon et al. (1989). However, it was not certain whether this result can be also applied to kaolinite specimens of other origins. Recently Johnston et al. (2008) examined various kaolinite specimens using low-temperature FTIR and reported that the spectrum from sedimentary kaolinite (Capim, Brazil) shows several bands that can be assigned to dickite and nacrite, in addition to those of kaolinite. HRTEM images from this specimen indicate that stacking faults are mainly caused by the coexistence of $\mathbf{t}_1$ and $\mathbf{t}_2$ interlayer shifts, and this type of disorder was observed as (1) isolated stacking faults (for instance, insertion of $\boldsymbol{t}_2$ shift in an ordered matrix with $\boldsymbol{t}_1$ shift) as well as (2) interstratification of two kinds of multi-layer blocks with $\boldsymbol{t}_1$ and $\boldsymbol{t}_2$ shifts. In contrast, the diagenetic kaolinite reported by Kogure & Inoue (2005) contains only defects of the second case. Besides, disorder induced by the displacement of the octahedral vacancy site in the dioctahedral 1:1 layer was occasionally observed in Capim kaolinite. Furthermore, SAED patterns along the $Y_i$ ([010], [310] and $[3\,\bar{1}0]$) directions sometimes have extra spots and/or streaks, suggesting incorporation of stacking sequences with (±60°, 180°) layer rotation and/or $(0, \pm\boldsymbol{b}/3)$ layer shift. This paper reports these HRTEM results to elucidate the nature of stacking disorder in kaolinite and its relation to the XRD patterns and geological origins.

**Keywords**: Kaolinite, Stacking disorder, High-resolution transmission electron microscopy.

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# INFRARED SPECTROSCOPY OF CLAY MINERALS FROM FIRST-PRINCIPLES

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Infrared (IR) spectroscopy is widely used to investigate the finely divided minerals occurring in soils and weathering environments. The resulting information ranges from the detection and identification of specific or minor mineral constituents to the determination of the stacking order and ordering pattern of substituting cations in clay minerals (Farmer 1974).
However, the straightforward interpretation of IR spectra is often difficult, in particular when considering divided and poorly ordered minerals, such as clays. It is experimentally difficult to measure the polarization properties of small particles and there is not always an evident relationship between the microscopic atomic structure and the vibrational modes observed with IR spectroscopy. An additional complexity of powder spectra also arises from the influence of particle shape on the infrared spectra.
The first-principles calculations of vibrational spectra thus represent an ideal tool to establish unambiguous relationships between the IR spectrum and the microscopic structure of minerals. T his is done by computing the phonon vibrational modes of the mineral from density functional perturbation theory. The same method is also used to obtain the low-frequency dielectric tensor and thus determine the influence of the shape of particles on the IR spectrum (via long-range electrostatic interactions). Combining first-principles calculations of crystal properties with a model taking into account the experimental and sample-dependent parameters, it is possible to significantly improve the comparison between theory and experiment. Several applications of this approach will be presented, including the interpretation of the OH spectrum of kaolinite-group minerals and Al hydroxides (Balan *et al.* 2005, 2006, 2008) and the investigation of radiation effects in clay minerals (Fourdrin *et al.* 2009).

**Keywords:** Infrared spectroscopy, Ab initio, OH.

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# INTERLAYER ORGANIZATION OF WATER IN SYNTHETIC SAPONITE BY COMBINATION OF MOLECULAR SIMULATION AND X-RAY/NEUTRON DIFFRACTION PROFILE MODELING

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As a function of relative humidity (RH) under non-saturated conditions, smectite typically shows a stepwise hydration behavior corresponding to the intercalation of 0, 1 or 2 discrete interlayer sheets of water molecules. Recent developments in X-ray diffraction (XRD) profile modeling provides increased sensitivity in characterizing the structural heterogeneity of smectite which results from the coexistence of different layer types within smectite crystals. It is also possible to refine the distribution of water molecules within the different types of expandable layers. The hydration behavior of two synthetic smectites (Na-saponite) with different layer charges (0.4 and 0.7 per $O_{10}(OH)_2$) was studied by recording XRD patterns as a function of RH from an almost saturated atmosphere (92% RH) to a dry one (~ 0% RH). Calculated XRD patterns were fitted to the data using a trial-and-error procedure and structure models were derived for hydrated smectite at each RH value. The results were then used to determine the water vapor conditions at which almost homogeneous mono-hydrated and bi-hydrated states could be obtained for each samples. Additional neutron diffraction experiments were performed on both $H_2O$ and $D_2O$ saturated specimens (D4 instrument, ILL, Grenoble) and used to increase the sensitivity of the modeling approach regarding the distribution of water molecules, especially hydrogen atoms, by taking advantage of the different cross-sections of hydrogen and deuterium and of the invariant scattering cross-sections over the entire angular range. The layer thicknesses derived from XRD profile modeling were used also as constraints to build a simulation box for Grand Canonical Monte-Carlo simulations (GCMC - $\mu$, V, T). The profiles of interlayer species obtained from GCMC simulation were then introduced for calculation of X-ray and neutron diffraction profiles and the amount of interlayer water was compared to that determined from gravimetric water sorption isotherms. The close correlation between numerical simulation and the diffraction methods provides i) a better understanding of the organization of water and cations in smectite interlayers, and ii) an experimental basis for discriminating among the diverse potentials and models used for microscopic simulations of confined water.

**Keywords**: Smectite, X-ray diffraction, Neutron diffraction, Grand Canonical Monte-Carlo simulation.

# ALKALI METAL ACETATE INTERCALATION OF KAOLINITE OBSERVED BY ATR-FTIR SPECTROSCOPY

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The intercalation of kaolinite with small polar molecules like urea, dimethylsulfoxide or potassium acetate is a widespread technique for the identification of kaolinite in the presence of other clay minerals. Such intercalation complexes are formed when the reactive guest molecules enter the interlayer spaces and expand the silicate layers. This pre-expansion with acetates can be used to modify kaolinite for the interaction with large polymer molecules like polyethylenglycol forming kaolinite-polymer nanocomposites.

Kaolinite is easily intercalated with potassium acetate and intercalation often approaches 100 % (Frost et al. 2001a). Similarly the intercalation with cesium and rubidium acetate occurs at high rates. However X-ray diffraction reveals the same increase in the *d*001 spacing of kaolinite from 0.7 nm to 1.4 nm for all three alkali acetates, independent of the ionic radius of the metal cation. FTIR ATR spectra of potassium-, rubidium- and cesium-acetate intercalated kaolinites are strongly affected by the migrating molecules especially in the OH-stretching region at ~3650 $cm^{-1}$ and in the Si-O stretching region at ~1000 $cm^{-1}$. Besides strong intensity decreases of all four OH-stretching bands (3693, 3668, 3650 and 3621 $cm^{-1}$) in intercalated kaolinites one new band occurs at ~3605 $cm^{-1}$ in all samples, this vibrational mode slightly shifts to 3600 $cm^{-1}$ with ongoing intercalation time. In potassium acetate intercalated kaolinite a small additional band occurs at 3590 $cm^{-1}$ after 30 hours of treatment time. The differences between the three intercalates are not pronounced in this spectral region because they display the interaction between the acetate C=O groups and the hydroxyls of kaolinite. These bonds are not affected by the metal cation of the acetate molecule, but rather by the amount of water molecules within the interlayer (Frost et al. 2001b). In contrast, the spectral changes in the Si-O stretching region depend on the migration of potassium, rubidium and cesium into the pseudohexagonal holes within the Si-O sheet. All spectra show band shifts to higher wavenumbers at 1026, 1000 and 936 $cm^{-1}$. Additionally, new bands occur at ~1114 and ~900 $cm^{-1}$.

**Keywords**: kaolinite, acetate intercalation, ATR FTIR spectroscopy.

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# CRYSTAL STRUCTURE OF BIRNESSITE: IMPACT OF pH AND LAYER CHARGE ORIGIN

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Birnessite is a lamellar manganese oxide whose sheets are made of edge-sharing Mn octahedra. Hydrated cations located in the interlayer region insure structural cohesion and compensation of the layer charge arising from the coexistence of the heterovalent Mn cations or from the presence of octahedral vacancies. Despite its low natural abundance, birnessite is ubiquitous in nature and is found to be a sink for numerous contaminants such as heavy metals (Zn, Pb, Cd, U …). The reactivity of birnessite is directly related to its surface area and layer charge deficit. The structural origin of this charge has direct consequences on the redox properties of birnessite, on its cation exchange and adsorption capabilities, as well as on its structural stability as a function of pH, thus impacting directly its long-term efficiency in the retention of the contaminants. Because of its unique behaviour, natural birnessite draws attention for its potential use in the reclamation of contaminated soils or water resources. However, the highly defective structure of natural birnessite can complicate the understanding of the adsorption mechanisms at the molecular level. A great effort has thus been devoted to unravelling the detailed structure of synthetic analogous and polytypic variants. The combination of chemical analyses, X-ray and electron diffraction and EXAFS spectroscopy has allowed demonstrating the direct link between crystal structure and the origin of the layer charge. In addition, it was shown that the charge origin is a key parameter for the stability of the crystal structure when the pH becomes acidic, and therefore has an important impact on its exchange and/or adsorption properties.

**Keywords:** Birnessite, X-ray diffraction, EXAFS.

# MODELLING X-RAY DIFFRACTION PATTERNS OF MIXED LAYERS BEYOND NEWMOD

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Modelling of experimental X-ray diffraction (XRD) patterns represents the optimum, and at present the sole, quantitative method allowing the structural characterization of mixed-layer phases. However, the limited availability of calculation routines has limited the use of this approach despite its interest for the clay community at large.

Routines allowing the calculation of diffraction effects from mixed layers were first written about forty years ago simultaneously by different groups over the world. They were popularized later by the wide availability and the user-friendly character of Newmod, despite its intrinsic limitations. Over the last decade, modelling of experimental XRD patterns has thus relied essentially on the matrix formalism described in details by Drits & Tchoubar (1990) so as to overcome these limitations. In particular, using a trial-and-error fitting approach, the multi-specimen method has allowed unravelling the actual structure of both synthetic and natural samples, including complex parageneses found, for example, in diagenetically altered shales samples. Such detailed modelling of experimental XRD data allows for a semi-quantitative phase analysis of the clay fraction including both discrete and interstratified clay phases in addition to their detailed structural characterization.

The new program includes all enhancements that proved necessary in recent studies, but no coupling with a minimization routine. The main improvement concerns however the graphic user interface that allows visualization of the data and of calculated patterns, and provides statistical assessment of the fit quality. Discrete and interstratified phases, whose relative proportions are optimized, may be combined to fit the data and optimized independently. An additional interface has been developed to ease the calculation of complex mixed layers for the non expert user. The possibility to modify all structural parameters, and to virtually calculate any structure, is however maintained for advanced users. The abundance of "unusual" mixed layers described recently in clay parageneses, together with the multiple improvements to the description of elementary layers, made this option essential to investigate the structures of mixed layers, and more generally of lamellar structures, with a renewed perspective.

**Keywords**: X-ray diffraction, Interstratification, Profile fitting.

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# X-RAY VIEWS OF THE DEFECT STRUCTURE AND CHEMISTRY OF LAYERED ENVIRONMENTAL NANOPARTICLES

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Major goals of environmental science are to control mobility of toxic elements and to remediate contaminated soils, sediments, and subsurface waters. These goals cannot be met without first having in hand a fundamental understanding of the elemental composition, defect structure, and surface properties of environmental nanoparticles. Key problems are their low dimensionality, short-range order and high density of defects, the multiplicity of reactive surface sites and bonding mechanisms of impurities, and the partitioning of elements into coexisting organic and inorganic phases. In most cases, the information sought can be obtained by application of synergistic synchrotron-based X-ray techniques, including microfluorescence (micro-SRXF), microdiffraction (micro-XRD), high-energy scattering (HEXS), and microspectroscopy (micro-EXAFS), and data modelling with meaningful structure models. In this approach, micro-SRXF is used to map trace contaminants among coexisting constituents in a natural matrix, thus determining their distribution and relative abundance with unrivalled sensitivity. Then, micro-XRD, complemented by powder XRD and HEXS, is employed to identify nanocrystalline minerals and, more importantly, to determine the nature of structural and chemical defects (stacking faults, cationic and anionic vacancies and occupancies, site occupation of impurities, stoichiometry) through modelling of their scattering properties. Finally, micro-EXAFS gives the uptake and complexation mechanism of trace contaminants by individual constituents. Since the distribution of trace elements is heterogeneous on nanometer to micrometer length scales and nanoparticles are generally aggregated in environmental systems, the combination of these three microscopic techniques provides just the tool needed to scrutinize the nature and fundamental properties of environmental matter. This new kind of hybridization of experimental and modelling approaches to the characterization of natural nanoparticles will be illustrated with examples that show its potential for expanding our knowledge in environmental science.

**Keywords**: Nanoparticles, Layer minerals, Defective structure.

# DO I-S MIXED-LAYER MINERALS INFLUENCE THE WORKABILITY OF TWO CERAMIC CLAYS FROM WESTERWALD, GERMANY?

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The ceramic industry requires tailored solutions to enhance the workability and performance of clays. A new interdisciplinary approach is the development of processing technologies for raw clay material driven by microbial reactions. In this context two ceramic clays with different extruding behaviour, named W1 and W2, from Westerwald, Germany, were investigated. The phase content was determined for both bulk material and several grain size fractions by X-ray diffraction (XRD) and Rietveld analysis. Kaolinite, illite, muscovite, quartz, orthoclase, plagioclase, rutile, smectite and illite/smectite mixed-layer minerals were identified. The quantitative phase content was crosschecked with the chemical composition by X-ray fluorescence (XRF). First results showed that W1 and W2 have nearly the same mineralogical and chemical composition. However, investigation of the <0.6 µm size fraction revealed differences in the composition of 2:1 layer silicates. The percentage of smectite layers in I-S mixed-layer minerals and the amount of illite and smectite in a physical mixture were estimated by calculation of one-dimensional XRD patterns (NEWMOD, SYBILLA). Best results were obtained by describing W1 as physical mixture of an illite-rich I-S (I>90%) and pure smectite, whereas W2 is characterized by a higher smectite percentage in the I-S phase.

Mineralogical results together with organochemical and microbiological results - which will be presented in a parallel contribution (Krolla-Sidenstein et al., 14ICC) - indicate that coupled mineralogical-biological processes do influence the workability of ceramic clays.

**Keywords**: Ceramic clays, Mixed-layer illite/smectite, Microbiology.

# SOFTWARE FOR AN ASSISTED DETERMINATION OF THE STRUCTURAL PARAMETERS OF THE MIXED-LAYER PHYLLOSILICATES

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The structural determination of a mixed-layer mineral (MLM) is classically derived from the modelling of its XRD patterns. This modelling is preceded by the following steps: 1) choice of mixed layer model, 2) setting up of the formalism for the calculation of the corresponding XRD intensities, and, 3) design of a computer program for these intensity calculations. The software is then run with different sets of structural parameters to get the best fit between the experimental and calculated intensities. This trial-and-error method used until now is time-consuming, even for R1 two-component MLM (e.g. I-S) for which all structural parameters of the components (atomic composition, atomic coordinates, *d*-values) are assumed to be known, and only two stacking parameters remain to be determined: the proportion of one component, and one junction probability. The trial-and-error method is more complicated for a three-component MLM structural determination (e.g. I-S-V) requiring at least two component proportions and four junction probabilities, with additional complications when more structural parameters are considered, such as the iron content of a component along with associated changes in layer *d*-spacing.

The purpose of this work is to present a computing tool that intends to automate the determination of the structural parameters. This tool associates the computer program described in the step 3 with a legacy general purpose non-linear least square program and a graphic user interface. Because the direct calculation is complex, a finite difference method is used to calculate the needed partial derivatives.

The user proposes a first approximation of the structural parameters under study. Then the software determines a set of parameter increments improving the fit between the experimental and calculated intensities. This incremental process is repeated until a convergence criterion is reached. The software enables to 1) weigh properly the so called error equations, and check correlations and error propagation, 2) lock or set free a subset of parameters as required to improve convergence and 3) follow and relax the iterations, with the help of a visual feedback of the calculations. This interactivity is often needed by non linear problems with many parameters (as in Rietveld refinement). All calculation steps and relevant covariance and correlation matrices can be checked on plain ascii files.

# MINERALOGY & CRYSTALLOGRAPHY

## SESSION MC8

## *Modeling diffraction effects from layered systems and nanomaterials*

# STRUCTURE/MICROSTRUCTURE ANALYSIS OF NANOCRYSTALLINE AND LAYERED SYSTEMS

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In the powder diffractionist's life it is not infrequent to meet patterns showing unexpected or unexplained features such as odd profile shapes or anisotropic line profile broadening.

Even apparently well-behaving data lead sometimes to questionable refinement results (e.g. unexpected polymorphism in transformations, unrealistic thermal parameters) in which materials' physics contrasts with the hypotheses on which the analysis method is based (e.g. perfect three dimensional lattice).

Complementary information is usually needed in those cases, together with new analysis tools able to cope with the real physical environment in which the problem is framed. A couple of such tools are the Whole Powder Pattern Method that can provide microstructure information in simple cases, and the DIFFaX+ approach, able to deal with traditional, layered/interlayered and modular structures showing a local or global reduction of the lattice symmetry due to the presence of defects.

Basics and examples of both methods will be shown and commented.

**Keywords:** WPPM, microstructure analysis, DIFFaX+.

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# POLYTYPISM AND DISORDER IN LAYERED DOUBLE HYDROXIDES

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The diffraction of X-rays by a crystalline solid yields a number of sharp Bragg reflections corresponding to the different d-spacings of the solid. The broadening of peaks in the PXRD pattern beyond what is expected from instrumental factors can arise among other factors due to (i) crystallite size effects and (ii) structural disorder. The anisotropy of bonding within a layered solid creates room for the inclusion of a number of types of structural disorder, important among these, being stacking faults. The line broadening caused by structural disorder has to be first discounted before estimates of crystallite size are made by applying the Scherrer formula. We first show how by using the Brass suite of programmes (http://www.brass.uni-bremen.de), the effect of structural disorder is distinguished from the effect of crystallite size. We use the layered double hydroxide (LDH) of Mg with Al as an illustration.

In a simple layered solid such as graphite, where the layer is one-atom thick, the stacking faults are simple. In a LDH, the layers are three-atoms thick and the stacking faults are diverse. The local structure of the stacking faults resembles the stacking patterns of different polytypes that are theoretically possible among the LDHs (Ramesh et al., 2006). This resemblance becomes a basis for the classification of stacking faults. DIFFaX simulations (Treacy et al., 1991) help in the quantification. Laboratory prepared LDHs are thereby shown to be intergrowths of the 3R1 and 2H1 polytypes (Radha et al., 2005). These stacking faults conserve enthalpy and contribute to the thermodynamic stability by enhancing disorder. The stacking faults are incorporated during crystal growth and, once incorporated, cannot be eliminated (Bellotto et al., 1996). This author has been greatly inspired by the work of Bookin and Drits (1993).

**Keywords:** LDHs, Stacking faults, DIFFaX simulations.

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# ONE DIMENSIONAL STRUCTURE OF EXFOLIATED POLYMER-LAYERED SILICATE NANOCOMPOSITES: A POLIVYNYLPYRROLIDONE (PVP) CASE STUDY

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The classical modeling of powder X-ray diffraction patterns of lamellar structures is applicable only to periodic or quasi-periodic structures. For non-periodic structures another approach is necessary. X-ray diffraction patterns of non-periodic structures contain relatively small amount of information, therefore some initial assumptions are necessary. In case of an exfoliated polymer-layered silicate nanocomposites it is possible to assume the chemical composition and the thickness of the clay layer but the structure of polymer remains unknown. A new approach, which can be used to solve the structure of the polymer is proposed. This approach is based on modeling of $LpG^2$ factors recorded from oriented samples in order to obtain the one dimensional structure of polymer.

In case of polivynylpyrrolidone (PVP) adsorbed on smectite it was found that, although $LpG^2$ factors for various smectites are quite different, the structure of polymer is not affected by the charge of smectitic layer, nor by the location of this charge in the tetrahedral or octahedral positions. There is an enhancement of the polymer concentration at distances closer to the clay layer, and it seems that PVP chains that are directly bonded to the surface are more rigid, while the outer parts - more flexible. It was also possible to obtain the thickness of the polymer layer adsorbed on the surface. The generalized configuration of PVP on smectite can be used as a model for other surfaces of smectitic character, e.g. the surface of illite fundamental particles.

# STRUCTURALLY BASED MODELLING OF THE X-RAY DIFFRACTION PATTERNS OF ILLITE/SMECTITE MIXED LAYER MINERALS WITHIN THE RIETVELD METHOD

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Recently, the Rietveld technique becomes a standard tool for quantification of complex mineral mixtures. Therefore, a structurally based modelling of stacking disorder is necessary to characterize clay minerals and quantify clay bearing rocks. Simple anisotropic line broadening models based on standard unit cells are unable to fit the diffraction patterns of mixed-layered structures. The recursive calculation of diffraction intensities (Treacy et al., 1991) opens an effective way to fit the patterns of disordered and interstratified lamellar structures. Inside the Rietveld approach, a definition of an extended supercell is necessary to approximate the statistical character of mixed-layered systems. This is possible by a combination of the single layer approach (Ufer et al., 2004) with the recursive calculation (Treacy et al., 1991). Instead of a hard coding of the mathematical formulations, the definition of the translational matrix as well as the entire recursive calculation were formulated within the "structure interpreter" language of the Rietveld program BGMN (Bergmann et al., 1998). This was possible because of the access of the complex structure factor within the program and the built-in function to solve equation systems. Thus, the BGMN structure interpreter language is flexible to create models containing different layers as well as different kinds of stacking faults and ordering.

Structural and order/disorder parameters were refined for several illite/smectite mixed layered minerals from conventional laboratory X-ray powder diffraction data. These testing materials vary in their proportions of smectitic and illitic layers, their degree of long range ordering of the illite/smectite sequences, and the nature of rotational disorder. It is shown that this new approach is flexible enough to model different degrees of ordering, even in the presence of additional components. Therefore, it is suitable for QPA.

**Keywords**: Rietveld refinement, Stacking disorder, Illite/smectite.

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# PARAMETRIC FITTING WITHIN THE NEWMOD ARCHITECTURE: SIMPLEX FITTING OF XRD PROFILES OF INTERSTRATIFIED PHYLLOSILICATES

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NEWMOD© was developed by R. C. Reynolds, Jr., particularly for the study of two component interstratifications of clay minerals (Reynolds 1989). One dimensional X-ray diffraction (XRD) profiles of an interstratified system of two clay minerals can be simulated using NEWMOD, given a set of parameters that describe not only instrumental factors and the chemical composition of the system, e.g., the concentration of Fe and interlayer cations, but also, more importantly, structural parameters, e.g., proportions of the two components, the nature of ordering, and crystallite size distribution. NEWMOD has served as the primary tool for quantitatively evaluating interstratified clay minerals for more than twenty years. However, a significant drawback to the NEWMOD approach is that analysis is done by forward simulation, making it sensitive to user input, and it has not been possible to extract information in a reverse manner using automated fitting. Other shortcomings with the hydrated smectite structure models were recently discussed by Ferrage et al. (2005). The program SMOD, was developed by incorporating recent progress on the structures of clay minerals into a user-friendly graphical user interface (GUI), thereby greatly facilitating automated fits to observed XRD data.

The most significant enhancement to parameter fitting in SMOD was accomplished by the development of an optimization routine using the Simplex method. A genetic algorithm (GA) was first introduced by Pevear and Schuette (1993) for parameter fitting within the NEWMOD architecture. Compared with the GA methodology, the Simplex method yields results in a deterministic way rather than based on random evolution under prescribed evolutionary rules. In addition, the Simplex method has significant advantages over the least-squares method in both its ability to adjust integer parameters and in calculation time. As a result, the Simplex method in SMOD is superior for fitting XRD profiles of interstratified phyllosilicates and can effectively eliminate operator bias.

**Keywords:** NEWMOD, X-ray diffraction, SIMPLEX.

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# NANO & POROUS MATERIALS

**NM1 • FUNCTIONAL HYBRID NANOFILMS**

**NM2 • INDUSTRIAL APPLICATIONS OF NANOCLAYS**

**NM3 • MESOPORUS SILICA AS MOLECULAR SIEVES**

**NM4 • METAL NANOPARTICLES CATALYZED ORGANIC SYNTHESIS**

**NM5 • NATURAL ZEOLITES: FROM GENESIS TO APPLICATIONS**

**NM6 • POLYMER-CLAY NANOCOMPOSITES: ADVANTAGES, PROPERTIES AND USES**

**NM7 • POLYMER-CLAY NANOCOMPOSITES: PREPARATION TECHNIQUES AND THEORETICAL FORMULATIONS**

**NM8 • SELF-ASSEMBLY FROM CLAY PARTICLES: FROM NANO TO MACRO**

# NANO & POROUS MATERIALS

## SESSION NM1

## *Functional Hybrid Nanofilms*

# LINEAR AND NONLINEAR OPTICAL PROPERTIES OF COMPOSITES CONSISTING OF CLAYS AND DYES

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Nonlinear optical (NLO) materials are the key materials for the fast processing of information and for dynamic and permanent optical data storage applications. Therefore, materials exhibiting large NLO coefficients are strongly desired. NLO coefficients of several organic materials are known to be three orders of magnitude larger than those of inorganic materials [1]. For practical NLO devices, however, only inorganic crystals are used, because it is very difficult to obtain an organic material suitable for an optical device in view of size and light-scattering.

We have developed fabrication techniques of composites consisting of clays and organic dyes of which the size and the extent of light-scattering are sufficient for NLO devices [2, 3]. Such composites are promising candidates of NLO materials in which the salient optical nonlinearities of organic dyes can be utilized. In the present paper, linear and nonlinear optical characteristics of such composites will be discussed. Hybrid Langmuir-Blodgett (LB) films consisting of a clay and nonamphiphilic organic dyes exhibit second-order NLO properties [2, 4]. The films can be fabricated making use of an aqueous dispersion of a clay exfoliated into single layers as a subphase instead of ultra-pure water. Since the surface of the clay is charged negatively, cationic molecules spread onto the surface of a clay dispersion are adsorbed onto the clay layers through electrostatic interaction. Owing to this interaction, a well oriented molecular array essential for a second-order NLO material can be realized, even when a non-amphiphilic organic dye is used as the guest molecule. Furthermore, the stability of the molecular orientation is considerably improved compared with that of conventional LB films [4]. Films fabricated under optimized conditions, by filtering a water dispersion of a clay-organic dye composite through a membrane filter, also exhibite superior NLO properties. A film fabricated by employing synthetic saponite and a diacethylenic dye was a prominent two-photon absorption material [3]. A composite consisting of synthetic saponite and a chiral metal complex shows characteristics of a quasi-phase-matchable optical second-harmonic generation device.

**Keywords**: Nonlinear optical property, Langmuir-Blodgett film, Two-photon absorption.

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# PHOTOELECTROCHEMICAL INDUCED UNDULATIONS OF CLAY FILM

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In this presentation the photoelectrochemical manipulation of $Ru(bpy)_3^{2+}$ to initiate changes in the macroscopic structure of thin montmorillonite films will be discussed. The technique makes use of the segregation of $Ru(bpy)_3^{2+}$ into confined domains within the clay. Alteration of the charge on the complex is accomplished by use of an electroactive planar waveguide. When the complex charge is altered two different events can be initiated: delamination of the overlying clay film or a capillary wave mechanism for dehydration of the overlying aquated clay. To the best of our knowledge this is the first time that the undulatory behavior predicted by computational models has been observed experimentally. The specifics associated with capillary wave dehydration are shown to follow standard theories for polymer thin films and provide a window into measurements on the surface tension of different domains within the clay film.

**Keywords:** Capillary Dehydration, Undulations, Photoelectrochemical Control, Planar Waveguide, Thin clay Films.

# CLAYS AS TEMPLATES FOR THE SYNTHESIS OF HIGHLY ORDERED TWO-DIMENSIONAL ORGANIC-INORGANIC HYBRIDS USING THE LANGMUIR BLODGETT APPROACH

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Much of the research effort concerning the nanoscopic properties of clays focuses on mechanical applications such as nano-fillers for polymer reinforcement. To broaden the horizon of what is possible exploiting the richness of clays in nanoscience, we developed a new bottom-up approach for the production of hybrid materials based on single and/or multi-layers of clay nanosheets as building blocks. Our method, based on combing self-assembly processes with the Langmuir Blodgett technique, uses the clay nanosheets as 2D template for reaction or grafting of a variety of guest species (in our case: $C_{60}$, $Ni_8$ molecular magnets, Prussian blue analogues) and allows for prefect layer-by-layer growth and control at the molecular level. We present a detailed study of this new approach with an emphasis on the crucial role of clays and illustrate the flexibility of our approach with T-dependant X-ray diffraction data, spectroscopic measurements, microscopy (AFM, STM), magnetic measurements of different new hybrid materials where clays act as structure directing interface and reaction media.

**Keywords:** Langmuir-Blodgett, Self-assembly, low dimensionality.

# PREPARATION OF AN ANION EXCHANGE MATERIAL BY IMMOBILIZATION OF IONIC LIQUID ONTO LAYERED OCTOSILICATE

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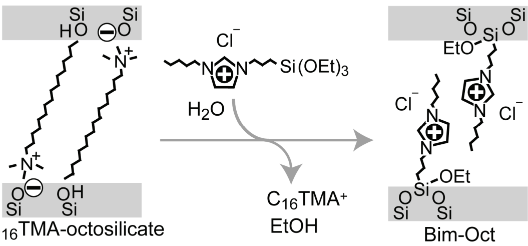
Layered anion exchange materials, such as layered double hydroxide (LDH), are of considerable interest because of their usability as adsorbents of drugs, dyes, biological molecules and oligosaccharides. However, the anion exchange capacity (AEC) of LDHs is limited because it depends on the degree of substitution of trivalent metal cations in the divalent metal hydroxides. Hata et al. reported the overcompensation of the interlayer charge of mica by intercalation of excessive polycations.[1] The concept of the interlayer charge reversal with organic species may lead to diverse compositional and structural design of layered materials. Here, we report the preparation of a layered anion exchange material through the immobilization of imidazolium cations on layered octosilicate. (Fig. 1)

Hexadecyltrimethylammonium-exchanged octosilicate was dispersed into toluene with 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride (BImCl), and the mixture was stirred for 1 day at 70 °C. After washing with hexane and acetonitrile, and drying for 1 day, the silylated material (BIm-Oct) was obtained.

The powder XRD peaks at 3.0, 1.5 and 1.0 nm assigned to a lamellar structure were observed for BIm-Oct. The $^{29}$Si MAS NMR spectrum showed the peaks assigned to $T^1$, $T^2$, $T^3$, $Q^3$, and $Q^4$ environments. The integral ratio of $Q^3/(Q^3+Q^4)$ was decreased from 1 to 0.18, suggesting that 82% of silanol groups were silylated with BImCl. The amount of immobilized BImCl was ca. 2 molecule/nm$^2$ on the silicate sheet (CHN analysis and TG-DTA). The adsorption capacities of BIm-Oct for an anionic prodrug (sulfasalazine) and dye (Orange II) were 1.7 mmol g$^{-1}$ (66 wt%) and 1.9 mmol g$^{-1}$ (66 wt%), respectively. In addition, a self-standing film (Fig. 2) was fabricated from BIm-Oct only.



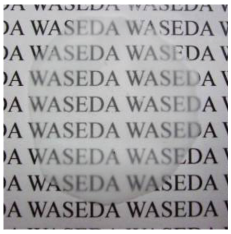


**Fig. 2.** Self-standing film of BIm-Oct

**Fig. 1.** Synthetic pathway of the layered material (BIm-Oct)

**Keywords:** Intercalation, Alkoxysilylation, Inorganic-organic hybrid.

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# CONTROLLING THE SURFACE PROPERTIES OF ULTRATHIN ORGANO-CLAY HYBRID FILMS FROM CATION-EXCHANGEABLE SURFACES TO ANION-EXCHANGEABLE SURFACES

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A smectite clay is exfoliated into negatively-charged elementary sheets with a thickness of 0.96 nm (clay nanosheets) in a dilute aqueous dispersion. When amphiphilic cations are spread at the air-clay dispersion interface, the clay nanosheets are adsorbed onto the floating mono-molecular layer of the amphiphilic cations by electrostatic interaction to form a hybrid clay monolayer. One of the interesting properties of the film is that the outer surface of the hybrid film transferred on a solid substrate has a cation-exchange capacity (CEC), because the positive charge density of the ammonium cation is lower than the negative charge density of the clay nanolayer. In addition, the CEC of the film can be controlled by changing the dispersion concentration. If the positive charge density of the cation is larger than the negative charge density of the clay, it is expected that the film surface has an anion-exchange property. This charge reversal has been impossible to realize for films of primary ammonium cations because of the equilibrium between the ammonium cations and the corresponding neutral amines.

In this work, the quaternary alkylammonium cations with long alkyl chains were employed: $CH_3(CH_2)_nN^+(CH_3)_3{\cdot}I^-$ , n=21, 25, and 29. When these water-insoluble ammonium cations were spread on the dilute clay dispersion at 2 ppm (mg dm$^{-3}$), the hybrid monolayers were formed. Their π-A isotherms and in-plane XRD patterns indicated that the alkyl chains lie down on the nanosheet and form an ordered structure due to the interaction between the long alkyl chains. This implied that the density of the cation was too low to realize the anion-exchange property.

Methanol was added in the clay dispersion (10 w%) to weaken the interaction between the alkyl chains in the floating monolayer. As a result, the density of the cations in the film was high enough to have an anion-exchange film, probably because the alkyl chains stand up on the nanosheets. Actually, the hybrid films prepared on the MeOH-mixed dispersions at 5 and 8 ppm adsorbed the anionic dye acid orange II. On the contrary, the hybrid films prepared on the dispersions at high concentrations (>15 ppm) adsorbed the cationic dye rhodamine 6G. In conclusion, the surface properties of the clay hybrid films of the quaternary alkylammonium cations with long alkyl chains can be controlled from being cation-exchangeable to being anion-exchangeable by changing the concentration of the clay dispersion.

**Keywords:** Langmuir-Blodgett Film, Quaternary Alkylammonium Cation, Clay Nanosheet.

# NANO & POROUS MATERIALS

## SESSION NM2

## *Industrial Applications of Nanoclays*

# NANOCLAYS AND MESOPOROUS NANOSILICATES: APPLICATIONS IN ENGINEERING POLYMER TECHNOLOGY

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Talc is the traditional cost-effective silicate mineral for the reinforcement of thermoplastic polymers, particularly polyolefins. Its importance as a thermoplastic filler is likely to continue into the future due in part to its low cost and recent technological advances that reduce the particle size of the mineral to the nanometric size domain. Smectite clays have the potential to out-perform talc as a filler for thermoplastics, particularly as gas barriers and as eco-friendly flame retardants, but applications in these later areas are limited in part by the need to chemically modify the basal surfaces of the nanolayers with organocations in order to achieve dispersion of the nanolayers in the polymer matrix. In addition to adding cost, organocations can function as thermally sensitive plasticizers and thereby compromise other desirable properties of the composite. These same considerations are relevant limitations for the use of organoclays in thermoset polymer systems.

Many of the disadvantages of organoclays as polymer reinforcing agents can be overcome by synthetic layered silicates (e.g., saponite) and mesoporous nanosilicates (e.g., MCM-41, MSU-H, SBA-15, among others). For instance, it is possible to modify the surface polarity of synthetic smectite clay through the strategic adjustment of the inorganic composition to achieve a layer charge and surface polarity suitable for dispersion of the nanolayers in the desired polymer matrix. Similar strategies can be used to achieve the dispersion of the mesoporous silicate nanoparticles in a polymer matrix without the need for an organic surface modifier.

Several examples of the limitations of talc and organoclays in comparison to synthetic clay and mesoporous nanosilicates for the reinforcement of thermoplastic polypropylene and thermoset epoxys will be discussed in this presentation. The comparison will show that synthetic clays and mesoporous silicates have significant competitive potential for commercial applications in polymer composite technology.

**Keywords:** Synthetic smectite clay, Mesoporous Nanosilicates, Polymer nanocomposites.

# INDUSTRIAL EUROPEAN APPLICATIONS OF CLAY-POLYMER NANOCOMPOSITES RESEARCH AND DEVELOPMENT OF NANOCLAYS

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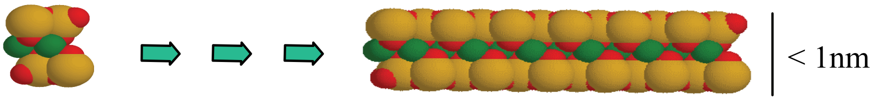
The wish to communicate on emerging subjects leads the material scientists to give different names to the same subject. For example, clay-polymer nanocomposites (CPN) are also considered as hybrid inorganic-organic nanocomposites where nanoclays are used as fillers. The major common denominator between several reviews and most of the recent focused papers interested on nanoresearch are the negatively or positively charged clay minerals which form a part of the class of 2D layered materials. Those concerned by this topic especially montmorillonite, and to a less extent kaolinite and sepiolite, belong to particularly 2D layered silicates.

Nanoclay: an inorganic nanopolymer



The growing interest to "nano" application area emerges recently after the beautiful pioneering results obtained by Toyota, on clay-nylon nanocomposite with remarkable mechanical properties. Since this time, the research on CPN attracts attention of many industrials interested by clay minerals as fillers to improve not only mechanical properties but also many other physical properties in different applications. However, it is interesting to note that clay scientists are involved in nanocomposites research since ever, ignoring that they are doing nanoresearch. Because clay minerals which have layer thickness (at least 1/3 dimension) at the nanometer scale, are considered by definition as nanominerals and as nanomaterials. Thus, a nanostructured mixture of clay minerals with any organic compounds such as polymers, leads to nanocomposites based on nanoclays.

Actually, it is well known and definitely recognized that nanoresearch is exponentially and exceptionally growing, but surprisingly effective commercial nanoapplications is far to follow this trend. What is the state of the art in established structure-properties relationship and what are the limits to commercial applications at the same level will be part of this talk.

The author will also try to update the various commercialised clay-polymer nanocomposites applications in Europe and particularly in France, through the patented literature and the accessible recent data.

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# DEVELOPMENTS FOLLOWED BY NCH

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A report of NCH; Nylon/Clay Mineral Hybrid (Usuki,1993), was followed by many proposals for nano-hybrid materials with organic polymers and clay minerals. The NCH, which was prepared by intercalation process (Fukushima,1988), have been attracted for their excellent gas-barrier properties beside mechanical properties (Yano, 1993), transparency, heat distortion property (Kojima,1993) and anti-flammability (Glimann,2000).

The gas-barrier effect has been one of the main targets in industrial applications. The barrier effect for oxygen permeation and transparency were attributed to apply the NCH-film for food packaging (Mori, 1997). A barrier property for fuel (Nakamura, 2002) is expected to use it in a fuel hose (Ube industry, 2007) or a fuel tank. A moisture proof acrylic or polyvinyl acetate resin coating with montmorillonite for wood, concrete or ceramic wall was reported by Toagosei Co., Ltd. 2003. Although an alternative diffusion for a blocked rout by silicate layers has been attributed for the barrier effect, molecular mobility of the polymer segment would also affect the permeability. The mobility is restricted by the influence from the inorganic layer surface.

Besides the phyllosilicate layer, other inorganic matters, such as fibrilliform sepiolite and imogolite (Yamamoto, 2006), oxide nano-sheets (Sasaki, 2002), layered double hydroxide; LDH, and nano-particles (DIC corp, 2008), have been proposed.

In-situ polymerization have been tried to alternate for the intercalation process. An organic-inorganic hybrid resin 〝CERANATER〞 developed by DIC Corporation (2008). An aqueous emulsion of acrylate resin with polysiloxane nano-particles is coated followed by cross-linked with Si-alkoxide to form a high weather-resistant, contamination resistance and adherability coating on metal walls. A bottom-up process, that is in-situ polymerization of inorganic and/or organic polymer, to form a hybrid has been offering a noble silica-polyamide hybrid; CERYLR, paper (DIC, 2000). Nano-size of the inorganic particle, high dispersion and strong interaction through Si-OH would be attributable for a low thermal expansion, high heat resistance property and high elastic modulus (Nakashima, 2008). The technology has been expanded polyamide-alumina, polyurea-silica, polyurea-alumina (Nakashima, 2008), and epoxy resin-silica hybrid (Arakawa Chemical Ind., 2008). These new materials have been expected to apply to coating, adhesive and sealant. Although we could have no doubt whatsoever that the organic-inorganic hybrids should innovate a material industry, we have only vague discrimination between hybrid, mixture, and composites. Organic-inorganic interfaces and interactions are key science for a surge of technical innovation.

**Keywors:** Hybrids, Organic polymer, Gas-barrier, In-situ polymerization.

# INDUSTRIAL APPLICATIONS OF NANOCLAYS

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Polymer/clay nanocomposites have become a leading industrial use of nanoclays. Three key aspects of this are the mechanism, methodology and measurement techniques. The commercial importance of polymers has lead to an increased interest in investigation of polymeric material nanocomposites of sizes between 1 to 100nm. Nanocomposites are materials that contain nanofillers, or fillers of nanometer dimensions. The successful synthesis of nylon–clay nano- composites ushered in nylon nanocomposites that could attain high modulus, heat distortion temperature, dimensional stability, impermeability, and strength with only a few percent modified clay nanofillers. The nylon–clay nanocomposites have since been commercialized and were utilized for automotive timing-belt covers and packaging barrier films. Commonly used 2:1 phyllosilicates include hectorite, saponite, montmorillonite, and synthetic mica. In particular, naturally occurring montmorillonite with CEC ranging from 0.9 to 1.2 meq/g, depending on the mineral origin, is most frequently used and was the type employed in the initial nylon–clay nanocomposites. Small amounts of well-dispersed natural clay can lead to environmentally friendly and inexpensive plastic composites with improved specialized properties. Addition of clay can make plastics less permeable to liquids and gases; more flame retardant and tougher. Lower permeability can make plastics like PET, the standard plastic used in soft drink bottling, suitable for bottling beer or wine. Adding clay to polymer blends is not a simple process as polymers and clays mix about as well as oil and water. However, if the clay is treated with an organic surfactant, a compound that allows the inert clay to mix with the polymers, much as soap allows oil and water to mix, the clays can be incorporated into the final product. The polymer clay blends, while containing only 1 to 5 percent clay, are actually nanocomposites. The addition of clay into the polymer blend does not alter the normal production and processing of the clayless polymer. New materials for car bodies may soon transform the auto industry. Auto engineers can mold these carbon-fiber-reinforced plastics into virtually any shape. The materials are both strong and light - increasing fuel efficiency and safety at the same time.

**Keywords**: Nanoclay, Polymers, Functional.

# GAS BARRIER PROPERTIES OF RUBBER/KAOLIN NANOCOMPOSITES

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Air-tightness is one of the most important properties for the rubber product such as inner tube and inner underlayer of tyre. Clay minerals with impenetrable lamellar structure are considered as the crude barrier nano-material. A kind of kaolin powder with 300-500nm average diameter and 20-50nm average thickness, was manufactured through combined intercalation-delamination techniques, and was applied into rubber by means of melt blending to form kaolin/rubber nanocomposite. The mechanical and gas barrier properties of rubber composite were tested according the national standard of China. The results show that the rubber composites filled with nanokaolin were found to have good mechanical properties, thermal stabilities, and elastomeric properties. Especially, the kaolinite flakes dispersed uniformly and in the nano-scale in the rubber matrix can notably reduce the permeability, and effectively improve the gas barrier property of rubber composite. The permeability of rubber has a great relationship with the rubber types, loaded amount of nanokaolin as well as temperature. The permeability of various rubbers filled with nanokaolin reduces 35%, 41%, 51% and 83% respectively for natural rubber (NR), ethylene-propylene diene methylene (EPDM), styrene butadiene rubber (SBR) and butyl rubber (IIR) compared to pure rubber, and decline with increasing loaded amount of kaolin, but increase as temperature rising.
The studies on XRD, IR and TEM for rubber composites showed that the good dispersion of nanokaolin and its parallel arrangement in rubber matrix, as well as the good interfacial interactions between nanokaolin and rubber chains give these rubber composites excellent processability, mechanical properties, and gas barrier properties.

**Keywords**: Nanokaolin, Rubber composite, Gas barrier.

# NANO CONFINED WATER IN CLAY MINERALS

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Kaolin-group minerals are among the most abundant and industrially important minerals on Earth. Halloysite, a naturally occurring hydrated polymorph of kaolinite, is emerging as an attractive material for use in a variety of industrial applications, which take advantage of the distinct nano-tubular morphology of this mineral as a reinforcing material in polymer nanocomposites, as well as a vehicle for the controlled release of drugs or enzyme immobilization.

From the perspective of surface chemistry, a unique attribute of hydrated halloysite is the presence of a confined monolayer of water between the siloxane and hydroxylated surfaces. Additionally, halloysite is typically characterized by a tubular or spheroidal meso-structure, leading to further organization of water molecules at the particle scale. Finally, the presence of some "free" water is apparently necessary to maintain the system fully hydrated.

While water plays a critical role in controlling the structure of halloysite, surprisingly, relatively little is known about the chemical and physical properties of water associated with halloysite. At the same time industrial applications of halloysite are limited by the presence of water on this strongly hydrophilic clay, making knowledge of the types of water and their properties critical to extend our ability to exploit halloysite as an industrial mineral.

The study presents an integrated experimental study of water on samples of halloysite which have been kept fully hydrated since collection, and samples prepared in the laboratory at different water contents. A novel application of low temperature differential scanning calorimetry is presented to identify and probe the nature of the three different populations of water molecules. In the fully hydrated halloysite, the calorimetry results show anomalies in the freezing and melting peaks with distinct peaks reflecting freezing of the bulk water and the capillary water confined inside the nano-tubular pores; the latter freezing process is observed to occur at temperatures as low as -37°C; upon re-heating two melting events are also observed, albeit in a much narrower temperature range. Air drying leads to the deintercalation of water but similar calorimetric curves are observed after rehydration of the clay. In all samples, a significant amount of water – as large as 16% w/w - is found not to freeze.

The calorimetric data are supported by: low temperature (~ 20 K) FTIR spectroscopy which shows clear changes that occur upon freezing in the vibrational bands of the water and of the clay itself; ATR-FTIR spectroscopy to study the nature of water in halloysite; and XRD for monitoring the loss of the interlayer water.

**Keywords:** halloysite, low temperature calorimetry, intercalation, meso-macroscopic superstructure

# DESORPTION FROM HETEROGENEOUS AND POROUS BODY BASED ON CLAY

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Adsorption is a transition of adsorbate molecules into a solid and porous adsorbent. Besides molecules, colloid particles, micro partials and ions can also adsorb. Desorption is a process opposite of adsorption and represents a transition of molecules from a solid adsorbent into a liquid or gaseous medium. The starting power of the process are different concentrations and the process is developing until the balance is achieved. If water is desorbed then it is a dehydration process.

In this paper the sorption characteristics of heterogeneous and porous materials based on clay are investigated, a small ball of clay-bentonite with addition of a filler and an additive: sand, polyphosphate, zeolite, water-glass and calcium hydroxide. Desorbed components are water, 95% ethyl alcohol and 50% acetic acid.

The aim of the work is to investigate desorption on a heterogeneous model of a porous body.

Bentonites are natural sorbents widely used in chemical processes. Due to their structure and composition, bentonites are very interesting to study. With the water loss, the mass of bentonites decreases for 8-15 % but they can also absorb water i.e. they can swell.

Experimental results show that no matter what the character of the mixture is, the process of ethanol desorption is much faster than the process of water or acetic acid desorption (which is logical taking into consideration the ethanol vaporization point (78,3 °C), water (100 °C) and acetic acid (118 °C). The presence of zeolite (porous stone) increases the desorption process. The ball mass in this case can be decreased to 75% of the starting mass. This phenomenon can be explained by great porosity of zeolite. The desorption process is slower with the mixtures that do not contain zeolite and 24 h later the ball mass decreases much less. The presence of polyphosphates in the mixture leads to the reduction of the desorption process. Polyphosphates bind water with stronger bonds, hydrates.

**Keywords:** Clay, Bentonite, Desorption.

# CLAY-POLYMER INTERACTIONS AND NANOCOMPOSITES

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The interactions of clay minerals with organic polymers enjoy wide applications in agriculture and industry. Indeed, it would be difficult to avoid using clay-polymer products in modern living as these materials occur in paper, plastics, and rubber goods (Theng, 1979).

In conventional 'microcomposites', the clay component consists of micrometer-size aggregates, and make up a substantial proportion (> 25%) of the system. Here clay is added as a filler or extender in order to reduce the cost, or improve the mechanical properties, of the product. In 'nanocomposites', on the other hand, the clay component seldom exceeds 5 vol%, while the nanoscale clay particles with a high aspect ratio (length/height > 300) are more or less dispersed in the polymer matrix.

Montmorillonite is the most widely used clay mineral species for the synthesis of polymer nanocomposites. Montmorillonite, however, is naturally hydrophilic, and hence "immiscible" with hydrophobic organic polymers. This surface-chemical incompatibility may be overcome by replacing the interlayer inorganic cations ($Na^+$, $Ca^{2+}$), initially present, with quaternary ammonium or phosphonium surfactants. When such organically modified montmorillonites ('organoclays') are incorporated into polymers, the resultant clay-polymer nanocomposites show substantially improved mechanical, thermal, and gas-barrier properties without much loss of optical clarity. The demand for clay-polymer nanocomposites for industrial applications (packaging, automotive, construction, coating) is estimated to be worth two billion dollars.

Clay-polymer nanocomposites may be prepared by one of three methods: (1) direct intercalation of preformed polymers from solution or melt; (2) intercalation of monomers and their in situ polymerization; and (3) template synthesis of clay minerals.

Before describing the synthesis of clay-polymer nanocomposites, we will outline the principles of polymer adsorption by clays, and how clays can activate the polymerization of some organic monomers. We will also briefly mention the interactions of montmorillonite with $C_{60}$ fullerene, a special all-carbon polymer.

**Keywords:** Clay, Polymer, Nanocomposites.

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# THE STUDY OF THE ADDITIVE FOR REDUCING THE PRINT-THROUGH PHENOMENON AND INCREASING THE CURING DEGREE OF UP COMPOSITES

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Recently, the vacuum-injection method has been considered the new approach to making yachts. However, there is a bottleneck, when it comes to the present materials, including the UP/fiber glass or Vinyl Ester/fiber glass composites. This is because the different degrees of cure within the UP resin result in the differential thermal contraction of materials, and thus the print-through phenomenon exists on the yacht surface.

According to the preliminary understanding, three possible factors which cause the print-through phenomenon are as follows. First of all, the differential shrinkage of composites; that is, there is a great diversity in the differential shrinkage of resin and fiber glass during the preparation. Second, the pattern and density of fiber-glass fabrics which make the print-through phenomenon emerge. Third, in terms of per unit of the composite resin, the different thicknesses make the surface become uneven and rough. Based on the literature, when forming the copolymer through the free-radical polymerization reactions of the UP/ST, the differential shrinkage is 7-10%. Therefore, they induce in twists and wrinkles on the surface. In this consideration, the addition of clay is applied to the present research expected to enhance the reaction of the LPA in the UP/ST/LPA system. On the other hand, the stability of the size could be improved. This study also discusses the features of the flame-resistant clay which served as flame retardants in the experiments. The UP/clay nanocomposites were measured by wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) techniques to study the dispersion of the UP/clay nanocomposite materials. Density measurement of the cured sample was employed to calculate the volume shrinkage of the resin system.

**Key words:** Clay, Unsaturated polyester, Print-through phenomenon.

# NANO & POROUS MATERIALS

## SESSION NM3

## *Mesoporus Silica as Molecular Sieves*

# FABRICATION AND CHARACTERISTICS OF SMART MAGNETIC NANOCOMPOSITES: ENCAPSULATED FERRITE OXIDE IN HOLLOW PERIODIC MESOPOROUS ORGANOSILICA

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Tailoring magnetic nanoparticles into related composites may exhibit exceptional properties compared to the conventional bulk magnetic materials. They also show extensively promising potentials in the field of high density data storage,[1] medicine and bioscience,[2] catalysis and magnetic separation.[3,4] The emerging of mesoporous silica with ordered pore-size at nanoscale and varied morphology makes it possible to fabricate magnetic nanocomposites with well-tuned particle size and distances. By careful control on composition of mesoporous hosts and fabrication procedures, it is potential to prepare magnetic nanocomposites with a desired set of properties.

Based on our previous work on hollow periodic mesoporous organosilica (HPMO)[5], here we report a kind of smart magnetic nanocomposites from ferrite oxide (Barium or Strontium) confined within inorganic- organic HPMO. This involves a combination process of precoating and encapsulation as compared to growing HMPO in quantum dots of iron oxide-containing surfactant solution. Effect of the ferrite oxides existence on the pore structure and morphology of HPMO was investigated. It is found that the formation of HPMO in the presence of ferrites oxide is quite sensitive; however optimal control on some parameters during synthesis, precoating, and encapsulation, will lead to Ferrite oxide-HMPO nanocomposites with much stronger magnetic response than quantum dots iron oxide. Characterization is performed through XRD, SEM, TEM, FT-IR and measurement of magnetic saturation. Some different magnetic characteristics could be attributed to the interaction between the ferrites and HPMO as the host matrix, and possible mechanism will be further proposed.

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**Keywords:** Periodic mesoporous organosilica, Magnetic nanocomposites, Encapsulation.

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# LAPONITE-DERIVED POROUS CLAY HETEROSTRUCTURES: FTIR STUDY OF THE STRUCTURE EVOLUTION

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The investigation of porous clay heterostructures (PCHs) is an attractive research area because of their possible applications as catalysts and adsorbents. Present work introduces the potential of the infrared (IR) spectroscopy in the middle (MIR) and near (NIR) regions to characterize the materials obtained during particular steps of Laponite-derived PCH synthesis. In the first step the clay interlayers are opened by hexadecyltrimethylammonium (HDTMA) surfactant cations. Displacement of hydrated $Na^+$ with $HDTMA^+$ cations significantly modifies the shape of the IR spectra of HDMA-L. In addition to new bands due to $CH_3$ and $CH_2$ vibrations of $HDTMA^+$, this cation affects also the vibrations of structural groups of Laponite. The OH and $Si\text{-}O_{apical}$ dipoles, perpendicularly oriented to the basal oxygens plane, are more aligned with one another and related OH and Si-O bands become narrower and their intensities increase. Next step of the PCH synthesis consists in addition of cosurfactant (dodecylamine - DDA) and Si source (tetraethylorthosilicate - TEOS) to HDTMA-L. While the MIR spectrum of TEOS shows several sharp well-resolved bands in the 1200-950 $cm^{-1}$ region assigned to Si-O and Si-O(C) stretching vibrations, a broad complex band at 1070 $cm^{-1}$ and the absence of SiO(C) band at 968 $cm^{-1}$ indicate that interaction between the micellar templates (formed by surfactant molecules) and TEOS leads to the creation of a silica network at the outer surface of the micelles. The NIR spectrum of HDTMA-L/DDA/TEOS shows in addition to $CH_3$ and $CH_2$ overtone (6100-5400 $cm^{-1}$) and combination (4500-4000 $cm^{-1}$) bands also overtones (6523 and 6478 $cm^{-1}$) and combination (4935 $cm^{-1}$) bands of primary amines. Only NIR spectra allows identification of $NH_2$ groups of DDA, because corresponding NH stretching (~3400 $cm^{-1}$) and bending (~1620 $cm^{-1}$) vibrations are overlapped with absorption bands of adsorbed water molecules. The final step of PCH synthesis consists of removal of the organic template by calcination. The characteristic vibrations of Laponite found at 1030 $cm^{-1}$ (Si-O) and near 7190, 3680 and 670 $cm^{-1}$ (OH) confirm that layered structure of clay mineral resists the thermal treatment. No bands due to $CH_3$, $CH_2$ or $NH_2$ vibrations in the spectra of PCH prove complete removal of organic template upon heating. The 1094 $cm^{-1}$ band belongs to the vibrations of three-dimensional silica framework created from TEOS during PCH synthesis. The SiOH overtone at 7315 $cm^{-1}$ confirms that SiOH groups are also a part of the silica network in Laponite-derived PCH.

**Keywords**: Laponite, PCHs, IR spectroscopy.

# SYNTHESIS, CHARACTERIZATION AND ITS APPLICATIONS OF A NOVEL MESOPOROUS HOLLOW SILICA, NANOCUBOIDS

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Since the discovery of mesoporous silica molecular sieves by Beck et al., mesoporous materials have opened many new possibilities for application in the fields of catalysis, separation, and nanoscience. In recent years, fabrication of silica materials with designed structure (e.g. thin films, monoliths, hexagonal prisms, toroids, discoids, spirals, dodecahedron and hollow sphere shapes) is an important research in modern materials chemistry. Among them the fabrication of monodispersed hollow spheres with control size and shape is fastest developing area. It is generally accepted that hollow sphere with mesopores will exhibit more advantages in mass diffusion and transportation as compared with conventional hollow spheres with solid shell. They can serve as a small container for application in catalysis and control release studies. The methods currently used to fabricate a wide range of stable hollow spheres include nozzle reactor processes, emulsion/phase separation, sol-gel processing, and sacrificial core techniques. The fabrication of hollow spheres has been greatly impacted by the layer-by-layer (LbL) self-assembly technique. This method allows the construction of composite multilayer assemblies based on the electrostatic attraction between nanoparticles and oppositely charged polyions. By varying the synthetic methodology and reactants, it is highly probable to achieve the materials with interesting morphology and properties. In the present study, an attempt was made to synthesize silica nanocuboids and investigated its host guest properties.

Synthesis of silica nanocuboids are as follows. 3.57 ml of triethanolamine was added to a solution containing 74 ml of ethanol and 10 ml of deionized water. 6 ml of tetraethylorthosilicates was added to the above prepared mixture at 298 K with vigorous stirring. The reaction mixture was stirred for another 1 h. A solution containing 5 ml of TEOS and 2 ml of octadecyltrimethoxy silane was added to the above solution (11 $SiO_2$: 6 TEtA: 1 C18TMS: 149 $H_2O$: 298 EtOH) and further reacted for 24 h. The resulting octadecyl group and or triethanolamine incorporated silica nanocomposite was retrieved by centrifugation. The sample was washed several times with distilled water, dried and calcined at 823 K for 8 h in air to obtain hollow cuboids silica material.

The resulting silica material found to have hollow (300 nm) nanocuboid (400 nm) property confirmed by X-ray diffraction, Scanning electron microscopy, Transmission electron microscopy, Thermogravimetry/Differential thermal analysis, Fourier transform Infrared spectroscopy and Nitrogen adsorption. Ibuprofen tablet storage capacity was also studied by Ultraviolet-Visible spectroscopy. A plausible synthesis mechanism was reported.

**Keywords:** Mesoporous, Hollow silica, Nanocuboids.

# SILICON QUANTUM DOTS FUNCTIONALIZED WITH BIOMOLECULES IN EXCITED STATES

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Surface functionalization is a critical step for silicon quantum dots (SiQDs) being used as biological probes and sensors. We systematically investigate the optical properties of SiQDs with various termination groups, including H, $CH_3$, $NH_2$, SH, OH, and some biological molecules. Our calculations reveal that capping SiQDs with alkyl group (-Si-C-) induces minimal changes in the optical spectra, while covering the surface with $NH_2$, SH, and OH results in evident changes compared to hydrogenated SiQDs [1-4]. The structural deformations and electronic property changes due to surface passivation were shown to be responsible for the above-described features. Interestingly, we find the optical properties of SiQDs can be controlled by varying the S coverage on the surface [5]. This tuning effect may have important implications in device fabrications.

**Keywords:** Silicon quantum dot, Optical property, Biological sensing.

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# SYNTHESIS, PHYSICOCHEMICAL CHARACTERIZATION AND CATALYTIC PROPERTIES OF ALUMINATED MESOPOROUS SILICAS OF FSM-16 TYPE

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Mesoporous silicas of FSM-16 type are materials obtained from synthetic mineral kanemite, which is a layered sodium silicate of the formula $NaHSi_2O_5 \times 3H_2O$. The FSM-16 solids are characterized by the presence of an ordered hexagonal array of uniform pores, whose diameters can be controlled in the range o several nanometers, high specific surface area, and good thermal stability. These features render them particularly attractive for application in sorption, catalysis, separation processes, and host-guest chemistry. Insertion of Al into the mesoporous FSM-16 silicas aims at development of cation exchange/acid properties, and extends further their potential. Mesoporous silicas of FSM-16 type were aluminated by direct addition of Al source to the synthesis gel or by post-synthesis impregnation of purely siliceous material. The solids were characterized with XRD, HRTEM, EDS, XRF, nitrogen sorption isotherms, $Al^{27}$ and $Si^{24}$ MAS NMR and $NH_3$-TPD experiments. Both applied methods of FSM-16 alumination result in substitution of Al for Si in the mesoporous silica framework. Only substitutional tetrahedral Al sites exist in directly aluminated samples, while in the post-synthesis impregnated materials a certain amount of Al remains at the extra-lattice positions. For a given level of doping the post-synthesis aluminated samples show better structural ordering within the hexagonal lattice than the directly aluminated ones. The as received post synthesis aluminated samples exhibit significantly higher acidity than the as received directly aluminated solids, due to the presence of sodium retained after synthesis in basic environment. The acidity of the directly aluminated samples can be recovered by transformation of sodium forms into hydrogen ones. The sites generated by direct alumination appear stronger than those produced by post-synthesis treatment. The materials are active in ethanol decomposition and the observed activity/selectivity patterns follow the trends of acidity as measured by $NH_3$-TPD.

**Keywords**: FSM-16, Alumination, Mesoporous silica.

# NANO & POROUS MATERIALS

## SESSION NM4

## *Metal Nanoparticles Catalyzed Organic Synthesis*

# $CO_2$ REFORMING OF $CH_4$ OVER Ni-Mg CONTAINING PHYLLOSILICATES AS CATALYST PRECURSORS

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$CO_2$ reforming of $CH_4$ (CDRM) to produce synthesis gas ($CO+H_2$) attracts many researchers for the chemical utilization of two green houses gases during last decade. It is known that synthesis gas is a versatile feed stock for ammonia, methanol and Fischer–Tropsch synthesis processes. The catalysts based on noble metals have been found to be highly effective for CDRM. However, considering the high cost and limited availability of noble metals, it is more practical from industrial standpoint to develop transition metal-based catalysts, such as Ni-containing catalysts with high performance. However, Ni-based catalysts are mostly deactivated due to the carbon deposition on their surface. High dispersion of Ni metal and use of basic supports can hinder the formation of coke. To the best of our knowledge, Ni-Mg - trioctahedral phyllosilicates (PS) have not been evaluated as catalysts precursors for CDRM. Our preliminary studies showed that Ni pure kerolite (structural formula of $Ni_3Si_4O_{10}(OH)_2$; 2:1 PS) were more attractive catalyst precursors for CDRM than the Ni pure lizardite (structural formula of $Ni_3Si_2O_5(OH)_4$; 1:1 PS). In the present study, Ni-Mg lizardite and – kerolite are evaluated for CDRM and compared to their Ni pure counterparts.

Ni-pure and Ni-Mg lizardite and kerolites are synthesized by hydrothermal treatment of a gel (prepared from sodium silicate and metal chloride solutions) at 80° and 200 °C. Synthesized samples are characterized by XRD, FTIR, TG-DTA, TPR, TEM and BET. FTIR patterns give evidence of a random distribution of Ni and Mg in the octahedral sheet of kerolite and lizardite. Kerolites are found to be more thermally stable than lizardites. The Ni- rich lizardite thermally treated at 700°C transforms into a transitional phase similar to Ni-2:1 kerolite. Ni-Mg-lizardites thermally treated at 900°C gives mainly olivine ($M_2SiO_4$,$M=Mg_{1-x}Ni_x$), while Ni-Mg -kerolite transforms into enstatite ($MSiO_3$,$M=Mg_{1-x}Ni_x$). Both Ni-Mg - lizardites and kerolites give different TPR patterns than those of their corresponding Ni pure counterparts. Thermal stability of PS regarding their structural transformation are correlated to their TPR pattern. $NiMg_2Si_4O_{10}(OH)_2$ (here labelled NiMg2-T-200-4) is found to be a good candidate for the CDRM over all the PS evaluated as precursors. Uniformly distributed metallic $Ni^0$ (average particle size of 10 nm) with unreduced PS structure as a support (that exhibits high BET surface area and a more basic nature) leads to better catalytic properties of activated NiMg2-T-200-4. Carbon deposition as carbon nanotubes is observed on spent catalysts of activated NiMg2-T-200-4.

**Keywords:** Ni-Mg containing phyllosilicates, TPR pattern, $CO_2$ reforming of $CH_4$.

# IMMOBILIZATION OF GOLD NANOPARTICLES ON THE EXTERNAL SURFACES OF CLAY MINERALS

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Gold nanoparticles have interesting physicochemical properties leading to a large variety of applications, in particular in the field of catalysis. Gold nanoparticles were immobilized successfully on a variety of metal oxides, such as $TiO_2$, $Fe_2O_3$, $CeO_2$ and $Al_2O_3$. Their preparation is usually based on the method of deposition-precipitation, implying the most common gold precursor $HAuCl_4$. Although clay minerals are known to be useful catalytic supports due to their strong thermal and chemical stabilities, their use in the preparation of gold catalysts is scarce.

This work shows the potential to use natural clay minerals (sepiolite, kaolinite, montmorillonite) for the development of novel advanced materials such as heterogeneous catalysts for oxidation reaction. The application of clay minerals for the preparation of new functional materials can be regarded as an alternative approach in the use of these raw materials and in the manufacture of more eco-friendly compounds. To improve the physicochemical properties of the clay minerals (adsorption, hydrophobicity,…), as well as to ensure a strong immobilization of the adsorbed species, natural clay minerals were functionalized by the addition of organic compounds (organosilane, polymer, aminoalcool). This functionalization is carried out by internal grafting in the case of kaolinite, external grafting in the case of sepiolite, or just by a simple intercalation in the case of montmorillonite. This organo-inorganic combination which occurs at the nanometric scale allows the creation of host-guest bi-functional materials, combining the chemical properties of the two partners. The combination of the nanostructures of clay minerals with gold nanoparticles should lead to new or improved properties of both constituents.

The preparation of the gold-clay nanoparticles was carried out by a wet chemical process using $Au(en)_2Cl_3$ salt as precursor. Characterization results by X-ray diffraction and XPS spectroscopy confirmed the presence of metallic gold. High resolution transmission electronic microscopy (HRTEM) showed an homogeneous distribution of the gold nanoparticles with an average diameter lower than 5 nm.

**Keywords:** gold nanoparticles, clay minerals, catalysis.

# CLAY-STABILIZED SILVER NANOPARTICLES AS CATALYSTS IN REDUCTION OF OLEFINS, NITROARENES AND CARBONYL COMPOUNDS

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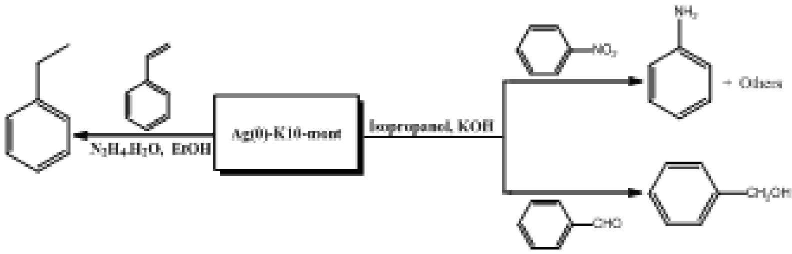
Nanoparticles find wide range of applications[1] in catalysis, electronics, materials science and also in biomedical sciences. Though nanoparticles of silver are prepared in various sizes, shapes and morphologies, studies on their catalytic activities are limited.[2,3] Our interest in catalysis by nanoparticles stabilized on clay matrix[4] prompted us to synthesize and characterize clay-entrapped silver nanoparticles in an unique approach.



In the present study, silver nanoparticles (particle size in the range of 15-30 nm and spherically shaped). are prepared from $Ag^+$-clay by hydrazine reduction. The nitrogen released during the reduction creates an inert atmosphere which prevents oxidation of Ag(0) nanoparticles. They are characterized by diffuse reflectance spectra (band at 403 nm), powder XRD, HRTEM and EDX analyses. Powder XRD data show that the unit cell of Ag(0) nanoparticles has the fcc structure. No oxides or hydroxides are observed, as evident from the phase analysis of XRD.

Arylarenes are reduced using hydrazine as a reducing agent in ethanol medium. In the reduction of carbonyl compounds and nitroarenes, they are reduced *in situ* by isopropanol/potassium hydroxide mixture which takes place *via* a mechanism involving a hydride ion transfer. The present approach involving Ag(0)-montmorillonite is economical and ecofriendly as it requires neither high temperature nor harsher acids. Other advantages include easy synthesis of catalyst and no need to use molecular hydrogen. The sterically hindered interlayer space of montmorillonite not only stabilizes the highly oxygen sensitive silver nanoparticles but also suppresses their agglomeration.

**Keywords:** Silver Nanoparticles; K10-Montmorillonite; Reduction.

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# NANO & POROUS MATERIALS

## SESSION NM5

## *Natural Zeolites: From Genesis to Applications*

# THE IMPORTANCE OF THE PARTIAL PRESSURE OF $H_2O$ IN ZEOLITE PHASE TRANSITIONS

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It is well known that most natural zeolites undergo a variety of phase transitions upon heating [1], generally as a result of (or concurrently with) dehydration. Thus, these transitions should exhibit a marked dependence on the partial pressure of $H_2O$ ($P_{H_2O}$). Most natural zeolites experience a gradual 2nd-order phase transition on dehydration, and these transitions are usually reversible and not hysteretic for heating below ~300ºC. Clinoptilolite and mordenite both show 2nd-order behavior, with gradual, reversible, anisotropic volume decreases on heating. Some zeolites, such as chabazite and erionite, show clear evidence of thermal expansion superimposed on dehydration-induced volume decreases. Interestingly, some zeolites show evidence for 1st-order phase transition(s) along with 2nd-order behavior. Laumontite shows both transitions as a function of either T or $P_{H_2O}$, and the structural changes are anisotropic and the 1st-order transition is hysteretic [2]. In general, zeolites having $H_2O$ and extraframework cations in fixed positions (low-entropy $H_2O$ molecules) exhibit marked $P_{H_2O}$-dependent behavior and 1st-order phase transitions. Evidence for this has also been observed in natrolite, which shows unique phase transition behavior. Previous research on natrolite and its high-T phases showed an intermediate-T form, α-metanatrolite, and a high-T form, βmetanatrolite. Controlled-atmosphere X-ray diffraction measurements to 450 ºC demonstrate that *two distinct* 1st-order transitions occur, depending on the T and $P_{H_2O}$ conditions of measurement [3], with α1-metanatrolite occurring at elevated $P_{H_2O}$ and α2-metanatrolite occurring at low $P_{H_2O}$. The discovery of α2-metanatrolite implies the existence of more than one 1st-order phase transition mechanism, which we correlate with the migration of $Na^+$ ions and the *rate* of evolution of $H_2O$ molecules. The phase transition behavior can therefore be rationalized in terms of two cooperating mechanisms: (I) Dehydration-induced processes, which determine the phase transition temperature; (II) Thermally induced processes, which determine how the framework and its extraframework cations are modified. Under higher PH2O conditions, it is possible to bypass the α2-metanatrolite phase, and natrolite goes directly to the α1-metanatrolite phase. It is noteworthy that variation of PH2O allows access to previously inaccessible transition space. For high thermal-stability zeolites (e.g., gottardiite), PH2O-dependent behavior is less likely because the framework is rigid at T < ~500ºC and there is no competition between thermally induced and dehydration-induced processes.

**Keywords**: Zeolite, Phase transition, Hydration.

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# PREPARATION OF ANTIMICROBIAL NATURAL ZEOLITE: ION EXCHANGE BY MICROWAVE IRRADIATON AND CONVENTIONAL WATERBATH

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Recent innovations in microwave chemistry lead scientists to focus on this phenomenon and early in the 1990s it has been began to be applied in different zeolite application. Natural zeolites have been an interest in engineering due to their unique sorption, catalytic and ion-exchange properties however owing to different cationic forms results with changes in their properties and applications. Ion exchange of natural zeolite in presence of microwave irradiation (MI) alternative to conventional waterbath (CW) method was studied since investigating the influence of microwave irradiation on ion exchange degree, process mechanism, structure and properties of the mineral has great importance and is the main purpose of this study. The clinoptilolite rich mineral from Gördes, W.Anatolia was used throughout the study. Near homoionic form of the mineral was accomplished by treating it with 1N NaCl at 80 °C for 10 days (NaCLI). It was then treated with 0.01 M $AgNO_3$ at 40°C, 60°C,80°C,0.01M $Co\cdot(NO_3)_2\cdot 6H_2O$ and 0.01M $Cu\cdot(NO_3)_2\cdot 5/2H_2O$ at 80 °C in CW and in the presence of MI. Solid: solution ratio, condition and time parameters effect on exchange degree were determined. The exchanged minerals were characterized by Inductively Coupled Plasma Emission Spectrometer, XRay Diffraction, Differential Thermal and Thermal Gravimetric Analysis, Fourier Tansform Infra-red Spectroscopy in order to determine if the microwave treated ones showed different properties and if microwave irradiated ion exchange enhanced the exchange degree while reducing time compared to CW method. Antibacterial activity of the exchanged minerals against *E.coli* was determined by Kirby–Bauer method.

Ion exchange was determined as controlling mechanism in NaCLI-metal solution systems, no surface precipitation and dissolution occurred for the utilized conditions. S/L ratio was found as an effective parameter. The microwave irradiated minerals has slightly higher exchange degrees compared to CW treated ones however different behaviors occurred depending on the metal ion to be exchanged and its concentration. XRD patterns and FTIR spectra of the exchanged forms of NaCLI showed no transition of clinoptilolite phase and no shift in characteristic peak positions. $Ag^+$, $Co^{+2}$ and $Cu^{+2}$ exchanged forms of NaCLI showed considerable superiority against E.Coli. For all cases negative $\Delta H^o$,$\Delta S^o$ and $\Delta G^o$ values were found. Consequently, MI can be proposed as an alternative and reliable method that can be used to prepare an ion-exchanged clinoptilolite mineral for different purpose.

**Keywords:** Zeolite, Ion-Exchange, Microwave-irradiation.

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# FAVOURABLE EFFECTS OF NATURAL ZEOLITES ON SOILS TREATED WITH MUNICIPAL SEWAGE

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A research was started aiming at evaluating the possible use of natural zeolites as soil conditioners to improve and make durable the soil resilience against possible adverse effects of anomalous waters used for irrigation.

This paper deals with a long-term study on a sandy, alkaline Entisol and a sandy-loam, acidic Alfisol (A horizons), conditioned by Neapolitan Yellow Tuff (NYT) or clinoptilolite-rich tuff (CLP), and treated with a “dirty” municipal sewage (DSW). NYT or CLP were added at ratios 25/75, or 50/50 tuff/soil (w/w). DSW was added at the ratio 5/1 DSW/sample (v/w). Twelve consecutive DSW treatments were performed within six-months experiments.

For both soils, the presence of NYT or CLP resulted in several favourable effects, usually increasing with the zeolite conditioning rates with respect to non-conditioned samples.

In soil solutions, Electrical Conductivity was lowered, and pH was buffered at physiological alkalinity. Sodium Adsorption Ratio also decreased, particularly in the presence of CLP, which released less $Na^+$ than NYT.

Ammonium was selectively taken up from DSW, by releasing alkaly and alkaly-earth cations into soil solution, with special reference to $Na^+$, $K^+$, and $Ca^{2+}$. Consequently, the zeolitized tuffs became almost saturated by $NH_4^+$, potentially playing a relevant role as a slow-releasing nitrogen fertilizer. At the same time, the $NH_4^+$ itself was protected against biological oxidation to nitrate, as well as against the polluting dispersion of nitrogen compounds in the environment. Concurrently, plants nutrients as $K^+$ and $Ca^{2+}$ were made available in soil solution.

Potentially toxic elements, such as Pb, Cu, and Zn, were continuously taken away from DSW, likely owing to precipitation rather than exchange reactions.

Magnesium appeared to be practically unconcerned in the complex soil/zeolite/DSW equilibria.

On the whole, the results obtained highlight the important role of natural zeolites in pedotechnique strategies to improve and preserve soil functionality and performance.

**Keywords:** Natural Zeolites, Municipal Sewage, Pedotechnique.

# NEW DATA ON PHILLIPSITES FROM NEAPOLITAN YELLOW TUFF

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Neapolitan Yellow Tuff (NYT) is one of the most studied Italian pyroclastic formation. Its formation is linked to one of the most powerful and largest phreatomagmatic eruptions of Campi Flegrei (Southern Italy), dated about 12.000 ybp. More than 50% of its volume was envolved in sin- and post-depositional epigenetic processes, leading to the crystallization of zeolites (mainly phillipsite and subordinately chabazite and analcime) (de'Gennaro et al., 2000).

Chemical composition of phillipsites was reported in previous studies by various Authors (Passaglia e Vezzalini, 1985; de' Gennaro et al., 1990; de' Gennaro et al.; 2000). The present paper reports new crystal-chemical data on different phillipsites from the major outcrops of the NYT, in order to: 1) obtain correct information on the extra-framework cation population and 2) verify if there is any variation according to their spatial distribution. Furthermore, the same phillipsite samples were investigated by XRPD to obtain crystal structure information using a new starting model (Gatta et al., in press) for the Rietveld refinement.

The use of this new structural model of the distribution of the extra-framework contents in phillipsites may help in understanding the "cation exchange capacity" (CEC) of this zeolite, as well as the discrepancies often found between the extra-framework population deduced on the basis of the CEC experiments and that calculated from chemical analyses

**Keywords**: Phillipsite, Neapolitan Yellow Tuff, Cation exchange capacity.

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# NATURAL ZEOLITE - A SPECIAL FUNCTIONAL MATERIAL IN CEMENT AND CONCRETE

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China is a country abundant with natural zeolite. There are over 120 zeolite deposits distributed in 21 provinces and autonomous regions. Three of the largest are Dushikou Deposit in Hebei Province with approximately 500 million tons of clinoptilolite, Jinyun Deposit in Zhejiang Province with approximately 100 million tons of mordenite, and Linhai Deposit in Heilongjiang Province with approximately 100 million ton of clinoptilolite.

Natural zeolite has been applied as a raw material to cement and concrete in China since 1978. It can be used as a blended cementitious material in cement, to improve quality of cement produce in shaft kilns. It can also be used as a mineral admixture in concrete to control the alkaline-aggregate reaction and enhance durability of concrete structures effectively. All these applications are fairly beneficial to energy conservation, resource conservation and environmental harmony. There are six types of application of natural zeolite due to the characteristics of natural zeolite. The six types of special zeolite functional materials described below have been successfully used in construction practice, and promote the development of concrete technologies.

(1) High performance mineral admixture of natural zeolite: Natural zeolite as a replacement of cement at 10%-15 % by mass, can significantly improve durability of concrete and enhance strength as well. With the aid of natural zeolite, high performance normal-strength concrete can be prepared. (2) Zeolite strengthening agent: Ultra-fine natural zeolite powder, as the replacement of 10% of cement, can acquire an increase of 10% in strength of concrete at a W/B ratio less than 0.38. (3) Zeolite gas carrier: As a gas carrier, natural zeolite can expanded in cement mortar. After setting and hardening of the expanded paste, cellular concrete can be produced. (4) Zeolite plasticity-maintaining agent: As a carrier of superplasticizer, natural zeolite may increase flowability of fresh concrete, and maintain its plasticity for five hours to meet the requirement of concrete construction, especially in hot weather or in summer. (5) Zeolite alkali absorbent: The application of natural zeolite can absorb a considerable part of solvable alkali, released from the aggregates in concrete, and hence prohibit the occurrence of alkali-aggregate reaction. (6) Zeolite water releaser: Harmful autogenous shrinkage and cracking can be minimized with ultra-fine zeolite powder, since water may be released gradually from zeolite for a relatively long period during the process of cement hydration.

**Keywords:** Natural zeolite, Cement, Concrete.

# TRANSITION METAL COMPLEXES SUPPORTED ON NATURAL ZEOLITES: NEW COMPOSITE MATERIALS FOR INNOVATIVE APPLICATIONS

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The zeolitic materials are not frequently used as synthesized or as obtained from the nature (unmodified), but their physicochemical properties are refined by chemical and/or thermal treatment. One of the novel procedures to obtain modified zeolites is the gradual loading of the crystals with transition metals and organic substances, which leads to complexes supported on the aluminosilicate zeolitic substrate. The coordination and organometallic compounds can either be encapsulated inside the micropores (intrazeolite complexes) or arranged on the surface of the crystals (surface complexes). The surface complexes are anchored by chemical bonds to active (Brønsted or Lewis) surface sites, whereas the intrazeolite ones are hosted into the channels allowing the zeolite to act as a “solid solvent”. In the latter case, the guest complexes principally retain all of their properties and, being isolated in the micropores playing the role of “inorganic molecular-scale microreactors”, are often more stable under dimerisation, auto-oxidation, clustering and thermal-degradation conditions. Moreover, in both cases the supported complexes are considered as “new” (not existing as individual chemical compounds) if oxygen-atoms of the zeolite lattice participate in the first coordination sphere. The above described solid systems constitute in fact an entirely new class of composite materials with great technological interest. The existing literature on synthetic zeolites (e.g. FAU-type) provides evidence for peculiar applications such as the shape/size-selective catalysis and even the biomimetic catalysis where the supported in the micropores “ship-in-a-bottle” complexes behave as the enzymes in the protein structure. These materials are the so-called “zeozymes” contributing to the establishment of the supramolecular solid-state science. The relevant research already performed using naturally occurring species is comparably limited and refers to FAU-type zeolites as well as to HEU-type zeolites (clinoptilolite/heulandite series, which are the most abundant zeolites on Earth). Different intrazeolite and surface complexes of various metals (Mn, Fe, Co, Ni, Cu, Ag) have been investigated in respect of the above zeolites and novel uses of the obtained composite materials have been pointed out including the development of specific sorbents and catalysts, environment-friendly pesticides and insecticides, and modern pharmaceuticals and nutritients.

**Keywords:** Natural zeolites, Intrazeolite complexes, Surface complexes.

# USE OF NATURAL ZEOLITES IN AGRICULTURAL AND ENVIRONMENTAL FIELDS

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Zeolites are natural or synthesized substances with a large group of hydrated aluminosilicates of alkaline and alkaline-earth minerals(3). They are made up of a framework of $(SiO_4)^{-4}$ and $(AlO_4)^{-5}$ tetrahedron linked to each other's corners by sharing oxygen atoms(1,3,4).

Natural zeolite mines in Iran are located in Semnan, Azarbayjan and Gilan provinces. One major form of the mineral in Iran is Clinoptilolite which is more available in these mines(1). Natural zeolites are mostly used in chemical processes ,in air enrichment, as filter in paper and rubber industry, for soil beneficiation, as animal feed supplement and in water and waste water treatment(2,5).

Recent advances in research activities has been directed toward using these minerals specially in the area of soil and plant enrichment and improvement ,control of soil and water pollution and also in the treatment of sewage and waste water with respect to environmental concerns(1,2,5).

This paper will present a review of the current research worldwide which can be used as basic information for new studies in these fields. The focus of the review on environmental issues will be toward heavy metal contamination treatments and in the field of agricultural studies use of zeolite for composting and improvement of soil properties to increase productivity will be addressed.

**Keywords:** Natural zeolites, Soil beneficiation, Heavy metal.

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# THE ENHANCEMENT OF NITRIFICATION IN AN ORGANO-ZEOLITIC-SOIL SYSTEM AND ITS EFFECT ON PLANT GROWTH AND QUALITY

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A zeolitic tuff containing an appreciable abundance of clinoptilolite was composted with animal waste to produce a dry friable non-odorous material that can easily be mixed with soil to produce an amended soil substrate. By the systematic analysis of aqueous leachates, taken from both unamended and amended substrates, it was found that samples taken from the amended substrates had nitrate concentrations an order of magnitude greater than those from the unamended substrates. Further, comparative analysis of separate batches of organo-zeolitic mixture show that those containing abundant zeolitic tuff have very much higher concentrations of nitrate, in their leachate samples, that those containing only animal manure. It is well known that clinoptilolite has an ion-exchange property that is highly selective towards ammonium ions and it appears that the clinoptilolite component in ion-exchanging ammonium, as it is liberated from the decomposing animal waste, “buffers” the loss of ammonia from volatilization and leaching.

Analysis of the electrical conductivity of aqueous leachate samples show a linear relationship with nitrate concentration, as would be expected as protons are produced at a rate depending on the degree of nitrification. Electrical conductivity measurements of leachates from amended substrates are always characterised by high values and it is thought that free protons, in reacting with the substrate porewater, would produce hydroxonium ions that would be unstable and rapid neutralization by oxy/hydroxy complexes and soil polymers to liberate cations from the soil that would produce such high ionic mobility.

The analysis of 21 elements in leaf and stem samples of plants growing in unamended mine waste, amended mine waste and clean soil identifies two trends in mineral uptake. In cases where a particular element concentration is low in a plant growing in the mine waste relative to that of a plant growing in the clean soil the trend in a plant growing in an amended mine waste is to increase the concentration of that element to approach that of a plant growing in the clean soil and vice versa. It therefore appears that the high ionic mobility of the amended substrate porewater allows a plant to self regulate its mineral uptake resulting in enhanced growth and, in the case of edible fruit, an improved quality.

# SORPTION OF HOMOLOGUES OF REDIONUCLIDES ON SYNTHETIC ION EXCHANGER

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Synthetic ion exchangers (analogues of nepheline, marialite and natrolite) have been chosen for the present study. These analogues has been characterized by techniques like X-ray Diffraction, EDXF's, TGA, FTIR & SEM. $UO_2^{+2}$, $Th^{+4}$, $Eu^{+3}$, $Sm^{+2}$, $Ru^{+3}$ and $Fe^{+3}$ are used as homologues of radionuclides. Sorption was observed to be pH dependent. The data revealed maximum sorption at pH 9 which could be attributed to hydrolysis of metal ions at higher pH. It has been found that sorption was enhanced by increasing the sorbent dose and reduced by increasing metal ion concentration. The data was analyzed by Freundlich sorption isotherm by varying metal ion concentration which was found to fit well at ambient temperature and is observed to be linear indicating the applicability of Freundlich isotherm model to the sorption of metal ions on these analogues which in turn indicates multilayer sorption behaviour of metal ions. Thermodynamic parameters were investigated by varying the temperature. The data was plotted as ln Kc Vs. 1/T; the values of $\Delta H$ and $\Delta S$ were calculated from the slope and intercept respectively. The negative values of Gibbs free energy demonstrate the feasibility and spontaneity of sorption process. The positive values of $\Delta H$ specify endothermic nature of sorption. The positive values of $\Delta S$ indicates an increase in randomness or disorder at solid-solution interface during sorption. Sorption was found to get affected in the presence of competing cations and was observed that it decreases with increase in the concentration of competing cations which may be probably due to the competition between these ions and the radionuclides. Desorption of radionuclides with different leachants as distilled water, citric acid, EDTA, DTPA and oxalic acid showed that water has negligible capacity of leaching in comparision to organic leachants.

**Keywords:** Analogues of Zeolite, Homologues of radionuclide, Sorption isotherm.

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# RECYCLING OF ZEOLITE FILTERS THROUGH THE USE OF ELECTRODIALYSIS

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Zeolites are clay minerals with multiple industrial uses. They are used to make cat litter, livestock feed additives, catalysts, and contaminant filters. Recently, more attention has been given to the use of different types of mineral clay to address environmental pollution issues. With concerns such as environmental protection and industrial process efficiency at the forefront of societal concerns, we thought it would be useful to determine whether or not zeolite filters could be recycled by using electrodialysis. We performed the following tests on the soil samples we collected from Presidio County: 1) $CaCO_3$ %; 2) Moisture content; 3) pH; 4) EC (saturated paste); 5) XRD. After running XRD, we concluded there was not enough zeolite in the samples to reasonably continue with the experiment. As an alternative we ordered different zeolite samples from St. Cloud's Mine in New Mexico. Preliminary characterization does indicate that these samples do contain the appropriate amount of zeolite for this experiment. Once the particle size fractions of the St. Cloud samples have been isolated, the following procedure will be followed: 1) Excess ions adsorbed to the zeolite very fine clay, fine clay, and clay/silt fractions will be removed, essentially purifying those fractions; 2) The fractions will be placed in a $Cd^{+3}$ wash; 3) The fractions with adsorbed $Cd^{+3}$ will be placed in an electrodialysis unit; 4) Electrodialysis will be conducted; 5) The particle size fractions will be analyzed for $Cd^{+3}$ content.

**Keywords:** Zeolite, Electrodialysis, Cadmium.

# NANO & POROUS MATERIALS

## SESSION NM6

## *Polymer-Clay Nanocomposites: Advantages, Properties and Uses*

# CLAY POLYMER NANOCOMPOSITES

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The initial promise which clay polymer nanocomposites were believed to hold has yet to be realized even though extensive research has been undertaken over the last three decades. Several of the critical barriers to the development of these materials were identified midway through this period. Limited processing window, insufficient characterization methods and incomplete fundamental understanding of structure property and structure processing relationships are issues which must still be overcome. However, a number of groups have made advancements in developing structure property and structure processing relationships, while other efforts have improved the characterization, synthesis, and processing methods. Our own contributions over the last decade to the first two challenges include: ion exchange methods for preparation of quaternary ammonium based organo-clays with improved thermal stability (~40 °C) [1] and therefore better processing window, synthesis and characterization of imidazolium based organo- clays which have improved thermal stability (~100 °C) [2], NMR characterization of mixing in montmorillonite (Mt) polymer nanocomposites, and preparation and characterization of fluorescent dye tagged organo-clays [3] (layered silicates and double layered hydroxides) which enable absorbtion and fluorescence spectroscopy of nanocomposites and quantitative laser scanning confocal microscopy (LSCM) of mesoscopic nanocomposite morphology [4]. We have also been focused on one of the major applications of clay polymer nanocomposites i.e., as flame retardants [5]. This presentation will cover our most recent research on elastic modulus and flammability properties, absorbtion and fluorescence spectroscopy, nanocomposite foams and sustainable fire safe products.

**Keywords:** Nanocomposite, Characterization, Flame retardant.

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# POLYSULFONE-SODIUM BENTONITE NANOCOMPOSITE MEMBRANES

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Polysulfone (PSf), a polymer widely used in membrane production, exhibits a low hydrophilicity, inducing fouling formation onto membrane surface, which results in water production fall [Wavhal; Fisher]. Moreover, polymer-clay nanocomposite (PCN) technology is known to be a successful way to improve several features, such as, thermal, mechanical and chemical resistance properties [Ray, Okamoto]. Then, nanocomposite membrane production is a method to produce an enhanced material, once PCN presents improved properties, with higher hydrophilicity, since sodium bentonite is a hydrophilic clay. Therefore, a comparison of properties of the pure polysulfone membrane and nanocomposite membrane, considering clay content, is the main aim of this study.

Membranes were prepared by wet-phase inversion method, by adding clay to the system PSf Udel® P-1700/ N-methyl-2-pirrolidone/ water, consisting to a variation of solution dispersion technique. Thermal properties were evaluated by thermogravimetry/ derivative thermogravimetry, tensile tests were performed to determine mechanical properties and contact angle measurements were carried out to provide hydrophilicity properties.

The increase of thermal stability, reflected by onset decomposition temperature, is a result of the interaction between clay platelets and polysulfone chains. Clay layers act as a heat barrier e improve total thermal stability. The increase of final decomposition temperature is due to labyrint effect created by the dispersed clay platelets in the material, rendering volatilization difficulties.

Slight improvements around 15% for elongation at break of nanocomposite membranes prepared form dispersions containing until 3,0wt%. A reason for this could be the rearrangement of clay platelets in the direction of deformation, allowing bigger deformations. It was observed an increase of tensile strength (around 20% for nanocomposites prepared from a 0,5 to 3wt% clay dispersion), caused by the interactions between clay platelets and polymer chains.

Apolar interactions were diminished by adding clay and the opposite effect was observed for the polar interactions, which means that nanocomposite membranes have a higher affinity for water molecules and a lower affinity for apolar molecules that can be reflected by a lower retention of substances onto membrane surface.

**Keywords:** Sodium bentonite, Polysulfone, Membrane.

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# DEVELOPING AND APPLYING POLYCATION-CLAY COMPOSITES FOR THE REMOVAL OF SELENIUM FROM DRINKING WATER

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Recently several wells have been closed due to high levels of selenium which may cause health problems. The WHO and the EU recommend an upper limit of 0.01 ppm selenium in drinking water. Common selenium removal methods are based on ion exchange, membrane filtration and iron hydroxides, technologies which are not selective, expensive and usually fail to lower selenium concentrations below the recommended limit. In the current study we designed polycation-montmorillonite composites for the efficient removal of selenate (a soluble form of selenium) from drinking water. We tested three polycation-montmorillonite composites (5 g/L) for the removal of very high selenate concentrations (0.64 ppm). In all cases selenate removal (74-99%) increased with the increase in polymer loading on the clay. Only the chitosan-montmorillonite composites succeeded to reduce the selenate concentration below its limit. We suggested that upon penetration of two layers of polycation (and not one) between the clay platelets an anion exchange composite is formed which promotes selenate removal. Indeed XRD measurements indicated that the basil spacing of the efficient chitosn composite increased to 2.18 nm which can account for an intercalation of two polymer layers. The concentration of selenate and of sulfate (competing anion) detected in a closed well in Israel were 0.11 and 13 ppm, respectively. The removal of selenium (0.11 ppm) by the chitosan-montmorillonite composites (5 g/L) was high (93-98%) for all polymer loadings on the clay (0.1- 0.43 g/g). Selenium (0.11) removal in the presence of sulfate (13 ppm) was complete only at high polymer loadings (0.43 g/g). The removal of selenate from a selenate solution and from the well water was studied in column filtration experiments. Columns were filled with the 0.43 g/g chitosan-montmorillonite composite and with basalt or aluminum oxide (to improve hydraulic conductivity) at a ratio of 1:19. Selenate removal from well water was nearly complete by the composite-oxide filter whereas, the composite-basalt filter was less efficient. This result indicates that the oxide also removes selenate and emphasizes the advantage of using it as a filling material. We suggest that the advantage of the composite-oxide filter in comparison with the oxide filter will be more pronounce when increasing the volume of water filtered.

**Keywords:** Polymer-clay nanocomposites, Selenium, Water treatment.

# THE INFLUENCE OF CLAY AND PLASTICISER ON THE BARRIER PROPERTIES OF STARCH NANOCOMPOSITE PAPER COATINGS

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The drive to improve the barrier properties of biopolymer coatings and films to replace petroleum derived materials in the packaging industry continues to gain momentum. Indeed, it was one of the major targets in SUSTAINPACK, an integrated project funded by the EU, which ended in September 2008. An important outcome of this project was a clay-starch-plasticiser formulation which exhibited a very competitive water vapour transmission rate (WVTR) of < 30 g $m^2$ $day^{-1}$ at 23 $^{o}$C and 50% relative humidity (RH).

The ability to achieve this attractive WVTR value depended on the type of plasticiser used in the coating formulation. The plasticiser was also a critical ingredient needed to overcome the inherent brittleness of the starch which becomes a major factor when the coated paper or board is bent or creased.

In order to better understand the contribution of the different components in the coating formulation an extensive survey was undertaken. The interaction of plasticisers such as glycerol, sorbitol and polyethyleneglycol with the bentonite used was studied in the absence and presence of starch using XRD. Particular attention was paid to how the d-spacings were influenced by factors including plasticiser and starch loading, the ambient humidity and the processing temperature.

There were important differences in the ordering of the clay platelets when different plasticisers were used. Polyethyleneglycol and sorbitol exhibited a range of spacings as the plasticiser loading was increased and polyethyleneglycol was particularly adept at enhancing the signal from the clay platelets even in the presence of starch.

**Keywords**: Nanocomposites, Starch, Paper coating.

# ORGANICALLY MODIFIED HYDROTALCITE-LIKE ANIONIC CLAYS, NON CONVENTIONAL FILLERS OF POLYMERIC COMPOSITES

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It is well known that the dispersion of inorganic particles, having at least one dimension in the nanometer range, into organic polymers is an efficient way to improve the mechanical, thermal and gas permeability properties of the original polymer. In order to obtain a homogeneous dispersion of inorganic nano-particles into the polymeric matrix and obtain a thermodynamically stable system, the interfacial adhesion between the two phases can be improved by anchoring organic species, compatible with the polymer, to the surface of the inorganic particles. The most common nano-particles used to obtain polymeric composites are organically modified layered silicates (nanoclays). The present communication will report recent results obtained by using as inorganic fillers of hydrophobic and hydrophilic polymers, exfoliated hydrotalcite-like anionic clays (HTlc), suitably modified. Zn-Al or Mg-Al - HTlc, modified by intercalation of hydrophobic anions such as stearate [1], oleate, 1-adamantanecarboxylate [2], have been successfully used as fillers in polyethylene nano-composites. In particular the flame retardant properties of the polymer in the nano-composites have been investigated. The results indicate that the presence of the hydrotalcite lamellae produces a good barrier effect to oxygen diffusion into the heated polymer. Moreover, the interlayer region of the hydrotalcites has been used to host several hydrophilic guests such bis(2-ethylhexyl) sulfo succinate anion (AOT), glycolate, lactate, gluconate and hydroxylate aromatic anions. The intercalation compounds have been used as filler of a water soluble polymer as the poly(ethylene oxide) (PEO) [3]. The polymeric films obtained have been characterized by XRD and thermal analysis. The lack of the typical reflections of the intercalation compounds in the XRD patterns is an indication of the nanocomposite formation. Thermal analyses indicate that HTlc functionalized with hydroxylate aromatic guests offers a barrier to the oxygen diffusion increasing the $T_{max}$ of PEO of about 40 °C.

**Keywords:** Polymeric nanocomposites, Hydrotalcite-like anionic clay, Flame retarding effect.

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# PREPARATION, CHARACTERIZATION AND MECHANICAL PROPERTIES OF CLAY-PVAc LATEX BASED NANOCOMPOSITES

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Nanocomposites produced from incorporating a small amount of nanoclay into matrix materials offers several advantages over the matrix polymer or classical composites and have exhibited large improvements in gas barrier properties, mechanical properties, thermal stability, fire retardancy, and other areas and this materials (1,2). Then, it is well known that changes in the structure of composites materials particularly affect the barrier characteristics and mechanical properties of the materials. Montmorillonite is the most widely used clay in polymer/clay nanocomposites because of its low cost, layered crystal structure, exchangeable interlayer cations and surface properties (3,4).

In this study, nano-clay particles were used with poly(vinyl acetate), PVAc, based latexes. PVAc latexes are widely used in a waterborne coatings and adhesives because of they are ready to application, compatible with the other materials and have a low cost. Although PVAc based latexes are used in various industrial applications, in many of these they are disadvantaged by the poor water resistance, poor creep and poor heat resistance of PVAc . Vinyl acetate (VAc) is copolymerized with another monomer such as ethylene, butyl acrylate, 2-ethyl hexl acrylate and methyl methacrylate. However, the some poor properties of these copolymers based vinyl acetate have been not exactly improved (5,6). In this study, the effect of clay particles prepared with a different methods on the structural, mechanical and thermal properties of the poly(vinyl acetate) based latex were investigated. The previously determined rheological and colloidal properties of montmorillonite dispersions and latexes were investigated. The physical mechanical properties, thermal stability, rheologic and electrokinetic measurements of clay-PVAc latex based nanocomposites are determined.

**Keywords:** PVAc, Clay, Nano-composites, Physical and mechanical properties.

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# EVALUATION OF DOMESTIC BENTONITE DEPOSITS FOR NANOCOMPOSITES

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The largest domestic bentonite mine in Mangatarem, Philippines is currently utilized as a bulk industrial material (i.e. feed additives, general purpose sorbent, coagulant), its value lower compared to its utilization for other purposes such as in clay-organic polymer nanocomposites and as a carrier for active ingredients in pharmaceutical products. However, it is necessary to evaluate its mineralogical purity and implement the appropriate beneficiation procedures prior to its utilization.

Two types of material are being produced from the mine: (1) an industrial bentonite (i.e. smectite clay) and (2) zeolites. XRD analyses conducted in this study have determined that these two materials are similar in terms of mineralogical composition. Both are dominated by smectite clay (i.e. montmorillonite) and a zeolite (heulandite-type) but differ in the amount of accessory minerals such as magnetite and calcite. This is reflected on the color and XRF-determined geochemical composition of the bulk materials. Bentonite is pinkish and contains a larger amount of Fe and Ca while zeolite is greenish with less Fe and Ca.

The main goal involves separation of the individual mineral components through combined physical and chemical treatments. Five (5) treatments were utilized to determine their effects on the bentonite and zeolite bulk (i.e. XRD and XRF) namely: (1) distilled water only; (2) NaCl-exchange; (3) alkaline treatment; (4) acid treatment; and (5) formamide only. Based on these results, a beneficiation procedure was formulated to primarily separate smectite from the bulk bentonite material. Magnetite can be separated by utilizing a very strong magnet. Calcite was primarily removed by acid treatment. Formamide can only be utilized when the smectite has been isolated from the bulk material. The smectite was utilized for a montmorillonite-PVA and montmorillonite-epoxy nanocomposite at different weight loadings (5 to 20% wt.).

**Keywords**: Bentonite, Nanocomposites, Mineralogy.

# REAL-TIME INVESTIGATION OF CRYSTALLIZATION IN PVDF-BASED NANOCOMPOSITES

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*Via* time-resolved Fourier transform infrared spectroscopy (FTIR), we examined the real-time investigation of the conformational changes of poly (vinylidene fluoride) (PVDF) chain segment during crystallization of neat PVDF and the corresponding nano-composites. It was shown that on the following crystallization processes the chain folding mechanisms of the crystal growth were virtually the same in both nano-composites and neat PVDF. We have examined an annealing at an infinitely long time at 200 °C (~20 min) to erase the thermal history in the nano-composites. The dispersed titanate nano-filler particles exhibited strong contribution to enhance the heterogeneous nucleation for the formation of both $\gamma$- and $\beta$-phase crystals.

**Keywords:** Poly(vinylidene fluoride), Nano-composites, Crystallization.

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# THE ENVIRONMENTAL STABILITY AND FLAMMABILITY OF POLYMER/CLAY NANOCOMPOSITES

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Environmental stability is a key factor for polymer materials in their processing and usage due to their degradation. It is even the case in polymer/clay nanocomposites (PCN). The present paper reports some results on the photo-oxidation, thermal degradation and oxidation, and flammability of polymer/clay nanocomposites.

PE/clay and PP/clay nanocomposites were prepared by melt compounding and their UV aging behavior were studied. The rate of photo-oxidation of PCN is faster than that of pure polymer. The effect of compatibilizer, organic modification of clay, nature of clay, transition metal ions in clay galleries and hydroxyl groups on layer side of clay, were investigated respectively. The compatibilizer can introduce some functional groups to polymer matrix; the complex crystallographic structure and habit of clay minerals result in some catalytic active sites; the decomposition of ammonium ions can create catalytic acidic sites on clay layers. All these functional groups and active sites can lead to the formation of free radicals and catalyze the UV aging of polymer matrix. The thermal degradation and thermal-oxidative degradation of PP/clay and PA66/clay nanocomposites were studied. On the one hand, the addition of clay could improve the thermal stability of PCN; on the other hand, it could catalyze the initial decomposition of polymer matrix. In thermal degradation of PP/clay nanocomposites, the reaction order was lowed to zero-order, whereas the activation energy had a dramatic increase. The kinetic analysis can provide additional mechanistic clues on thermal stability and flammability of PCN.

PP/clay and PA66/clay nanocomposites were prepared to investigate their combustion behaviour by cone calorimeter. The influence of organic modification of clay, nature of clay and dispersion state of clay is considered respectively. The decrease of heat release rate (HRR) of PCN is not only due to the barrier effect of clay layers. The active sites on clay layers and acidic sites created by the decomposition of organoclay can catalyze the dehydrogenation, crosslinking and charring of PCN. The protective coat-like char and physical-chemical crosslinking effect should be responsible for the decrease of HRR in PCN.

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**Keywords:** Polymer/Clay Nanocomposites, Stability, Flammability.

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# PREPARATION AND THERMAL STABILITY OF NOVEL FLUOROALKYL END-CAPPED OLIGMERS/CLAY AND /SILICA NANOCOMPOSITES

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Fluorinated polymers are attractive functional materials due to exhibiting excellent chemical and thermal stability, low surface energy, and low refractive index which cannot be achieved in the corresponding non-fluorinated polymers.[1] Therefore, it is in particular interest to explore novel fluorinated polymers/inorganic nanocomposites from the developmental viewpoints of new composite materials possessing unique characteristics imparted by fluorine. In this study, we would like to demonstrate on the preparation and thermal stability of fluoroalkyl end-capped N-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer/clay and /silica nanocomposites. Fluoroalkyl end-capped N-(1,1-dimethyl-3-oxobutyl) acrylamide oligomer [$R_F$-(DOBAA)$_n$-$R_F$]/clay nanocomposites were prepared by the interaction of the corresponding oligomer with organically modified clay in 1,2-dichloroethane. The size of the obtained composites was nanometer-size controlled, and these fluorinated clay nanocomposites were applied to the surface modification of the traditional organic polymers such as poly(methyl methacrylate) to exhibit a good surface active characteristic imparted by fluorine on their surface. $R_F$-(DOBAA)$_n$-$R_F$/silica nanocomposites were prepared by reactions of the corresponding fluorinated oligomer with tetraethoxysilane and silica nanoparticles under alkaline conditions. These fluorinated oligomer/silica composite thus obtained is nanometer size-controlled very fine particles possessing a good dispersibility and stability in a variety of solvents including water. TGA (thermogravimetric analyses) showed that $R_F$-(DOBAA)$_n$-$R_F$/clay nanocomposites exhibited a clear weight loss at 800 $^{o}$C, which corresponds to the content of the oligomer; however, $R_F$-(DOBAA)$_n$-$R_F$/silica nanocomposites, in which the oligomer contents are 18 ~ 72 %, were not observed at all even at 800 $^{o}$C, as well as the original silica nanoparticles.

**Keywords:** Fluorinated Oligomeric Nanocomposite, Clay, Silica.

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# TRANSPARENT EPOXY-CLAY FABRIC FILMS COMPOSITES WITH HIGH GAS BARRIER PROPERTIES

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We have developed epoxy-clay fabric film composites with high $O_2$ gas barrier properties by impregnating self-supported clay fabric films with epoxy pre-polymers [1]. In order to improve the interfacial adhesion between the oriented clay particles and the epoxy matrix, homoionic organoclays and homostructured and heterostructured mixed inorganic-organic ion clay films were prepared. Naturally occurring $Na^+$-montmorillonite (MMT) and synthetic $Li^+$-fluorohectorite were exchanged with cetyltrimethylammonium ($CTA^+$), choline $(CH_3)_3N^+CH_2CH_2OH$, glycidyltrimethylammonium ($GTA^+$) and diprotonated primary α, ω-diamine $H_2NCH(CH_3)CH_2[OCH_2CH(CH_3)]_xNH_2$ (denoted Jeffamine D2000 with $x = 33.1$). In comparison with the parent inorganic clay films, which show no adhesion toward the epoxy matrix, $CTA^+$, choline and $GTA^+$ clay films present substantially improved interfacial adhesion. The large interlayer spacing of ~27 Å for $CTA^+$ organoclay (42% onium ion exchange) and the functional –OH and epoxide groups in choline and $GTA^+$, respectively, may facilitate the solvation of clay nanolayers by epoxy precursors and promote adhesion. Clay films partially exchanged by di-protonated Jeffamine D2000 provide the best adhesion to epoxy polymer and impart the high optical transparency. The di-protonated organocations play a dual role of organic modifier and curing agent for the thermoset epoxy matrix. Thus, the clay fabric films links to the epoxy matrix by forming covalent bond at the interface of the two phases. An interesting finding based on XRD and SEM-EDS measurements is that polymer adhesion improves with the increasing degree of clay platelet orientation at the surface of the fabric film. Also, fabric films assembled from fluorohectorite plates are very robust paper-like materials, whereas most of the organo-MMT films are very fragile. The difference in durability is correlated with the aspect ratio of the platelets. The pristine clay films are very permeable to oxygen due to the micro- to sub-micro size voids formed between clay nanolayer edges. However, the epoxy-clay fabric composite films show 3-4 orders of magnitude decrease in $O_2$ permeability with respect to the parent clay films. The enhancement in barrier properties is attributed to the efficient diffusion of epoxy monomer and curing agent into the clay film and to the blocking of the voids between clay platelet edges upon curing.

**Keywords:** Epoxy, Adhesion, Permeability.

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# EFFECT OF IMPROVED D-SPACING OF MONTOMORILLONITE ON PROPERTIES OF POLY (VINYL CHLORIDE) – NANOCOMPOSITES

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Surface modification of montomorillonite for improvement in d-spacing was done using quaternary long chain ammonium salt with cation exchange capacity of 110 meq/100 g. Organically modified montomorillonite (OMMT)/ poly (vinyl chloride) (PVC) nanocomposites were prepared through direct melt compounding on a conventional twin screw extruder. Due to improved d-spacing of OMMT the polymer chains get exfoliated in between the plates of clay and dispersed uniformly. The mechanical properties of the nanocomposites were found to be appreciable at 12 wt % loading of OMMT. Moreover, rheological data like torque, fusion time, viscosity and shear rate were also recorded on Brabender Plasticorder. The improvement in mechanical properties with increase in amount of OMMT loading is evidenced from reduction in shear viscosity and torque. Also nanoclay is acting as a lubricating agent with packing effect, which reduces the torque with decrease in viscosity along with increment in elongation at break. Due to soft nature of OMMT and improvement in d-spacing the processing of PVC becomes easier and hence OMMT is playing a dual role as a i) good processing aid ii) filler.

**Keywords:** Poly (vinyl chloride), Montomorillonite (OMMT), Mechanical properties, Thermal properties, Rheological Properties.

# MONTMORILLONITE NANO COMPOSITES FOR ORAL DRUG DELIVERY SYSTEM

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The need for safe, therapeutically effective and patient-compliant drug delivery systems has continuously led the researchers to design novel tools and strategies. The main objective of this study was to develop a drug delivery system based on clay composites. Which is expected to be resistant to different pH and enzymatic conditions present in the gastrointestinal tract. Such delivery systems is likely to offer numerous advantages like improved efficacy, reduced toxicity, improved patient compliance and increase bioavailability of the drug.

The present work descibes the possibility of using poly (D, L-lactide-co-glycolide) montmorillonite nanocomposites (PLGA - MMT) with propranolol hydrochloride as the model drug. Propranolol hydrochloride loaded PLGA - MMT nanocomposite was prepared by the simultaneous emulsification/solvent diffusion method.

Propranolol hydrochloride containing PLGA - MMT nanoparticles were found to be spherical in shape, with sizes ranging from 80 – 150 nm, with a polydispersity of less than 0.14. Physical state of propranolol hydrochloride in the PLGA - MMT nanocomposite was investigated by DSC which confirms the presence of drug in the nanocomposites in its original state.

XRD and SEM with EDAX studies confirm partial exfoliation of MMT layers, the drug and the polymer form the inner core with a protective outer layer of silicate.

**Keywords:** Montmorillonite nanocomposite, Drug delivery system, Propranolol hydrochloride.

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# STUDY OF NYLON 6/CLAY NANOCOMPOSITES BY CONTINUOUS SONICATION PROCESS

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Nylon 6/clay nanocomposites were prepared by the single screw extruder with attached die of ultrasound of variable amplitude. The structure and morphology of nanocomposites were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM). Mechanical properties such as Young's modulus, elongation, breaking stress, toughness, yield stress and yield stain of ultrasonically treated nanocomposites were changed significantly in comparison to untreated nanocomposites. Complex viscosities of nanocomposites were increased with clay loading and decreased after ultrasonic treatment. XRD, differential scanning calorimeter (DSC) and $^{15}$N-NMR spectra were used to investigate the structural change in nylon 6/clay nanocomposites. The results indicate that the addition of the intercalated organoclay can induce generation of $\gamma$-form of crystal of nylon 6 and substantially affect the arrangement of molecules in the $\alpha$-form crystal. From the DSC results it was found that the addition of clay in the nylon 6 matrix leads to decrease of crystallinity and this property increased ultrasonic amplitude. A substantial reduction in oxygen permeability was observed by increasing clay loading.

**Keywords:** Sonication, Nanocomposites, $^{15}$N-NMR, Crystallinity, Permeability.

# PREPARATION, STRUCTURE, PERFORMANCE, INDUSTRIALIZATION AND APPLICATION OF ADVANCED RUBBER/CLAY NANOCOMPOSITES

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Clay/polymer nanocomposites have attracted great interests in the field of materials science and engineering for some superior properties. However, further development is limited by reasons like high price/performance ratio and deficiency in some properties. To break through the bottleneck we have to (1) develop preparation techniques with low cost; (2) exploit the acquired excellent properties and find optimum application fields. In this report, the compositing method using pristine clay and commercialized rubber latex to produce layered silicate/rubber nanocomposites, namely latex compounding method, is introduced. The unique compositing mechanism and structure of the obtained nanocomposites are discussed, and properties of series of clay/rubber nanocomposites prepared by this method are systematically presented. Latex compounding method is a low-cost and easily controlled process, and quite promising to be industrialized. The structure of the nanocomposites is either “Separated Structure” or “Intercalated Structure”. The nanocomposites show desirable properties, such as excellent tensile strength, superior gas barrier property, improved flame retardant property, outstanding anti-fatigue properties, etc. As a result, the first production line of kiloton clay/rubber nanocomposites materials in China was established and ten thousands tons scaled production line is being constructed. The applications of the nanocomposites in tyre inner tube, tyre inner liner, OTR tyre tread and conveyor belts are presented.

**Keywords**: Clay, Rubber, Nanocomposites, Multifunctional performance, Preparation.

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# NANO & POROUS MATERIALS

## SESSION NM7

## *Polymer-Clay Nanocomposites: Preparation Techniques and Theoretical Formulations*

# INTERACTION CHARACTERISTICS OF POLYMER NANOHYRIDS WITH POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (POSS)

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Polyhedral oligomeric silsesquioxane (POSS) reagents show unique hybrid chemical compositions with nano-sized cage structures that are of comparable dimensions with those of most polymer segments and coils [1]. Thus, incorporation of POSS into polymer chains can be used to modify the local structure and chain mobility in polymeric materials. Also, the wide variety of functional groups and the solubility of POSS in both organic solvents and comonomers allow them to be easily adopted as the comonomer feedstock and/or graftable reagents [1]. In this study, we attempted to present a generalized functionalization scheme for POSS suitable for various polymer systems using the theoretical and experimental approaches. The polymer nanohybrids containing various functionalized POSS were prepared by melt compounding. For the theoretical considerations the thermodynamic interaction energy density and thermodynamic solubility parameter were used to study the specific interaction between polymers and the functionalized POSS. The thermodynamic interaction energy density was determined by the melting-point depression method using differential scanning calorimetry, based on the classical Flory-Huggins theory [2]. And, the thermodynamic solubility parameters of polymers and the functionalized POSS were calculated using the method of Hoftyzer and Van Krevelen, and Hoy [3]. The interaction characteristics of nanohybrids were further characterized by measuring the activation energy and by following the weighted relaxation time obtained by the stress relaxation experiment. Thermal, mechanical, rheological and morphological properties of nanohybrids were analyzed to correlate theoretical and experimental results.

**Keywords:** POSS, Interaction Energy Density, Solubility Parameter, Nanohybrid.

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# HALLOYSITE CLAY TUBES AS BIOCOMPATIBLE NANOCONTAINER FOR SUSTAINED RELEASE OF PROTECTIVE AGENTS

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One way to utilize the high functionality and stability of bio-related materials is to create hybrids consisting of materials of biological origin and inorganic materials. Among other templates employed for biomineralization, halloysite, a naturally occurring aluminosilicate nanotube, has been undeservedly forgotten. Halloysite is defined as a 1:1 layered aluminosilicate, chemically similar to kaolin, which has predominantly hollow tubular structure in the submicron range.[1-3] Halloysite is an economically viable raw material that can be mined as a raw mineral. As for most natural materials, the size of halloysite particle varies within 1-2 microns of length and 15-100 nm of inner diameter depending on the deposits or even within different locations in a specific deposit. Halloysite nanotubes are efficient nano-containers capable of entrapping a range of active agents[2] within the inner lumen (as oxygen corrosion and biological protection, expecially for ship protection), followed by their retention and slow release[3]. Halloysite is a green environmentally friendly object available in commercial quantities. The lumen of the halloysite tube accommodates globular protein diameters, allowing their entrapment within the inner lumen of the halloysite while retaining their activity for use in biocatalysis. In this work a combination of Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) and Scanning Force microscopy (SFM) imaging have been employed to elucidate the structure. We have investigated their visco-elastic properties by force-indentation measurements and performed MTT test, utilizing neoplastic cell lines (i. e. breast cancer cells). The results indicate that halloysite clay nanotubes exhibit a high level of biocompatibility and very low cytotoxicity, rendering them an ideal candidate as a therapeutic and protective nanocarrier.

**Keywords**: Halloysite, Clay, Nanotubes, Nanocarriers.

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# MIXED MODIFIER ORGANOCLAYS - CONTROLING CLAY DISPERSION IN POLYMERS

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The current focus on the dispersion of organomodified clays into both petroleum and plant derived polymers presents significant challenges; particularly given the very restricted range of organomodifiers used in the production of commercially available organoclays. Successful development of commercial nanocomposite products requires a secure source of reproducible organoclays. The purpose of the organomodification is to increase the platelet-platelet separation, decrease the platelet-platelet attraction and make the clay surface more compatible with the host polymer. The work presented here will describe the strategy, production and characterisation of a series of commercially available organoclays which have been modified by incorporation of a second organomodifier of much shorter chain length than the commercial organomodifier. The influence of the solvent system on the redistribution of the original modifier and the incorporation of the second modifier will be presented.

X-ray diffraction evidence indicated that the short chain and long chain modifiers did not segregate into different interlayers. Except at a 50% loading of the shorter chain modifier the mixed-modifier clays exhibited a single diffraction peak (of varying breadth). The d-spacing varied from the 19.5 Å spacing of the commercial clay to 14.5 Å for the modifier with the shortest alkyl chain. The mixed modifier distribution will also be discussed with reference to TG-MS, 'H NMR and carbon/nitrogen analysis data.

Representative examples of the dispersion of these mixed modifier clays into solvent-cast polycaprolactone films will be described. Transmission electron micrographs confirmed that a mixed modifier clay with 20 wt% of the shorter chain modifier represented the optimised clay for polycaprolactone because the clay layers were completely delaminated and dispersed through the polymer matrix.

**Keywords**: Polymer-Clay Nanocomposites, mixed modifier organoclays.

# PHYLLOSILICATE/ORGANIC HYBRIDS WITH COVALENT BONDS BETWEEN INROGANIC AND ORGANIC MOIETIES: VERIFICATION OF STRUCTURES AND PREPARATION OF HETEROGENEOUS SYSTEMS WITH LUMINESCENCE

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Lamellar hybrids with covalent bonds between inorganic and organic moieties are very attractive materials, because it would be possible to tune the electronic structures and the properties of both the inorganic and organic moieties and control arrangements of the organic moieties within two-dimensional nanoscaled galleries. They have also merits in formation of inorganic-organic hybrid nanosheets and its application to polymer-clay nanocomposites. In this study, we focus on the structure of the phyllosilicate/organic hybrids we prepared and its application to preparation of heterogeneous systems with luminescence.

The structure of the hybrid, especially the covalent bonds between the inorganic and organic moieties, plays an important role in preparing the heterogeneous systems, for the covalent bonds suppress deintercalation and segregation of two functional organic species. Therefore, first we prove the structure of the model hybrid - phyllosilicate/alkylammonium hybrid with the covalent bond between inorganic and organic moieties. The structure of the hybrid is supported by all experimental results such as elemental analysis, high-resolution solid-state nuclear magnetic resonance as well as discussion including *Sc* (the silicate surface area covered by the organic cations). The experimental results are inconsistent with other models, e.g. mixtures of phyllosilicate and polycondened organosiloxane.

Next, we report application of the phyllosilicate/organic hybrids to heterogeneous systems with luminescence. Phyllosilicate/coumarin hybrids (host hybrids) are synthesized and the structures of the host hybrids are verified in a similar manner to the above model hybrid. Coumarin/cyanine heterogeneous systems are prepared by intercalation of cyanine into the interlayer space of the host hybrids. Absorption peaks are observed around 488 and 463 nm for the coumarin/cyanine heterogeneous systems by ultraviolet–visible (UV-vis) measurement, and these absorption peaks become more intense as the cyanine content increases. These UV-vis results indicate that cyanine is incorporated in the interlayer space, resulting in the coumarin/cyanine heterogeneous systems. The deintercalation of the coumarin moiety and segregation of the coumarin moiety and cyanine are suppressed by the covalent bond between the phyllosilicate and coumarin moieties. Both the coumarin moiety and cyanine fluoresce. Interestingly emission from cyanine is observed even when the coumarin/cyanine heterogeneous systems are pumped at 320 nm.

**Keywords:** Phyllosilicate/organic hybrid, Covalent bond, Fluorescence.

# DIVERSIFIED NANO-HYBRIDS OF POLYAMIDESPRDUCTION METODS AND STRUCTURE

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Poly-amide was picked from among several candidate polymers in the early stages in my development for hybrid materials. Diversity in polymerization methods was one of the significant factors to choose the Nylon. Ring opening metathesis polymerization, dehydration condensation and interfacial polymerization provide various sorts of poly-amides.

The ring opening polymerization of caprolactam to form 6-Nylon has been applied for NCH; Nylon-Clay mineral Hybrid (Fukushima,1988). Van der Waals attraction between poly-amide chain and silicate surface and the interface structure would be attributable to the mechanical, gas barrier and other properties of NCH.

Nylon-66 which is prepared by dehydration condensation of hexamethylene diamine and adipic acid was also tried to use in the hybrid materials. However, an ionic character of the monomer molecules interfered with the formation of the dispersed structure like the NCH.An organic derivative zirconium phosphate, where the organic pendants are bind covalently to the phosphate layer, was used as a host for Nylon-66 – inorganic hybrids. As a distribution of the organic pendants to form the amide amide binding, arrangement of the poly-amide chains could controled easily. A successive growing of Nylon-66 type polymerization was observed. We also made a smectite like layers which have similar organic pendants on the silicate surface, which was layerd organic-inorganic hybrid polymer (Fukushima, 1995). The hybrid polymer is expected an expanding the nano-hybrid technology.

Poly-amides are formed at the interface between an organic solvent dissolving acid halide and aqueous solution of diamine. A group of DIC corporation tried to make a silica-polyamide hybrid by the interfacial polymerization (USPatent, 1998). They used adipic acid dichloride toluene solution and 1,6-diaminohexane aqueous solution, in which sodium silicate was also dissolved. A hydro chloride generated by the polymerization reaction of the acid dichloride with the diamine reacted with sodium silicate to form silica nano particles. Uniform dispersion of silica particles with several nm size, and any binding between silica and amide part in poly-amide chain realized excellent properties (Deguchi, 2003).

We have diversified possibility in hybrid technology. We have also many typical hybrid materials in biological systems, or traditional mortars, which we should refer for planning the future directions of new-materials.

**Keywords:** Polyamide, Polymerization, Phyllosilicates, Silica.

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# STRUCTURE AND CLEAVAGE ENERGY OF SURFACTANT-MODIFIED CLAYS: INFLUENCE OF CEC, HEAD GROUP, AND CHAIN LENGTH

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Upon exchange of alkali cations on clay mineral surfaces with alkylammonium or alkylphosphonium surfactants, the approximate tilt angle and occurrence of thermal transitions of the surfactants can be estimated from the packing density, defined as the cross-sectional area of all-anti-configured alkyl chains in relation to the available surface area per chain. This simple propensity rule is supported by experimental data including X-Ray, NEXAFS, AFM, TEM, IR, SFG, NMR, DSC, however, the detailed molecular structure, the surface energy, and transition temperatures depend on the CEC, head group chemistry, and chain length of the surfactants. We discuss the gallery spacing, the interlayer density, the backbone conformation, and the cleavage energy as a function of these variables for more than 40 different alkylammonium montmorillonites using molecular simulation and experiment. At low CEC, alkyl monolayers, bilayers, trilayers etc parallel to the surface between the clay mineral layers are seen with increasing chain length, and such step-wise patterns weaken at higher CEC. Primary ammonium head groups, in contrast to quaternary head groups, form additional hydrogen bonds to the silicate surface which results in reduced mobility and simpler thermal behaviour. Chain conformations range from between 15% and 35% gauche in the hydrocarbon layers parallel to the surface to only 5% gauche in well-ordered, upright oriented layers for multi-arm surfactants at high CEC. The range of distinct patterns and interlayer densities also results in variable cleavage energies between 30 and 100 mJ/m$^2$ for organically modified clay minerals with different surfactants in contrast to cleavage energies of >100 mJ/m$^2$ for alkali clays. These data have implications on the miscibility with various polymers of a similar surface energy (20−60 mJ/m$^2$), assuming that exfoliation in nanocomposites requires a negative or minimal positive interface tension. We also present the tensile, shear, and bending properties of mica-type minerals as a function of CEC including a proposed failure mechanism.

**Keywords:** Polymer-clay nanocomposites, Surface properties, Organoclay.

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# LAYERED DOUBLE HYDROXIDES INTERCALATED WITH DERIVATIVES OF ACRYLIC ACID AND THEIR APPLICATION IN PREPARATION OF LDH/POLYMER NANOCOMPOSITES

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Layered double hydroxides (LDHs) intercalated with various organic anions are often used for preparation of LDH/polymer nanocomposites, in which inorganic nanoparticles are dispersed in low concentration in polymer matrix [1]. Monomer anions containing vinyl group, namely acrylate, methacrylate, 2-acrylamido-2-methyl-1-propan sulfonate (AMPS), and vinylbenzoate, polymerization initiator (4,4'-azobis(4-cyanopentanoate)), and hydrofobizing agent (dodecylsulfate) were intercalated into Zn-Al LDH host structure. A direct coprecipitation of Zn and Al nitrates in the presence of organic anion or anion exchange using coprecipitated Zn-Al-$NO_3$ LDH precursor were applied for preparation of intercalated products. The intercalated LDHs dispersed in aqueous phase were then used as comonomer and initiator for preparation of polybutylmethacrylate-modified LDH hybrid latexes, when the emulsion polymerization was performed in the presence of inorganic (nano)particles. Nanostructured hybrid materials containing low amount (1 – 3 wt%) of inorganic nanofiller were obtained. The mean particle size and structure of the synthesized latexes were characterized by using dynamic light scattering and X-ray scattering (WAXS and SAXS) techniques; particles with mean size of 65 – 100 nm were detected. A minor part of methacrylate or AMPS anions was incorporated into solid during anion exchange, when LDH intercalated with dodecylsulfate was used as precursor; a slight change of LDH basal spacing was observed in powder XRD patterns. After addition of these partially exchanged products, nanocomposite latexes with butylmethacrylate were obtained by *in situ* emulsion polymerization; the nanocomposite was not formed, when LDH intercalated only with dodecylsulfate was applied. A modification of intercalated LDHs with photoactive porphyrin anions and application of modified products in nanocomposite preparation were also examined.

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**Keywords**: Layered double hydroxides, Intercalation, Polymethacrylate nanocomposite.

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# PREPARATION OF POLYMER-HECTORITE NANOCOMPOSITES USING LIQUID CRYSTALLINE SUSPENSIONS OF ORGANOPHILLIC HECTORITE

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In the field of clay-polymer nanocomposites most attention has been given to the use of the smectite clay Montmorillonite. Here we report the preparation of nanocomposites of natural smectite Hectorite particles. Sterically stabilized Hectorite particles (average length 288 nm, average width 43 nm, average thickness 6 nm) were prepared by a novel method in which amino-modified poly-isobutene chains were grafted on the clay surfaces followed by a freeze-drying step, in which water is removed. Redispersion of the organically modified clay particles in toluene led to stable dispersions. These were shown to form permanent birefringent nematic phases -a result of self organization of the highly anisotropic particles- as well as strong flow-induced alignment in the coexisting isotropic phase.

Replacement of the toluene by a monomer solution of divinylbenzene led to stable dispersions that were polymerized using a UV-sensitive initiator (Igacure). The resulting polymer films (0.15 mm) are homogeneously translucent. Submicron thick samples from the bulk of the polymer film were prepared using a Focused Ion Beam setup to obtain Transmission Electron Microscope images of the nanocomposite. These images show that the exfoliated Hectorite particles are freely dispersed in the poly-vinylbenzene matrix. This novel route to the preparation of clay-polymer nanocomposites appears to be general and promising.

**Keywords**: Bentonite Clay, Liquid Crystals, Nanocomposite.

# PREPARATION OF REGULARLY INTERSTRATIFIED LAYERED SILICATE-POLYMER NANOCOMPOSITE

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Most of the previous research on nanocomposites has dealt with layered silicate-polymer nanocomposites that are based on smectite clays. Morphology controlling techniques provide effective alternatives to achieve further improvements in nanocomposite properties. However, studies on other types of layered silicate-polymer nanocomposites have been conducted to a much lesser degree due to the relatively greater difficulty in preparing polymer-intercalated compound composites. Recently, an exfoliated non-expandable mica–polymer nanocomposite was successfully prepared for the first time using a conventional polymer process with a three roll mill.[1] The non-expandable mica platelets strongly resemble clay platelets in their shape and crystal structure, although their absolute size is approximately 1000 times larger than that of clay. Hence, the morphology of the nanocomposite exhibited silicate nanolayers that possess extremely high aspect ratios which are of several dozen to hundreds of times greater magnitude than that of conventional exfoliated clay-polymer nanocomposites.

In this study, a method to control the number of layers of dispersed silicate platelets was investigated using regularly interstratified layered silicates. In order to achieve control over the number of layers, a layered silicate with two antagonistic properties, swelling and non-swelling, was prepared in each particle. A new regularly interstratified layered silicate composed of talc/talc/smectite (TTS) in an ordered sequence was synthesized using a hydrothermal technique.[2] Novel layered silicate-polymer nanocomposites were then prepared through exfoliation of the regularly interstratified layered silicates (rectorite and TTS). The controlled morphology of the nanocomposite resulted in the silicate nanolayers (consisting of 2~3 layers/group) being uniformly dispersed in the polymer matrix. This would appear to be a new method (in polymer nanocomposite technology) that will enable the control of the number of dispersed layers in a nanocomposite.

**Keywords:** Interstratified layered silicate, Polymer, Nanocomposite.

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# POLYMER-γFe2O3-MONTMORILLONITE NANOCOMPOSITES: PREPARATION, CHARACTERIZATION AND PROPERTIES

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Polymer-clay nanocomposites are gaining a widening range of applications, for example in food packaging and automotive industry. Indeed, incorporation of clays in a polymer matrix can improve gas barrier and mechanical properties but also heat stability. Beside clays, other inorganic nanoparticles, such as iron oxides and especially maghemite ($\gamma Fe_2O_3$), are of particular interest in the field of polymer nanocomposites. Their superparamagnetic properties can be used in electromagnetic devices like those uses for electromagnetic interference suppression or for biological applications.

The aim of this work was to develop a new method to obtain a multi functional nanocomposite combining the properties of clays and maghemite. An original method was used to prepare the nanofillers mixture by generating maghemite nanoparticules in the interlayer space of synthetic montmorillonite. The preparation of polymer-$\gamma Fe_2O_3$-montmorillonite nanocomposites was then performed by photo initiated polymerization of difunctional acrylate monomers containing small amounts (1 and 2 wt%) of nanofillers mixture. UV light induces polymer formation allows a fast transformation of the liquid monomer into the solid film to be obtained. Moreover, as this process is solvent-free and do not need heat as in a traditional thermal curing, it is environmental-friendly and guarantees the saving of energy. The formation of iron oxide nanoparticles in the interlayer space of montmorillonite leads to a partial exfoliation. Incorporation of the nanofillers has no effect on the polymerization process as proven by real time infrared spectroscopy. Nanocomposites materials could thus be obtained within seconds. An interesting improvement of the storage modulus was obtained for 2 wt% of nanofillers. The surface roughness caused by the nanofillers leads to small decrease of the gloss.

The elaboration, the structural mechanical characterizations, and properties of these new multifunctional nanocomposite will be discussed in details.

**Keywords**: maghemite, clays, UV curing.

# NANO & POROUS MATERIALS

## SESSION NM8

## *Self-Assembly from Clay Particles: from Nano to Macro*

# SELF-ASSEMBLY AND DYNAMICS OF CLAY PLATELETS IN A MAGNETIC FIELD

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Diffusion-weighted magnetic resonance imaging (MRI) provides a vivid description of the roles played by wall anchoring and applied magnetic fields in the self-assembly of clay platelets in aqueous suspension. The anisotropy of the self-diffusion coefficient of water, caused by directional differences in the tortuosity of the diffusive paths in a system of ordered thin platelets, can be incorporated into MRI contrast yielding a powerful technique for studying various phenomena. In-situ diffusion-weighted MRI measurements have been performed [1] in suspensions of synthetic Na- Fluorhectorite where the polydisperse clay platelets separate, under the action of gravity, into various phases [2]. For a certain range of clay concentration and added salt a gel phase was found to coexist with nematic order [1,2]. Face to face anchoring of the platelets to the walls favors a homeotropic order in the gel phase. The application of a 2.0 T magnetic field very slowly changes the order to a true nematic one where the normals of the platelets become perpendicular to the magnetic field and to the walls of the cylindrical container. Although the dynamics of platelet reorientation in the gel phase is heavily damped it can be monitored in a time scale of ~$10^5$ s using diffusion-weighted MRI. From the difference between torque-free evolution and forced evolution in the presence of an aligning magnetic field it has been possible, using Fokker-Planck´s equation, to extract parameters characterizing the time evolution [3].

**Keywords:** Magnetic Resonance Imaging, Diffusion-weighted imaging, Na-fluorohectorite, Nematic order.

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# PHASE TRANSITIONS IN AQUEOUS SUSPENSIONS OF SWELLING CLAYS MINERALS

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The phase behaviour of swelling clay minerals that are strongly anisotropic bidimensional colloids has been studied for nearly one century as these natural materials control various environmental processes and are extensively used in industry. The occurrence of an isotropic/nematic (I/N) transition in clay suspensions has been debated since Langmuir's pioneering work who reported a macroscopic phase separation in hectorite suspensions. Such a behaviour was subsequently rationalized by Onsager on the basis of a competition between orientational entropy and the packing entropy governed by the excluded volume. However, in most clay minerals studied so far, a sol-gel transition is systematically observed, that hinders the I/N transition. Furthermore, the structure and formation mechanisms leading to the gel remain rather ill-defined. By working on a natural clay, nontronite, we recently evidenced a true I/N transition occurring at a lower concentration than that of the sol-gel transition. In this talk we will analyze in detail for this particular sample the influence of particle anisotropy on the phase diagrams. We will focus on the evolution of both the sol/gel and I/N transitions by combining optical observations, SAXS experiments and rheological measurements. We will show that the system is purely repulsive at low ionic strength and that the I/N transition can be rationalized on the basis of Onsager's approach. Though the structure of the gel remains somehow elusive, we will show that some of its rheological features can be understood through an approach based on effective volume fraction and orientational effects.

**Keywords**: Liquid crystal, Isotropic/nematic transition, Sol/gel transition.

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# AVALANCHE BEHAVIOR IN CLAY SUSPENSIONS

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We show that above a critical stress, typical yield stress fluids (Bentonite suspensions) and soft glassy materials (the colloidal glass of Laponite) start flowing abruptly and subsequently accelerate, leading to avalanches that are remarkably similar to those of granular materials.

Rheometrical tests reveal that this is associated to a bifurcation in rheological behaviour: for small stresses, the viscosity increases in time: the material "ages", and eventually stops flowing. For slightly larger stresses the viscosity decreases continuously in time: the flow accelerates and we observe a "rejuvenation" of the material by the flow.

We show that for the Laponite system, both the aging and the shear rejuvenation can be observed directly using Diffusive Wave Spectroscopy. We propose a simple physical model capable of reproducing the rheological observations.

**Keywords:** Avalanches, Clayey soils.

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# PHASE TRANSITION OF CONDUCTING POLYMER/CLAY NANOCOMPOSITE SUSPENSIONS UNDER ELECTRIC FIELD

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Due to nanoscale polymer-clay interactions, various polymer/clay nanocomposite systems are currently being adopted as novel functional materials. Among these, conducting polymer based clay nanocomposites are known to provide better processability as well as enhanced electric properties [1]. In this work, nanocomposites of the conducting polymers such as polyaniline and polypyrrole with clay are investigated especially for electrorheological (ER) materials. ER fluids are smart materials which can be transformed from a fluid-like state to a solid-like state by an applied electric field [2], thus making electrorheology one of good examples of the self-assembly of clay guided by an external field [3]. This phase transition implies not only interesting physics but also huge engineering applications. Conducting polymer/clay nanocomposites were prepared via in-situ polymerization, emulsion polymerization or solvent intercalation [4] in this study. Compared with the conventional intercalated structure, a unique morphology of clay sheets wrapped polyaniline nanobeads was also introduced. Internal structure and thermal properties of these nanocomposites were examined via WAXD, TEM, and thermogravimetric analyzer. Electrical conductivity of the nanocomposite materials with different clay loading was also characterized. The intercalated nanostructures analyzed via WAXD and TEM were correlated with the electrical and thermal properties change originated from the nanoscale interaction between clay and conducting polymer. Moreover, their ER behaviors were measured via a rotational rheometer with external electric field controller [5]. ER fluids based on different conducting polymer/clay nanocomposites demonstrated diverse ER characteristics such as yield stress, flow curve, viscoelasticity and dielectric spectra.

**Keywords:** Clay, Conducting polymer, Electrorheological fluid.

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# HIGHLY ORDERED NEMATIC PHASES AND EMERGING POSITIONAL ORDERING IN AQEOUS DISPERSIONS OF SODIUM-FLUOROHECTORITE

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We study liquid crystalline phases in dispersions of synthetic sodium-fluorohectorite clay nanoplatelets suspended in saline water. Sedimentation in Earth's gravitational field size-separates the initially isotropic dispersions into several strata [1], of which some display anisotropic properties attributable to the presence of nematic ordering. Small-angle x-ray scattering profiles from gravitationally settled samples show that the preferred direction of order in the nematic phases is perpendicular to the platelets' optical axes, and that the order parameter $S_2$ assumes negative values.

In the current work, size-selecting gravitational sample sedimentation procedures [1] were combined with a slow partial evaporation of the water, and we observe that these combined processes lead to a striking increase in the overall order. This is evidenced both by high optical birefringence orders of monodomains in the upper parts of 2 mm diameter glass capillaries and by measured values for the order parameter $S_2$ reaching positive values as high as 0.91, based on intermediate-angle x-ray data and our previously developed method [2]. Strongly anisotropic small angle x-ray scattering profiles indicate that this new and highly ordered phase is a true uniaxial nematic, where the clay platelets are lying horizontally face down, and where the preferred direction of order corresponds to the average direction of the platelets' face normals. Relatively broad and marked peaks in the small angle x-ray scattering profiles of the partially evaporated samples may be identified as possible pre-transitional features of a nematic-to-columnar phase transition [3].

**Keywords**: Sodium-fluorohectorite, X-ray scattering, Liquid crystals.

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# ISOTROPIC-NEMATIC INTERFACES IN SUSPENSIONS OF NA-FLUOROHECTORITE SYNTHETIC CLAY – ORDER, ORIENTATION AND MAGNETIC FIELD RESPONSE

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Colloidal suspensions of platelet-shaped anisometric synthetic clay Na-fluorohectorite (NaFh) in saline water exhibit coexisting isotropic and nematic phases, due to gravitational separation and ordering of the polydisperse particles [1]. In this work we have studied the ordering of the NaFh platelets near the isotropic-nematic (I-N) interfaces, where a sharp horizontal layer appears. We have also studied the magnetic field response of a liquid nematic region situated between the I-N interface and the viscous nematic gel. We utilize four complimentary experimental techniques: Visual observations of birefringence, Magnetic Resonance Imaging (MRI) and synchrotron X-ray Scattering, both Wide Angle (WAXS) and Small Angle (SAXS).

We find that the particles are lying horizontally at the interfaces, i.e. with the mean particle director along the vertical direction, perpendicular to the isotropic-nematic interface. With externally applied magnetic field, we observe a reorientation of the particles in the liquid nematic region. As previously observed [2], our clay platelets reorient in magnetic field so that their plate normal is perpendicular to the magnetic field lines. Using a combination of magnetic field and sample rotation, we show that the entire liquid nematic region can be made uniaxially nematic with particle orientation equal to that at the interface.

**Keywords**: Clays, Nematics, MR Imaging, WAXS, SAXS, Birefringence, Particle orientation.

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# ISOTROPIC-TO-LIQUID CRYSTAL PHASE TRANSITION OF LAYERED CLAY MINERAL COLLOIDS

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Introduction Colloidal sols of inorganic nanosheets obtained by exfoliation of layered materials were recently found to form lyotropic liquid crystal phases[1] which are useful to fabricate various advanced materials.[2] However, only very limited numbers of clay mineral colloids were reported to form liquid crystal sols,[3], [4] while they usually form birefringent gels. Here, we demonstrate quantitatively the liquid crystal phase transition behaviors of some layered clay mineral colloids as the functions of concentration and particle size of the clay minerals. Experimental The synthetic clay minerals, fluorohectorite and fluortetrasilisic mica, were purified, dispersed in water, and ultrasonicated, to obtain stable nanosheet colloids with varied lateral sizes. The clay colloids in cells or capillaries were observed with crossed polarizers by optical microscopy. Small-angle neutron scattering (SANS) measurement was performed with SANS-J-II at Tokai, Japan. Results and Discussion Observation of the clay colloids with crossed polarizers characterized the formation of liquid crystal phases. We observed textures typical to liquid crystals and permanent interference colors of birefringent liquid crystal domains. SANS observation clarified that the liquid crystals of clay colloids has a lamellar structure with the basal spacing of up to ca. 60 nm. The colloids were macroscopically separated into upper isotropic and lower liquid crystal phases after standing in a glass capillary. Detailed observation of the phase separation behavior quantitatively clarified that both the nanosheet colloids form liquid crystal phases at higher concentration and larger lateral size. These results are basically rationalized by excluded volume effect.

**Keywords:** Liquid crystal, Fluorohectorite, Fluortetrasilisic mica.

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# GELATION/GLASS FORMATION VERSUS LIQUID CRYSTAL PHASE TRANSITIONS IN SUSPENSIONS OF CHARGED COLLOIDAL PLATELETS

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The equilibrium and non-equilibrium phases of suspensions of charged colloidal gibbsite ($Al(OH)_3$) platelets are investigated with Rheological and Optical Measurements, Small Angle X-ray Scattering and Cryo-Electron Microscopy. By variation of the colloid concentration and ionic strength we are able to tune the balance between attractive and repulsive interactions. This leads to a competition between liquid crystal formation and gelation/glass formation. We find nematic (N) and columnar (C) liquid crystal phases wedged between an attractive gel and a repulsive gel/glass. The structures of these states are discussed.

**Keywords:** Phase Separation, Liquid Crystal, Gel.

# LIQUID CRYSTAL PHASES IN AQUEOUS SUSPENSIONS OF NATURAL BEIDELLITE

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Nematic ordering in colloidal clay platelets suspensions has been studied since Langmuir[1] reported a phase transition on sols of California bentonite. During the last two decades, different minerals compounds have been found to exhibit nematic phases and recently, Michot et al[2] evidenced an isotropic/nematic transition before the gel state in aqueous suspensions of natural nontronite clay (NAu2).

The present study focuses on the phase behaviour of natural beidellite suspensions (SBId-1). Beidellite is formed of subhedral lamellae with a disklike morphology, i.e. a simpler situation than that of lath-shaped nontronite. After size-selection, a wide concentration range of beidellite suspensions at various ionic strengths was obtained using osmotic stress experiments. All samples were analyzed by combining optical observations under polarized light, rheological experiments and SAXS experiments. The phase diagrams (volume fraction $\phi$/ionic strength) reveal, for ionic strength below $10^{-3}$ M/L, true isotropic/nematic transitions before the gel transition. This transition line displays a positive slope for increasing ionic strength and shifts towards lower volume fraction with increasing particle size. The swelling laws derived from the interparticle distances obtained by SAXS display a transition from isotropic swelling at low volume fractions to lamellar swelling at higher volume fractions. The combination of these data with osmotic pressure measurements reveals that the system is controlled by repulsive interactions whereas a modelling of rheological curves provide relevant information on the orientational order of the platelets under flow.

**Keywords**: Isotropic-nematic transition, Phase diagram, SAXS.

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# FIELD-INDUCED ORIENTATIONAL ORDER IN AQUEOUS BEIDELLITE SUSPENSIONS

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Suspensions of hard anisotropic particles exhibit a first order phase transition between an isotropic and a nematic phase. As developed in liquid crystals studies[1,2], the role of external fields on the orientation of particles provides viable thermodynamic information on the system and could be used for designing novel materials.

Beidellite suspensions display a liquid crystalline character. Therefore, external electric and magnetic fields have been applied on the isotropic, biphasic and nematic phases of beidellite suspensions. Electric field experiments were carried out using a specially developed electro-optical set-up. Platelets orientations under electric field were observed for ionic strength below $5.10^{-3}$ M/L in the isotropic and nematic regions of the phase diagram whereas gel samples could not be oriented. SAXS experiments under electric-field were carried out to better assess the orientation and to follow changes upon switching on and off the field. They reveals that platelets were oriented parallel to the field with some degeneration around it. Magnetic-field experiments were carried out by placing the samples at high field strength (8 Tesla) into a NMR solenoid. Optical birefringence and SAXS measurements were performed ex situ. Nematic beidellite suspensions are clearly aligned and SAXS experiments show an alignment of the particles perpendicular to the field. No orientation of the isotropic phases could be evidences. This is likely due to orientational relaxation occurring too quickly after removing the field to be observed by either optical observations or SAXS.

**Keywords**: Nematic liquid crystal, electric and magnetic fields, SAXS.

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# DYNAMIC COLUMN FORMATION OF NA-FLHC CLAY PARTICLES: WIDE ANGLE X-RAY SCATTERING AND RHEOLOGICAL STUDIES

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Electrorheological fluids (ERFs) are liquids that solidify, or become very viscous, under an electric field. The transition from liquid into a solid-like state indicates that there is an inner ordering of the ER-constituents, which leads to a change in the rheological properties. Application of an electric field induces polarization of the suspended dielectric particles and a chain-like structure can be formed along the electric field direction [1]. Recently, the Giant Electrorheological (GER) fluid was discovered and it differs from the conventional ER fluids by exceeding the theoretical upper bound [2] of the yield stress, reaching 250kPa at 5kV/mm [3]. That discovery opens new horizons in the field of ER systems and inspires rheologists for working on further developments of such systems. In order to predict the response and behavior of ERFs under an applied electric field, it is important to gain an understandable knowledge of the physical mechanism of the chain and column formation and its dynamics. In the present study, synthetic clay particles Na-fluorohectorite (Na-FLHC) suspended in insulating, non-polar silicone oil form with time chain-like structures when subjected to an external electric field. The time needed to create columns of aggregated particles varies as the electric field (0.35, 0.5 and 0.75kV/mm) increases. Wide Angle X-Ray Scattering (WAXS) diffraction patterns reveal changes of the direction of the dipolar moment induced in clay particles when the electric field is applied. The anisotropic arrangement of particles forming the chain can be described by the global order parameter S. The detail description of the system geometry, fitting procedure and calculations of S parameter can be found in the report of Meheust Y, et al. [4]. In-depth analysis of the system measured can be obtained using rheometry. The shear stress $\tau$ as a function of a shear rate $\gamma$ can reveal the type of ER fluid and in case of samples of this study the shear stress is represented by the Bingham plastic model [5].

**Keywords:** Chain and column formation, Electrorheology, clay particles.

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# LIQUID CRYSTAL PHASE TRANSITIONS IN A SYSTEM OF COLLOIDAL PLATELETS WITH A BIMODAL ASPECT RATIO

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Bidisperse colloidal systems have given rise to rich phase behaviour, ranging from remarkable superstructures to multiphase equilibria. In a system of charged colloidal gibbsite platelets with a bimodal distribution of the aspect ratio (diameter / thickness), we find an isotropic-nematic density inversion and a three phase equilibrium, with a nematic phase at the top, an isotropic middle phase and a columnar bottom phase. To relate this phase behaviour to the bimodal particle aspect ratio distribution, we calculate the liquid crystal phase behaviour of binary mixtures of thick and thin colloidal platelets for various thickness ratios, by combining Onsager-Parsons theory for the isotropic-nematic (I-N) transition with a modified Lennard-Jones-Devonshire cell theory for the columnar (C) state. For sufficient difference in aspect ratio, the phase diagram features an I-N density inversion and a triphasic I-N-C phase coexistence, in agreement with experiment. Furthermore, fractionation with respect to aspect ratio of the platelets in the different phases, which is predicted by the theory, is confirmed experimentally. At very high particle concentration, theory predicts a coexistence of two columnar phases. This is not observed in our experimental system, which at high particle concentration becomes kinetically arrested in a glassy phase with columnar features.

**Keywords:** Liquid Crystals, Gibbsite, Bimodal.

# MICROTEXTURE AND MECHANICAL PROPERTIES OF SELF-ASSEMBLED SMECTITE FILMS

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Thanks to excluded volume forces, evaporation of dilute sols of smectite clays on a support leads easily to highly oriented thin deposits which can be peeled off as self-supporting thin films. This property has been extensively used for spectroscopic purposes (it provides a simple way to record spectra), but little effort has been devoted to the mechanical properties of those films.

The present work is an attempt to establish the quantitative relationships between the macroscopic mechanical properties of the films (elastic modulus, ultimate strength, strain hardening, creep behaviour) and the mesoscale organization of the films, in particular the orientational correlations between the individual clay sheets. In order to put this on a broad perspective, six cation-exchanged montmorillonite film samples were compared to each other. The film mechanical properties were measured in tensile loading, while simultneaously measureing the film microtexture by opticalmicroscopy and atomic force microscopy. Furthermore, the film microtexture was correlated to the aggregation of clay sheets in the parent suspensions.

The main result is that the mechanical properties of the films are totally controlled by the inter-particle connectivity in the films but, contrary to the intuitive expectations, optimal connectivity is not obtained by increasing the interlayer attractive forces, but by decreasing them to the lowest level compatible with a compact structure.

**Keywords:** Thin films, Mechanical properties, Self-assembly.

# SOILS & SEDIMENTS

## SS1 • CLAYS AND SOIL FORMING PROCESSES: AN EVERGREEN

## SS2 • CONTRIBUTIONS OF SOIL MINERALOGY TO SOLVE AGRICULTURAL, ENVIRONMENTAL, TECHNOLOGICAL AND OTHER PRACTICAL PROBLEMS

# SOILS & SEDIMENTS

## SESSION SS1

## *Clays and Soil Forming Processes: An Evergreen*

# GENESIS AND TRANSFORMATION OF FERRIMAGNETIC MINERALS IN SOILS AS AFFECTED BY ENVIRONMENTAL FACTORS

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Pedogenesis under aerobic conditions usually increases magnetic susceptibility, most often by raising the concentration of magnetite and/or maghemite. While there is wide consensus that the nanosized crystals of these two ferrimagnetic minerals are mostly pedogenic, their formation pathways remain a matter of debate. Inorganic or bacterially mediated neoformation of magnetite —subsequently oxidized to maghemite in soil— has been proposed by several authors; this mechanism, however, requires the presence of $Fe^{2+}$ in solution, which, in well-drained soils, is restricted to specific microenvironments. Other authors have recently postulated that nanosized maghemite is an intermediate product of the transformation of ferrihydrite into hematite under aerobic conditions. This hypothesis is supported by *in vitro* experiments where ferrihydrite doped with some ligands (phosphate, citrate) evolved to a maghemite-like magnetic phase (“hydromaghemite”) and on to hematite (Barrón and Torrent, 2002). Moreover, this hypothesis is consistent with the facts that (i) soils poor in hematite generally exhibit little magnetic enhancement; and (ii) the concentrations of pedogenic hematite and maghemite in aerobic soils are mutually correlated (Torrent et al., 2008). It has been speculated (Liu et al., 2008) that, should this model apply to soil, the particle size distribution of maghemite and the maghemite/hematite ratio should depend on the rates of (1) weathering of Fe-bearing minerals to produce ferrihydrite; (2) transformation of ferrihydrite into hydromaghemite; (3) growth of hydromaghemite particles from the superparamagnetic (SP) to the single domain (SD) region; and (4) transformation of SD hydromaghemite into hematite. Such rates, and the contents in all these Fe oxides in soil, are influenced by the moisture and temperature regimes of the soil, its chemical environment (e.g., the concentration of phosphate and other ligands in the soil solution), and the duration of pedogenesis. In summary, accurately reconstructing hematite-containing soils in paleoenvironmental terms entails considering various factors including the particle size distribution of maghemite, the quantitative relationships between the different Fe oxides (including goethite, which is the most common pedogenic one), and any indices reflecting the degree of weathering and that of transformation of ferrihydrite into other Fe oxides.

**Keywords:** Maghemite, Magnetite, Magnetic susceptibility, Soil.

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# GENESIS AND DISTRIBUTION OF CLAY MINERALS IN A TRANSECT OF GYPSIFEROUS, CALCAREOUS AND SALINE MATERIALS (SOUTHERN IRAN)

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The clay mineralogy of soils and parent rocks on a transect of gypsiferous, calcareous and saline materials of Bakhtegan lake marginal (Fars province, southern Iran) was investigated to determine the genesis and relationship between type of clay minerals and physiographic units. The study area is located between Zagros orogenic area and Bakhtegan lake with dry xeric and thermic soil moisture and soil temperature regimes, respectively. Representative pedons were classified as Xerorthents, Haploxerepts, Calcixerepts, Haploxeralfs, Calcixererts and Aquisalids. XRD, TEM, EDX and FTIR analyses indicated that chlorite, illite, palygorskite, kaolinite, smectite and interstratified minerals are the dominant clay minerals in both soil and rock samples. The presence of kaolinite, illite and chlorite abundance can be related to the parent rocks and inherited origin. Illite and chlorite are generally considered to be weatherable and could be changed because of transformation reactions into interstratified expansible minerals and smectite. The results showed that smectite constitutes a high portion of clay minerals in well drained Alfisols, some what poorly drained Vertisols and soils with alkaline and saline ground water. Therefore, it can be concluded that in well drained soils it increases because of transformation of interstratified minerals and illite and it can increases in low-lying topography due to transformation, transportation of upslope to down slope (detrital origin) and neoformation. There were not evidences of vermiculite in the studied soils due to unstable condition of its formation. The region is arid with a $P/ET^{\circ} \sim 0.1$, a part of the post-Tethyan sea environment rich in the evaporates (salt and gypsum) and it has affected by saline and alkaline Bakhtegan lake, so it is deduced to be suitable and stable environment for considerable palygoeskite formation in all soils. Presence of large amounts of highly crystalline elongate palygorskite can be an indicative of in situ neoformation in saline and alkaline and gypsic evaporate environment. SEM images show the authigenic origin of palygorskite in the gypsiferous soils and soils with pedogenic calcic. FTIR spectra are a method accompanied with TEM, XRD and SEM for recognizing the structure of clays. There is overlapping in mixed clay samples and it cannot be suggested as a single method in impure clay samples.

**Keywords**: Clay mineralogy, Arid climate, Bakhtegan Lake.

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# MODIFICATIONS OF THE MINERALOGICAL COMPOSITION OF SOILS AS RELATED TO STEPPE CLIMATE DYNAMICS

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During last years the authors carried out the complex investigations of palaeosol from archaeological sites in Russian steppe (the Lower Volga area, the Cis-Ural, the Northern Caucasus). The investigation of burial mounds palaeosol of the Bronze epoch (within a time span of 1000 years) testifies to the considerable changes in the clay mineralogy, molar chemical ratios, magnetic mineralogy, and surface properties of the soils and permits us to assess the rates of the mineralogical transformations caused by the climate dynamics in intervals of <~100 years. The investigated soils have developed on Late Pleistocene marine loam (Q3) overlain by loess. The clay fraction of the soil-forming material is rich in the smectite phase. In addition, the clay contains dioctahedral mica, vermiculite, chlorite, and kaolinite. The clay fraction of the soils developed on these deposits (light chestnut soils with different development of solonetzic and salinity features) is formed under the influence of chlorite and smectite transformation, as well as the profile redistribution of smectite depending on the solonetzic process. To assess the intensity of the mineral transformations in the upper horizons of the paleosols, we used the illite–smectite index. This parameter represents the illite–smectite ratio multiplied by 10, and it is physically based on the resistance to weathering, which is high for illite and low for smectite. Similar to the chemical coefficients of the weathering, the minimal intensity of the soil-forming processes and the mineral soil mass transformation are registered for the age of about 4000 years ago (aridization period). The ratio of Rb in humus horizon to the background concentration of Rb can be considered by analogy with illite–smectite index. The relationship of this Rb indicator with changes of atmospheric precipitation (rainfall) was observed. The magnetic properties of the soils (minerals of iron oxides) may be regarded as quickly altering parameters with their characteristic transformation periods ranging from tens of years to one hundred years. The state of the iron compounds reaches equilibrium with the climate similar as in the case of the salt and carbonate profile. The mineralogical transformation in the soil solid phase results in the changing surface properties of the studied soil sequence. Depending on the soil-formation conditions, the pore space and the surface of the soil particles are filled either with carbonates (upon aridization) or with iron oxides (upon climate humification). The investigation of the proportion between the mineral phases as a consequence of the transformation of the chemical composition and the surface properties of the buried soils testifies to the primary importance of climate factors as affecting the intensity of the mineral transformations in comparison with the total duration of the weathering process, or the soil age.

**Keywords**: Paleosol, Clay mineralogy, Climate change.

# EVOLUTION OF EXPANDABILITY DURING EXPERIMENTAL ALUMINIZATION OF VERMICULITE INTERLAYERS. AN X-RAY DIFFRACTION PERSPECTIVE ON STRUCTURAL MECHANISMS

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The conversion of expandable 2:1 phyllosilicates (smectite, vermiculite) into aluminium hydroxy-interlayered minerals is commonly reported in acidic soils and sediments. This important process occurs through the adsorption and polymerization of aluminium ions in the interlayer space of the original expandable mineral and strongly modifies its physico-chemical properties (e.g., cation exchange capacities and swelling properties) as well as the properties of the soil/sediment. In the present work a natural well-crystallized vermiculite (Santa Olalla, Andalusia, Spain) was aluminized at fixed pH and temperature conditions in stirred flow-through reactors. The 200-400µm size fraction of the macro-crystalline vermiculite was separated first, iron impurities were removed using magnetic separation before Na exchange and drying. Experiments were performed at 50°C by adding 4mL of HCl (pH = 2.3) to ~0.25 g of vermiculite with a 0.042 mL/min flow rate for solution renewal. Several experiments were performed simultaneously and stopped at different times for liquid and solid analysis. After 0.5, 1.5, 2.5 4, 7, 10 and 28 days of reaction time, the altered solids were washed in water and Na-saturated to exchange all non-fixed interlayer species. X-ray diffraction (XRD) analysis was performed on oriented preparation at a controlled relative humidity (20%RH) to maximize the layer thickness contrast between expandable (basal *d*-spacing ~12.5 Å) and aluminized (basal *d*-spacing ~14.5 Å) interlayers and the hydration homogeneity of expandable interlayers.

Experimental XRD data were then fitted using a trial-and-error approach based on the direct comparison between experimental and calculated patterns. This technique allowed the quantification of the relative proportion and the stacking mode of unaltered and aluminized layers in the complex interstratified structures observed along the progressive aluminization of vermiculite interlayers. Constrains on the reaction mechanisms of vermiculite aluminization and on the reactivity of aluminized layers will also be discussed.

**Keywords**: Vermiculite, X-ray diffraction, Aluminization process.

# DISSOLUTION OF LATH-SHAPED CLAY MINERALS: EVIDENCE FOR BASAL SURFACE REACTIVITY OF NONTRONITE

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Phyllosilicates play an important role in many geochemical processes occurring in soils and sediments (nutrient release, element cycling, contaminant availability or sorption..). In this context, understanding the mechanisms of phyllosilicates dissolution and the factors that influence their weathering is a key question. Mineral dissolution is surface-driven and depends on physico-chemical conditions (pH, Eh, ligands…), microbe-mineral interactions as well as crystallographic and textural properties of crystal faces. The latter can be important in the case of lath-shaped mineral particles characterized by strong shape anisotropy. Several authors consider the edges as the sole or a major reactive faces with regard to phyllosilicates dissolution (1-2), implying that the rate of dissolution also depends on the distribution of reactive faces and therefore on the particle size (amount of edge faces increases with decreasing particle size). However, most experimental dissolution studies have been limited to micrometric-scale mineral particles, which is partly due to specific problems encountered when dealing with colloidal size particles such as flocculation. In this study, we developed an original approach for studying the dissolution of colloidal size mineral particles. Using a sol-gel process, size-selected Na-exchanged nontronite particles were stably and homogeneously immobilized in a porous silica gel. Four size fractions with evolving size and shape were incubated under acidic conditions. The results showed that for a given pH, a decrease in particle size significantly increased nontronite dissolution. For instance at pH 1.5, 7.5% of the total iron of the highest size sample was released in solution whereas this proportion rose to 28% for the smallest size fraction. However, the observed increase in dissolution is not directly correlated to the increase in the amount of edge faces. This suggests that basal faces of nontronites also play a significant role in the weathering process. In the present case this may be related to the fact that 8% of total iron of used nontronite is in the tetrahedral sheet. The use of other clay minerals with distinct crystal chemical properties could certainly help in assessing in more details the respective role of the different crystallographical faces on dissolution processes.

**Keywords:** Phyllosilicates Weathering, Nontronite, Reactive surfaces.

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# KAOLINITE AND GIBBSITE FROM SUB-TROPICAL SOILS, DISTRITO FEDERAL, BRAZIL

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Distrito Federal (DF), in Brazil central area, the dominant wheathering processes are monosialitization and alitization,under a sub-tropical climate.

In DF, soils are developed on the precambrian sedimentary rocks of the Paranoá Group, which from the base to top comprises bottom shale, rhythmites, sandstones, upper shale and carbonate rocks.

Soil mineral composition defined by X-ray diffraction shows kaolinite as a major or minor constituent in all samples, whereas illite, quartz, gibbsite and goethite are variable; hematite, anatase and vermiculite may occur as trace constituent. Different compositions reflect the range of parent materials. However, even soils from similar pelitic rocks contain different mineralogical assemblage.

In order to understand these differences, two weathering profiles developed on pelitic rocks were studied: a ten meters high profile developed on the bottom shale (WP 1) and another twenty-two meters on the upper shale (WP 2). Samples were collected at one- meter intervals in both profiles. The samples were analyzed as a whole soil and as a clay fraction. The basal levels of both profiles are constituted by illite and kaolinite, characterized by XRD as high and straight reflections. Toward the top, illite reflections became lower and broader, disappearing at 7-8 and 13-14 meters deep in WP 1 and WP 2, respectively. Kaolinite is more stable, but at the upper profiles it changes in a new type of kaolinite. Their main reflections at 7,1 and 3,56 A became lower and broader in WP 1, whereas in WP 2 they are maintained high and straight, beside an asymmetric pick at 4,48. The change of the kaolinite coincides with the illite disappearing in WP 1 and occurs at 15-16 meters deep in WP 2, down the illite limit. In samples from both profiles, under heating at 490$^{o}$C, the characteristic reflections remain in the kaolinite from the base, and are lost by the upper kaolinites. Such behavior may be the reflex of a positive relationship between dehydroxylation temperature and degree of order of kaolinite.

In WP1, at the level where illite disappears and the kaolinite becomes disordered, the gibbsite appears and becomes the main constituent toward the top. Otherwise, gibbsite does not occur in WP2, kaolinite is the only major constituent.

Beside illite and kaolinite, the whole samples from upper levels of both profiles contain quartz as constituent trace. However, quartz appear in the clay fraction from WP2, but it does not exist in WP1.

This result suggests that gibbsite was not formed where silica is available in fine fraction. Silica has remained in the profile WP2, where the leaching seems have been less intense than on WP1. Seeing that the parent rocks from both profiles are similar, the differences on the weathering products are attributed to local geomorphologic conditions.

**Keywords:** Kaolinite, Weathering, Gibbsite.

# SOLVING COMPLEX PEDOGENESIS: USE OF DIRECT XRD PATTERN FITTING TO QUANTIFY CLAY MINERAL ASSEMBLAGE CHANGES

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The cultivated soil studied here is a polygenetic cambisol developed on a paleo-oxisol (INRA Lusignan, France). It is characterised by silty surface horizons (loess deposit) overlying a reddish paleosol. From field observations, the soil has been divided in five horizons. Degradation tongues are present through the three deeper horizons (from 40 to 180 cm). The clay mineral assemblage was determined from the < 2 µm fraction for the five horizons (matrix, 5 samples) and along soil tongues (6 samples). The direct XRD pattern fitting approach, developed first for diagenetic clays, has been applied for the first time to soil samples. The crystallographic characteristics of the different clay mineral species are adjusted in order to fit directly the calculated $00\ell$ reflections on the experimental ones (angular range: 3- 35 °2θ CuKα in the air-dried (AD) and ethylene glycol solvated (EG) states). When achieved, the fit provides a semi-quantification of the different clay minerals species composing the < 2 µm fraction. The clay species having a low Coherent Scattering Domain size (CSDS < 10 layers) are mainly mixed layers: illite/smectite (R0 85/15), smectite/illite (R0 40/60), kaolinite/illite (R1 segregated 79/21) and kaolinite. The clay species having a high CSDS (> 10 layers) are: illite, chlorite, kaolinite and illite/chlorite/smectite mixed layers (R0 60/26/14). The same clay mineral assemblage is relevant for all the soil samples studied both in the soil matrix and in the degradation tongues. Only variations among the relative proportions occur.

The large relative content of high CSDS kaolinite (~20%) and the increase of low CSDS kaolinite with depth from 5% at soil surface to 20% in the deepest horizon are typical of the paleo-oxisol. Illite, chlorite and illite/chlorite/smectite mixed layers amounts slightly decrease with depth. This is due to the incorporation of silt material from the loess in the upper horizons. The smectite/illite mixed layers relative content is low (~5%); it varies in the soil profile because of leaching. The degradation tongues are more depleted in kaolinite and smectite/illite mixed layers.

The influence of the pedogenesis under tropical climate is preserved along the soil profile. The silt deposit (loess) is detectable through the incorporation of 2:1 clay minerals in the upper horizons. The current pedogenesis under temperate climate does not induce significant modifications of the clay minerals at the crystal scale. The XRD fit method highlights the active pedogenic process: a redistribution of the clays minerals at the profile scale due to degradation tongue formation.

**Keywords:** Polygenetic soil, Clay mineral quantification, X-Ray Diffraction.

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# SOME PROPERTIES OF PALLID ZONE KAOLINS FROM WESTERN AUSTRALIA IN RELATION TO GROUNDWATER COMPOSITION

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Acidic, hypersaline groundwater affects large areas of Western Australia (WA) and land management is, and will be increasingly, impacted as water tables rise. Dissolved toxic metals will potentially have adverse effects on the surface and near-surface environment, and thus on agricultural sustainability. Also these changing landscape conditions have had unknown effects on the regolith characterised by a very thick (up to 20m) pallid zone that consists predominantly of kaolinitic clay. This study investigated some characteristics of these kaolins and their relationships with groundwater. Samples (57) from 2.5m to 36m depth were collected from 13 sub-catchments of the Avon River Catchment in the north-central wheatbelt of WA. The clay was separated and both this and the bulk samples were analysed by XRD, XRF, ICP-MS and OES, BET surface area, and TGA. Water from the boreholes from which the samples came was analysed by ICP-MS and OES. Zeta potential (ZP) curves (pH 2.0 to 12.0) were measured for 15 clays, chosen after XRD for their apparent monomineralic (kaolin) composition and anomalous dispersion behaviour. These 15 samples exhibited a wide range of characteristics (range for all samples in brackets) i.e. surface area from 9.39 to 30.55 (9.39-123) $m^2/g$; $Al_2O_3/SiO_2$ from 0.61 to 0.92 (0.57-0.92); Hinckley index from 0.50 to 1.28 (0.32-1.39); Hughes and Brown index from 15 to 55 (6-70); and the main endotherm from 513 to 536 (491-549) $^oC$. Only two samples gave a PZC (at pH 2.70 and 4.30). Negative ZP over the entire pH range may be partially explained by a large face to edge surface area ratio which in turn may explain the difficulty in dispersing the original samples. The pH of the water from the boreholes from which the 15 kaolins came varied from 2.47 to 6.90 (range for all samples 2.36-7.29) and the EC from 3.59 to 85.70 (3.59-150) dS/m. ICP-OES showed high concentrations of the easily soluble elements i.e. Ca (17-441 mg/L), Mg (14-798 mg/L), K (7-312 mg/L), Na (102-16000 mg/L), and S (9-886 mg/L), with Cl the dominant anion. Trace amounts of Sr, Ba, Co, Fe, Mn, Ni, Rb, Zn and U were also present. Only three samples contained measurable amounts of Al (64-218 mg/L) and these coincided with the highest Si concentrations (60-65 mg/L). These data will be discussed in relation to dispersion behaviour of the kaolins, the interrelationships between the characteristics measured and the possible impacts of the hypersaline groundwater on the pallid zone minerals.

**Keywords**: Kaolin, Pallid zone, Hypersaline groundwater.

# MINERALS AND ORGANICS IN SOIL FORMATION IN ALKALINE SUBSTRATE

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Deposits of industrial waste and by-products become increasingly important as substrates for soil formation. Here we report the (1) mineral formation and alteration and (2) accretion of organic matter (OM), mainly by organic–mineral interactions during the first seven decades of soil formation in a well-defined time series of undisturbed, homogeneous waste deposits of industrial soda production exposed to natural weathering and under natural succession from grassy to woody vegetation. Samples obtained from several sampling points and soil depths were characterized by X-ray diffraction, X-ray fluorescence and density fractionation.

Soils were calcareous Regosol, with the depth of development (structure, colour) increasing with time after exposition to weathering. Within 70 years, the pH (initially at 12.0) decreased to 8.1 due to reaction of carbonic acid (biotic and abiotic origin) or other acidic deposition from the atmosphere with $CaO•H_2O$ and $Ca(OH)_2$, the main constituents of the deposited material. This resulted in increasing amounts of calcite. Other minerals forming include thaumasite, ettringite, hydrotalcite and hydrocalumite. The kinetics of ettringite and thaumasite formation and transformation was rapid, along with the change in soil pH. Hydrotalcite and hydrocalumite, both layered double hydroxides (LDH), were detected in all soils, likely existing as solid solutions with a larger proportion of hydrotalcite. The two minerals form in the early phase of weathering, under the alkaline conditions with sufficient Mg and Al available, but seem stable under less alkaline conditions.

Organic carbon (OC) concentrations and stocks increased with time. The dominant portion (61 ± 13%) was in heavy density fractions of $d = 1.6–2.2\ g\ cm^{-3} > 2.2\ g\ cm^{-3}$; assumingly associated with minerals. The lighter of the two fraction held the larger share of the soil OC. Fractions from the older soils revealed the lignin signature of the initial grass vegetation, indicating longer mean residence times of contained OM. LDH dominated the lighter and calcite heavier fraction. The OC concentration in lighter fraction ($80 \pm 29\ g\ kg^{-1}$) exceeded that in heavier one ($8 \pm 4\ g\ kg^{-1}$), suggesting organic–LDH associations to cause the rapid stabilization and accumulation of OM in the soils. Increasing OC concentration in the lighter fraction with site age indicated that the capacity of LDH for accretion of OM has not been reached. Laboratory sorption experiments confirmed the large capacity of hydrotalcite to bind OM under pH conditions such as those in the study soils.

The results underline the mutual interactions of mineral formation and transformation and OM accretion during pedogenesis.

**Keywords**: Layered double hydroxides; Organic matter, Soil formation.

# INITIAL STAGES OF SOIL AND CLAY MINERALS FORMATION IN THE MORTERATSCH PROGLACIAL AREA (UPPER ENGADINE, SWITZERLAND)

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Investigations in Alpine soils indicate that mineral weathering is much faster in 'young' soils (< 1000 years) than in 'old' soils (10,000 years). However, little is known about the initial stages of weathering and soil formation, i.e. during the first decades of soil genesis. In this study we investigated rock-forming minerals weathering and clay minerals formation during this time span. Due to the continuous retreat of the Morteratsch glacier (Upper Engadine, Swiss Alps), the proglacial area offers a full time sequence from 0 to 160 years old surfaces. Reduced elevation stacks, low slope and absence of glacier advancement within this time span and soil formation process interruption, contributed to the choice of Morteratsch proglacial valley as case study, as well. The area is also well documented regarding vegetation and soils. The morainic material was produced through glacial transport within a small area of relatively homogeneous parent material. The lithostratigraphic unit is the Bernina-crystalline, mainly constituted of diorite and granodiorite; consequently, the glacial till shows an acidic character. Accordingly, special emphasis has been given to the weathering of biotite, the 'chlorite' group, amphiboles and apatite in the soils. Mineralogical measurements were carried out for the clay as well as for the bulk soil fraction using XRD, DRIFT and total chemical analyses. In addition to the soil mineralogy, analyses of the main stream water, tributary rivers and the rainwater were performed with a special focus on Sr isotopes ($^{87}Sr/^{86}Sr$). The water measurements supported the findings of mineral analyses. The high Ca/Sr as well as $^{87}Sr/^{86}Sr$ ratios confirmed that biotite and other Ca bearing minerals are weathering and transforming at very high rates in the proglacial area. Also in cryic, ice-free environments, chemical weathering rates are high leading to the formation and transformation of clay minerals. Biotite (clay fraction) transforms relatively quickly into hydrobiotite and in a following step into expandable minerals or into HIV. Also the process of 'chlorite group' minerals (clay fraction) transformation into HIV seems to be a fast process. Disseminated calcite in granitoid rocks, not only confined to carbonate geology, also plays a role in subglacial environments. It is, however, not known for how long such an influence is significant and measurable. The high Ca/Na and Ca/Sr ratio in the stream and tributary waters showed that calcite significantly contributes to the Ca solubility although the ion activity product calculations clearly demonstrate that the waters are undersaturated with respect to calcite.

**Keywords**: Proglacial area, Biotite weathering, Clay minerals.

# GRANITE WEATHERING IN THE DAMMA GLACIER FOREFIELD

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In alpine regions weathering processes are of particular interest with respect to the effects of climate change. Large areas of bare rock will be exposed as glaciers retreat. Weathering includes both, mechanical as well as chemical processes. In pristine alpine areas, where soil formation has not yet occurred physical weathering is the main initial process and includes tectonic forcing, thermal expansion and contraction of rock, alternate freezing and thawing of water between the rock's cracks and fissures, and pressure release after erosion of overlaying rock material or glacier retreat. Physical weathering causes the disintegration and breakdown of rock into smaller fractions, or into its constituent minerals. Chemical weathering primarily affects the mineral composition of the parent rock material through alteration and redistribution. In contact with liquid water, rock minerals are subject to dissolution, carbonation, hydration, and oxidation. Dissolution of most primary rock-forming minerals is limited by slow kinetics of the reactions at the mineral-water interfaces. Dissolution rates depends on extrinsic factors (T, pH, Eh, and exudates from microbes and plant roots) and on intrinsic factors (mineral surface properties and weathering state).

The presented research is part of an interdisciplinary study of the initial phase of weathering to obtain a detailed picture of the processes occurring at the biosphere-hydrosphere-geosphere interface (http://www.cces.ethz.ch/projects/clench/BigLink). For our studies we established a grid for representative sampling of soil evolution along the chronosequence up to 150 years in the forefield of the retreating Damma glacier in Central Switzerland. To document both, the influence of physical and chemical weathering, we investigated a.o. the grain size distribution and the mineralogical composition of the soil samples in different horizons.

As expected, the amount of the clay fraction <2 µm increases, but only slightly with increasing soil age. Despite the inhomogeneous metagranitic mineralogy of the Damma granite only little variations in the mineralogical composition of the soil samples up to an age of 130 years could be found. Only the older soils, particularly in the fraction <2 µm, show a significantly increased content of 14 Å clay minerals (up to 50 wt%!) and a strong decrease in the feldspar and mica content.

**Keywords**: Alpine glacier forefield, Mineral weathering, Initial soil formation.

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# MICROCRYSTALLINE PYRITE IN ENDOAQUODS ON THE SWAN COASTAL PLAIN, WESTERN AUSTRALIA: PROPERTIES AND ENVIRONMENTAL CONSEQUENCES

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The reducing chemical environment within saturated horizons of very sandy humus podzols on the Swan Coastal Plain provides a favorable condition for pyrite ($FeS_2$) formation. As these profiles desiccate due to water extraction and climate change the oxidation of pyrite acidifies groundwater. We used scanning electron microscopy and synchrotron X-ray diffraction to characterize and quantify pyrite and associated, potentially pH buffering, minerals in these podzols. Thirteen coffee rock (indurated B horizon) samples and 35 other horizon samples were collected from seven podzol profiles in Perth on the Swan Coastal Plain. Typical soil profiles featured an A horizon rich in decomposing organic matter, followed by a light colored sandy albic E horizon, and by a dark colored spodic B horizon (coffee rock) over a gray sand horizon. Some profiles seem to contain several E and B horizons which may be regarded as remnants of palaeopodzols that formed when the water table was at lower positions. These palaeomaterials also contain pyrite. Soil samples were kept in a wet condition in a cool room until analyzed and novel preparation procedures were employed to limit microbial activity and oxidation. X-ray diffraction patterns show that the clay fraction contains *inter alia* the following minerals that contribute variously to pH buffering: kaolin ($Al_2Si_2O_5(OH)_4$), gibbsite ($Al(OH)_3$), goethite ($\alpha$-FeOOH), lepidocrocite ($\gamma$-FeOOH), akaganéite ($\beta$-FeOOH), allophane ($Al_2O_3(SiO_2)_{1.3\text{-}2}(H_2O)_{2.5\text{-}3}$). Sand contains abundant quartz and a little K-feldspar, zircon and ilmenite none of which provide appreciable buffering against acidification. Pyrite framboids (5-20 µm diameter) occur within the E horizon. However, pyrite single crystals (0.5-1 µm diameter) were also highly abundant. Synchrotron XRD analysis confirmed the presence of pyrite in the gray sand horizon and coffee rock. Apparently, it is the microcrystalline nature of much of the pyrite that causes rapid acidification of desiccated podzol materials.

**Keywords:** Microcrystalline pyrite, Endoaquods, Spodic B horizon.

# THE ORIGIN OF Fe-KAOLIN FROM PRECURSOR BEIDELLITE AND INTERSTRATIFIED KAOLIN-SMECTITE IN MOIST TROPICAL SOILS

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Fe-rich kaolins in soils from a terrace chronosequence in the moist tropics of Costa Rica are derived from the transformation from smectite via interstratified kaolin-smectite (K-S). The smectite is ferruginous beidellite (10.1 $\pm$ 3.7 % $Fe_2O_3$) that forms early during pedogenesis from basaltic-andesitic parent material and is the dominant mineral in $\leq$ 5 ka soils. Interstratified K-S with 60 – 90 % kaolin layers is the dominant mineral in 10 ka soils, while 125 ka soils contain a physical mixture of Fe-kaolin (6.0 $\pm$ 1.9 % $Fe_2O_3$) and K-S with $\geq$ 80 % kaolin layers.

K-S is indicated by X-ray diffraction (XRD) data that reveal asymmetric 001 peaks between 17.5 and 17.8 Å (ethylene glycol-solvated) and irrational 00*l* peaks that exhibit Méring-like behaviour, and by transmission electron microscopy-analytical electron microscopy (TEM-AEM) data that document single crystals of K-S with compositions intermediate to those of end-member crystals of beidellite and kaolin. Lattice fringe images from high resolution TEM (HRTEM) show lateral transitions from smectite layers to kaolin layers via a cell-preserved, layer-by-layer transformation mechanism, and changes in the compositions of tetrahedral and octahedral sheets, notably decreases in octahedral Fe and Mg and tetrahedral Al, indicate that the reaction is accompanied by localized dissolution of smectite 2:1 layers that proceeds laterally. Fourier transform infrared (FTIR) and XRD data indicate that kaolin layers are a mixture of kaolinite and halloysite, and differential thermal analysis-thermogravimetry (DTA-TG) combined with data from XRD and TEM-AEM indicate the development of Al-hydroxy interlayers in K-S with time.

The soil-forming factors that appear to control formation of K-S are (1) basaltic-andesitic parent that produces high concentrations of base cations and Si in young ($\leq$5 ka) soils, and (2) moist tropical climate (3085 mm MAP, 27.3 $^{o}$C MAT) with a short dry season that fosters formation of beidellite in $\leq$5 ka soils. By 125 ka, soils are dominated by Fe-kaolin and K-S, helping to constrain reaction rate. The relatively high cation exchange capacity (CEC) of the Fe-rich kaolins (18 $\pm$ 12 $cmol_c/kg$) relative to many tropical kaolinites is attributed to small amounts of octahedral Mg and tetrahedral Al inherited from precursor ferruginous beidellite layers. Accordingly, the origin (from beidellite) and relatively high CEC of the K-S and Fe-kaolin has potentially important implications related to clay mineral reactions and elemental cycling in moist tropical soils.

**Keywords:** Beidellite, Moist tropical soil, Interstratified kaolin-smectite.

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# THE NATURE OF INTERLAYERING IN CLAYS FROM A PODZOL FROM THE TATRA MOUNTAINS, POLAND

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Interlayered clays are common constituents of several soil orders. The presence of interlayering is indicated by modified thermal stability of soil vermiculites and smectites. In most studies the clays have been reported as Al-hydroxyinterlayered minerals. Despite the abundance of organic compounds in many soils, potential organic-clay interactions have rarely been considered. In the present study three clay sub-fractions separated from the eluvial (E) horizon of one podzol from the Tatra Mts., Poland, were analyzed by X–ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), in the natural state and after being subjected to organic matter removal, saturation with different cations, and heating at 330ºC and 550ºC. All fractions contain a "~14Å clay". In the natural state the "~14Å clay" shows high thermal resistance, manifested by only a partial shift to 10Å after heating at 550ºC. This behavior strongly suggests the presence of interlayering. After saturation with $K^+$, some shift of the 14Å reflection toward 10Å occurs at room temperature, and the thermal resistance diminishes, which indicates that part of the interlayer fillings are in the form of charged molecules. After treatment with $H_2O_2$ and NaOCl, the "~14Å clay" becomes more unstable during heat treatment, and its 001 reflection shifts to ~10Å after heating at 330ºC, possibly suggesting the organic nature of the interlayering. The organic nature of the interlayering is also indicated by FTIR spectra. The obtained results show that for accurate characterization of interlayered clays, consideration of the possibility of the occurrence of both hydroxy and organic interlayers is required, and these can be evaluated by a combination of XRD and FTIR methods.

**Keywords**: Hydroxy-interlayering, Clay- organic matter complexes, Soil clays.

# PALEOSOLS IN AUSTRIAN LOESS DEPOSITS

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Soil characteristics of paleosols in loess deposits give information on past climate and vegetation (VANCAMPENHOUT et al., 2008). Clay minerals, soil organic matter and carbonate content are indicators of environmental conditions during former pedogenesis (BAJNÓCZI et al., 2006; KARLSTROM et al., 2008). Loess deposition occured during cold, glacial climates, pedogenesis during relatively warm interglacials and interstadials.

Different loess-paleosoil-sequences from three sites in Lower Austria (Wolkersdorf, Niederabsdorf and Krems) were studied. The mineralogical composition (bulk sample and clay fraction < 2 µm) was determined using X-ray diffraction. Dominating clay minerals in samples from all sites are chlorite, illite, and smectite, in some of the samples considerable amounts of vermiculite were found.

Grain size analysis were made by a combination of wet sieving and sedigraphy.

Soil analyses included chemical parameters like pH-value, C/N-ratio, carbonate content and cation exchange capacity of the fine soil as well as of the clay fraction.

The type of humus substances may serve as an indicator of the conditions under which ancient soils have been formed. The composition of soil organic matter was characterised using Fourier transform infrared (FT-IR) spectroscopy, thermogravimetry and differential scanning calorimetry.

**Keywords:** Paleosol, Clay minerals, Organic matter.

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# SOILS & SEDIMENTS

## SESSION SS2

## *Contributions of Soil Mineralogy to Solve Agricultural, Environmental, Technological and other Practical Problems*

# SOIL MINERALS IN THE ENVIRONMENT, INDUSTRY AND THE JUSTICE SYSTEM

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Without question, the refinement of soil mineral identification techniques, along with the development of new field protocols/approaches to systematically collect samples for detailed mineralogical characterisation has created a revolution in soil mineralogy investigations. This has led to new discoveries of minerals in previously unreported soil environments and more basic information about soil mineral structures, composition, crystallinity and the processes leading to their formation or transformation. Soil minerals research is becoming highly multi- and inter-disciplinary. Soil mineralogists are collaborating closely with pedologists, chemists, geochemists, engineers and police/detectives, like never before to help understand, predict and solve complex soil problems for a multiplicity of practical purposes. These interactions and the astounding advances and employment of *in situ* molecular scale techniques (e.g. synchrotron XRD methods), along with information technology/geographic information systems (GIS) and biogeochemistry have changed the field of soil mineralogy. Through case studies, this presentation will demonstrate how: (i) new sampling protocols/procedures involving selective removal or isolation of mineral-rich layers/crusts from the rest of the soil volume are used to develop appropriate soil processes models, (ii) soil mineralogical information is extrapolated from microscopic to landscape scales to produce coherent mechanistic models and soil mineral maps, and (iii) pathways of mineral transformation are verified by synthesising natural minerals in the laboratory and conducting *in situ* experiments on natural and synthetic samples (e.g. mechanisms of dehydration and hydration). Soil mineralogical information has been critical in solving practical soil problems for a broad range of stakeholders, for example:
(i) Environment, public health and mineral exploration: Extreme drought conditions in Australia is causing water levels to recede and expose extensive areas of sulfide-containing soils previously formed under reducing conditions in lakes and rivers. As water levels recede, sulfide minerals oxidise to form sulfuric acid with soil pH levels as low as 1 and the acidic pore waters evaporate at the soil surface precipitating many new assemblages of hydrated sulfate-containing evaporite (e.g. sideronatrite) and Fe-oxyhydroxysulfate (e.g. schwertmannite) minerals. As such, these minerals are environmental indicators of changing soil-water processes because they are formed by the unique soil and ground water geochemistry of the specific landscape (e.g. diurnal, rainfall event and seasonal variations, redox, pH and rates of availability of S and other elements such as Cu, Pb, Zn, Se and As). Hence, identification of these soil minerals is used as a new tool for mineral exploration.
(ii) The Justice System: where soil minerals in very small samples from shoes and clothing are compared with samples from crime scenes to help solve a range of criminal and environmental soil forensic investigations.

**Keywords**: Soil-water process models, Forensic science, X-ray diffraction.

# SPATIAL RELATIONSHIP BETWEEN CLAY CONTENT AND GEOPHYSICAL DATA

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Agricultural soils vary significantly causing within-field variability in crop yield. An important attribute for soil use is clay content, because it greatly effects the water holding capacity and the hydraulic properties of a soil. The soil surveys are generally time-consuming, labour-intensive and costly, while geophysical methods, such as Electromagnetic Induction (EMI) and Ground Penetrating Radar (GPR), offer a rapid, inexpensive and noninvasive approach to map soil features. Clays are hydrated minerals with high porosities and low permeabilities but their surface causes an excess of cations in the pore fluid immediately adjacent to the clay surfaces. The result is high conductivity near the clay surfaces and that may cause propagation velocity of the EM wave to be lowered. This phenomenon may be advantageously used to estimate clay from geophysical data, objective of this study.

EMI soil survey allows measuring apparent electrical conductivity, function of various soil properties as clay content [1]. The GPR produces a high-frequency EM wave, which propagates at the velocity determined by the soil dielectric permittivity [2]. To make easier the interpretation of these measures, soil cores were collected and analysed in laboratory for clay content. The EMI data were interpolated using ordinary cokriging [3]. The GPR data are elaborated with standard processing and the envelope of the filtered GPR data of all transects are used to produce 3D maps of the kriged estimates [4]. Multi-Collocated Cokriging was applied to integrate secondary information in primary variable modelling. The spatial correlations between the EMI and GPR measurements with clay content were evaluated from the cross-variograms of the corresponding gaussian variables. The spatial correlation was high and positive between EMI and clay content, whereas it was negative between the GPR measurement and clay content.

In this work multivariate geostatistical analysis has shown a relationship between the EMI and GPR observations with clay content to occur. So, the EMI and GPR data could be used to improve the precision of the estimate of the clay using geostatistical approach. However, the relationships between geophysical data and clay content appear complex because these measures are influenced by many factors, so these maps cannot substitute soil sampling, but only optimize it.

**Keywords**: EMI induction, Ground Penetrating Radar, clay content.

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# ROLE OF CARBONATE ON SWELLING/SHRINKAGE OF CLAYEY SOILS

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In the past decades, the succession of several periods of drought caused damage on individual constructions in France. After the summer heat in 2003, an increasing number of pathologies with cracks appeared consequently to soil deformation under foundations because of the presence of sensitive clay. Indeed, smectites may swell and shrink when the soil water content varies. So characterization of the swelling/shrinkage potential of soils after identifying the presence of clay represents a real challenge to reduce expensive reparations on damaged constructions and to prevent new buildings from sinister.

Experiments were conducted on the two major clayey materials named as Romainville's green clay and Argenteuil's blue marl and at the origin of the pathologies encountered near to Paris. After the geotechnical, physico-chemical and mineralogical characterization of materials extracted from a gypsum carrier, mechanical tests were applied to better understand the relation between microstructural characteristics of soils and macroscopic behaviour. An automated instrumented apparatus developed in LCPC to measure the volumetric shrinkage was used as well as the free swell test (Makki, 2008). Several parameters impacting on the soil behaviour were identified as the soil density, the numbers of humidification/desiccation cycles, the sample structure (intact or compacted after destructurated soil sample) and the presence of carbonates. This last parameter appears to be determining as it can modify the soil sensitivity, compared to the same soils with similar clay. Between aggregates, the carbonates may form cementation that is submitted to alteration under dry/wet cycles. This cementation, that we tried to show from observations by scanning electron and optical microscopies, completed by porosimetric measurement by mercury intrusion, reduces the soil deformation. Therefore such parameters must be considered in the classification of soil sensitivity to swelling-shrinkage.

**Keywords**: shrinkage, carbonates, building foundations.

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# VARIABILITY OF CLAY MINERALOGY IN A VERTISOL IN A FLAT CALCAREOUS LANDSCAPE AND ITS EFFECT ON PASTURES

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This study was motivated by the concerns of land owners on saline Vertisols in South Australia about isolated patches of land that are almost devoid of plants. Land owners have been fearful that these may spread to occupy more of the landscape.

A representative site has been investigated over a variety of scales by geophysical methods. An exploratory trench was then excavated to groundtruth the geophysics, providing the opportunity to observe deep soil features in the flat landscape and to collect samples for analysis. Soil profiles could be separated into two main types based on their morphological, chemical and agronomic properties. They each have either one or two carbonate layers, of variable thickness, within their profiles. Soils were alkaline, saline and sodic to varying extents with depth.

X-ray diffraction (XRD) showed that clay fractions at all depths (including below the single carbonate layer at 50-70 cm) of the soil in unproductive patches was dominated by a smectite. In contrast, there was no smectite above the upper carbonate layer (at *ca.*30 cm) in the most productive soil and only broad or poor smectite peaks below it. Instead, illite was dominant, with kaolinite also often present, in the upper horizons of this soil type. XRD and Transmission Electron Microscopy (TEM) also showed sepiolite and palygorskite in both productive and unproductive soils. Both of these Mg-rich minerals were more common at depth, usually below the upper carbonate layer.

The deeper, and thicker, carbonate rock below the unproductive soil has resulted in impeded drainage leading to the neoformation of smectites, which themselves give rise to a low porosity that limits the leaching of salts from the profile. The root zone of this soil has also developed a high pH. By contrast, the lack of smectite in the more productive soil has led to better conditions for plant growth. A thinner upper carbonate layer higher in this profile, together with another carbonate layer below, has insulated the root zone from the upward movement of salts from the groundwater while its dominant non-swelling clays have provided a relatively porous structure, enabling leaching to occur.

It is concluded that the problem soils result from their mineralogy, which are a product of, and also affect, their drainage; they will not spread with time.

**Keywords:** Smectite, Drainage, Alkaline.

# ADSORPTION BEHAVIOR OF ZINC ON CLAY MINERALS AND ITS VARIABILITY IN DIFFERENT SOILS

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The bioavailability of trace elements including Zn, decreases with the clay mineral content in soils. The type of mineral has a great role on the adsorption of heavy metals. Surface samples (0-30 cm) selected of two acid, two calcareous and two gypsiferous soils were collected from the Fars province, Iran. The mineralogy of fine and coarse-clay fractions was analyzed by X-ray diffractometry. XRD studies indicate palygorskite, chlorite, illite, smectite, quartz and interstratified minerals are the major clay minerals within the soils. Two grams of each soil sample were placed in separate centrifuge tubes and mixed with 20ml of a series of different electrolyte solutions containing $ZnSO_4$. Adsorption isotherms most frequently used are Freundlich, Langmuir and Temkin equations. Langmuir isotherm adsorption was found to be more suitable for this research than the two other equations. The effects of different background solutions on the sorption of Zn by various clay minerals were tested. Zn sorption capacity correlates with soil contents of aluminosilicate clays, metal oxides and carbonates. The magnitude of surface charge and its origin (tetrahedral or octahedral) should determine the selectivity of silicate surfaces for different metal ions. The mineralogy of gypsiferous soils showed that Palygorskite is the main mineral. High sorption of Zn by Palygorskite is due to its large surface area (300-600 $m^2$/gr). The amount of Zn sorption by calcareous soils, in which Smectite and Vermiculites are dominant clay minerals, is high but not as much as gypsiferous soils. The acid soils with Illite showed the least Zn sorption. Incorporation of Zn into hydroxyl-Al interlayer phyllosilicates was confirmed in an acid subsoil of a contaminated site by x-ray absorption spectroscopy. The interaction between Zn and Fe or Al oxides through the formation of covalent bonds with surface aqua and or hydroxo groups have been proved to be the major mechanism of Zn retention by acid soils so that the formation of Zn-Fe precipitates such as $ZnFe_2O_4$ (Franklinite) occurs in both acid and calcareous soils. Increase in the nonlabile fraction of sorbed Zn in calcareous soils is largely due to the formation of Zn-phosphate precipitation such as $Zn_3(PO_4)_2$ $4H_2O$ (Hopeite). The presence of various ions and minerals changed both the capacity and specificity characteristics of Zn sorption in all soils. Hence the best indications of mineral effects requires Microprobe & Microscopic studies.

**Keywords**: Gypsiferous soil, Calcareous soil, Zn Sorption.

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# AUTHIGENIC PALYGORSKITE IN VALLEY FLOOR SOILS IN WESTERN AUSTRALIA

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The Wheatbelt of Western Australia is characterised by an ancient deeply weathered landscape formed under humid conditions which is now experiencing a semiarid climate. The region is predominately underlain by Achaean granitic and gneissic rocks that have been weathered to form lateritic profiles up to 30 meters or more in depth. The main weathering products are kaolinite and iron oxides with primary quartz also abundant. However carbonates and many evaporite minerals are present, having accumulated in valley floor situations under current semi-arid conditions over a long history of weathering.

Six sites across the Wheatbelt were sampled with kaolinite, illite and smectite being present in soils at most sites. Authigenic palygorskite occurs at one site; an area where salts are dominated by calcite and dolomite. Palygorskite only occurs in association with dolomite.

This paper reports on the first comprehensive characterisation of soil palygorskite from Western Australia. Analysis has shown that the crystals are large for a soil palygorskite, extending upto 10µm in length. Techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal gravimetric analysis (TGA), differential thermal analysis (DTA), synchrotron x-ray diffraction and x-ray fluorescence (XRF) were used to provide chemical, morphological and structural information.

**Keywords:** Palygorskite, Characterisation, Morphology.

# IDENTIFICATION AND QUANTIFICATION OF SOIL REACTIVE CLAYS MINERALS BY DIRECT XRD PROFILE FITTING

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Soil clay mineral assemblages are most often heterogeneous mixtures of numerous clay species formed by the weathering of primary silicates or nucleation-growth of neoformed species. X-Ray diffraction (XRD) is routinely used for their identification; however, as the several clay mineral species are often poorly ordered and interstratified, their diffraction bands are wide and overlapping and consequently difficult to interpret. We applied, for the first time to soil samples, the direct XRD profile fitting method which has been developed for diagenetic mixed layer minerals (Sakharov et al., 1999). The crystallographic characteristics of the different clay mineral species are adjusted to reproduce the positions, widths and relative intensities of the experimental $00\ell$ peak series in the air dried (Ca saturation) and ethylene glycol saturation states (from 3 to 35 °2θCuKα). A significant advantage of this method is that it provides quantitative analysis of discrete species and mixed layers present in the assemblage. The clay mineral assemblage of the < 2 μm fraction from a horizon of a cambisol developed onto a paleo-oxisol (INRA Lusignan, France) was characterised using a two step method. Firstly, XRD profile fitting was performed on the experimental patterns of the < 0.05 μm fraction. Secondly, the clay mineral species identified in the < 0.05 μm fraction were implemented in the calculation of the complete < 2 μm fraction.

The clay mineral species forming the < 0.05 μm fraction do not present diffraction bands but wide modulations of the diffracted intensity. They contribute to the so-called “background” of the XRD patterns of the < 2 μm fraction in spite of the fact that they represent approximately 30% (weight). The < 0.05 μm fraction concentrates clay species having a low Coherent Scattering Domain Size (CSDS). These mineral phases are: smectite rich mixed layers-like illite/smectite (R0 85/15; CSDS 8; 9% and R0 40/60; CSDS 3; 4%) and kaolinite/illite (R1 segregated 79/21; CSDS 7; 17%). In contrast, discrete clay mineral species having a higher CSDS such as illite (CSDS 22; 16%), chlorite (CSDS 10; 2%), two kaolinite populations (CSDS 19; 22% and CSDS 5; 6%) and illite/chlorite/smectite mixed layers (R0 60/26/14; CSDS 14; 24%) are identified in the > 0.05 μm fraction.

This study reveals that direct XRD pattern fitting allows identification and quantification of the complete soil clay mineral assemblage including the most reactive species in the < 0.05 μm fraction.

**Keywords:** Clay mineral quantification, Mixed layer minerals, Modelisation.

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# MINERALOGICAL FORMS OF Pb AND Zn IN SOIL SAMPLES FROM A FORMER Pb MINING AREA IN MOROCCO AND INFERENCES FOR SPECIATION

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In soil heavy metal partition among the various geochemical phases is a determining step for the evaluation of the mechanisms of retention and release involved in the process of migration and decontamination of metals at past mining sites. Chemical extraction techniques used for this purpose are inevitably operationally defined. A more direct approach to the identification of mineral forms can be made by mineralogical techniques such as X-ray powder diffraction (XRPD) coupled with Spray-drying sample preparation and quantitative determination of phases by the Rietveld method and a full pattern fitting method. In this study this approach was used to define Pb and Zn mineral forms in the soils from the mining district of the High Moulouya valley (Morocco), as to assess metal mobility. The Upper Moulouya district displays 3 main types of lead ores in the Hercynian domain: Aouli vein-type deposits hosted in the Hercynian basement (1926-1985), Mibladen carbonate-hosted stratabound and karstic mineralisations in the Mesozoic cover (1936-1985), and Zeïda Triassic sandstone-hosted (1972-1985). Due to the location of the sites, the mine wastes and tailings can be considered the only sources of metals in the area. Surface (0–10 cm) soil samples were taken at various locations around each mine site. Soil profiles were opened, described and sampled at selected locations. Total metal analysis were made on the soils along with pH, EC, OM, total carbonates and texture. Mineralogical analysis was undertaken on the bulk soil (<2 mm) and on the <2 μm fraction from the most contaminated samples, by XRPD using a Siemens D5000 diffractometer with a θ/θ goniometer and Co-Kα radiation. The Rietveld method was applied to the XRD data using the software package Siroquant V3. Most studied soils are alkaline as a consequence of $CaCO_3$ abundance (average: 41%). The total Pb and Zn concentrations have a very wide spread (Pb: 8–31092 mg $kg^{-1}$; Zn: 31–190577 mg $kg^{-1}$), the most contaminated samples being from Mibladen. In total, 36 crystalline phases were identified from the 3 mining sites investigated. Seven out of these minerals contain Pb and Zn in their structures: cerussite, anglesite, hydrozincite, smithsonite, sphalerite, willemite and hemimorphite. Quantitative analysis indicates that cerussite is the most important Pb-host in all mining sites. Hemimorphite and smithsonite are the main Zn sources, although the occurrence of this contaminant and its minerals is restricted to Mibladen. In relation to the minerals solubility, the mobility of Pb and Zn within the studied environment is limited and most likely occurs through physical transport of fine particles.

**Keywords**: Heavy metal mobility, Quantitative mineralogical analysis, XRPD.

# RHEOLOGICAL INVESTIGATION OF PADDY SOILS WITH MIXED MINERALOGY

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Soil strength is a complex soil property resulting from water content, size and shape of particles, their arrangement in space, physico-chemical behaviour and soil forming processes including impact of man and controls many ecological functions of soils. Rheological investigations as a new tool in soil physics allows potentially to discriminate between the influence of soil inherent parameters (e.g. clay content, mineralogy, content of organic matter and Fe oxyhydroxides) and soil forming processes (e.g. ped formation or destruction) on soil strength.

We tested four paddy soils from China (Red Soil Station, Jiangxi Province), each with three horizons (puddling horizon, plough pan, horizon below plough pan). Two soils are coarse grained (13 to 25% clay) and two fine grained (19 to 40 % clay). One of the pairs was 15 to 20 years (young) and one 120 to 150 years (old) under paddy use. The highest content of organic carbon is 2.2% and content of dithionite soluble Fe varies between 0.6 and 2.6%. The mineralogy of the clay fraction is of mixed type, with quartz, kaolinite, illite, 10-14nm mixed layer silicates and hydroxy interlayered vermiculite as dominant minerals.

Measurements (disturbed and homogenised fine earth, three replications per horizon at 0 and -60hPa water suction) were done with a Modular Compact Rheometer (MCR 300, Paar Physica) with an oscillating upper plate and a fixed lower plate, both with structured surface and a distance of 4 mm. The shear deformation was regulated from 0.0001…100% with a constant frequency of 0.5Hz and registration of 30 readings within 15 minutes. During the tests a power of 0-12N was generated for sandy to loamy samples and up to 30N for clayey samples.

The linear viscous-elastic range of all samples increased significantly with the content of organic matter and decreased less pronounced with the content of quartz. Clay content (13 to 40%), saturation of the exchange complex with multi valent cations (67 to 82%) as well as content of certain clay minerals or content of Fe oxyhydroxides has no pronounced influence. Deformation (point where the elastic module is equal to the viscous module) was in tendency higher with increasing content of clay and Fe oxyhydroxides. Long time puddling of the upper horizon resulted in a loss of soil strength in comparison to younger paddy soils, the plough pans and the horizons below.

**Keywords:** Rheology, Paddy soils, Soil strength.

# LOCATION OF NICKEL IN RAPIDLY DEHYDROXYLATED GOETHITE IN OXIDE-TYPE NI LATERITE ORES: EXAFS AND XANES INVESTIGATION

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The crystal chemistry of Ni in iron oxides in various oxide-type Ni laterite ores that were rapidly dehydroxylatied by shock heating at 220-800°C was investigated using synchrotron based XRD, X-ray absorption fine structure (XAFS) spectroscopy and TEM. Acicular nano-sized goethite was the main constituent of the samples with minor to trace amounts of quartz, talc, kaolinite and Mn oxides. Goethite was partially dehydroxylated to OH-hematite at 340-400°C and had completely altered to well ordered hematite at 800°C.

Congruency of acid dissolution experiments indicated that Ni was uniformly distributed in the goethite structure. However, nickel may not be completey compatible with the neoformed hematite structure and is therefore either exsolved from the crystal structure where it may reside on the crystal surface, or, forms a more soluble Ni mineral than the precursor goethite (Landers *et al.*, 2009). XAFS (XANES and EXAFS) data were collected across the Ni (8333keV) and Fe (7112keV) *K*-edges at ambient temperature for reference materials and samples shock heated at several temperatures. Due to the relatively low Ni contents and the high Fe content of the iron oxide samples Fe strongly interferes with the Ni signal. Detector saturation was minimised and the signal to noise ratio was optimised by varying sample thickness and use of fluorescence filters. Results provide information of the Ni bonding environment and inform on whether Ni is incorporated into the neoformed hematite phase and/ or if it exists as a discrete phase (i.e. cluster) on the hematite surfaces.

These results may contribute to the development of more efficient procedures for the extraction of Ni from lateritic nickel ores as well as provide valuable information on the probable effects of natural heating on pedogenic iron oxides.

**Keywords:** XAFS, Lateritic nickel, Dehydroxylation.

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# SHALLOW SOILS FROM BASIC AND ULTRABASIC ROCKS, RUSSIA: MINERAL COMPOSITION AND CHEMICAL PROPERTIES

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Mineral associations of clay size fractions of shallow, cobble soils underlain by basic rocks: Lithic Leptosol from amphibolites and Epileptic Entic Podzols (WRB, 2006) from (i) metamorphized gabbro - diabases (East Fennoscandia), (ii) meta-gabbro amphibolites (northern taiga area of Polar Ural) and (iii) traprocks (basalts, Central Siberia) and Haplic Cryosols Reductaquic from serpentinous olivinites (mountainous tundra, Polar Ural) were determined by X-ray Diffraction.

Shallow soils from basic substrates are acid. Sola of East Fennoscandia are illustrated a rare variant of soil formation from the basic substrates with phyllocilicate absence or with small content in sola because of initial absence of phyllosilicates in the bedrocks. The pedogenic alteration of the initial mineral is very weak and does not lead to a significant accumulation of clay minerals in the soils. The recent pedogenic processes of mineral matrix transformation are rock disintegration, and binding of iron released from the weathered silicate minerals. Enrichment of fine size fraction by phyllosilicates of sola (Ural Mountains and Central Siberia) is due to their inheritance from basic substrates. It was shown on the example of Epileptic Entic Podzol from meta-gabbro amphibolites that pedogenesis enhances the phyllosilicate transformation which was advanced by epigenic rock alteration: recent vermiculitization of chlorite that is followed by destruction of inherited vermiculite. The latter process takes place not only in the clay-size fraction but in coarser fractions. The only pure pedogenic process is illite degradation.

Haplic Cryosols Reductaquic from serpentinous olivinites (Ural Mountains) are cobble, “gleeish” colored and alkaline due to pH data in bulk samples. Serpentinous olivinites are a source of easy weatherable minerals that leads to soil formation on the matrix that is enriched by phyllosilicates: saponite, chlorite, serpentine and talc. The results of pedogenesis are (i) serpentine increase in the upper horizons and (ii) saponite destruction that is the most unstable in the mineral associations. In spite of alkaline conditions the saponite destruction is due to biota (moss and lichens) influence. Strong lichens and moss influence upon the mineral matrix is possible only in the case of rock enrichment by phyllosilicates which are not stable in acid conditions. It was shown on the example of studied sola that the mineral matrix destruction and transformation depends more on rock composition than on climate conditions.

**Keywords:** Basic and ultrabasic rocks, Mineral transformation.

# INVESTIGATION OF PHYSICAL, CHEMICAL AND MINERALOGICAL STUDIES OF TRANSPORTED SEDIMENTS IN SEFID-ROOD DAM

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The objective of this study was to investigate the physical, chemical and mineralogical properties of transported sediments in Sefid-Rood dam reservoir site that is located in conjunction of two major rivers in the area named Shahrood and Ghezel-Ozan rivers. 8 different blocks in the area were used to collect samples. block 1, 2 & 3 for Shahrood river basin area , blocks 4 & 5 for the areas between the two major rivers, and finally block 6, 7 & 8 for Ghezel-Ozan largest sediment deposits. Clay deposits were subjected to petrographical, mineralogical and geochemical investigation to examine their origin. The mechanical analysis results shows that these river deposited sediments are poorly graded for engineering practical purposes. The permeability of them categorized as low permeable. Other physical characteristics were analyzed and reported. The chemical and mineralogical analyses of the sediments reveal that the clay minerals of Ghezel-Ozan deposits were dominantly Kaolin and Montmorillonite group minerals. In Shahrood river deposit the clay minerals were Chlorite & Vermiculite like minerals deposits and the area between the two major rivers was Illite or Mica groups. Absence of Smectite and Illite/Smectite mixed layers and deterital nature of Illite and Kaolinite suggest that Illite was formed as a result of hydrothermal alteration of acidic to intermediate igneous rocks then transported to the depositional basin rather than its formation as a result of diagenesis of precursor clays. The Nb/Y-Zr/TiO2 discrimination diagram indicated that the studied illitic clay deposits were derived from Trachy-Andesite source. The study suggested that these mineral deposit can be excavated and use for different purposes. For example, Kaolin for ceramic industries, Illite for break industries and Montmorillonite & Vermiculite for agricultural industry. The quantities of sediment deposit behind the Sefid-Rood dam are so large that it has already diminished the effectiveness and usefulness of dam water project purposes. For this reason, flushing method is used to reduce the volume accumulation of sediment deposited. The study suggested that in order to minimize the transport of sediment behind the Sefid-Rood dam, pools should be constructed along the river deposit, long before the sediment can be reached to the reservoir areas.

**Keywords:** Transport of sediment, Reservoir areas, Precursor clays.

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# SUITABILITY OF VOLCANIC SOILS AND SEDIMENTS IN METRO MANILA, PHILIPPINES FOR LANDFILL LINER MATERIAL

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This study investigates the mineralogy and geochemical characteristics of Metro Manila soils and sediments for landfill liner material. Samples were taken at different locations around Metro Manila and were analyzed for its clay content using XRD and XRF. Generally the results show smectite-type clays dominate Metro Manila soils. This clay mineral group has high compressibility and high swelling potential which can be utilized for a landfill liner. Surface soils in Fort Bonifacio, Taguig City have little smectite clays but contain primarily quartz and calcite. In Tondo, Manila City, soils are largely smectite-type clays. For Makati City soils, amorphous silica related to the original volcanic glass fragments is dominant. Soils in Fortune, Marikina City and Pasig area are abundant in smectite-type clays. The same clay minerals were also found in Taft, Manila City. Most of the smectite-type clays are potentially weathering products of the volcanic glass derived from andesitic pyroclastic rocks. The dominance of smectite-type clays is due to the degree of volcanic glass-water interactions. These interactions can be traced based on the drainage system of Metro Manila – more water means more smectite-type clays.

**Keywords:** volcanic soils and sediments, landfill liner, Metro Manila, Philippines.

# IMPORTANCE OF CLAY MINERALOGY IN THE FORENSIC COMPARISON OF SOILS

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Rapidly developing advances in scientific instrumentation, analytical methods and sampling techniques continue to find increasing application in areas of criminal and environmental soil forensic investigations. Whilst X-ray powder diffraction (XRD) methods are arguably the most significant for both qualitative and quantitative analyses of solid materials in forensic soil science, it is also a reasonably mature technique and continues to remain of great importance because of its non-destructive nature; often allowing further investigations of original intact specimens. The major strength of XRD is the ability to identify and interpret crystalline components "directly". XRD can be used to analyse all manner of crystalline materials from crime scenes such as; explosive residues, paint chips, adhesive tapes, building materials, minerals, alloys, ceramics, gemstones and drugs.

Soil and clay materials are frequently part of evidence recovered from crime scenes. These materials may require a variety of procedures for analysis, especially in combination to achieve reliable, definite and accurate results to provide additional information about the mineralogical, chemical and physical properties of the suspected soil material (Fitzpatrick et al. 2008). Various systematic sample preparation techniques are employed depending on the quality and quantity of evidence available. Materials can either be analysed undisturbed on the carrier object or removed and analysed separately. Mounting the specimen in the instrument is also dependent on the size and shape of the items being investigated.

Several case studies will be presented outlining aspects of XRD analysis where soil and clay mineralogy provided vital information to help solve a wide range of criminal (e.g. murder, rape and hit-and-run) and environmental soil forensic investigations. Emphasis will be placed on case investigations where new approaches have been applied to analyse very small samples from shoes and clothing, and preparation procedures to obtain representative samples. These case studies include pinpointing the location of buried bodies and comparing soil material from clothing to crime scenes.

**Keywords:** Forensic science, Soils, X-ray diffraction.

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# COMPOSITION OF CLAY MINERALS IN AGGREGATES AND THEIR EFFECT ON AGGREGATE STABILITY IN RED SOILS UNDER DIFFERENT EROSION FROM CHINA

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Soil degradation is a key factor on sustainable development in red soil region of China, and their essential is the deterioration of soil structure. Our research focused on the red soil (Ferralisols) with different erosion intensity, which possessed a high content in clay mineral, and low in organic matter. The composition of clay minerals in red soils derived from Quaternary red clay was determined. The effect of clay on aggregate formation process and aggregate stability under different erosion were discussed. The clay minerals of soils from ChangSha, XianNing and ChiBi were mainly kaolinite, hydromica and 1.4 nm intergrade minerals. The amounts of free iron-aluminum oxides/hydroxides (Fed and Ald) content, point of zero charge (PZC), specific surface area (SSA) and cation exchange capacity (CEC) of the soils increased with the increment of soil erodibility. However, the water stability of micro-aggregate, the amount of pores and percent of pores in soils decreased with the increment of erodibility.

The amounts of Fed and Ald in the exterior of the aggregate were higher than that in the interior. Their different degree between interior and exterior aggregates increased with the increment of erodibility. This dissimilarity was according to the diversity of heavy eluviation. For the phyllosilicate, the amount of 1.4 nm intergrade mineral and kaolinite in the exterior was higher than that in the interior of the tested aggregate, but the amount of hydromica was reverse. The weathering or binding during aggregate formation was different, which resulted in the different composition of phyllosilicate.

Micromorphology by SEM clearly showed that the morphology of the micro-aggregate under different erosion was different. The rotundity, ellipse or round surfaces could be observed in micro-aggregates undergoing heavy erosion. Iron preferred to distribute in surface of aggregates from the result of electron probe. Fe oxide acted as a “bridge” when two micro-aggregates cohered to large aggregates in the tested samples.

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**Keywords**: Soil, Clay mineral, Erosion.

# MINERALOGICAL IMPLICATION FOR AGRICULTURAL USES OF SOILS DEVELOPED ON CALCITE BEARING ROCKS

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Fourteen soils in Northern Thailand were selected for this study to determine the relationship between their spatial mineralogical compositions and chemical characteristics in order to evaluate soil constraints on crop production. The study included analyses on field morphology, chemical and mineralogical properties of the soils. These soils were developed on colluvium, alluvium and wash over residuum derived from calcite bearing rocks such as calcareous shale, limestone and calcite bearing phyllite. Land uses are mainly vegetables and ornamental plants, strawberry and maize. This area is under a tropical savannah climate with an elevation range of approximately 540-590 m above mean sea level.

All soils are deep and slightly to moderately developed mainly with genetic Ap/Apk-Bw/Bk-Ck horizon sequence. There is evidence of $CaCO_3$ accumulation in some soils. Soil texture ranges widely from loam to clay and most have an alkaline reaction (pH 7.8-8.4). Extractable Ca is a dominant cation among bases with the range of 1.49-11.24, 0.19-1.43 and 0.01-1.95 cmol $kg^{-1}$ for Ca, Mg and K, respectively. Their mineralogical compositions exhibit small variation. Smectite is present in the highest proportion followed by kaolinite and illite except for the soil located on dissected footslope where a small amount of smectite can be found only at depth. This is probably due to their high pH, Ca and Mg under restricted drainage conditions which favours smectite formation. This predominant group of clay minerals shows good correlation with CEC values which are moderately high to high (15-30 cmol $kg^{-1}$). Major constraints of these soils are low availability of plant trace elements due to high soil reaction in combination with phosphorus fixation. High contents of smectite also cause difficulty in workability on the soils, ploughing in particular. The increase of organic matter content by application of manures and composts may alleviate the latter problem by loosening the topsoil and improving its structure stability increasing in available moisture. Single application of fertilizers is recommended as leaching is unlikely to be pronounced in these soils and acidic fertilizer is more appropriate for reducing soil pH.

**Keywords:** Calcareous soils, Clay mineralogy, Soil constraint, Thailand.

# CLAY MINERALS AND THEIR INFLUENCE ON MASS MOVEMENTS

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Mass movements are a threat to buildings and the people who live in them. Therefore it is important to know what contributes to the development of landslides, etc. An important factor is the presence of expandable clay minerals contained in sedimentary rocks which influence the mechanical behaviour of rocks very strongly due to their small grain size and other specific properties.

In Austria, flysch sediments reach from Vienna in the East to Vorarlberg in the West. They consist of very stable sandstones on the one hand and soft, unstable clay marls on the other hand. These marls have been known responsible for mass movements in this geological zone for a long time.

This project deals with the classification of mass movements and clay minerals. Their properties are explained and special attention is paid on how clay minerals contribute to the formation of gliding layers.

This knowledge has been applied on two locations in Upper and Lower Austria, Windischgarsten and Gresten, where slope instabilities caused damage on buildings. Since this is also an economic issue, counteractions must be taken.

From both sites, samples have been taken from drill cores, testing pits, and dynamic probes in order to determine the bulk and clay mineralogy. High amounts of mixed layer minerals and illite were found. There is a correlation between the occurrence of those minerals and the gliding tendency of observed slopes.

**Keywords:** Mass movements, Clay minerals, Mixed layer.

# CLAY MINERALOGY OF SOILS DERIVED FROM SANDSTONE ALONG A TOPOSEQUENCE IN NORTHEAST, THAILAND

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A study on clay mineralogy of soils along a toposequence was carried out in Khon Kaen province, Northeast of Thailand. Five soils occupying the summit, upper-slope, mid-slope, lower-slope and toeslope were selected to investigate the influence of landscape positions on mineralogical compositions using XRD, XRF and chemical measurements. These soils were developed on sandstone/or siltstone under rubber tree plantation in a tropical savannah climate with an elevation ranging from 165 to 181 m above mean sea level.

Quartz, smectite and kaolinite are the predominant constituents in the clay fraction with some illite and trace amounts of feldspar and goethite. The basal 001 spacing values of these kaolinites ranged from 0.7167 to 0.7392 nm, this may be due to them consisting of kaolinite-smectite mixed layer clay minerals (K-S). Kaolinite increased with increasing depth within the same profile as well as smectite except for the soil located on toeslope where the trend is converse. This may possibly be due to the translocation of the fine clay mineral of smectite to downslope. Quartz is the major component in the silt fraction with small amount of feldspar and trace of goethite. Therefore, the clay minerals in these soils may be assumed to be derived from the pedogenic alteration of feldspar over the toposequence. The poorly crystalline kaolinite of these soils along the slope may formed by pedogenesis under an intermediate to poorly drained whereas these soils had a dense clay layer at 50-70 cm depth which produced water logging in the rainy season. The major elements in these soils are Si, Al, Fe and K which correspond to the XRD results in both of the clay and silt fractions.

CEC values of the soils along this toposequence have a significantly positive relationship with the clay content (r = 0.89**). When each soil profile is considered separately, only the soils developed on mid-slope, lower slope and toeslope that have these relationships (r = 0.98**, 0.99** and 0.95**, respectively). However, there is no significant relationship between CEC and organic matter content, indicating that clay minerals play a vital part in contributing on the CEC of these soils.

**Keywords**: Smectite, Kaolinite, Toposequence, Tropical soil, Sandstone.

# REHYDROXYLATION OF HEATED GIBBSITE, KAOLINITE AND GOETHITE: AN ASSESMENT OF PROPERTIES AND ENVIRONMENTAL SIGNIFICANCE

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Soils mostly provide humid environments so that minerals that are dehydroxylated in bush fires may tend to rehydroxylate in the soil. The absence of large amounts of dehydroxylated minerals in frequently burnt soils supports this proposition. Few studies have investigated the rehydroxylation of metakaolinite, goethite and gibbsite and the relevance of such changes to soils, which are the topics of this paper.

Pure gibbsite, kaolinite and goethite were heated at temperatures above and below DTA dehydroxylation maxima. Gibbsite was heated between 250°C and 350°C and formed boehmite. Goethite altered into hematite after heating between 250°C and 350°C. Kaolinite, dehydroxylated at temperatures above 500°C to form metakaolinite.

For rehydroxylation experiments, all dehydroxylated minerals were mixed with deionised water before heating in an oven for 0, 14, 70 and 200 days at several temperatures (RT, 55, and 95 °C). The changes in mineral properties were studied by thermal analysis, X-ray diffraction, electron microscopy, specific surface area measurement (SSA), inductively coupled plasma mass spectrometry of extracts and phosphorus sorption.

Rehydroxylation of heated gibbsite was extensive during hydrothermal treatment at 95°C and after 14 days had formed bayerite and gibbsite, the process was much slower at lower temperatures. Metakaolinite and also hematite formed from goethite showed no change in XRD patterns but SSA and P sorption capacity of the three dehydroxylated minerals increased substantly with period of rehydroxylation time. These results suggest that dehydroxylated minerals and their partly rehydroxylated forms may exert significant effects on the chemical behaviour of heated soils.

**Keywords**: Dehydroxylation, Rehydroxylation, Reversion.

# MISCELLANEOUS

## UM1 • TEACHING CLAY SCIENCE

## UM3 • GENERAL TOPICS

# MISCELLANEOUS

## SESSION UM1

## *Teaching Clay Science*

# WHITHER CACT (COMPUTER ASSISTED CLAY TEACHING)?

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This presentation reviews the current status of computer-assisted teaching of clay mineralogy and attempts to project where these learning tools might take us. In the previous two decades the computer has played a significant role in support of learning objectives by making the material used in our courses available on demand and providing superb audio visual tools. Animations, narrated slide shows and movies, archived literature, and Internet posted course notes are available. Difficult concepts, such as X-ray diffraction by mixed-layered materials, can be explored with computer applications.

I foresee continued expansion of computer-assisted learning by more active involvement of students in group learning through the use of threaded discussions and the construction of Wikipedia-like summaries of important basic concepts and techniques. Self-tutored modules constructed by experts from around the world will replace standard university lecture courses. Professors on site will become facilitators challenging the students to apply their skills to solve problems.

**Keywords**: Teaching, Learning, Computer.

# SMECTITE CLAY ADSORPTION OF AFLATOXIN ILLUSTRATES APPLIED CLAY SCIENCE TO THE PUBLIC

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Texas has a vast array of corn production that is prone to be infected by aflatoxin produced by mold. The major area extends from the Red River at the Oklahoma border to the border with Mexico in the south and the infection extends into Mexico. Aflatoxin infects corn less grown in the High Plains of northwest Texas where irrigation is frequently utilized. Plant scientists have investigated the aflatoxin problem for many years yet amending animal feed with smectite clay is the most effective solution thus far.

Presenting this solution to the public includes grain producers, grain dealers, animal producers, and biologically oriented colleagues who are mostly unfamiliar with clay minerals and their unique properties. Recent research has extended into the medical community investigating the use of smectite in human diets in Africa as a preventative medication where aflatoxin is suspected in local grains. This wide array of professions can benefit from clear authoritative images of smectite clays and how they adsorb aflatoxin in the digestive tract of the consuming animals.

Research has revealed some of the basic cause and effect relationships between aflatoxin molecules and the clay structure such as interlayer adsorption of the molecules and their resistance to removal by washing. Particle size analysis by laser diffraction illustrates the very fine crystallites of smectite clay and how it correlates with amount of aflatoxin adsorption. Electron micrographs illustrate the platy nature of smectites. X-ray diffraction (XRD) illustrates the closure of smectite layers on almost planar aflatoxin molecules. XRD also provides clear evidence of inert prismatic minerals that usually dilute smectite clays in bentonites. Clay structures differ in composition as indicated by their differences in color and range of adsorption of aflatoxin. These subtle properties are analyzed by the infrared absorption curves produced by smectites of different compositions. The platy morphology of fine smectite particles is indicated by their smooth sticky consistency when moist.

Smectites in bentonites are typically dissolution and precipitation products of volcanic ash deposited in marine environments. These colloidal adsorbents occur in many parts of the world and have the potential to reduce liver cancer and other diseases caused by aflatoxin in animals and humans. These clays are usually available at modest cost. The use of natural smectite clays to bind afatoxin may bring the importance of clay science to many people in the world that were not motivated to learn about it in the past.

**Keywords:** Bentonite, Mycotoxin, Cancer.

# ARGUMENTS IN FAVOUR OF KAOLIN REDEFINITION

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Targets, concepts, principles, methods, evolution, interdisciplinarity, systems, and implications on society are common fundamentals to any science. Concepts can be expressed differently by people from different educational backgrounds and experience. Concepts can evolve over time. The concept or definition of kaolin is of paramount importance from scientific, industrial, and legal purposes. The term “kaolin” is often defined and used differently in science than in industry. These differences may have legal implications. In defining kaolin, some questions can be raised. What is kaolin? Is all kaolin equal? What properties must clay exhibit in order to receive the name kaolin? What definition of kaolin would meet the joint approval of academia, industry, and government agencies? Science privileges the fundamental properties of this geological product, such as, genesis, mineralogy, and chemistry. Industry, on the other hand, privileges other properties of this industrial mineral such as colour, mean grain size and grain size distribution, chemical inertia, plasticity, rheology, abrasiveness, and refractoriness, properties that can condition certain applications and functions. An extensive review of the historical evolution of the definition of kaolin, from the beginnings of clay science up to the present time, will be presented. This will include the fundamental geological, mineralogical and technological properties of kaolin as defined by various authors, although in a not satisfactorily integrated way. In regard to kaolin geology, the origins are diverse, the occurrences being diverse too. Both the volume and quality of a kaolin deposit determines the economics and legality of its exploitability. Kaolin mineralogy and chemistry are the fundamentals of kaolin quality, decisive in terms of industrial applications and functions. The white or near white colour in bulk, and after drying and firing, is important for the industrial applications of kaolin. Other clays, however, can exhibit white colour, and even kaolin can exhibit other colours. Hence other basic arguments contemplating genesis, mineralogical, and chemical data common to all types and varieties of kaolin should be considered. The emphasis on one or more than one particular property depends greatly on the academic background or professional experience and interest of the individuals seeking to define kaolin. As a result, developing a consensual definition is difficult. A proposal for a new kaolin definition, characterized by its more comprehensive character, able to integrate kaolin geology (origin and occurrence), mineralogy, technological properties, as well as the always decisive economic and legal criteria, is put forward Kaolin is a fine grained natural or engineered product predominantly composed of clay minerals classified into the kaolin sub-group minerals; to fulfil the diverse and important industrial functions kaolin is extracted from geologic deposits of quality and economics previously assessed, and appropriately refined and beneficiated in order to achieve its required ultimate white colour and other relevant properties.

**Keywords:** Kaolin, Fundamentals, Redefinition.

# COMPUTER MODELS OF TERNARY SYSTEMS: SPACE DIAGRAMS WITH MATERIAL BALANCES

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Computer models and attendant software make it possible to visualize and investigate phase diagrams (PDs) in 3D [1-2]. This makes it possible to decipher the horizontal and vertical sections of the surfaces and phase regions by means of the special tables, to simulate the tie-lines and crystallization paths, and to calculate the mass-balances.

A kinematical method of PD surfaces description has the most potential [1]. Any surface is presented as a pseudo-ruled surface, when a space curve, given by the interpolation polynomial, moves along the analogously given directing curves. Complex surfaces with holes, folds and complex contours are formed from the separate fragments or by means of auxiliary templates.

Material balances can be shown as vertical diagrams – for the given centre of masses (in the temperature interval), or as horizontal diagrams – an isothermal one, which coincides with the isopleth section [2].

T-x-y diagram computer model development starts with its geometrical description, when all types of points, lines, surfaces and phase regions are named uniquely and informatively. Traditional tabular schemes of phase reactions are added by these designations. Resulting schemes of monovariant states in 3-phase regions, including the beginning and ending concentration of the phases, permit the designation of the boundaries of two-phase regions also.

Working with real systems it is possible to use a universal algorithm to convert the concentration coordinates [3]. Computer models permit the use of phase diagrams as an instrument to solve different applied tasks of heterogeneous design and physics-chemical analysis. For example, they are very useful to compare and analyze the contradictions between the 3-phase region eutectical and peritectical fragments borders determination methods.

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# EXPERIMENTS ILLUSTRATING THE INFLUENCE OF THERMODYNAMICS PARAMETERS ON SORPTION ON CLAY MINERALS

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Enthalpies of adsorption are considered in most cases exothermic[1]. The explanation for this outcome stems from the definition of changes in Gibbs' free energy (G) for an isothermal process:

$$\Delta G = \Delta H - T\Delta S \qquad [1]$$

where $\Delta H$ denotes changes in enthalpy, T the absolute temperature and $\Delta S$ is the change in entropy during the process. Since adsorption is spontaneous, $\Delta G$ must yield negative values. The general assumption is that during adsorption molecules that had freedom of mobility in the solution become attached to the surface, leading to a decrease in the distribution of energy. In other words, the entropy of such a process is usually considered negative. The absolute temperature is by definition positive - thus in order to conform to a negative value of $\Delta G$, the reaction should be exothermic, i.e. $\Delta H<0$. However, for adsorption on clay minerals, the statement that $\Delta S<0$ may not always be correct. Since adsorption to phyllosilicates is often accompanied with exchange of ions, and in several cases hydrated water molecules are also released due to adsorption, the change in entropy might be positive, and consequently endothermic heats of adsorption are possible[2,3].

In previous studies[4], enthalpies of adsorption of some organic cationic dyes on clays were measured, showing that in some cases the enthalpy depends on the different steps of the adsorption, being endothermic for part of the processes, and exothermic for the rest. Such results were obtained by microcalorimetry, but simple experiments based on Van't Hoff's equation can elucidate such processes[5]. For example, adsorption of dyes on clays and organoclays can be performed at three or four temperatures. Analysis of the data can improve student understanding of the influence of thermodynamical parameters on the sorption process. Detailed descriptions of such experiments and how they can be used in the classroom will be presented.

**Keywords:** Gibbs' free energy, Entropy, Adsorption.

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# MISCELLANEOUS

## SESSION UM3

## *General Topics*

# SPECTRO-MINERALOGICAL CHARACTERIZATION OF BRAZILIAN AGALMATOLITES USING REFLECTANCE SPECTROSCOPY AND ASTER IMAGERY ANALYSIS

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Agalmatolite is a peculiar rock commonly known by its high concentration of pyrophyllite and largely used worldwide in the ceramic industry. Along the manufacturing chain, it is used to control granulometric composition of materials, as lubricating binders for ceramic extrusion and to avoid extensive shrinking during ceramic sintering, yielding low porosity, highly reflective, white ceramics. In Brazil, chief agalmatolites resources are hosted by meta-volcanic-sedimentary rocks of the Archaean Rio das Velhas greenstone belt that occur NW of Belo Horizonte, capital of Minas Gerais State. The deposits are placed along a SE-NW, 150km-long, 30km-wide, strike-slip fault, which cross-cuts the Archaean stratigraphy and is associated with metamorphic-metassomatic-hydrothermal events. Considering the intrinsic complexities involved in characterizing such materials by conventional methods (i.e., specifics on sample preparation), and using the type area of occurrence of agalmatolites in Brazil as a control, this works aims to (i) evaluate the potential of reflectance spectroscopy (RS) as a complementary (or substitutive in relation to optical microscopy and XRD), expedite and portable method to characterize sheet silicates; including definition of their type, composition and crystallinity; (ii) to seek a possible relation between spectral characteristics of these minerals and their use in the ceramic industry, and (iii) to evaluate the potential of ASTER multispectral data and image products to map agalmatolite-related minerals remotely. RS allowed the distinction of several mineral types and sub-types, including pyrophyllite, kyanite, andalusite, diaspore, micas, diasper, dumortierite, tourmaline, plus other ‘clays’. RS also allowed these minerals to be grouped into three zones, which were further validated by XRD analysis. These zones typified in the agalmatolite deposits have a specific application in the ceramic industry, indicating the prominent potential of RS to characterize such industrial materials and help defining their use. Information extracted from ASTER data, comprising visible and infrared wavelengths, allowed the mapping of podiform structures along the shear zone containing similar mineral zoning. These results have important implications for regional exploration of these agalmatolite bodies and to detailed mapping of mine faces and boreholes, with enormous potential benefits for the ceramic industry.

**Keywords:** agalmatolites, reflectance spectroscopy, ASTER imagery.

# ENVIRONMENTAL TEM TECHNOLOGY: EMERGING RESEARCH PATHWAYS AT THE FOREFRONT IN GEOMATERIALS, ORGANO-CLAY COMPLEXES, AND BIOGEOCHEMISTRY: DYNAMIC OBSERVATIONS AT THE MICRO-NANO- AND MOLECULAR SCALES OF INTERACTION

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Environmental Transmission Electron Microscopy (ETEM) is at the forefront in providing new observational capabilities and technology in a myriad of research science and engineering disciplines. Initial studies and testing have shown that ETEM is capable of high-resolution imaging of wet materials and resovling real-time dynamic environmental processes at micro- and nano-scales for high resolution observation. This technology is presently engendering new paradigms through observational and quantitative interdisciplinary research and is contributing to new and exciting opportunities for fundamental scientific modeling at micro- nano- and molecular scales. ETEM technology opportunities will attract investigators in all disciplines of sciences (physical, natural and medical) and engineering. The emerging technology in ETEM enjoys a relatively brief history of high-level developments and experiments in Europe, Japan and the U.S.; and portends the evolution of challenging future multi-disciplinary, international, basic research programs. Optimum success in nano and molecular level research will require the support of leading academic materials science Departments and Institutes with other high-tech instrumentations (i.e. EDS, EELS and EFT (Energy Filter TEM)) and capabilities that provide a fundamental underpinning required to support the development of ETEM R&D Centers for national and international programs. Smectite and other materials were selected for ETEM study, and the results will be presented/illustrated. Early research and testing of ETEM instrumentation and capabilities have been demonstrated by Bennett et. al. (unpublished) performing tests of biological sample collagen in an early environmental (wet cell) TEM built in the US, and also with the same ETEM system Hulbert et. al. (unpublished) used to conduct geochemical experiments depicting chemical reactions in the wet cell. Chiou et. al. (e.g., 1999) demonstrated excellent ETEM in-situ observation of various materials and clays at nano-scale. These experiments signify the opening of new opportunities in fundamental, organic matter and inorganic nano- and molecular scale, "in-situ" dynamic processes research.

**Keywords**: Environmental/in-situ TEM experiments, Dynamic TEM observation.

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# CLAYEY SOIL - WATER INTERACTIONS: STUDIES, TESTS AND MAIN RESULTS

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Basic statements have already pointed out the strict dependence of clayey soil properties on salt concentration and chemical composition of pore fluids. Present developments, besides adding new support to these statements, emphasize the need to integrate theoretical issues and laboratory test results in the natural environment.

This effort identifies, in determining the behaviour of the clayey soils, the differences locally existing between the chemical composition of pore waters and those peculiar to ambient waters freely circulating within the clay masses as a critical consideration. The extent and direction of related phenomena depend on a series of geological and hydrogeological boundary conditions, which define type and range of concerned differences and time limits of acting processes.

This way, more importance is assigned to the variation of salinity and chemical composition of pore waters rather than to the absolute values of the parameters. The study was performed on blue clays belonging to the wide region geologically known as Bradanic Foretrough and located in Southern Italy.

The interaction between different fluids, environmental or free circulating and pore waters of different chemical composition, involves the variation of various measurable clay properties: suction, osmotic pressure, dielectric constant, composition of the diffuse double layer, and the electrical force field inside the double layer.

Long term or seasonal variation of ionic concentration in waters circulating mainly along clay fractures determines unsteady-state conditions and causes disequilibrium, caused by natural or human changes of existing environmental conditions, between exchange complex and interstitial water.

These phenomena have been evaluated, up to now, in terms of swelling pressure, by geotechnical equipment. However, a better understanding can be gained using energetic terms: the energy balance is well correlated to the energy released by the soil volume when interacting with external waters. The chemistry of pore water was determined on samples extracted from core samples by means of a pressure squeezing technique.

On the basis of the experimental results and in situ surveys from several areas with different geomorphological and hydrogeological situations with swelling or non swelling clayey soils. it is possible to conclude that a complete site characterization must include the evaluation of both pore water and ambient water chemical composition.

**Keywords:** Clay, Interstitial water, Swelling.

# CHARACTERIZATION AND CHEMICAL TREATMENT OF BRAZILIAN VERMICULITE

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Vermiculite is a clay mineral which exhibits a crystalline structure similar to that of the montmorillonites. However, the electrostatic charge of the vermiculite layer is larger than that of the montmorillonite due to a higher substitution in their structure [1]. It also has the potential to generate platelike aluminosilicate layers with high aspect ratio [2]. Unfortunately, the high charge of the layer makes it difficult to disperse in water. On the other hand, a chemical treatment can cause a decrease in the charge of the vermiculite layer. Therefore, the present work aims to study the effect of three different chemical treatments using inorganic solutions, on the swelling and particle size of a Brazilian vermiculite. The raw material used in this study was from the State of Piauí, northeastern Brazil. The as-received material was characterized in terms of its cation exchange capacity, particle size distribution, and mineral (XRD) and chemical (XRF) compositions. The XRD analysis demonstrated the presence of vermiculite as the major phase. Other minerals are present in trace amounts. The XRF analysis showed a high quantity of silica (40.6 wt.%), and also alumina (12.4 wt.%), magnesium (24.0 wt.% of MgO), and iron (8.4 wt.% of $Fe_2O_3$). These are the characteristic oxides found in vermiculites. The as-received material was then milled in a rotary knife grinder, sieved, and the size fraction between 63 and 150 μm (average particle of 101.7 μm) was subsequently chemically treated. The clay mineral was chemically attacked with solutions of sodium and lithium chlorides of several concentrations, at $90^{O}$C, and long enough for the complete drying of the solution (up to 144 hours). Treatments with 2M HCl solutions at room temperature, for various times, were also applied. The results showed that all samples had their Foster swelling in water increased after the chemical treatment. Additionally, mechanical delamination was also tested in all samples. The highest rates of swelling in water were obtained after mechanical delamination, and followed the order: HCl>LiCl>NaCl. These results suggest further research exploring the acid activation method for the disaggregation of vermiculites in order to produce higher swelling capacities, thus allowing a broader industrial use for the vermiculites.

**Keywords:** Vermiculite, Chemical treatment, Acid activation.

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# AN OVERVIEW OF KAOLIN DEPOSITS AND OCCURRENCES IN AFRICA: GEOLOGY, MINERALOGY, CHEMISTRY AND UTILISATION

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Kaolin exploitation remains a financially sustained profit making mining industry that continues to contribute positively to national economies of the world. Its occurrence in Africa is not properly documented and adequately investigated. This overview deals with a summary of the geology, mineralogy, chemistry and usage of over two hundred kaolin deposits and occurrences in Africa including Algeria, Botswana, Burundi, Cameroon, Egypt, Eritrea, Nigeria, South Africa, Tanzania and Zimbabwe. Utilisation of African kaolin in bricks, ceramics, fibre glass, plastics, pottery, pharmaceutics, paint, rubber, among others is mentioned. Market economics including cheap labour, must be considered by prospective companies interested in investing in kaolin exploitation in the continent. With increasing and new industrial applications and continuous price increase, any promising deposit or occurrence of kaolin in Africa is worth investing in.

**Keywords:** Genesis, Investment opportunities, Kaolinite.

# COMPLEX PHYSICAL PHENOMENA IN A CLAY

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We have for a number of years studied interconnected complex physical phenomena in one model clay, fluorohectorite, using a variety of experimental techniques: Synchrotron X-ray scattering (SAXS/WAXS) [1,2,3], neutron scattering (SANS) [4], magnetic resonance (NMR and MRI) [5,6], and rheometry [7]. Phenomena studied include: (i) Intercalation processes and water structuring in fluorohectorite nano-stacks [1,5], obtaining new information regarding structure and dynamics of intercalated water; (ii) Spontaneous gravitationally induced phase separation and nematic self-organization in systems of fluorohectorite nanoparticles in aqueous suspension [2,8], mapping out the parameter space controlling the phase separation; (iii) New on transitions from biaxial to uniaxial nematics by application of external magnetic fields of anisotropic (diamagnetic) fluorohectorite nanoparticle systems [6]; (iv) Experimental studies of guided self-organization into chainlike structures of polarized fluorohectorite nanoparticles in oil suspension when subjected to external electrical fields [3], and experiments describing the stability and rheology of such structures [7]. Synchrotron experiments were performed at LNLS-Brazil, PLS- Korea, BNL-USA and ESRF-France, magnetic resonance at Universidade Federal de Pernambuco in Recife, Brazil, neutron experiments at IFE-Norway, and home X-ray and rheometry in our home laboratory at NTNU, Trondheim, Norway.

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**Keywords:** fluorohectorite, water-structure, self-organization, clay rheology.

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# MECHANOCHEMICAL PHENOMENONA ASSOCIATED WITH FINE COMMINUTION OF CLAY MINERALS

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To decrease the particle sizes and increase the specific surface areas of clay minerals are two of the most energy-intensive technological processes in the ceramic industry. In spite of the relative small particle sizes of clay minerals in nature, a large amount of energy is required to produce powders with average sizes less than 100 nm. The energy required to obtain clay mineral powders with specific surface areas larger than 35-40 square meters per gram is especially large. These small grain sizes and large specific surface areas are often required to produce frost-proof bricks and freeze resistant ceramic roof tiles with high thermal insulation properties and with nano-porous structures [1]. Energy consumption problems also can be observed during application of ceramic glazes from clay minerals to increase antifreeze properties of the ceramic facing bricks and roof tiles, or just to make them more aesthetic and more competitive [2]. During the fine comminution of clay minerals losses of energy can be observed accompanied by an appreciable change of chemical composition and mineralogical structure, because of the mechanochemical phenomenon, taking place during fine crushing. The mechanochemical investigations and laboratory experiments made by the author have shown a relative slow growth of the specific surface areas of different clay minerals, while the volumes of Muscovite-2M1 – $(K,NH_4,Na)Al_2(SiAl)_4O_{10}(OH)_2$ – decreased and the volumes of Illite-1M (NR) - $K_{0.7}Al_2(SiAl)_4O_{10}(OH)_2$ – and of Quartz – $SiO_2$ – increased considerably depending on crushing time. Increasing the crushing time the Albite – $NaAl_{0.91}Si_3O_8$ - was unstable too, but its volume did not vary as much as Muscovite-2M1 or Quartz and Illite-1M. The mechanochemical processes achived in laboratory were confirmed by industrial experiments [3]. Analytical methods applied in this research were laser granulometry, scanning electron microscopy, X-ray diffraction and energy dispersive spectrometry. Digital image analysis was applied to microscopy results, to enhance the results of transformations.

**Keywords:** Clay minerals, Mechanochemistry, Comminution, Nanoparticles.

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# EVALUATION OF THE MAXIMUM POTENTIAL AMMONIA VOLATILIZATION FROM CLAY AND SOIL SURFACES IN SOME CALCAREOUS SOILS

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The process of ammonia diffusion from the soil surface to the atmosphere is called ammonia volatilization [1]. Ammonia volatilization is often affected by many factors Including the amount of ammoniacal $N$ present, pH, cation exchange capacity, temperature, and soil water content [2]. The objectives of this study were to evaluate the maximum potential ammonia volatilization from clay and soil surfaces of four calcareous topsoils of Iran using a new approach. The soil samples were selected based on mineralogical properties. The clay fraction was separated by sedimentation. The samples were then saturated with magnesium. A new system was designed to estimate $NH_3$ volatilization in the samples. In this system, the air continuously is transported over the samples with boric acid solution. Hence, partial pressure of ammonia decreases and the following equilibrium chemical reaction improves the forward, $NH^+_4 + OH^- \leftrightarrow NH_3\uparrow + H_2O$. During this process, ammonium ion is transformed to ammonia. The increase in the potential ammonia volatilization of the sample causes an increase in the ammonia volatilization. Two distillation pipes were used in this study. The first involved treatment of the clay or soil with a known amount of $NH^+_4$-salt solution and the other one included a known amount of boric acid solution. After turning the air pump on for 24 hours, the maximum ammonia volatilization was determined by titration of distilled steam with 40% NaOH. Results showed that the mean maximum potential $NH_3$ volatilization from the clay and soil surface were 0.02 and 18.5%, respectively. The maximum Potential $NH_3$ volatilization is substantial in the soil samples presumably, as a result of buffering capacity of soils. Whereas, the soil treatments provide $OH^-$ and so, the reaction improves the forward. Another reason, that can be mentioned, is ability of clay to absorb cations. Since ammonium is a cation so it can be absorbed by clay component. Hence, volatilization declines in clay samples in relation to soil samples.

**Keywords:** Volatilization, Ammonia, Boric acid.

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# KAOLIN DEPOSITS OF SABZEVAR (EASTERN IRAN)

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Clay minerals are abundant south of Sabzevar . They are identified by their light color in the field. XRD and XRF studies of the clays indicated that the main minerals are kaolinite , illite and dickite. Pyrophyllite is a minor clay mineral . Quartz and sanidine are present with the clay minerals .The $Al_2O_3$ content is about 40 percent. The deposits are very good for industrial minerals .Basic to acidic volcanic rocks are clay mineral parent materials. . South of Sabzevar town tthe kaolin deposits include volcanic and volcaniclastic rocks. Geochemical and petrographic studies showed that their compositions are generally acidic and intermediate and are dacite, rhyolite and andesite rocks that have changed into clay minerals.

**Keywords:** Kaolinite, Volcanic rocks, Sabzevar, Iran.

# BEHAVIOUR OF CLAY MINERALS IN THE ALBERTA OIL SANDS DURING NON-AQUEOUS BITUMEN EXTRACTION

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Abstract: Although non-aqueous bitumen extraction from the Alberta oil sands has not yet been used commercially, it is important to study due to its potential for high bitumen recovery with no sludge tailings ponds. Lack of information about the behaviour of clays in nonaqueous bitumen extraction was the main inspiration for this work. Two oil sand ores were studied, a high grade, low fines, good processing ore and a low grade, high fines, poor processing ore. The clay mineralogy of the solids separated from the extraction products, the supernatant and the tailings, as well as the raw oil sands ores was studied by x-ray diffraction (XRD). Based on the XRD results, the kaolinite to illite ratio is higher in the supernatant than in the raw ore. Morphology of the solids, mainly aggregates of clays and bitumen, in the extraction process was studied using a low-pressure scanning electron microscope (SEM). SEM observations show some major differences among various samples in terms of the amount of aggregates in the tailings and the settling behaviour of the supernatant. Morphology and clay mineralogy of several samples were studied by transmission electron microscopy (TEM) as well. In order to understand the behaviour of clay minerals in the extraction process, cation exchange capacity (CEC) of the samples was measured and compared to one another.

**Keywords:** Clay minerals characterization, Alberta oil sands, XRD.

# DIELECTIC PROPERTIES OF MICAS DETERMINED BY TERAHERTZ TIME-DOMAIN SPECTROSCOPY

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The optical anisotropic properties of micas as known in the visible spectral region were investigated in the far infrared region using terahertz time-domain spectroscopy (THz-TDS). This technique allows determination of the complex index of refraction – refractive index and absorption index, including sample thickness determination from single sample and background measurement in the frequency region from 0.1 to ~1.2 THz (3.3 to ~40.0 cm$^{-1}$). Main advantage of the THz-TDS is the coherent nature of measured transmitted electric field, providing high sensitivity and resolving phase information (Ferguson and Zhang 2002). This technique easily delivers as well the frequency dependence of material complex dielectric permittivity related to the refractive properties through Maxwell´s relationships.

The samples were characterised by X-ray diffraction, Fourier transform infrared spectroscopy and chemical analyses by Energy dispersive X-ray spectroscopy. Investigated samples differed significantly in chemical composition of structural cations and ratios of interlayer cations. For instance the structural iron content as determined by EDS increased in muscovite, phlogopite and biotite on the levels of 1.3, 2.0 and 8.0 atomic %, respectively. The angular dependence of changes in complex refractive indexes as function of incident polarised beam angle and sample orientation around the c axes were found. The results of frequency dependent complex index of refraction ($\tilde{n}_s = n_s - i\kappa_s$) of used micas were determined.

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**Keywords:** Micas, Dielectric properties, THz-TDS.

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# PRODUCTION OF CLAY BRICK INCORPORATING RED MUD AND CLAY WASTE CONTAINING BORAX

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It is well know that, in spite of technological advances, many waste materials are produced as a result of various production steps. All these wastes are viewed as nuisance and problems on Earth due to the pollution of the environment. In the light of the above, the possibility of using some waste materials as a raw material for clay brick was investigated. Red mud (RM) taken from Seydişehir (Turkey) is a waste material consisting mainly of hematite and sodium hydrosilicate minerals. CWD and CWS wastes consisting mainly clay and borax were obtained from dsm sieve and second step of the plant in Kırka Borax Company (Turkey) respectively. They were dried, crushed and ground. Secondly, both of wastes which consist of borax were separately mixed in proportions (5, 10 and 15 %) with RM. After molding, samples were fired at three different temperatures (700$^o$C, 800$^o$C and 900$^o$C) in a laboratory furnace. Dry shrinkage of green body, bending and compressive strength, firing shrinkage, water absorption, frost resistance and harmful magnesia and lime tests on heat-treated bodies were performed. In addition these tests, samples were examined by a color analysis apparatus. The color, mineralogical and mechanical tests showed that usability of boron wastes as flux materials in the production of RM bricks was possible.

**Keywords:** Clay brick, Red mud, Borax wastes, Color analysis.

# CORRELATION BETWEEN HYDRATION AND IONIC TRANSPORT IN HOMOIONIC MONTMORILLONITE

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Ionic transport of a series of homoionic alkali exchanged montmorillonite (Wyoming) [1] is studied at different dehydration states [2]. More specifically, we investigate, the last stages of dehydration, i.e. when the number of adsorbed water molecules corresponds, at maximum, to a monolayer. Weight losses are measured at several constant temperatures, i.e. treatment temperature (TT), as a function of time by thermo-gravimetric analysis. Application of Van't Hoff's law yields dehydration enthalpy. Comparison with X-ray data and with the dissociation enthalpy of alkali cation/water complexes shows that dehydration of weakly hydrated homoionic alkali montmorillonites results from the competition between opposite energy contributions due to: i) the cation solvation, ii) the hydration of the silicate interlayer surface and iii) the structural swelling. So, depending on the balance between these various energy contributions, different behaviors are observed accordingly to the nature of the alkali cation.

Besides, we investigate dc conductivity of the same series of homoionic montmorillonite treated at various TT. When dehydrated, dc conductivity follows an Arrhenius behavior. In contrast, this behavior is no longer observed as long as water molecules are adsorbed and, hence, in interaction with the alkali cations. In that case, the results are well described by the empirical Vogel–Tamman–Fulcher (VTF) form, i.e. $\sigma_{dc} = \sigma_0 . \exp\left(-\Delta E / k(T - T_0)\right)$, suggesting order/disorder transition in the water/cation sub-network even at low hydration state.

**Keywords:** Water desorption, Dehydration enthalpy, Cation solvatation.

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# EFFECT OF VARIABLES ON ACID DISSOLUTION OF CLAY MINERALS

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Acid activated bentonites, well known as bleaching earths, have been widely used for a broad range of decolourising applications, as solid acid catalysts and catalyst supports. Other clays are less frequently treated with acids; however, several studies have been published. The acid treatment of a bentonite removes readily soluble phases such as carbonates or iron oxides. It also affects the main mineral, smectite, via the exchange of the interlayer cations for hydrated protons and the removal of octahedral cations and any isomorphously substituted tetrahedral cations from the clay matrix. The extent of smectite dissolution affects the properties of the product obtained.

Many laboratory assays of acid treatments under various conditions provided valuable information on the reactivity of different minerals with acids and on the kinetics and mechanisms of these reactions. Very important is that direct comparison of the results obtained in different laboratories is difficult because various variables of the experiments, e.g. acid concentration, temperature and time of the treatment, clay/acid ratio, intensity of stirring of the reaction mixture, etc., which affect substantially the reaction process and the results obtained, are rarely sufficiently characterized. The extent of clay mineral dissolution is affected by several variables, which can be divided into four groups: 1) Reaction conditions: temperature, time, type and concentration of the acid used, clay/acid ratio, and stirring of the reaction mixture; 2) Type of clay and its dominant mineral; 3) Substitutions in the structure; 4) Particle size and swelling of the interlayers.

The variables of the first group may be well defined, the only exception being stirring. The reaction rate may depend substantially on the intensity of stirring. This is why any comparison of the results on acid dissolution of smectites obtained in different laboratories is difficult, if possible at all.

Effect of chemical composition of layers can be well illustrated on smectites; trioctahedral minerals dissolve in acids much faster than their dioctahedral counterparts. Comparable reaction rates were reported for a hectorite in 0.25 M HCl at 20 °C and for an Al-rich montmorillonite in 6 M HCl at 95 °C. Octahedral Fe(III) and/or Mg(II) substitution for Al(III) in the octahedral sheets increases substantially mineral dissolution rate. The effect of Mg(II) is more pronounced than Fe(III). Protons attack the clay structure not only from the particle edges, but also from the interlayers. Mixed-layer clay minerals, typically illite/smectites, occur frequently in bentonites. Higher content of non-swelling layers decreases the dissolution rate of these minerals in HCl. Most recent results show that the effect of chemical composition of the layers predominates that of swelling interlayers.

**Keywords:** Smectite, Swelling, Octahedral substitution.

# RELATIONSHIP BETWEEN UNDRAINED SHEAR STRENGTH AND SHEAR WAVE VELOCITY IN CLAY WITH CONSOLIDATION STATE: IN-SITU UNDRAINED SHEAR STRENGTH ESTIMATION TECHNIQUE FOR CLAY USING SHEAR WAVES

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The undrained shear strength is a critical parameter in the evaluation of ground resistance and stability in soft clay. This study attempts to estimate the in-situ undrained shear strength using the measured undrained shear strength($S_u$)-void ratio($e$)-shear wave velocity($V_s$) relationship under fully saturated conditions. Empirical models are presented to infer the undrained shear strength from the shear wave velocity with different (over and normally) consolidation states. According to the empirical model, the undrained shear strength and shear wave velocity relationship shows bi-linearity at the pre-consolidation stress state point. To verify the developed empirical model, the shear wave velocities of clay are measured under different void ratios by means of piezoelectric bender element sensors inserted in consolidation cells. In addition, laboratory vane shear tests are performed with different void ratios.

To confirm the relationship between the undrained shear strength and shear wave velocity, the in-situ undrained shear strength profile can be estimated from the developed empirical model using the in-situ shear wave velocity profile. Using a probability analysis, the inferred undrained shear strength profile is compared with the measured in-situ undrained shear strength profile.

**Keywords:** Undrained shear strength, Shear wave velocity, Consolidation state.

# EFFECT OF CHEMICAL KINETICS ON PERMEABILITY OF A POROUS ROCK: SCALING BY CONCENTRATION OF ACTIVE MATERIAL IN FLUID

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Pores and fractures in rocks are continuously being reshaped through different chemical and physical processes. Fluids filling the pore space and carrying different chemical species are responsible for these changes. In the present work we study the effect of chemical kinetics on the reshaping of pore structure and thereby on permeability. A simulation study is carried on a 2-dimensional random porous structure. The particles permeate with a constant peclet number and their diffusion is represented through a random walk. Changing the probability of interaction varies the strength of the chemical reaction between the fluid and the rock. This study is done for different concentrations of the active material in the fluid. A scaling law is found to exist between the changes in permeability with reaction rate. The scaling exponent is found to be nearly 2.

**Keywords**: Permeability, Chemical kinetics, Scaling.

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# HYDRATION SEQUENCE OF SWELLING CLAYS

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Swelling clays present a multi-scale structure and therefore a multi-scale porosity: macroporosity between aggregates– inter-particle mesoporosity – microporosity in the interlayer spacing, as shown by mercury intrusion porosimetry, nitrogen adsorption and XRD experiments. In this work, we propose to couple DRX results and thermoporometry results, to look at the evolution of porosity in mesoscopic pores and interlayer spacings. Thermoporometry is based on the phase transition of a fluid confined in a porous media. This method is used to calculate the pore size distribution (2 nm < pore radius < 50 nm) from transition temperatures. Usually this technique is performed with completely saturated samples. The originality of our work consists in the study of unsaturated samples, equilibrated at different relative humidities. The aim is to track the penetration of water inside each scale of porosity as a function of the relative humidity (RH). Thermoporometry experiments bring an important information: the mesopores (with a mean radius from 2 nm) start to swell at 54% RH for homoionic Li- and Na-montmorillonites The interlayer spacing is only filled with one or two layers of water at RH < 60%, and swelling starts only at RH > 80%. It has been checked that the total saturation of mesopores is reached using nitrogen adsorption isotherms (BJH treatment) and by thermoporometry calculations in solidification and fusion modes. At this stage, we can propose the following hydration sequence for Li- and Na- saturated montmorillonites: hydration of mesopores surfaces, hydration of interlayer spacing with one layer of water, complete saturation of some mesopores, hydration of interlayer spacing with a second layer of water and swelling in mesopores. At higher RH osmotic swelling in interlayer spacing can occur. For others cations (K, Na/Ca, Ca) placed in the interlayer spacing, we observe the same behaviour for the mesoscopic porosity, but for higher RH.

**Keywords:** Hydration sequence, Thermoporometry, Osmotic swelling.

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# STORAGE AND SUPERMOBILITY OF $H_2$ AND $CH_4$ IN PROMISING NEW FLEXIBLE METAL-ORGANIC FRAMEWORK MATERIALS

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Developing new porous materials that can adsorb and store $H_2$ or $CH_4$ is of great current economic interest. The flexible MIL-53(Al, Cr, …) MOF solids, synthesized by the group of Férey in Versailles are probably some of the most exciting MOFs because of the combination of a low framework density and very high capacity of adsorption. Furthermore, the presence of both inorganic and organic moieties exhibits the possible interaction with polar and apolar. Moreover the MIL-53(Cr) presents a fascinating breathing character upon adsorption of some gases, strongly higher than in the similar solids and comparable with clays. Combining experimental (Quasi-Elastic Neutron Scattering (QENS) and gravimmetry) measurements with molecular simulations bring information on the microscopic mechanism of adsorption and diffusion for various gases in these MOF materials leading to a deeper understanding of the breathing mechanism. Here the adsorption and diffusion of $H_2$, $CH_4$ in both flexible MIL-53(Cr) and rigid MIL-47(V) systems has been successfully characterized by both experiments and calculations. In MIL-53(Cr), the observation for the first time of a 1D "supermobility" of these adsorbates along the tunnel of the MIL materials[1,2]. The understanding of this phenomenon has been elucidated using Molecular Simulations. In the same way, the adsorbed amounts have been simulated by Grand Canonical Monte Carlo Simulations and compared with experimental data to determine the interaction sites for each gases and investigate the influence of the different part of the structure.

**Keywords**: Metal-Organic Framework; Adsorption and Diffusion; Molecular Simulations.

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# MINERALOGICAL AND MICROMORPHOLOGICAL PROPERTIES OF ARGILLIC HORIZON IN ARIDISOLS FROM IRAN

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Illuviation of clay is considered to be an important pedogenetic process in soil formation. Clay accumulation in soils is an established fact for argillic horizon genesis (Pal et al. 2003). To investigate genesis of argillic horizons in aridisols of Iran, 8 pedons were described according to soil survey manual (1993). Mineralogical, micromorphological and physico-chemical properties were studied on samples in the laboratory (Sparks, et al, 1996). Thin sections showed that the illuviated form of clay includes: infillings on channel, coating on pendant, on nodules and on grains at lower depths, and juxtaposed calcite needles on void argillan in upper parts of the profiles.

Mineralogical results showed fine clay in argillic horizon, too. In fact, smectite clay was dominant in lower part of pedon confirming movement of clay in soils. The general distribution of clay minerals was: illite >>>chlorite >> kaolinite. Also, comparison between the texture of soils shows that there is an abrupt textural change from clay loam to sandy.

Considering depth and forms of these pedofeatures, we concluded that, the observed argillic horizon at lower depth must be the result of the more humid climate of the past, where the carbonates have been removed completely as pendant, nodules or coating to considerable depth, following processes, clay has been dispersed and also translocated to these depths.

**Keywords:** Argillic Horizon, Mineralogical properties, Micromorphology.

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# NMR SPECTROSCOPY STUDIES OF WATER INTERCALATION IN NA-FLUOROHECTORITE

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Proton and deuterium NMR measurements heve been performed in Na-fluorhectorite powdered samples [1]. The results are related to X-ray scattering results from the same type of samples [2,3,4], and have been compared with data from NMR data from other 2:1 clays, as well as with recent results of molecular simulations.

The results yield new information about the factors governing the geometry and dynamics of intercalated water in these materials. In the one-water layer regime, two different sites were identified, permitting us to elucidate the structure of interlamellar water. The role of proton exchange appears to be more pronounced in Na-fluorohectorite than in Na-vermiculite and is not limited to the 2WL regime. It appears to be promoted by a considerable amount of interlamellar water outside the hydration sphere of the cation.

**Keywords:** NMR spectroscopy, Synchrotron X-ray scattering, Na-fluorohectorite, Water intercalation dynamics.

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# KINETICS OF COMPETITIVE FIXATION OF POTASSIUM AND AMMONIUM IONS BY SOME SOILS AND THEIR CLAY AND SILT COMPONENTS

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Even though there have been a number of studies on the kinetics of fixation of potassium and ammonium ions in soils and clays, however, investigations on the kinetics of competitive fixation of these ions have been few, if any. In this study, kinetics of fixation of potassium and ammonium were examined in four different soils and in their clay and silt components. At first, the clay and silt fractions of the soils were separated through sedimentation and then homoionized with $Mg^{2+}$ions. The mineralogy of the fractions was also identified by X-ray diffraction. The kinetic studies were performed separately as well as in the presence of both ions for time periods varying from 10 min to 360 hrs. At the given time periods, soluble and exchangeable potassium and or ammonium were extracted using 0.5M $MgCl_2$. The results indicated that the rate of fixations of these ions were high at first, but quickly diminished with the time of incubation. Furthermore, fixation of potassium over ammonium was strongly preferred in the silt and clay samples. The quantity of potassium fixed was from 2.0 to 8.8 times more than ammonium. This study also showed that the silt fraction of the soils fixed a considerable amount of $K^+$ and some $NH_4^+$, due to the presence of mica or illite and some vermiculite in the samples. In order to describe the fixation kinetics mathematically, seven models were examined. A comparison of these models based on both the coefficient of determination and the standard error of the estimate showed that zero order, first order, second order, parabolic diffusion, power function and simplified Elovich equations did not satisfactorily describe the kinetics of fixation of $K^+$ and $NH_4^+$, while pseudo-second order equation described the fixation of by the silt samples in a satisfactory manner.

**Keywords:** Kinetics, Ammonium and Potassium, Pseudo-second order.

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# GEOLOGICAL AND ENGINEERING CHARACTERSITICS OF SAM-TEKIN CLAYS (BOZOVA-SANLIURFA-TURKEY)

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A borrow pit for Sam-Tekin clays is located close to the Atatürk Dam, between villages of Sam and Tekin belonging to Bozova district of Şanlıurfa city. Pliocene aged clays were chemically changed by the temperature effect of Karacadağ volcanism, the most active volcanic activity of the region. The clays had been used as raw material for cement by Şanlıurfa Cement Factory and also employed in the impervious clay core of Atatürk main dam body. Laboratory and in-situ tests were carried out in order to investigate its suitability for these purposes.

In addition to mineralogic analysis on the samples taken from quarry, the suitability of the material was investigated in terms of engineering characteristics and the potential interaction of cement mixtures with any other materials. Other characteristics of clay such as specific gravity, weigtht per unit volume, swelling ratio, natural water content were determined on the core samples taken from the same quarry at the site laboratory of Atatürk Dam. Grain size distribution, Atterberg limits (liquid and plastic limits) and classification according to Unified Soil Classification System (USCS) were also measured. Maximum dry weight per unit volume and optimum water content were determined. The impervious core material was transported to filling area of the main dam body and spread as approximately 30 cm layers at optimum water content and compacted by rollers.

For the impervious core, clay compaction procedure was completed to achieve at least 95 per cent of maximum dry unit weight determined in the laboratory at optimum water content $\pm$ 2%.

The Sam-Tekin clay was classified as appropriate material in some ways for both proposed applications even though it lacked ideal characteristics in terms of both mineral content and grain size distribution.

**Keywords:** Sam-Tekin clays, Laboratory tests.

# NANOINDENTATION TESTING OF LAYER SILICATES

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Layered hydrous aluminosilicates including all types of clay minerals and micas occur abundantly in the geosphere. Determining their elastic modulus (*E*) and hardness is of importance for predicting the behavior of clay-rich geomaterials in various scientific and technological applications. The elastic constants (e.g., Young's modulus, shear modulus, and bulk modulus) are among the basic physical or mechanical properties controlling a material's response to force within the elastic regime. On the other hand, hardness (*H*), the resistance of a material to permanent penetration by another harder material, is closely related to plastic yield stress and provides information on compressive or tensile strengths.

Nanoindentation, also named depth-sensing indentation or instrumented indentation, is based on conventional theories of contact mechanics. The test results provide information on elastic modulus, hardness, strain-hardening, cracking, phase transformations, creep, and energy absorption. It is widely used in the characterization of mechanical properties of thin films, coatings, and other nanomaterials. To date, this non-destructive testing technique has been used in limited cases restricted to aggregates of layer silicates in clayey materials such as shales.

This presentation describes the nanoindentation testing procedure and presents initial results for muscovite and rectorite (Zhang et al., 2008). *E* and *H* in the direction normal to the basal plane of muscovite and rectorite are 79.3±6.9 GPa and 5.14±0.82 GPa, for muscovite and 18.3±4.6 GPa and 0.73±0.17 GPa for rectorite, respectively. Observed differences are a consequence of differences in the crystal structure of the minerals.

**Keywords:** Nanoindentation, Elastic modulus, Hardness.

Zhang, G., Wei, Z., and Ferrell, R. E. (2008) Elastic modulus and hardness of muscovite and rectorite determined by nanoindentation. Applied Clay Science, doi:10.1016/j.clay.2008.08.010.

# SHAKEDOWN ANALYSIS OF OFFSHORE PLATFORM SAFETY UNDER VARIED COMBINED LOADING CONDITIONS

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In the field of offshore engineering, environmental conditions result in the footings of platform being subjected to complex vertical loading , moment loading and horizontal loading generally, and the amplitude of loading components is varying with time which is called varied combined loading. In order to evaluate the safety of foundation under varied combined loading, a statically admissible residual stress field of shakedown analysis is presented, based on Melan lower bound theorem. The paper presents many kinds of varied loading combinations, and compares the different shakedown loading. The shakedown loading is less than the ultimate bearing capacity. Furthermore, the shakedown under bi-directional varied loading is lower than the unidirectional varied loading. By analyzing the failure mechanics of foundation under varied combined loading, the failure modes of varied combined loading are achieved, and the failure mode under combined loading and the failure mode under varied combined loading are compared in detail.

In order to verify the accuracy and rationality of the method presented in this paper, the general-purpose FEM analysis package ABAQUS was employed. A residual stress field is achieved by using elastic-plastic finite element analysis. Based on the residual stress field, the shakedown loading due to varied combined loading is obtained. The numerical results of ABAQUS are consistent with the results of the method presented in this paper.

Finally, some conclusions can be drawn that the lower bound shakedown method presented in this paper is valid and accurate, and the shakedown loading is less than the ultimate bearing capacity under general circumstances. In order to study the safety of offshore platform under varied combined loading, the shakedown should be taken into account.

**Keywords:** Varied combined loading, Offshore platform, Shakedown analysis, Melan theorem.

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