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MECC'08

ABSTRACTS

MECC'08

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MECC'08

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1. *Crystal chemistry, structure and synthesis of clay minerals* – Sabine Petit, Tamas Weiszburg

2. *Fe-rich phyllosilicates and Fe oxy-hydroxides in terrestrial, marine and extraterrestrial environments* – Javier Cuadros, Andrzej Wiewióra

3. *Kaolinite group minerals: properties, modifications and new applications* – Ivan Kraus, Leszek Stoch

4. *Sorptive, chemical and physical properties of clays and their derivatives* – Jerzy Fijał, Marian Janek

5. *Layered double hydroxides and nanohybrid materials* – František Kovanda, Miroslav Pospišil

6. *Clay minerals as a tools in geological processes interpretation* – Béla Raucsik, Darko Tibliaš

7. *Clay minerals in soil environment* – Jacek Długosz, Jerzy Weber, Zbigniew Zagórski

8. *Clays in oil and gas industry* – Douglas McCarthy, Jan Środoń

9. *Drilling industry - clays - environmental problems* – Lyudmyla Wilson, Andrzej Gonet

10. *Industrial applications of clays* – Marek Tokarz, Piotr Wyszomirski

11. *Environmental interactions, clay barriers and waste management, geotechnics* – Ivan Janotka, Frantz Ottner, Edeltrauda Helios-Rybicka

12. *Geology of clays and related deposits* – Béla Raucsik, Darko Tibliaš

13. *Man and clays: health, history, environment* – Derek Bain

14. *Clay minerals as nanomaterials in current and prospect applications* – Peter Komadel, Jana Madejova, Krzysztof Bahranowski, Ewa M. Serwicka

Plenary lectures:

Derek BAIN, Victor DRITS, Goran DURN, Claude FORANO, Marian JANEK, Tamas WEISZBURG

Papers in this issue were reviewed

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CONTENTS

KEY-NOTE LECTURES

CONTRIBUTIONS

Key-not lectures

MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
www.Mineralogia.pl

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How to succeed in publishing research in refereed journals

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Intended mainly for young researchers publishing their research for the first time, this paper will describe the various stages in the process used from submission of manuscripts to publication in refereed journals. The author will draw on experience from being editor of clay journals to provide guidance on how to prepare manuscripts for submission to refereed journals, particularly those publishing clay research, so that they will have the best opportunity of being accepted for publication. This will include details of how manuscripts should be formatted, organised and prepared for submission. Comments, hints, recommendations and guidelines will be provided to enable research to be presented in a succinct, unambiguous, to-the-point manner, unencumbered by flowery prose, complicated jargon, convoluted reasoning or wild speculation.

The process followed by editors on receipt of manuscripts will be described along with how referees are chosen and how the reviews process operates. Advice will be given on what is needed to satisfy referees and editors. Possible pitfalls will be pointed out and indications on how referees reports should be handled and appropriate revision carried out.

A paper published by Mumpton in 1990 is still very appropriate and should be consulted by authors before preparing a manuscript.

Reference:
MUMPTON F.A., 1990: The universal recipe or how to get your manuscript accepted by persnickety editors. Clays and Clay Minerals 38, 631-636.

MINERALOGIA - **SPECIAL PAPERS**, 33, 2008
www.Mineralogia.pl

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Trans-vacant and cis-vacant 2:1 layer silicates: Structural features, occurrence and identification

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For a long time it was commonly accepted that dioctahedral 2:1 phylosilicates have a *trans*-vacant (tv) structure. This view was based on single crystal structural refinements of muscovite, phengite, paragonite, and margarite and persisted in both the generally accepted structural classification of dioctahedral clay minerals and their identification by diffraction and other methods. Numerous structural investigations show, however, that illites, smectites and 2:1 layers in interstratified structures are characterized by a wide occurrence of *cis*-vacant (cv) layers in these mineral varieties.

Crystal chemical analysis of various dioctahedral 2:1 layer silicates consisting of tv and cv layers indicates that there is compositional control in the distribution of octahedral cations over *trans*- and *cis*-sites. In dioctahedral smectites the formation of tv and cv layers is related to the layer composition and local order-disorder in the distribution of isomorphous cations. Dioctahedral 1*M* micas with abundant Fe^{3+} and Mg occur only as tv varieties. In contrast, compositional restrictions control the occurrence of 1*M*-cv illite, as well as cv layers in illite fundamental particles of I-S which can form only as Fe- and Mg-poor varieties.

High octahedral and tetrahedral Al causes a small difference between individual K-O bond lengths and minimizes repulsion of basal oxygen atoms across the interlayer and is the main factor responsible for the stability of cv illites where the interlayer environment is similar to that in $2M_1$ muscovite. However, the asymmetry of the cv octahedral structure decreases the stability of 1*M*-cv minerals. In contrast, the symmetrical structure of the tv layers in 1*M*-tv illite is favorable despite the less stable arrangement of the interlayer configuration. Because of structural control, the occurrence of 1*M*-cv illite, its association with 1*M*-tv illite and interstratified cv-tv layers in illite fundamental particles is confined by certain physical and chemical conditions.

Identification of tv and cv mica varieties is based on (1) powder XRD patterns calculated for different polytypes consisting of either tv or cv layers, (2) on simulation of experimental XRD patterns corresponding to illite or illite fundamental particles in which tv and cv layers are interstratified, and (3) on the semi-quantitative assessment of the relative content of the layer types in the interstratified structures by generalized Mering's rules.

A simple and effective method for identification of *tv* and *cv* layers in dioctahedral 2:1 layer silicates employs DTA in combination with evolved-water analysis. For *tv* layers dehydroxylation occurs at temperatures at or below 600 °C, whether these layers are in illite or smectite. In *cv* structures dehydroxylation is accompanied by a complex structural re-arrangement and occurs at temperatures higher than 600 °C. Problems related to interpretation of structural features and identification of *tv*- and *cv* 2:1 layer silicates will be discussed in detail.

MINERALOGIA - ***SPECIAL PAPERS****, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Origin of terra rossa soils in the Mediterranean region

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Terra rossa is a reddish clayey to silty/clayey soil that is especially widespread in the Mediterranean region, where it overlies limestones and dolomites. In some classification systems based on the Mediterranean climate as the major soil differentiating criterion, the term terra rossa is used as a name for the soil subclass “Modal Fersiallitic Red soil” when situated on limestones (Duchaufour, 1982). However, several national soil classifications (e.g. Croatian, Italian, Israeli) retained the term “terra rossa” for the hard limestone derived red soils. The nature and relationship of terra rossa to underlying carbonates is a longstanding problem that has resulted in contrasting opinions with respect to their parent materials and origins. In some isolated karst terrains, terra rossa may have formed exclusively from the insoluble residue of limestone and dolomite, but it most commonly comprises a variety of external materials, including aeolian dust, volcanic debris and clastic sedimentary particles that were carried to the carbonate terrain by various transport mechanisms. Some recent investigations in Indiana, USA (Merino and Banerjee, 2008) show that terra rossa forms by replacement of limestone by authigenic clay at a moving metasomatic front.

Terra rossa covers limestone and dolomite in the form of a discontinuous layer ranging in thickness from a few centimetres to several metres. It is also found along cracks and between bedding surfaces of limestones and dolomites. Thick accumulations of terra rossa like material are situated in karst depressions in the form of pedo-sedimentary complexes. Different authors have considered terra rossa to be soil, vetusol, relict soil (non-buried-paleosol), paleosol or pedo-sedimentary complex (soil-sediments). However, most authors today believe that terra rossa is a polygenetic relict soil formed during the Tertiary and/or hot and humid periods of the Quaternary. Investigation in the Atlantic coastal region of Morocco (Bronger & Sedov, 2002) shows that at least some terra rossa previously referred to as polygenetic relict soils should be regarded as Vetusols (soils that are marked by a continuity of pedogenic processes) according to the concept of Cremaschi (1987).

A bright red colour is a diagnostic feature of terra rossa and is a result of the preferential formation of haematite over goethite, i.e. rubification. Boero & Schwertmann (1989) concluded that it is of little relevance for the process of rubification whether the primary Fe sources are autochthonous or allochthonous as long as the general pedoenvironment remains essentially suitable for the formation of terra rossa. This pedoenvironment is characterised by an association of Mediterranean climate, high internal drainage due to the karstic nature of a hard limestone and neutral pH conditions. Terra rossa is formed as a result of: (1) decalcification, (2) rubification and (3) bisiallitization and/or monosiallitization. Since Fe_d/clay ratios are relatively uniform in most terra rossa, translocation of clay particles is responsible for the distribution of the red colour throughout the whole profile. However, since terra rossa soils have been exposed to various climatic fluctuations they can be affected by eluviation, yellowing and secondary hydromorphy. Erosional and depositional processes operating on the karst terrains, induced by climatic changes, tectonics and/or deforestation might be responsible for both the patchy distribution of terra rossa and the thick colluvial or alluvial terra rossa accumulations in uvala and dolina type of karst depressions.

The main objective of this lecture is to give an overview of terra rossa soils in the Mediterranean region based on different aspects (bulk and clay mineralogy, heavy and light mineral fractions, grain size distribution, iron-oxide phases and distribution of Fe_t, Fe_d and Fe_o, geochemical fingerprinting). Examples from Istria will be used to demonstrate these aspects (Durn, 2003; Durn et al., 1999, 2001, 2007).

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Trends in hybrid layered double hydroxides intercalation chemistry

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Due to their high versatility of chemical composition, high anion exchange capacities and opened framework for intercalation of a large variety of anions, Layered Double Hydroxides are a unique class of materials under great investigations for a wide range of applications such as catalysis, environmental remediation, molecule delivery, polymer reinforcement or modification.

Intercalation of organic entities in LDH has been envisaged either for surface modification opening the field of colloidal chemistry of LDH or for functionalization in order to develop new physical properties or chemical reactivities. Indeed, exfoliation of LDH has been obtained through anion exchange of carboxylate anions or intercalation of polar solvent molecules such as formamide leading to new intercalation capability and access to thin film elaboration. Interestingly LDH are good candidate matrices for the immobilization of reactive organic molecules (redox species, organometallic complexes, enzymes) or organics with specific optical or magnetic properties, for the vectorization of drugs or phytoactive molecules, for the removal of toxics from waste waters. Hybrid organic-inorganic LDH are also good fillers for modified polymers. The presentation will focus on the new trends in the development of hybrid LDH in terms of preparations and properties. Structure and bonding of hybrid LDH will be discussed on the basis of both specificities of the inorganic layers and organic entities.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Application of terahertz time-domain spectroscopy for investigation of layered hydrosilicates

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The terahertz time-domain spectroscopy (THz-TDS) was used to determine the dielectric properties for selected layered clay minerals such as micas in a far-infrared region of 3.3 to about 40.0 cm^{-1} corresponding to 0.1 and 1.2 THz, respectively. Investigated samples were selected from different localities in such manner that differed significantly in chemical composition of structural cations and also ratios of interlayer cations. For instance the major type of the interlayer cation present e.g. magnesium in a hydrated state in vermiculite was compared with different dehydrated cationic species, mainly potassium present in phlogopite, biothite or muscovite. The main advance of the THz-TDS is coherent measurement of transmitted electric field providing high sensitivity and resolving phase information (Ferguson, Zhang, 2002). It 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 above mentioned frequency region. The data were accounted by a model concerning absorption in a disordered ionic crystals (Schlömann 1964; Strom, Taylor, 1977)

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Iron dominated dioctahedral TOT clay minerals: from nomenclature to formation processes

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Though some of the iron dominated clay minerals (*e.g.* celadonite, glauconite) were among the first clay minerals discovered in the 18-19th centuries, our understanding of them is still limited. GUGGENHEIM *et al.* (2006) summarizes the recommended nomenclature also for these minerals, however, application of these recommendations in the given subgroup is not easy in the daily practice. The difficulties, additional to the normal limits of the non-iron based clay mineral determination, are related to the changing valence state of iron and the changing octahedral occupancy. These factors strongly limit the practical value of the IMA nomenclature approach, adopted fully by GUGGENHEIM *et al.* (2006) for the related micas and interlayer deficient micas.

Another difference of these Fe-based phases, as compared to *e.g.* Al-dominated TOT layer silicates, is the dominance of K in the interlayer also in the smectite range, so that, from the chemical point of view, there is a continuous transition between smectites and interlayer deficient micas. That structural and chemical continuity may be the background of the (non p,T-driven) chemical evolution well known in the subgroup (glauconitisation).

Based on, mostly Central European, examples we point out the typical pitfalls one should expect when working with these phases and we recommend a unified crystal chemical and graphical approach, slightly different from that of GUGGENHEIM *et al.* (2006), applicable also for the iron-based clay minerals.

References:

GUGGENHEIM S., ADAMS J.M., BAIN D.C., BERGAYA F., BRIGATTI M.F., DRITS V.A., FORMOSO M.L.L., GALÁN E., KOGURE, T., STANJEK H. 2006: Summary of recommendations of nomenclature committees relevant to clay mineralogy: Report of the AIPEA Nomenclature Committee for 2006. Clays and Clay Minerals 54(6), 761-772.

CONTRIBUTIONS

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

The response of two bentonites to an acid and/or thermal attack

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The stability/degradation of properties has been studied on two Slovak bentonites (concerning barriers in a deep underground repository of high level radioactive waste). J250 is originally an in-situ formed bentonite (Ca-smectite >80%) from the Jelsovy Potok deposit in the Neogene volcanic Kremnicke vrchy Mts.; L250 is a re-deposited bentonite (Ca-Mg-smectite >60%) from the near Zvolenska kotlina Basin (Lieskovec). Both bentonites were industrially dried and milled to ≤ 0,250 mm. One part of J250 has been mixed with H_2SO_4 acid (1 M, 2 M and 4,5 M) and then washed using distilled water and centrifugation until the supernatants were free of acid. Both, original samples and chemically treated ones have been exposed to 120°C temperature during 30 days. Finally, high-density cylinders (h = 20 mm, d = 50 mm) have been pressed from all samples.

Compacted samples (dry density 1,6 to 1,8 $g.cm^{-3}$) were necessary for the swelling pressure tests. It has been measured indirectly in oedometers with attached water column (i = 25) as the pressure necessary for the step-wise suppression of the occurring vertical increase of the sample.

All other tests used powder material. Besides XRD, FTIR and TGA analyses, also BET tests of "outer" specific surface, tests of the total specific surface (water absorption from atmospheres with controlled relative humidity), as well as water absorption tests according to Enslin-Neff have been carried out. Also MLC, CEC and exchangeable ions have been tested.

As expected, J250 showed higher swelling pressures than L250 at equal dry densities, but good compaction improves the behaviour of L250 considerably. Swelling pressure increases also after treatment with acid in following order, in spite of high temperature: $J250 < J250_{4,5M\ 120C} < J250_{2M\ 120C}$. No change in the mineral composition has been found after attack. But water absorption tests showed better hydration of the smectite after 2 M acid treatment, which explains the higher swelling pressure. At 4,5 M concentration, degradation of the octahedral sheets of smectite started, which yielded certain drop in the swelling pressure and could be recognised also in other properties. Further results will be shown at the conference. Partly financed from the Slovak Ministry of Education, project VEGA 1/4045/07.

MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Phase composition and microstructure of brick-clay soil and fired clay-bricks from some areas in Peshawar, Pakistan

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Bricks are the most frequently used product in the local construction industry. However, there has been very little or no relevant information about the manufacturing standards and quality of locally-made bricks as compared to the situation in developed countries.

XRD revealed that the raw soils used by the local brick-industry are comprised predominantly of quartz, albite and chlorite along-with illite, melilite, calcite and orthoclase. In the processed brick-samples, mullite and cristobalite were not observed indicating the use of a low-firing temperature (~1000^{o}C) and absence of kaolinite in raw materials. Consequently, the local-brick specimens were expected to be more porous and mechanically weak as compared to those from advanced countries. Naked eye examination revealed that the sample bricks have had non-uniform colour and that pebbles are present – being a further indication of processing of initial raw ingredients. Cracks found in the fired brick samples were seen as further indication of improper heat-treatment and processing. The transformation of calcite into CaO takes place at around 900°C. CaO readily reacts with moisture to form $Ca(OH)_2$. This results in a volume increase (“lime blowing”) leading to further increase of brick porosity. $Ca(OH)_2$ eventually becomes $CaCO_3$ in the presence of atmospheric CO_2. These reactions result in an increase of volume and cause the formation of fissures, which cause further increases of porosity.

Within the limitations of this study, the following conclusions may be made:

1. Quartz, calcite, and albite in raw materials while quartz, albite and chlorite were found to be the major constituent phases found almost in all fired brick samples.
2. The absence of mullite or cristobalite in the fired samples might be due to the commonly used low firing temperature (~1000^{o}C) and absence of kaolinite in the raw materials.
3. The local brick was also found to be more porous, and thus it could be mechanically weak as compared to that from advanced countries because of improper and non scientific method of their processing and heat treatment.
4. The cracking observed in some of the bricks might be due to abrupt change in temperature and inappropriate processing.
5. The transformation of calcite into CaO in the presence of atmospheric carbon dioxide, might cause the formation of fissures, which results in further increases of porosity.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Syhtnesis and characterization of dipentaerythritol-intercalated layered double hydroxide

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Layered double hydroxide (LDH) is well-known as hydrotalcite-like compound, anionic clay, host-guest material. In recent, LDH has received considerable attentions due to their potential technological applications such as antacid, anion-exchangers, stabilizers and reinforced fillers for synthetic or natural organic polymers. On the other hand, polyhydric alcohol is a versatile building block for a preparation of many polymer compounds, and dipentaerythritol (Dpe) is a component of polyvinyl chloride (PVC) stabilizers and olefin antioxidants. In our previous studies, we have succeeded the intercalation of non-ionized guests such as sugars, cyclodextrins and polyhydric alcohols into LDH interlayer by the calcination-rehydration reaction (Hirahara et al., 2004).

In this study, we investigated the intercalation of Dpe into Mg-Al LDH interlayer both by the calcination-rehydration reaction and thermal reaction using molten guest substance (Carlino and Hudson, 1994).

In the intercalation test of Dpe into LDH interlayer by the calcination-rehydration reaction, Dpe was found to be hardly intercalated not like polyhydric alcohols because Dpe formed a strong intramolecular hydrogen bonding. However, in the thermal reaction at 200~235°C, the solid product has the well-ordered layered structure. The expansion of d-value was generally observed due to the intercalation of guest molecules into LDH interlayer space. The d-value of the resulted LDH containing Dpe decreased to 0.68 nm from 0.78 nm of the pristine carbonated LDH, suggesting that the reduction of interlayer distance was caused by decarboxylation and dehydration of the carbonated LDH and the formation of a strong hydrogen bond between hydroxyl group of the intercalated Dpe and the LDH basal layer. The results of FT-IR, TG-DTA and chemical analysis also exhibited that Dpe was well stabilized in the LDH interlayer space.

We will also propose the application results of the Dpe/LDH as novel stabilizer and filler for PVC.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

A blend of Al-rich and Fe-rich sodium bentonites – a potential filler for geosynthetic clay liners?

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Enhancement of geotechnical parameters of Fe-rich bentonite of lower smectite content (L = Lieskovec, Slovakia, 29-56% montmorillonite) by addition of an Al-rich bentonite of higher smectite content (JP = Jelšový potok, Slovakia, 64% montmorillonite) is discussed. L:JP mass ratios of 65:35, 75:25, 85:15 were tested. Addition of more expensive Ca^{2+}-JP to Ca^{2+}-L bentonite caused increase in some geotechnical properties, such as liquid limit (w_L) by 20% and water adsorption measured by Enslin test (E_S) by 50% compared to raw Ca^{2+}-L samples; however, the parameters were still insufficient for applications of Ca^{2+}-blends for sealing purposes.

After natrification of the blends with soda ash the geotechnical parameters markedly improved. The primary factor affecting the geotechnical properties of the blends in this series was the smectite content in L bentonite along with the L:JP ratio. Higher smectite and higher JP contents caused increased liquid limit and water adsorption by Enslin test values and decreased permeability coefficients. The highest w_L and E_S values for the Na-L11/JP blend resulted from the highest smectite content in L11 (56%), while low values for Na-L5/JP blend were the consequence of the lowest smectite content in L5 (29%). The natrification process of Ca^{2+}-L samples to their Na^+-counterparts resulted in increased liquid limit values by 95% in comparison with the Ca^{2+}-forms and water adsorption by Enslin test by 65%.

Permeability coefficients of the order of 10^{-11} m.s^{-11} for all the blends were sufficiently low. The liquid limit and water absorption values of the blend containing 65 mass % of Na^+-L and 35 mass % of Na^+-JP bentonites fulfilled all the requirements on geotechnical parameters of bentonites used in GCLs.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Detrital mica transformed to mixed-layer illite/smectite under early diagenetic conditions. Back-reaction processes

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The study by HRTEM of marly samples of the Upper Cretaceous materials from the Alava Block (Basque-Cantabrian Basin), to understand their diagenetic evolution (ARROYO et al., 2007), has shown the beginning of the transformations in some detrital micas under early diagenetic conditions.

The textural study has been focused in the phase-relationships between some detrital micas and mixed-layer illite/smectite (I/S). The results obtained using HR images, SAED patterns and microanalyses show in some cases altered micas with the crystal edges transformed to R1, R3 or R>3 I/S, which indicates back-reaction processes occurring under early diagenetic conditions. This transformation coexists spatially and temporally, in the same samples, with the normal prograde transformation of smectite to mixed-layer I/S.

It is important to highlight the use of the term "*back-reactions*", which we apply to differentiate this genetically prograde process from "*retrograde diagenesis*" (NIETO et al., 2005), which implies the superposition of low-grade minerals on higher-grade assemblages via fluid-mediated processes.

It can be concluded that ordered mixed-layer illite-smectite can be produced in diagenetic conditions through prograde reactions both from smectite and from detrital micas by back-reactions, which can only be appreciated unambiguously when textural relations can be directly observed, for example by HRTEM.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Physicochemical and magnetic properties of aluminium and zirconium pillared clays

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Among pillared clays, the Al-PILCs have been the focus of investigation, while the Zr-PILCs have received relatively little attention because of the sensitivity of the Zr(IV) species to environment conditions.

Calcination converts the different polyoxycation precursors into their corresponding oxide pillars. Dehydration and dehydroxylation of the charged pillars during calcination give rise to neutral oxide particles. The heating process also affects porosity, stability and acidity.

Novel aluminium and zirconium magnetic pillared clays were prepared at ambient temperature through ion exchange followed by reduction with sodium borohydride. The influence of calcination temperature on the physicochemical and magnetic properties of the resultant Al and Zr pillared clays was investigated using X-ray diffraction (XRD), N_2 adsorption-desorption at 77K, magnetization measurements (alternating gradient magnetometer, AGM), infrared-spectroscopy with attenuated total reflection (FTIR-ATR), and simultaneous thermal analysis (STA).

For gas adsorption a new advanced evaluation method was used. This method is based on DFT (density functional theory) and provides reliable information on the porosity and pore size distribution of PILCs and their magnetic forms.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Titanium magnetic pillared clays Ti-M-PILCs: A Mössbauer spectroscopy and superconducting quantum interference devices (“SQUID”) study

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Titanium magnetic pillared clays (Ti-M-PILCs) were prepared from ion-exchanged Fe-titanium pillared montmorillonite by reduction with sodium borohydride at ambient temperature.

The magnetic properties of Ti-M-PILCs were investigated using superconducting quantum interference devices (“SQUID”) and Mössbauer spectroscopy. The measurements were done at low temperature because of the potential technological applications of Ti-M-PILCs.

Here we present preliminary data on the magnetic behaviour of titanium pillared clays obtained using SQUID, such as the hysteresis parameter at different temperatures, and magnetization measurements after cooling in zero field (ZFC) and in low magnetic field (FC).

Mössbauer spectroscopy is used to assess the valence state of iron, and the presence of iron oxide phases, in Ti-M-PILCs.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Middle Jurassic black shale (Skrzypny Shale Formation) – palaeoenvironmental significance one of the oldest deposits of the Pieniny Klippen Belt

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Toarcian-Lower Bajocian *Bositra* ("*Posidonia"*) black shale with spherosiderites (Skrzypny shale formation) are one of the oldest rocks of the Pieniny Klippen Belt. This deposits represent of widespread Tethyan *Fleckennmergiel* facies appearing during the earliest stage of the Pieniny basin history. The Skrzypny Shale Formation of the Niedzica Succession exposed in the outcrop below the Czajakowa Klippe in the upper part of the Homole Gorge has been investigated. They consist of dark olive grey shale with small flakes of micas. Loaf-shape siderite concretions occur within this shale. The components of the shale are clay minerals and micas such as: high illitic I/S, illite, kaolinite, biotite partially alters to a chlorite and white mica. Small grain (up to 15 µm) of quartz and feldspars and calcite occur as well. SEM/EDX images of the shale show the orientation of clay minerals flakes approximately horizontal. Large mica and chlorite flakes have been rotated 30 to 90°, so that incipient slaty cleavage is developed. Microstructures and clay minerals assemblage of the rocks studied developed in high grade diagenetic conditions. Organic matter occurring in them (TOC app. 1%) shows high thermal maturity as well. As indicators of the source of the organic matter *n*-alkanes and izoprenoids have been used. According to the obtained data, mixed terrestrial/marine organic matter occurs in the rocks studied but the later of them strongly prevails. The ratio of pristane/phytane is 1.8. It is ambiguous but indicate rather oxic condition of deposition. TOC value, occurring of siderite concretions and molluscs fossils in the rocks under consideration confirm the sedimentation in oxidizing water column and oxygen-depleted pore water.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Sorption of chromate by clinoptilolite, glauconite and montmorillonite modified with alkylammonium surfactant

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Clay minerals and zeolites have a very limited capacity for sorbing anions. The anion exchange capacity of these silicates, however, can be considerably improved by attaching cationic surfactants to their surfaces. Here we compare the chromate sorption capacity of selected minerals that have been modified with hexadecyltrimethylammonium (C16) cations.

Clinoptilolite (Cl) from Dylągówka, glauconite (Gl) from Lubartów and montmorillonite (Mt) from Chmielnik (all localities in Poland) were used as starting materials. Their cation exchange capacities (CECs), determined by adsorption of C16 ions, are 16, 18, and 95 cmol/kg, respectively. The minerals were then treated with solutions of C16 bromide at concentrations equivalent to 0.25–2.0 times the CEC. The products were characterized by IR spectroscopy, XRD, and their C and N contents.

The sorption of chromate by the organically modified silicates was measured spectrophotometrically as a function of pH (1.3–10) and Cr(VI) concentration (0.02–6.24 mmol/dm^3), using a solid/solution ratio of 20 g/dm^3.

The amount of chromate removed from a solution with an initial Cr(VI) concentration of 2.11 mmol/dm^3 decreased with increasing pH in the range 1.3–10. Under these conditions, the silicates treated with C16 surfactant at 1.0xCEC showed widely different capacities for sorbing chromate (e.g. Mt: 103–16 mmol/kg and Gl: 65–23 mmol/kg). By contrast, the amount of chromate removed by the minerals modified with 2.0xCEC concentration of the surfactant was similar (94–41 mmol/kg).

Maximum sorption of Cr(VI) (280-125 mmol/kg) was observed at pH 2.6–4.1 with organo-silicates modified at 1.5 or 2.0xCEC concentration of the surfactant. Considerably lower values (168–46 mmol/kg) were obtained with minerals prepared using 1.0xCEC concentration of the C16 ions, especially glauconite (102 mmol/kg) and clinoptilolite (46 mmol/kg).

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***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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Clay minerals in organic and mineral soils and sediments from the Unisław Basin (Poland)

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Organic and mineral deposits are typical sediments occurring on the plain of the Unislaw Basin, a part of the lower Vistula valley. They are mainly extra-channel sediments of lacustrine (peats, gyttias) and fluvial (alluvium) origins developed over many sedimentary cycles (KORDOWSKI, 2003). The mineral part of these deposits is composed mainly of clay, comprising up to 80% of the sediments.

The objective of the study was to determine the mineralogical composition of these clay fractions in the context of their differentiation and the effect of late post-sedimentation processes on the composition of clay minerals. The soil samples were prepared according to method of Jackson and analyzed by X-ray diffraction using a HZG-4 diffractometer.

The investigations showed that smectite minerals dominated in the deposits under study. They occurred in the form of pure smectites or as mixed layer illite/smectite with more than 80% smectite. This could be caused by a high percentage of the fine and very fine clay fraction, which confirmed the peligenic character of the sedimentation. The presence of illites and chlorites was also considerable. The highest amounts of illites were found in the fraction isolated from the surface horizons. This was probably caused by an illitisation process, which was more intense during fertilization, especially with potassium. On the contrary, the percentage of chlorites found in the investigated deposits was uniform in all the samples. Those were mainly „pedogenic chlorites". The only exceptions were two horizons with detrital chlorites.

The composition of the clay fraction of the deposits studied showed a high uniformity. It was similar to that of the same fraction of glacial clay occurring in the area of a morainic plateau surrounding the investigated terrain.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Heavy metal ions removal from wastewaters using natural clays

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A bentonite sample from Petreşti deposit, Cluj county (Romania), was used to remove heavy metal ions (Pb^{2+}, Cd^{2+}, Cr^{3+}) from wastewaters. A representative sample of bentonite from Petreşti (Cluj county) was characterised by means of surface specific area (BET), wet chemical and thermal analyses, X-ray diffraction (XRD) and Fourier transformed infrared (FTIR) spectroscopy. The bentonite deposit from Petreşti formed at the contact between Upper Jurassic limestones and basaltic andesites and subordinately basalt bodies. These rocks are composed of clay minerals (mainly smectite), and subordinately opal, quartz, feldspar, and mica/illite; as minor phases, clinoptilolite.

The bentonite sample was used as powder, particles with grain size smaller than 0.2 mm, without any chemical treatment. We studied the influence of the working regime, static and dynamic (3D shaker) over the process efficiency. We worked with a solid: liquid ratio of 1:10. In order to determine the exact concentration of heavy metal ions, water samples were taken every 24 hours in static regime and every 15 minutes in dynamic regime, until the equilibrium was reached. Cadmium and lead ions in solution were determined using an ion selective electrode and a pH meter, while in case of chromium ions we used a spectrophotometric method. Experiments were carried out at 20°C without pH modification for the synthetic solution. We used monocomponent synthetic wastewaters containing cadmium, lead and chromium ions. Removal efficiencies (%) and adsorption capacities (mg M^{n+}/g) were calculated in order to establish the effectiveness of the considered bentonite sample in the heavy metal ions removal process.

The bentonite sample proved to be efficient for the removal of the considered heavy metal ions, removal efficiencies up to 97.82% (cadmium removal in dynamic regime) were reached.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Thermal behaviour of lead-containing bentonite from Gador

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The treatment by smectites (e.g., montmorillonite, bentonite) of effluent water for uses other than human consumption, has been the subject of several reports (MELLAH & GHECROUCHE, 1997; BARBIER et al., 2000). The process generates sludges containing different types of pollutants (organic compounds and heavy metal ions) among which lead is of special concern because of its toxicity.

One possible solution to this problem is to convert the sludges into ceramic-like solid materials for potential application in the building and construction industries. A thorough knowledge of the thermal, physical, and mechanical properties of lead-containing smectites is required for developing and optimizing the production of ceramic materials.

To this end, we have investigated the thermal behaviour of a Pb^{2+}-bentonite, formed by saturating a Na^{+}-bentonite from Gador (Almería, Spain) with Pb^{2+}, using ETA, DTA/TG, XRD, and SEM. The emanation thermal analysis (ETA), based on the ratio of radon released from labeled samples, can reveal microstructural changes due to interlayer collapse during sample dehydration (BALEK et al., 2008).

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MINERALOGIA - ***SPECIAL PAPERS***, *33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Clay minerals in zeolite deposit of Poljanska, Croatia

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Clay minerals in the Lower Miocene zeolite (analcime) deposit of Poljanska (southern slopes of Mt. Papuk, Slavonia, northern Croatia) have been investigated. Complex analyses of lithological members of Poljanska area provide insight into their modal composition and origin (physico-chemical conditions of sedimentation, diagenetic alteration and genesis). Among different sedimentary members contemporary dolomicrites, miscellaneous pelites (shales, dolomitic marls), tuffs, tuffites and tuffaceous sandstones can be distinguished. Variability of mineral composition, texture and structure of sediments belonging to different parts of sedimentary column indicate changes of climate, depth and expansion of the lake, in which sedimentation took place, the kind and amount of detritus. Sediments deposited in fresh- to brackish-water lake, represented by calcareous-marly rocks, in which clay minerals are represented by montmorillonite as a product of a volcanic glass alteration can be found in the bottom and in the middle of the sedimentary column. With increasing salinity and alkalinity of lake water, quantity of montmorillonite diminishes. Illite is the dominant clay mineral in the layers of authigenic analcime bearing dolomicrites, pelites and tuffites deposited in the saline-alkaline lake.

MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Bentonite modifications with new biopolymers for HDD mud

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Bentonite is a naturally occurring material composed primarily of fine-grained montmorillonite. Its high ability to adsorb water and unique rheological properties make bentonite clay, extremely widely used in the entire drilling industry.

HDD drilling fluids have some important functions. A good drilling fluid should provide optimal cutting transport, have high lubrication in stem and drill bit lubrication as well as stabilize the borehole permanently by sealing the walls of the drill well. These functions are desired to enable entirely efficient drilling process.

The most widely used drilling fluids for HDD applications are based on bentonite. Our laboratory research is focused on modification of selected bentonites by new biopolymers to reach certain range of required parameters such as low viscosity, high yield point and ability to create gel structure. It is also important to note that minimizing of filtration is highly desirable.

Based on the research, it can concluded that the observed HDD fluids exhibit good technological parameters, as well as low filtration. Our laboratory research proves to be effective at bentonite modifications with the use of new biopolymers.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Using an attapulgite clay for the removal of Pb (II) from solution

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Many industrial processes, in particular in metallurgy, tanneries and in chemical manufacturing, discharge aqueous effluents containing heavy metals. These heavy metals are not biodegradable and tend to accumulate in living organisms causing health problems (POTGIETER et al., 2006). Accordingly over many years various technologies have been developed for the removal of metal ions from aqueous solutions. These include chemical precipitation, filtration, membrane systems and more recently the use of natural absorbents such as mineral clays (AYARI et al., 2005). Here we present the results of a study to evaluate the use of an attapulgite clay from the Biskra region of Algeria, for the removal of lead from wastes solutions.

Mineralogical characterization of this alumino-silicate shows that it has a fibrous structure and presents a high surface area with a certain porosity. The retention process is characterized by adsorption isotherms and we examine the influence of the contact time between attapulgite and lead, as a function of the pH of the solution and the concentration of lead in the solution. The amount of lead adsorbed on the clay was measured using an ÌCP Spectrometer.

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Amorphous Fe and silicate phases of hydrothermal origin from the British HMS Challenger expedition 1872-6

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The HMS Challenger went around the world in 1872-6 in an expedition devoted to Natural History. Among other specimens, the scientists aboard collected samples from the seafloor, and thus this became the first oceanographic expedition. Some of the seafloor samples collected in the south-east Pacific were metalliferous sediments produced by the hydrothermal activity at the East Pacific Rise. They are part of the collection at the Natural History Museum in London and have not been studied since short after the expedition, in the late XIX century. We analysed some of these samples to study the authigenic Fe and clay phases, using chemical analysis (ICP AES), XRD and SEM-EDS. The samples closer to the continent display a significant detrital mineral component from the Andes (chlorite, plagioclase, illite, smectite, kaolinite and quartz). This component decreases rapidly away from the continent and samples become increasingly dominated by biogenic calcite and amorphous phases. After calcite removal, the XRD patterns of the amorphous phases are compatible with Fe oxyhydroxide and silicate phases. SEM-EDS analysis revealed abundant mineral grains of small size and quasi-smectite composition. No smectite signature can be found in some of the samples and thus these grains are interpreted to lack a crystalline structure. Chemical analysis of calcite-free samples reveals that they are composed of two types of phases: Fe-Mn-rich and Si-Al rich. The former is the product of metal precipitation from the hydrothermal plume. The latter is a mixture of detrital phases from the continent and the amorphous aluminosilicate phase, likely precipitated by reaction of the Si-rich hydrothermal fluid with seawater. The amorphous silicate phase has the interest of providing an example of the early stages of smectite (?) formation from fluids in a submarine hydrothermal environment.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Detoxication of drilling waste contaminated with oil products and their management in ground environment on the example of the Podkarpacie district

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The results of analyses of oil-products removal from drilling waste using a complex chemical-biological method are presented in the paper. The waste management in ground environment has been considered. The results of chemical and porosity analyses of mineral-phase have been considered. They document transformation of waste in the course of detoxication processes. The quality of anthropogenic ground system containing detoxicated waste-ground composite was evaluated based on laboratory results of plant species growth and observation of the reclaimed area. The results of experiments showed the opportunities of treated drilling waste management in ground environment.

MINERALOGIA - ***SPECIAL PAPERS****, 33, 2008*

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Spectral characterization of Nigde-Dikilitas clays (Central Anatolian region, Turkey) and petroleum

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Characterization of Nigde-Dikilitas clays in the Central Anatolian region (Turkey) were carried out and results were interpreted in terms of petroleum exploration. The clay samples taken from Nigde-Dikilitas studied area were investigated by means of spectroscopic methods. Chemical analyses reveal that the samples chemically consists of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, Cr_2O_3 and P_2O_5. DTA and TGA measurements have been carried out for the determinations of the thermal behaviour of the clay samples.

Firstly, the FTIR spectra of the clays known as standard clays such as illite, illite-smectite mixed layer, montmorillonite, Ca-montmorillonite, Na-montmorillonite, nontronite, kaolinite have been taken, and then the spectra of anhydrite, gypsum, illite + quartz + feldspar, quartz + feldspar mineral associations have been taken together with the standard clays. The minerals included in samples taken from Nigde-Dikilitas study area were identified by comparing their FTIR spectra with those of the standard clay minerals and XRD analysis results. Moreover, to see whether any change occur or not in the structure of the clay samples which have been affected by thermal process, FTIR spectrum of the sample belonging to the lower level (D_1 in clay profiles) has been taken. The clay samples have included Na-montmorillonite, amorphous silica, feldspar and quartz, and they have a T-O-T (tetrahedral-octahedral-tetrahedral) structure.

In recent years, two of the methods for petroleum exploration are organic maturity and diagenesis of the clay minerals. During the diagenesis and metamorphism, changes in the clay structures due to the temperature will reflect degree of diagenesis and metamorphism. Factors including temperature, pressure, depth and burial that are all influential during these changes along with hydrocarbon formation and the primary migration of the hydrocarbons could be explained through the diagenesis of clay minerals and organic maturation. Required temperatures for these changes in the clay structures are in the same range with the required for petroleum formation (60-150ºC). Results acquired by using the organic maturation could be obtained through the spectral studies of the clay mineral structures.

MINERALOGIA - **SPECIAL PAPERS**, 33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

BestRock - mineralogy, chemistry, and mineral surface property optimization to calculate petrophysical properties of the mineral matrix

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BestRock is both a computer program and analytical method that has been designed to determine the chemical composition of individual minerals in rock formations and to use as a tool for wireline log mineral modeling by Formation Evaluation analysts. Many minerals have fixed chemical composition; while others are characterized by isomorphous substitutions (e.g. clays, feldspars, and carbonates). Elemental and mineral concentration data are optimized to determine individual mineral compositions. BestRock then calculates the petrophysical and wireline log response parameters of the rock matrix. This includes the distribution of wireline log sensitive trace elements (*e.g.* B, Li, Ba, Sr, Sm, Gd, Eu, U, Th) into individual minerals. The actual values of the rock matrix petrophysical properties of the particular formation may differ significantly from the default values used in mineral modeling programs, which are in turn used to calculate hydrocarbon and water saturation values that are used in reserve estimates.

This approach combines results from whole rock quantitative phase analysis (QPA), chemistry, cation exchange capacity (CEC) and dehydration at 110ºC. The program allows the user to define the allowable error limits in all the experimental input data in order to deal with the analytical uncertainty. This can be done for each sample individually or for a group of samples being optimized. A primary assumption in the procedure is that the composition of individual minerals doesn’t change, but their concentration does for any chosen group of samples. BestRock can also consider compounds that may be present, but not detected by QPA, such as amorphous Fe hydroxides and volcanic glass. Such compounds my significantly affect the rock properties and the mass balance of the mineral and chemical analyses. BestRock uses a non-linear large-scale mathematical engine for optimization procedure, based on the minimization of errors between the experimental and calculated data.

BestRock output includes: individual mineral structural formulae, grain density, hydrogen index, oxygen index, photoelectric absorption factor, volumetric absorption index, sigma, API Gamma-ray response, CEC, and adsorbed water.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Diversity of natural nanoparticles in soils and causative factors implied

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Ferrihydrite and lepidocrocite crystals grow and dissolve seasonally in rice paddies. In acid soils goethite crystals are very small influenced by structural Al. Todorokite grows on siderite boulders and in certain Vertisols. Birnessite is disorderly in soils apparently from the decline in Mn concentration. The major Mn oxide in Ultisols and Oxisols is lithiophorite that contains an octahedral sheet of Al hydroxide and they grow well beyond the nanometer range. In many soils of Texas there is a small amount of opal-CT that is a mixed structure in the colloid particle size range. Palygorskite and sepiolite occur in soils mostly inherited from the parent sedimentary rocks. Colloidal allophane and imogolite form in volcanic soils and weathered rocks. Halloysite nanoparticles form in vesicular volcanic glass. Smectite owing to water and ions between the layers is characteristically a nanoparticle. Smallness factors: time, solution composition, crystal structure constraints, pH, redox conditions, surface adsorption.

MINERALOGIA - ***SPECIAL PAPERS***, *33, 2008*
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Clay minerals in Histosols formed on outcrops of greenschists from the Svanoy Island (Norway)

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The material for investigation was isolated as clay fractions from mineral horizons of 4 Histosols developed on the outcrops of greenschists located in the southern part of the Swanoy Island. These greenschists occur as thin layers in calcareous metagraywackes. They were developed in the medium and lower Herland belonging to the middle Ordovician period (Andersen et al. 1990, Skjerlie 1974). The soils developed on these rocks are very acidic (pH 3.2-4.2) and have been subjected to diverse oxido-reductive conditions, gleying processes being evident in profiles 1 and 2). The mineralogical composition of the isolated clay fraction ($< 2\ \mu$m) was assessed in oriented preparations by X-ray diffraction.

The analysis showed that the clay fractions of the soils under study were dominated by trioctahedral chlorites. Besides there were reflections indicating the presence of large amounts of amphiboles and albite. The occurrence of amphiboles was the most evident in the humus horizon (A) of Profile 1. Mica occurred as an accessory mineral in all samples. Probably this was comminuted biotite, as shown by strong (001) and (003) basal reflections at about 1.1 nm and 0.335 nm, with a very weak (002) reflections at 0.5 nm.

The composition of the investigated fraction was similar to that of the greenschists described by Skjerlie (1974) and Anderson et al. (1990), suggesting that the weathered rock was developed mainly because of physical weathering. Soil-creating processes occurred predominantly in the organic horizons. Gleying has not yet caused any significant changes in the mineralogical composition of the clay fraction of the soils under study.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Development of novel synthetic layered complex metal silicates with enhanced performance properties

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Rockwood Additives manufactures a range of synthetic layered complex metal silicates under the trade name Laponite®.

Laponite® resembles the natural clay mineral hectorite in both structure and composition and shows a number of distinct advantages compared with natural clays. Its efficiency as a rheology control agent is many times higher and it can be dispersed rapidly in water to give colourless, transparent, highly thixotropic gels.

The unique properties of synthetic layered silicates have lead to them being used in highly specialized and niche applications. They offer scope for use in a wide range of water based systems particularly those which are gelled or contain suspended solids. Very high viscosity build at low shear, combined with very low viscosity at high shear allows use in sprayable systems or formulations that can be pumped, rheology “engineering” by combination with other thickeners to meet specific application requirements and stabilization of multi-phase systems e.g. water based multicolour paint.

Synthetic silicate particles have an electrically charged, platy structure with very high surface area, BET ~400 $m^2 \cdot g^{-1}$ and physical surface ~1000 $m^2 \cdot g^{-1}$. This makes it useful as an antistatic agent, a barrier for macromolecules, an adsorbent and a carrier for other chemical agents. Laponite® is chemically pure and consistent in its properties as it is synthesized under carefully controlled conditions.

The presentation will summarise our research programme to develop new synthetic layered silicates with enhanced properties. We are able to carry out custom modification of synthetic silicate structures and composition to change particle size and charge, morphology etc and develop new materials that meet specific requirements. These changes have led to new materials with improved performance properties; this in turn has expanded the range of industrial application fields where synthetic layered silicates can be used effectively. We have carried out organo-modification of these structures to develop new properties such as anti-microbial activity and adsorption of specific/targeted molecules.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Mineralogical reactions in a multi-layer hydraulic sealing system during saturation with a rock salt brine

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An innovative multi-layer hydraulic sealing system for application as component of the geotechnical barrier in hazardous or radioactive waste deposits was developed and its functionality was demonstrated in semi-technical experiments (HTV-1 and HTV-2) (KÖNIGER et al., 2008). A rock salt brine was used because any observed parameters are of conservative character (SITZ et al., 2003). The new sealing system combines sealing layers (DS) of Ca-rich bentonite with equipotential layers (ES) of silty materials of different hydraulic properties. Although bentonite is well established as a component of sealing constructions, there is a notable lack of experimental data on the bentonite reactions during the saturation process of sealing constructions. Dismantling of HTV-1 and HTV-2 yielded more than 1000 samples and analysis is still ongoing. However, our preliminary results already provide insight into the time-depended bentonite transformation under defined saturation conditions that simulate the underground pressure regime of the penetrating brine. Both experiments lasted more than one year each. Contact time of the rock salt brine with the bentonite in different distances from the liquid supply within the column (d=0.8 m and h=1.8 m) varied for several month leading to different transformation states although the salt-water ratio of the brine of 0.26 was evenly detected within all moistened DS and ES.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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Destabilization of colloidal microstructure of used drilling mud by reactive composites – management of treated wastes

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Experimental results have been reported on the treatment of colloidal drilling waste. It was dealing with destabilization of the sludges and their management. Reactive composite and nanoconposite materials have been used for brigding and cross-linking the waste components. The way of treatment depends on the properties of the used drilling mud: (I) its chemical and mineral composition, (II) salinity, and (III) the content of toxic admixtures. The mechanism of transformation reaction of the colloidal wastes is discussed based on the results of chemical analysis, scanning electron microscopy and mercury porosimetry.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Fe L-edge X-ray absorption spectroscopic study of iron in ferruginous smectites

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As part of the commissioning experiments of the soft X-ray beamline (ID-14-01) facility at the Australian Synchrotron, we collected Fe L-edge X-ray absorption spectra on well-characterized nontronites (Gates et al., 2002), saponites and other iron-enriched smectites (Gates, 2008; Cashion et al., 2008). The beamline uses an elliptically polarized undulator insertion device to direct an X-ray light source through a plane grating monochromator into a full UHV surface science end station with an accessible energy range of ~90 to ~2500 eV. The highly collimated and polarized beam is provided as a high flux density (~5.5×10^{11} photons/s/200 mA at the sample) area of about 15x150 µm.

Fe L-edge spectra of several nontronites, ferruginous smectites, saponites and reference high spin minerals were collected using different methods to determine spectral sensitivity, resolution, energy drift characteristics and sample stability. Samples were mounted as undiluted powders on carbon tape and the signal was monitored as excitation energy was scanned from ~690 to ~760 eV.

Measurement using drain current enabled probing samples with as low as ~2.5% Fe_3O_3 (~1.3 mol% Fe). Spectra were of sufficient quality to enable full resolution of the multiplet structure of the L_3 and L_2 edges. Octahedral Fe(II) can be discriminated from octahedral Fe(III) because these two oxidation states have different spectral shapes and energies for a similar crystal field environment, and the multiplet structure for Fe(II) is broader than for Fe(III). The presence of tetrahedral Fe(III) causes a subtle change in spectral shape, due to decreased crystal field splitting upon mixing with octahedral Fe(III) in smectites. Distortions of Fe(III) sites due to increased Al and Mg substitutions and normalization issues diminish the general utility of this method.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Clay rocks and mining wastes from Greece as raw materials for lightweight aggregates

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Present study focus on the use of bentonitic rocks waste materials and clayey diatomites occurring as lignite overburden, as raw materials for the production of lightweight ceramic materials having well-defined properties. These ceramic materials could be used in the construction industry as insulation materials. Tests were performed on samples collected from two occurrences from Greece (Drymos old quarry, Thessaly and Kleidi area, in western Macedonia Prefectures). The Drymos sample is included in the Sarantaporo-Elassona diatomite deposit, and mineralogically consists of various amounts of quartz, feldspar (albite/anorthite), muscovite, clinochlore, and dolomite.

Another bulk rock sample was collected from the thick clayey diatomite deposit in Kleidi lignite basin, where the diatomaceous rocks occur as thick overburden of xylite-type lignite. The main mineral components are: quartz, feldspar (albite/anorthite), muscovite, clinochlore, and hornblende. There are differences concerning the chemical compositions of the analysed samples. However, because their trace element content is low, therefore there is no risk in using them as raw materials.

Thermal analyses show similar effects: an endothermic effect at temperature range 20-200°C and an exothermic one between 300-600°C. No or small thermal effects were noticed above this temperature. In order to obtain the lightweight ceramic materials, the raw clayey materials were wet mixed, passed through an extruder, plastic formed and then they underwent heating treatment at temperatures of 600º, 700º, 800º, 900º and 950ºC in a laboratory kiln. The sintered products were tested by measuring their apparent density and apparent porosity, absorption capacity, and compressive strength. The phase composition and microstructure evolution of the samples were documented using XRD, IR, optical and electron microscopy. The preliminary results show that the clayey rocks could be used to produce lightweight aggregates. A good combination of compressive strength, porosity and apparent density could be obtained using combustible materials (sawdust) during firing at a temperature about 1100ºC.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Phase composition and technical properties of the Petreşti bentonite (Cluj county, Romania) as raw materials for ceramic products

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Clayey raw materials represent one of the most important types of raw materials used in industrial areas such as ceramic industry or environmental protection. In such applications, the type of raw material, especially concerning chemical and mineralogical compositions as well as technological behavior, is essential for obtaining materials with properties suitable to the specific usage function. The mineralogy and chemistry of the Petreşti bentonite were investigated, followed by the technological characterization for establishing the best way of their usage.

The X-ray diffraction, IR spectroscopy and thermal analyses were complementary used in the view of establishing the mineral composition, *i.e.*: montmorillonite – $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2\cdot xH_2O$, the main minerals, muscovite-2M2 – $(K,Na)Al_2(Si,Al)_4O_{10}(OH)_2$, clinoptilolite-Ca – $KNa_2Ca_2(Si_{29}Al_7)O_{72}\cdot 24H_2O$, orthoclase – $K(AlSi_3)O_8$, quartz – SiO_2, tridymite M low – SiO_2, cristobalite beta (high) – SiO_2.

The grain size distribution analysed by a laser granulometer has evidenced two fractions in the 0.5-10, and respectively 10-50 μm ranges, classifying the material as fine clay. In order to study the physical-chemical transformations of the bentonite (*i.e.* dehydroxylation of the clay minerals, carbonate decomposition, formation of new phases, etc), the samples were treated at different temperature 650º, 700º, 750º, 800º, 850º, 900º, 950ºC in a laboratory kiln.

The technological characteristics (water absorption capacity, apparent density and porosity, compressive strength) and the microstructure (by optical and electron microscopy) of the fired samples were evidenced. The samples derived from Petreşti bentonite show high compressive strength. To obtain the lightweight ceramic materials with a higher porosity, saw dust must be added to the clayey raw material, using a higher firing temperature (~1150° C). The samples with a low apparent density and a low compressive strength could be used in hydroponics, also as herbicide and fertilizer carrier as well as decorative ground.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Diversity of smectite minerals in the Polish Flysch Carpathians marls: crystal-chemistry and origin

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The marls occurring within flysch deposits of the Polish Outer Carpathians are smectite minerals-rich rocks. The smectite minerals in 15 marls samples (<0.2 μm size fraction), Jurassic to Oligocene in age, from all tectonic units of the Outer Carpathians were studied to investigate their origin and to determine a geological significance of this rocks

The description of the smectite minerals was made by profile fitting of X-ray diffraction traces using oriented preparations in different saturated state (Na, Ca, K, K-Ca and Li) to investigate their swelling behavior. The structural formulae has been determined from chemical analysis, NMR, Mössbauer and IR spectroscopy and the octahedral vacancy pattern by using thermal analysis.

According to obtained data the smectite minerals of the Carpathians marls are mixed-layered illite-smectite consist of a high-smectitic-phase (up to 95%) and a low-smectitic phase in different proportions. K and subsequently with Ca treatment indicate occurring of low-, intermediate-, and high-charge smectite layers, with a high amount of second of them. The layer charge originate from octahedral substitutions (Hofman-Klemen test, NMR, Mossbauer, IR spectroscopy and chemical analyses data). With a high proportion of low-smectitic phase the layer charge originate also from the tetrahedral sheet. The structure of the octahedral sheet for all samples investigated is similar. The average structural formulae shows Fe,Mg-rich smectite minerals (0.20-0.46 Fe^{3+} and 0.20-0.26 Mg atoms per $O_{10}OH_2$) similar to the Wyoming standard smectite. The difference is that thermal behavior of the smectite minerals studied indicate *trans*-vacant octahedral sheet and small amount of *cis*-vacant one.

The structural similarity of the octahedral sheet in all samples studied suggested that *trans*-vacant Fe,Mg-rich illite-montmorillonite occurring in the Carpathian marls is a product of diagenesis of a smectite which formed primary in similar environment from a parent material of the same origin.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Diagenesis of pelitic sediments in the Sava Depression (Croatia)

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Mineralogical investigations of the Miocene pelitic sediments were performed on samples from six wells from the Sava Depression (sub-basin in the SW part of the Pannonian Basin System). The main goal was determination of mineral composition including determination of smectite content in illite-smectite and illite and chlorite crystallinity indices. Paleotemperatures were estimated from vitrinite reflectance and Thermal Alteration Index (TAI) measurements on eighteen samples.

The main components of the pelitic sediments are carbonate minerals and clay minerals together with ubiquitous quartz. In certain samples, smaller amounts of feldspars, pyrite, opal CT and hematite were found. In greater depths, smectite and illite-smectite content in <2 μm fraction decrease, simultaneously with illite and chlorite content increase. It has been established, that smectite illitisation is primarily influenced by temperature and depth increase, mineral composition of the rocks (potassium availability) and exposure time.

Based on X-ray diffraction investigations of pelitic sediments from the Sava Depression, three stages of diagenesis have been revealed:

1. Early stage of diagenesis is characteristic for rocks from depths <1.8 km. In those rocks smectite, illite-smectite of the randomly interstratified (R0) type and detritic illite are present.
2. Intermediate stage of diagenesis, marked with the appearance of ordered type of illite-smectite was recorded at the depths >1.8 km and temperature higher than 80°C.
3. At depths >4.6 km coresponding to temperatures ≥190°C, late stage of diagenesis, characterised by appearance of illite-smectite with <10% smectite, has been established.

Transformation of randomly interstratified R0 type of illite-smectite into R1 type, as well as transformation of R1 into ordered R3 type fit to catagenesis of organic matter.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Analysis by Cu-trien as a tool to chemostratigraphic correlation of sediment series

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Clay mineral analysis is rarely used to stratigraphic correlation of high-resolution sediment sequences because of insufficient productivity of common procedures, their empirical and semi-quantitative nature, and large sample numbers required to such correlations. Cation exchange with Cu-trien introduced by MEYER & KAHR (1999) overcomes most of these hindrances whenever the geomaterials analyzed contain at least 5% expandable clay minerals. Analysis of Cu-trien has been validated for pure expandable clay minerals, but it becomes increasingly popular also to characterization of sediments (GRYGAR et al. 2005) and in the last two years even to analysis of recent soils and paleosoils.

We tested the stability of the analysis of montmorillonite samples with Cu-trien, checked the influence of common mineral admixtures, and compared the Cu-trien analysis results with the results obtained by traditional $BaCl_2$ method in analysis of recent and buried soils. The method with Cu-trien permits reliable analysis of real materials in large sample series whenever stoichiometry of Cu-trien solution and sample weight are controlled. However, we found that the results of Cu-trien and $BaCl_2$ ion exchange analyses are not equal if recent and buried soils are dealt with.

The method with Cu-trien allowed us to successfully perform stratigraphic correlations in two case studies: Two sediment cores of a Stephanian B lake from Czech Permocarboniferous Basins, and many sections of recent flood plain sediments of Morava River, Czech Republic.

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MINERALOGIA - ***SPECIAL PAPERS****, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Intercalated surfactants in SWy-2-montmorillonite

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Surfactants are present in various every day's life products from detergents to pharmaceutical drugs and cosmetics whose toxicity notably on the membranes of the biologic cells and some aquatic invertebrates has been highlighted several times (Talmage, 1994). The preservation of the environment can be realized by the capture of these substances by using smectite clays. Moreover of the environmental interest, the confinement of surfactants into clays rises some fundamental questions. Indeed, the guaranty of the stability of the surfactant-clays composite materials is strongly related to the interaction between the smectite surface and the surfactant which is far from being well understood (Mahadevaiah et al., 2007).

For this purpose, we study the confinement of two kinds of surfactants, a cationic (the benzyltetradecyldimethyl ammonium chlorure (BDDAC) and a non ionic (the mono n-decyl-ether triethyleneglycol ($C_{10}E_3$) surfactant into the SWy-2-montmorillonites exchanged by calcium and sodium ions. With the use of several complementary techniques (X-Ray diffraction, Raman scattering, Infrared spectroscopy and adsorption isotherms), we show that the surfactant molecules are intercalated in the interlayer sheets space of the clays. Several confined surfactant molecule organizations, depending on the molar quantity of surfactant inserted, can be highlighted from one adsorbed layer to paraffin or micellar structures.

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***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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Thermal, phase and micro-structural characterization of locally available kaolin clays

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Thermal, phase and micro-structural analysis of kaolin samples collected from the North-West Frontier Province of Pakistan were investigated. Dehydration of these clays occurred at ~90 to 150°C, followed by dehydroxylation at ~500 to 530°C. The crystallization of γ-alumina-type spinel phase or primary mullite began at temperatures ranging from ~990 to 1000°C. The major crystalline phases observed includ kaolinite, paragonite, halloysite and illite with distinct morphologies along with other feldspathic minerals such as albite.

Powdered KN and KB (Swat China Clay Pvt. Ltd.), KE & KD (Akbari Traders & Durr Industries) were dried at 110°C and sieved before analysis using thermal analyses (TG/DTA) X-ray diffraction (XRD), scanning electron microscopy (SEM), EDS and XRF.

Dehydration completed by <160°C and the dips in the curves at ~534°C for KE, ~514°C for KD, ~509°C for KB and ~498°C KN indicate dehydroxylation. The crystallization of mullite were observed at ~991°C for KE, 992°C for KD, 981^{o}C for KB and 991°C for KN showing the crystallization of Al_2O_3-rich mullite consistent with DTA results. The weight loss observed at ~40-160^{o}C was due to dehydration, followed by dehydroxylation at ~400-500°C, which is more (~4%) for KB and KN than KD and KE (~ 3%). At 500-600°C, the weight loss is ~7% in KE, ~4% in KD & KB and ~3% in KN. The variation in wt. loss may be due to percentage of pure kaolinite present in KE (~13.6 wt.%) at 500-600°C in pure kaolinite. XRD revealed the presence of kaolinite and illite in KE and kaolinite, illite, qaurtz and albite in KD, paragonite, kaolinite, albite, montmorillonite, and halloysite in KB, and paragonite, kaolinite, albite, montmorillonite, and quartz in KN.

Secondary electron microscope SEM images of samples revealed book- and flake-like grain morphology in KE, soft, mealy and hexagonal shaped grains in KD and rod-shaped halloysite and clinochlore grains in KB and KN, respectively.

The phase transformation temperatures are different for different clays due to variation in composition and level of feldspathic minerals present. The crystallinity in KB and KN is lower than KE and KD as revealed by XRD peaks for the former samples. KB and KN are composed of rod-shaped hallosite/clinchlore grains whereas the microstructure of KD and KE comprise mealy hexagonal and book-/flake-like grains, respectively.

MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

The effect of organocations on the mechanochemical activation of montmorillonite

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Grinding of clays produces substantial changes in the specific surface area and structure as well as partial-to-complete material amorphization. Dry grinding is also an effective way of obtaining ultrafine powders. Because of their small particle size and high surface area, these nanoscale materials have found industrial applications. In this work, an industrial product JP A030 (Envigeo Inc., Slovakia) based on Jelšový Potok bentonite (Slovakia) and three organoclays were ground in a high-energy planetary mill with steel balls. The duration of grinding varied from 1 to 20 min. The organoclays were prepared from the JP A030 material through ion-exchange with tetramethylammonium, octyltrimethylammonium, and octadecyltrimethylammonium cations, and denoted as TMA-JP A030, OTMA-JP A030, and ODTMA-JP A030, respectively. The ground products were characterized by XRD, TA, SEM and EDX analysis.

The decrease in dehydroxylation temperature as grinding time increases, is related to the breaking of hydrogen bonds between the montmorillonite layers. The relative mass loss also decreases with an increase in grinding time. All three organoclays are more resistant against mechanical destruction by dry grinding than the initial Ca-JP A030 material. ODTMA-JP A030 seems to be the most resistant in this regard. The long-chain organic cations apparently protect the organoclay particles. Grinding decreases layer ordering in ODTMA-JP A030 although the bonds between the octahedral and tetrahedral sheets are not substantially destroyed. Amorphization of montmorillonite caused by intense grinding is markedly retarded after replacing the inorganic cations with alkylammonium cations, especially long-chain species.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Rubber-layer silicate (nano) composites

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This work is oriented towards investigation of organic modifications of clay materials and their possible applications in polymer composites. Bentonitic industrial product Jelšový Potok A030 (JP A030) from Slovakia was ion-exchanged with tetramethylammonium (TMA) chloride, octyltrimethylammonium (OTMA) bromide and octadecyltrimethylammonium (ODTMA) bromide to prepare the organoclays TMA-JP A030, OTMA-JP A030 and ODTMA-JP A030. The parent clays and the organo-clays were used as aluminosilicate fillers for preparation of natural rubber-layer silicate (nano) composites.

Results of the EDX analysis confirm successful ion exchange of inorganic cations with the organic species. The X-ray diffraction data show that the long-chain alkylammonium ions ODTMA$^+$ are intercalated between the layers, adopting a pseudotrimolecular conformation, while OTMA$^+$ and TMA$^+$ ions show the monomolecular arrangement.

Polymer-layer silicate (nano) composites were prepared by direct polymer melt intercalation; in some cases the mixtures of rubber and clay contained also 15% of silica as conventional reinforcing filler. The effect of the clay or organoclay loading on the tensile properties was measured in the range 1 to 10%. Stress at break, strain at break and modulus M100 were evaluated from the tensile tests.

ODTMA-JP A030 modified sample appears to be the most effective filler among the organoclays. Similar values of composite elongation are obtained with ODTMA-JP A030 and unmodified JP A030. Organoclays with shorter alkyl chains are less effective. Mechanical properties of natural rubber with silica are enhanced upon addition of hydrosilicate filler. The highest stress and strain at break values of composites with silica filler are obtained for blends containing JP A030. Silica addition leads to significant increase in mechanical properties of composites with TMA-JP A030. Addition of 10% of JP A030 causes increased strain of the composite by 52% in comparison with the one containing 15% of silica, while the stress values are comparable. This is promising for substitution of more expensive silica with unmodified clay JP A030 in natural rubber-composites.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Aspects of the evolution of green pelletal clay

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The transformation of detrital clay to iron-rich clay minerals is a complex process involving mixed layer clays and it is not yet well understood (McCarty et al. 2004; Huggett et al. 2006). Nor is the geographic and environmental distribution of glaucony and verdine as clear cut and simple as was once thought. If we are to use these clays as environmental or reservoir quality indicators we need to understand what controls their formation rather better than we do at present. Temperature, water depth, latitude, rate of deposition, Eh, organic matter abundance are all factors that have been invoked as controls on which iron-rich clays form and the intensity of the mineralisation. This talk will examine all of these potential controls, and attempt to make sense of them through analysis of both new and published data.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

A detailed investigation of the process of low temperature illitisation of smectite in a palaeosol from the Isle of Wight, UK

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Illite has formed at the expense of smectite in palaeosols soon after deposition, in the Late Eocene Solent Group of the Isle of Wight, UK. HUGGETT et al. (2001) demonstrated the association between variegated palaeosols (gley soils) and ephemeral lacustrine sediments and illite enrichment, which they attributed to low temperature formation of illite by wetting and drying. HUGGETT and CUADROS (2005) carried out a more detailed analysis using a variety of techniques from which it was inferred that the wetting (reducing) caused Fe^{3+} reduction, and that on drying (oxidizing) re-oxidation was never complete. This would have created layer charge that enabled K^+ to become fixed in the interlayer sites. In this study we have investigated a single 120 cm thick clay bed that shows increasing illitisation towards the top. Our aim was to investigate whether detailed study of the illitisation over this single bed could confirm the role of Fe^{3+} reduction, and demonstrate the origin of the K^+ and its mechanism of fixation. Samples were analysed by XRD of the bulk rock and the <0.5µm fraction to determine the mineralogy and clay assemblages, while total iron was measured by ICP-AES and Fe^{3+}/Fe^{2+} analysis by titration. The results of these analyses will be discussed in the presentation.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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Method of thermal utilization of used drilling muds

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The increasing requirements of environmental protection force us to search for more effective methods of neutralizing, management and utilization of waste. From the point of view of rational waste management one should prevent the formation of waste, and if such waste does form one should cultivate it properly or re-use again.

Certain quantities of waste is produced in oil industry during drilling operations, mainly used drilling fluids and drilling cuttings which create management problems.

The article presents the results of laboratory tests on thermal processing of aggregates obtained from waste drilling fluids. This method enables utilization of used drilling fluids.

***MINERALOGIA** - **SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Metakaolin sand - a prospective substitute for Portland cement

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Metakaolin is known in the building industry as a silica-aluminate-based pozzolan, enabling partial cement substitution. Its reaction with free CaO during cement hydration reduces $Ca(OH)_2$ content and produces more CSH gel and additional gel-like alumina-containing phases (C_4AH_{13}, C_3AH_6, C_2ASH_8). The permeability is significantly decreased, and strength increased when metakaolin sand is blended with Portland cement and this system is left to hydrate.

Calculated supplies of kaolin sand in the deposit from Vyšný Petrovec, Slovakia are slightly over 20,000 kilotons. Two types of raw material – original kaolin sand (OKS) were used for the experiment: OKS I was ground and sieved to <60 μm and OKS II to <100 μm and 60 μm. The OKS was heated for 1 hour at 650°C with 10^{o}C/min temperature increase. Besides metakaolinite the metakaolin sand samples contain illite and muscovite together with non-clay minerals quartz and feldspar. Contents of metakaolinite in burnt kaolin sands are: BKS I (60 μm) 20%; BKS II (60 μm) 36% and BKS II (100 μm) 31% by mass.

Mortars made from the blends of Portland cement with metakaolin and standard sands (cement to standard sand 1:3 by mass) having bottom mass percentage cement substitution were prepared: MK type I (60 μm): 5%; 10%; MK type II (60 μm): 5%; 10%, MK type II (100 μm): 5%; 10%; 15%; 20%. Non metakaolinite constituents substitute sand fines in the mortar. Tests on reference mortar with 100 mass % of PC served for comparison. All mortars were adjusted on the constant workability: 180 ± 5 mm flow. Evident gains in compressive strength of MK-containing mortars relative to the reference mortar after 90-day water cure were found. Flexural strength of reference mortar is 10.2 MPa; relevant flexural strengths of MK-containing mortars vary between 9.9 and 12.3 MPa. Compressive strengths of the mortars made from the above blends were between 81.2 and 93.5 MPa whereas that of reference one is 53.5 MPa only, though still very high.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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Adsorption of an acidic textile dye to organo-bentonite

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Montmorillonite, the principal component of bentonite rocks, is widely used as an alternative material for sorptive, catalytic and rheological applications. Because of its high cation exchange capacity, extensive surface area, and low cost, montmorillonite is particularly attractive as an adsorbent. The inorganic cations, balancing the negative surface charge of the clay mineral, can be replaced by quaternary ammonium cations containing long-chain alkyl groups. By this means, the hydrophilic surface of montmorillonite becomes hydrophobic. As a result, such organically modified montmorillonites (‘organoclays’) can serve as powerful adsorbents of organic compounds.

A major problem associated with the textile industry is the generation of coloured wastewater (effluent) from the dyeing process. The degree of colouration depends on the colour/shade and type of dye used. Moreover, some dyes might be toxic to various organisms. Because of charge-charge repulsion, anionic dyes would interact weakly with negatively charged clay mineral surfaces. Little information, however, is available on the adsorption of anionic acid dyes to organoclays.

Here we investigate the adsorption of Acid Red 88, an industrial anionic textile dye by organobentonite. The adsorbents were prepared by mixing bentonite from Ivancice (Czech Republic) with solutions of octadecyltrimethylammonium (ODTMA) bromide at concentrations equivalent to 10, 30, 65, 100, and 200% of the cation exchange capacity. By replacing the inorganic cations on the clay with ODTMA ions, we obtained a series of partially and fully exchanged organo-bentonites. The surfactant-modified samples were characterized by FTIR spectroscopy.

The adsorption capacity of fully exchanged ODTMA-bentonite (105 $mg.g^{-1}$) was 50 times greater than that of the original Na-bentonite (2 $mg.g^{-1}$). The uptake of Acid Red 88 from water increased as the ODTMA content of the organo-bentonite increased. We propose that the dye is adsorbed by electrostatic attraction between the anionic group of Acid Red 88 and the positively charged ODTMA-modified bentonite surface.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Effect of the layer charge on the thermal behaviour of NH_4^+-vermiculites

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We have previously shown that the thermal decomposition of Santa Olalla vermiculite is a multi-step process, attributable to the pattern of octahedral substitution of M^{3+} for Mg^{2+}. Here we extend this investigation to different vermiculites, namely, Eucatex, Santa Olalla, Ojen and Beni-Buxera with varied amounts of substitution in the tetrahedral and octahedral sheets. The d_{001}-spacing of the various ammonium vermiculites decreases from about 11 Å to 10.2 Å as the total layer charge increases. The presence of NH_4^+ ions in the interlayer space expands the range of thermal decomposition. The bulk of ammonium is lost at temperatures higher than 500 ºC, and decomposition is complete at ~900 °C. The TG curves of NH_4^+-vermiculites show two main steps that are separated by about 120 °C for samples with a total layer charge ≤ 0.62, and by ~85 °C for those vermiculites with a higher layer charge. Evolved gas analysis (EGA) shows that NH_3 is also liberated in two main steps. The low temperature peak decreases in intensity and shifts towards higher temperatures with decreasing layer charge, and merges almost completely with the high temperature peak for vermiculites of low layer charge (Beni Buxera and Ojén). The IR spectra of vermiculites with a high layer charge (Eucatex and Santa Olalla) show that a large part of the NH_4^+ is lost at 750 ºC, while the residual NH_4^+ is lost at higher temperatures. On the other hand, for Beni Buxera and Ojén vermiculites, the NH_4^+ is completely lost at 750 ºC.

The IR spectra of the OH-stretching region look very similar except for Ojén and Eucatex. This feature is indicative of vacancies in the octahedral sheet. The Mössbauer spectra of all the vermiculites are also very similar except for Eucatex. The latter two specimens show additional features that are indicative of Fe^{3+} in the tetrahedral sheet. The thermal decomposition of NH_4^+-vermiculites is correlated with the pattern of isomorphous substitution in the octahedral sheet.

MINERALOGIA - ***SPECIAL PAPERS***, *33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Comparison of very low-grade metamorphism in the Medvednica Mts. (Croatia) and the Bükkium (N Hungary)

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The similarities between Palaeozoic rock series of the Bükk Mts. and the Internal Dinarides were recognized in the 1930s. Since then several papers have been dealing with the structural evolution of the triple junction zone of the Alps, the Dinarides and the Pannonian Basin, i.e. the Zagorje–Mid-Transdanubian Zone, however, no systematic metamorphic petrogenetic correlation of these units has been carried out so far. Comparing the grade of the low-temperature alteration in the Medvednica Mts. with metamorphic P–T data published from the Bükkium (Szendrő, Uppony and Bükk Mts. – N Hungary, ÁRKAI, 1983) it is noticed that similar lithotypes (siliciclastic, carbonate and volcanoclastic rocks) that are widespread in the Palaeozoic–Mesozoic Complex (PMC) of the Medvednica Mts. occur also in the Szendrő and Uppony Mts. Metamorphic P–T conditions estimated by organic (e.g. vitrinite reflectance, "graphite ordering" and Raman parameters) and inorganic "thermobarometers" [e.g. phyllosilicate "crystallinity" indices, results of chlorite Al(IV) thermometers and the thermobarometer of VIDAL & PARRA (2000)] for the PMC, may approach the ones published from the Szendrő Mts. K/Ar ages of ca. 120–80 Ma obtained from the PMC coincide with age values published by ÁRKAI et al. (1995) from the Bükkium.

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***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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K-Ar ages versus grain size, phyllosilicate „crystallinity” indices, crystallite size and lattice strain data: a case study of fine-grained siliciclastites of various metamorphic grades

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K-Ar dating of various grain size fractions of fine-grained siliciclastic rock samples affected by various grades of alteration is a useful tool for tracing prograde reaction process of the smectite–illite–mica transformations. Age data obtained on the <0.6, 0.6-2, 2-4, 4-8, 8-16 and 16-32 μm size fractions of three selected samples, previously studied by ÁRKAI et al. (1996), from the Bükkium (N Hungary) are correlated with illite Kübler and chlorite “crystallinity” indices, and crystallite thickness and lattice strain data calculated on illite–K-white mica and chlorite reflections using the Voigt method. Clearly visible correlations are obtained for crystallinity indices and crystallite thickness data both with grain size and K-Ar ages of diagenetically altered (NHA-3), anchimetamorphosed (NHA-2) and epimetamorphosed (NHA-1) rocks samples. These trends can be explained by the increasing detrital influence and the decreasing reset of the K-Ar system with increasing grain size for NHA-2 and NHA-3. Decreasing cooling ages with decreasing grain size are obtained for epimetamorphosed metapelite NHA-1. The lack of bench-type age–grain size profiles refers to incomplete resetting of the K-Ar isotopic system even in the epizonal sample.

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***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Comparison of phyllosilicate reaction progress indicating parameters and organic maturity in the western Greywacke Zone

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The low-grade metamorphic rocks of the western Greywacke Zone are separated from formerly deeply buried rocks of the low- to high grade metamorphic Penninic Tauern Window by the sinistral transpressional Salzachtal-Ennstal Fault Zone (SEFZ). The Cretaceous tectono-metamorphic overprint of the Greywacke Zone was succeeded by a local Latest Eocene/Oligocene heating of the contact between the Greywacke Zone and the Tauern Window.

Along the SEFZ, epizonal illite Kübler index (KI) values differ from high-temperature anchizonal KI data within the internal parts of the Greywacke Zone. By the application of the "Raman spectroscopy of carbonaceous material thermometer" a narrow zone along the SEFZ is mapped as a thermal aureole with peak metamorphic temperatures close to 400°C, resembling the metamorphic temperatures at the northern margin of the Tauern Window (FRANK et al., 1987). The combined use of the "Raman spectroscopy of carbonaceous material thermometer" and "crystallinity" index measurements proves the effect of an Oligocene to Miocene thermal pulse inducing advective heat transport and circulation of fluids overprinting the Cretaceous high-temperature anchi-epizonal metamorphic pattern of the Greywacke Zone.

Acknowledgements: Financial support of the Austrian Academy of Science is gratefully acknowledged.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

A preliminary approach to palygorskite occurrence in Middle Miocene dolomitic sendiments of alluvial fan in Çanakkale, NW Turkey

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The middle Miocene alluvial fan type sedimentary units in the southern part of the eastern edge of the Çanakkale pass composed of claret red and reddish conglomerate, sandstone, mudstone units of alluvial fans alternated with white to brown colored dolomitic unit. The alluvial fan is derived from the micaschist, marble, quartsite, serpentinite, andesite and tuffaceous type basement rocks croped out in the eastern part of the study area. Dolomite and rarely dolomite associated with magnesite are dominant in the dolomitic units. These are accompanied mainly with palygorskite and rarely accessories of smectite, kaolinite, heulandite, alunite, quartz, illite, feldspar and talc in places.

In nature, palygorskite has been formed either as detrital, or diagenetical transformation of precursor minerals such as smectite, illite or volcanic glass, or by direct precipitation from solution (authigenically). Closs association of palygorskite with dolomite and non-existence or rarely occurrence of smectite and illite type precursor as accessory, as well as quartz, feldspar and talc type detrital minerals, reveal that palygorskite is formed authigenically from solution rather than transformation of precursor minerals or transportation. Therefore, the alternation of palygorskite-bearing dolomite, thin palygorskite layers with mudstone, sandstone and conglomerate was possibly as a result of periodic climatic changes. In wet periods Mg-rich water seeped upward through permeable zones by capillary action and by evaporation close to the surface causes concentration of the solution and consequently an increase in pH and salinity favoring precipitation of nodular, lenses, column, tubule and crack-filling type dolomite. These conditions are also favorable for palygorskite precipitation in association with dolomite when the activity of silica and magnesium are high and aluminum is low in the circulated water. Silicon, Mg and Al in solution may have been provided by degradation of minerals derived from the basement units in addition, Mg may also obtained from the coprecipitated dolomite.

MINERALOGIA - ***SPECIAL PAPERS****, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Mineralogy, geochemistry, and origin of the Sogut kaolin deposits in Paleozoic Saricakaya granite and granodiorite complexes in Bilecik, Northwest Turkey

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Kaolin deposits occur in granite and granodiorite complex units, which are cut by aplite and pegmatite in Çaltı, İnhisar, and Küre, all located in the Söğüt region of Turkey. These units are crosscut by networks of fractures and poor zones filled with hydrothermal injections of iron-bearing solution materials, which resulted in the degradation of primary minerals, such as feldspar crystals. Feldspar crystals are either sericitized or kaolinized, and mica is generally iron oxidized and chloritized. Some kaolinite exhibits either authigenic vermiform or plate stack forms having contact with degradated feldspar crystals, which, on occasion, exhibit thick, platy, and subparallel orientation to micro-fractures, which is the pathway of hydrothermal fluid injections. Relict of altered feldspar crystals and their alteration products are generally associated with quartz crystals and illite. Increases in the Al_2O_3/SiO_2 ratio in kaolinized units (in comparison to granite and granodiorite complexes in host rocks, and silicified hard materials) and the presence of Cu, Ni, Ba, high Fe_2O_3 + TiO_2 content, as well as goethite, limonite, lepidocrosite, rutile, pyrite, and manganite are characteristics indicative of hydrothermal alteration. These results are supported by negative isotopic ^{18}O and D values for the analyzed kaolinite fractions, indicating depletion, which occurred during hydrothermal activity.

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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Mineralogy, geochemistry and origin of alteration minerals and their effect on health: a case study from the Zonguldak region, NW Turkey

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The Cretaceous-Eocene volcano-sedimentary units of the Zonguldak region at the western Black Sea were sampled for mineralogical and geochemical analyses in order to understand environment-health interactions. The rock units consist of subalkaline andesite and tuff, and sandstone dominated by smectite and kaolinite with accessory chlorite, illite, mordenite and analcime associated with feldspar, quartz, opal-CT, amphibole and calcite. Kaolinization, chloritization, sericitization, albitization, Fe-Ti-oxidation, and the presence of zeolite, epidote and illite in andesitic rocks, and tuffaceous materials developed as a result of the degradation of a matrix of glass shards with enclosed feldspar and clinopyroxene type phenocrysts, possibly due to diagenesis or hydrothermal processes. The association of skeletal feldspar and glass shards with smectite and kaolinite, and the sub-orientation of feldspar-edged subparallel kaolinite plates to fracture axes may reveal an authigenic smectite or kaolinite. The presence of organic materials, micro-organisms and filaments in the altered units, and increased degree of alteration upwards resulting in a gain of Al, Fe, and Ti and depletion of Si, Na, K, and Ca, is due to alteration following possible diagenesis and hydrothermal activity. Micromorphologically, fibrous mordenite was detected in the altered units and needle-type chrysotile in the residential buildings in which people with cancer lived. In addition, the segregation pattern of cancer susceptibility in the region strongly suggested an environmental effect and a genetic influence on the increased cancer incidence in the region. However, the geological environment on the health problems in Zonguldak Region may have had a secondary role, with genetic factors having a primary role in the development of disease in the region.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Compressibility and swelling pressure of clays

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The compressibility properties of remolded and reconstituted clays are basic characteristics of clayey soils. The properties of natural clays differ from reconstituted due to the influence of soil fabric and cementation.

Different oedometer testing procedures were proposed to characterize the compressibility. Those tests are time consuming and therefore researchers have correlated compressibility characteristics with various parameters of index properties, e.g. different void ratios and plasticity index.

In this work we investigated Na- and Ca-bentonite, illite, kaolinite and natural clayey soils. From compression tests the normal logarithmic-linear relationship was derived. The calculated compressibility constant gives a correlation with the void ratios at 1 kPa and at the liquid limit. Two main linear regions can be shown. The first region at low vertical pressure begins from void ratios little above liquid limit and ends near the void ratio at plastic limit. At first the capillary water between the grain and aggregates is pressed out and then the clays were dehydrated from about four layers to one layer and below void ratio of about 0.9 (simple cubic packing) the grains were compacted to a more dense package. The second linear region at higher pressure begins at around 1 MPa and can only be seen on more or less pure clays. A combined equation with introduction of the limited consolidation pressures at the plastic limit and shrinkage limit is derived for both regions.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Morphological diversity of digenetic kaolinite in Cracow Sandstone Series sandstones (Upper Silesia Coal Basin)

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Numerous diagenetic processes that caused significant modifications in primary composition in rocks have been recognized in Cracow Sandstone Series (CSS) sandstones: mechanical compaction, crystallization of diagenetic siderite, dolomite, ankerite, pyrite, illite, kaolinite and quartz in pore spaces, replacement of framework grains and older cements by carbonates, and dissolution of quartz and feldspar. Processes and the degree of their advancement depend on the diagenetic potential of individual rocks and local conditions during diagenesis.

Crystallization of kaolinite and kaolinization of feldspar, biotite and matrix components are the most widespread and advanced diagenetic processes. Different morphological types of kaolinite are related to these processes.

The most abundant kaolinite type occurs as *big platy crystals* (from 5 to 50 μm in diameter, but usually not >20 μm), with irregular edges, which form vermicules but also occurring as thin plates which extend curvilinear in length to dozens of μm, and as booklets (up to 0.2 μm thick).With increasing well depth, the kaolinite crystals become thicker.

Vermicules and booklets usually fill pore-spaces in fine-grained sandstones. In coarse-grained sandstones, massive infilling in pore-spaces (compacted infilling) is more typical. These types of kaolinite are also present in the kaolinized rock matrix. Sometimes dispersed biotite relicts are visible among pore-spaces infilling massive kaolinite.

Another type of kaolinite morphology is massive and elongated, usually related to K-feldspar grains. This type of kaolinite occurs as infillings in dissolution voids in feldspar or in pore-space close to partly dissolved K-feldspar.

It is possible to notice two different types of kaolinized biotite. Kaolinite formed multiple intergrowths within biotite flakes, expanding along cleavage planes (displacive growth). The advance of this process depends on grain size in sandstones. In conglomerate and very-coarse-grained sandstones, intergrowths usually are typical for the biotite edges. In coarse- and medium-grained sandstones this process is more advance and usually only relicts of biotite are visible. Formation of kaolinite intergrowths within biotite is often accompanied by crystallization of Fe oxides, Ti oxides or pyrite along biotite flakes. Crystallization of abundant fine-grained Fe oxides between biotite plates inhibits formation of regular kaolinite crystal intergrowths.

Morphological diversity of kaolinite crystals is not related to the mineralogical composition of the rocks. Formation of different kaolinite types is related to variations in rock grain size, size of pore-spaces, size of grains acting as seeds for kaolinite crystallization, and, perhaps, to local changes in chemical composition of pore-fluids.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

The influence of exchangeable cations on the pH value of bentonite suspensions

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Adding bentonites to water is known to affect the pH value of the suspension. This is largely due to the (partial) dissolution of carbonate constituents in the bentonites.

Here we test the hypothesis that the nature of the exchangeable cation on the bentonite is an additional factor determining suspension pH (Kaufhold et al., 2008). To this end, we have taken 38 different bentonites from all over the world and measured the pH of the corresponding aqueous (2% w/w) suspensions. The pH of Ca-bentonites is typically 6–8, while Na-bentonites are more alkaline (pH 8–10). The range of pH values for Ca-bentonites can partly be ascribed to hydrolysis of Ca^{2+}. On the other hand, the pronounced alkalinity of Na bentonites may be attributed to the hydrolysis of montmorillonite (Na^+ is exchanged for H^+ from water). Since Ca^{2+} is more strongly bound (than Na^+) to the montmorillonite surface, such hydrolysis is inhibited. However, this process is important only at low pH values (e.g. < 5), and cannot account for the high pH (up to 10) of carbonate-free Na-bentonites.

An alternative proton binding mechanism is proposed. Increasing the Na^+ content results in a high degree of delamination which, in turn, increases the *Stern layer* volume. As a result, the concentration of H^+ and Na^+ ions in solution decreases and pH increases. Both montmorillonite hydrolysis and delamination depend on ionic strength. The quantitative differentiation between these two processes remains an analytical challenge.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Chloritization of maffic target rocks in the impact-induced hydrothermal system at Kärdla impact crater, Estonia

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Impact-induced hydrothermal (IHT) systems are specific sites of clay formation that are recognized in a number of terrestrial environments and that also may occur in extraterrestrial environments. In this contribution we study authigenic clays in an IHT system at a small-to-medium size impact crater in Kärdla, Estonia. It is a 4 km-diameter complex impact structure formed in a shallow sea about 455 Ma ago into a target composed of a thin sedimentary layer on the top of Paleoproterozoic crystalline basement of retrograde amphibolite-facies maffic rocks. The clay minerals in Kärdla IHT system are represented by authigenic trioctahedral Fe-rich chlorite, mixed-layered corrensite, and corrensite-chlorite minerals that replace hornblende and pyroxene and/or biotite in amphibolitic rocks. Chlorite occurs as aggregates of microscopic, radially oriented, masses of euhedral flakes lining the walls of fractures and cavities. The inner parts of the fractures and cavities are typically filled with carbonates and/or quartz and K-feldspar. The authigenic chlorite also occurs sparsely throughout the studied sections in all types of the breccia matrix where chlorite and/or corrensite replace both amphibole and/or devitrified glass and melt clasts. The alteration intensity (i.e., the mode and abundance) varies with the location within the structure. At the rim wall, the alteration is localized along fractures and impact-injected breccia lenses, where the chloritization is restricted to the fracture planes and grain boundaries and probably also to metastable melt/diaplectic glass fragments within the breccia lenses. More prolonged and intense alteration is evident within the crater depression where alteration zones reach progressively outwards from the fractures into the host rock, and up to one-third of the plagioclase and hornblende/pyroxene volume is replaced with the secondary minerals. IHT alteration was most widespread and complete in the upper portion of the allochthonous breccias in and around the central peak. In this area practically all hornblende and plagioclase, along with the impact glass, is replaced mainly by clay (chlorite/corrensite) and K-feldspar minerals.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Interactions of methylene blue with montmorillonites

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The metachromatic behaviour of methylene blue was first reported by BERGMAN & O´KONSKI (1963). The interactions between clays and cationic dyes have since been intensively studied but the underlying mechanisms are still not fully understood. Suspensions of methylene blue with montmorillonites (MB/MMT) in aqueous solutions absorb visible radiation at 650–675 nm (dye monomer), 590–610 nm (dye dimer), 570 nm (higher dye aggregates), and 763 nm (protonated methylene blue, MBH^{2+}, and/or J-aggregates). The adsorption of methylene blue from neutral (e.g. BUJDAK et al., 2002, 2003) and acid aqueous solutions by two original and reduced-charge montmorillonites (SWy-2 and Cheto) has been investigated together with the properties of the resultant complexes.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Influence of water on stability of geopolymers investigated by NMR solid state spectroscopy

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Layered aluminosilicates (bentonite, montmorillonite, illite, kaolinite, etc.) find applications in many professional human pursuits (building industry, foundry industry, ceramics, etc.) Therefore, aluminosilicate materials play an important role in our world. Among others these materials are exploited in the preparation of zeolite (catalysts) and in the preparation of geopolymer systems which exhibit large chemical and structural potential.

Geopolymers are usually prepared through reaction of alkali solutions and calcined aluminosilicate layered minerals – at the room temperature and normal/atmospheric pressure. Ideally they should have non-crystalline structure, which keeps molecular water inside the 3D framework. However, in time – at some circumstances, these materials can undergo gradual transformation into zeolite structures. These transformations are accompanied by loss of water and change of mechanical properties. Zeolites, which are originating mainly in closed systems (autoclaves) or from dilute solutions, have a crystalline structure. Zeolite sorption (desorption) of water occurs without a change in chemical structure. Stability of system is important for keeping of mechanical properties. This is the reason why this work is focused on the deep investigation of the role of water during these processes.

We prepared the stable and unstable systems of geopolymers and focused to kinetics of beginning steps. For such task we used very powerful method – the solid-state NMR. This is a physico-chemical method exploiting interaction atomic nuclear (with nonzero nuclear spin) with magnetic field. To gain structural information provided by solid-state NMR we used not only simple one-dimensional experiments on various nuclei like ^{1}H, ^{23}Na, ^{27}Al, ^{29}Si but also the two-dimensional multiple-quantum experiments – that were modified to indirectly detect water molecules that are closed in selected structural units. By this way we were able to resolve additional structural units in geopolymers that are responsible for their instability. We have tested large scale of NMR techniques involving also ^{1}H-^{1}H correlation experiments, cross-polarization transfer as well as relaxation experiments to locate and describe properties of clusters of water molecules.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Characterisation of porous mineral materials using time domain reflectometry methods

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The bulk characteristics (capillarity, storage of moisture and nutrients, accumulation of metals) of heterogeneous, porous materials like soils and clays are substantially defined by their content of fine grained particles (D <2 µm). The hydraulic behaviour of these materials is described by the relation of suction to moisture saturation. This relation is subject to a strong hysteresis, depending on whether the material is moistened or is drained (SCHUHMANN, 2003). The influence of the hysteresis can be reduced substantially by determing the water content. A suitable measurement procedure is based on the difference in permittivity (□) of fluids like water or brines and solid materials. The time domain reflectometry method leads to an integral water content, using a calibration procedure based on material density and electrical conductivity.

Material composits like soils and clays are mostly unsaturated. The improved understanding of materials on different scales explored by using lysimetres enables a synthesis of materials that meet a certain purpose and to understand their hydration behaviour. Examples are the development of capillary material for equipotential segments in underground multi-layer hydraulic sealing systems (KÖNIGER et al., 2008), or mineral sealings on landfills with required monitoring.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Permeability testing of geosynthetic clay liners

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Coefficient of permeability is the most important design parameter of clays and geosynthetic clay liners (GCLs) for landfill liner applications. It can be determined using conventional (constant- or variable-head method) or modern test methods like flow-pump testing (Veinovic et al., 2003). By applying flow-pump method, permeability measurements can be obtained much more precisely and rapidly, which is particularly important for low permeable and soft materials.

In our study, samples of one type of reinforced GCL were tested for the determination of permeability by two methods: constant-head (samples 1 and 2) and flow-pump (samples 3 and 4). The obtained values of permeability were quite similar in both cases. The major advantage of flow-pump method was that the duration of permeability testing phase was only several hours comparing to several days in case of constant-head method (Blazevic, 2007).

Sample	Effective stress (kPa)							
	35				70			
	L (mm)	Δu (kPa)	i	k (m/s)	L (mm)	Δu (kPa)	i	k (m/s)
1	8.4	15	182	1.76E-11	7.36	15	208	8.66E-12
2	8.4	15	182	1.69E-11	7.45	15	205	6.66E-12
3	9.22	10	111	1.38E-11	8.69	21	246	1.18E-12
4	10.20	11	110	1.85E-11	9.03	22	258	1.13E-12

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Formation of layered double hydroxides at alumina/water interface in aqueous solutions containing divalent metal cations

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A deposition of layered double hydroxides (LDHs) on supporting materials would be advantageous for various applications, e.g., in heterogeneous catalysis. The formation of LDH phases on the Al_2O_3/Al support prepared by anodic oxidation of aluminum foil was studied in an aqueous solution of Co, Mn, and/or Ni nitrates. The method reported by CHEN et al. (2006) was adopted, when the reaction under hydrothermal conditions at 80-180°C for time ranging from 8 to 168 hours was applied.

In initial stages of the reaction, a hydration of alumina was observed. The LDH phase was formed after long-term deposition at 120-160°C and only a slight incorporation of Mn into the deposited LDH was found. In solutions containing only Co and Mn cations, SEM images showed a gradual growth of platy crystals resulting in formation of spacious and separated aggregates with size of several tenths of microns. When Ni cations were present in the solution, they were preferentially incorporated into the LDH phase; a homogeneous layer was formed, with single platy crystals oriented perpendicularly towards the support surface. Temperature of 140°C and time of 3-4 days were chosen as suitable conditions for deposition of LDH precursors on Al_2O_3/Al support.

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***MINERALOGIA** - **SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Mixed oxides formed during thermal treatment of Co-M^{III} layered double hydroxides (M^{III} = Al and/or Fe)

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Layered double hydroxides (LDHs) are often used as precursors for preparation of mixed oxide catalysts and therefore it is useful to know in detail their thermal behavior. The Co-Al, Co-Fe-Al, and Co-Fe LDHs with Co:Fe:Al molar ratio of 4:0:2, 4:1:1, and 4:2:0, respectively, were prepared by coprecipitation of corresponding nitrate solutions and heated in air at various temperatures up to 1100°C.

The prepared LDHs were decomposed at about 200-260°C; thermal stability decreased with increasing Fe content. Thermal decomposition of LDHs resulted in a formation of rather amorphous spinel-like mixed oxides; their gradual crystallization with increasing calcination temperature was observed. Raman spectroscopy indicated a segregation of Co-rich spinel, i.e., Co_3O_4 or slightly Al-doped one, in Co-Al samples obtained at lower temperatures (300-600°C). A recrystallization of primary Co-rich spinel accompanied by incorporation of Al into the spinel lattice at higher temperatures can be considered.

In the Co-Fe samples, a segregation of two spinel-like phases, Co_3O_4 and $CoFe_2O_4$, was observed by XRD at temperatures higher than 600°C. The Co-Fe-Al calcination products contained a Co-Fe-Al spinel only, which lattice parameter gradually increased with increasing calcination temperature. In the Raman spectra of the samples obtained at 500-1000°C, a new band at 696 cm^{-1} was found. A partial decomposition of the primary Co-Fe-Al spinel to form Co_3O_4 and CoO was detected by XRD in the sample calcined at 1100°C. A formation of CoO to the detriment of spinels was observed at high temperatures with all examined samples.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Mg-Al layered double hydroxide intercalated with porphyrin anions: Molecular simulations and experiments

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Molecular modeling combined with X-ray diffraction, temperature X-ray diffraction and thermogravimetry was used for structure analysis of Mg_4-Al_2 Layered Double Hydroxide intercalated with porphyrin anions (5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin – TPPS). Molecular modeling was carried out in *Cerius*^{2} modeling environment. Models with various concentrations of TPPS anions (25, 50, 75 and 100% of exchange capacity) and interlayer water in the interlayer space were calculated and described. TPPS anions adopt a tilted orientation with respect to the LDH layers. The tilted angle is about 70°. The guest anions are horizontally shifted with respect to each other and the shift is equal up to a half of a diameter of guest anion. Most of the interlayer water molecules are arranged near the LDH layers together with SO_3^- groups of guest anions and a smaller amount of water can interact with the porphyrin core via hydrogen bonds. Temperature X-ray diffraction (25- 180°C) showed a dependence of the value of basal spacing on temperature (decrease from 22.1 Å to cca 21.1 Å). The decrease of the interlayer distance due to decrease of interlayer water leads to a lower tilted angle of TPPS anions with respect to the LDH layers that is in the range of 55-60°. We obtained a good agreement between the calculated and measured X-ray diffraction pattern and between the calculated basal spacing (22.0 Å) and experimental basal spacing (22.1 Å). This work is based on recently published article by Lang et al. (2007).

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Reconstruction of the diagenetic history of sedimentary basins revealed by the analysis of smectite illitization in shales: example from the basement of the Carpathians and the Carpathian Foredeep

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Reconstructions of diagenetic histories of sedimentary basins are crucial for proper modeling of oil and gas generation processes. That modeling provides a way of establishing the time relationships between the generation, expulsion, migration and accumulation of hydrocarbons, leading to the identification of traps existing during the time of generation.

Presented diagenetic reconstruction revealed by the analysis of smectite illitization in shales was conducted for the rocks of the Małopolska Massif, i.e. the basement of the Carpathians and the Carpathian Foredeep, the region known for its gas deposits. The study was done with the use of the XRD methods: the percentage of the smectite layers in illite/smectite, the Kübler index, the distributions of thickness of illite particles, combined with K-Ar dating of clay fractions.

The Ordovician, Silurian and Carboniferous rocks of the basement are treated as the source rocks in that region. The Miocene age of generation was assumed for them (Karnkowski, 1993).

The performed reconstruction proved that the time of maximum generation was different and much older. The diagenetic discontinuity between the basement and the autochthonous Miocene and the flysch Carpathians was found. The results of K-Ar dating showed that the post-Cambrian Paleozoic rocks reached the maximum of diagenesis (15-24% S in I/S, which correspond to the paleotemperatures > 130-160ºC) during the Upper Carboniferous time. Another thermal episode took place probably in the Lower Cretaceous. Thrusting of the Carpathian nappes influenced mainly the diagenesis of the Upper Cretaceous and the autochthonous Miocene rocks.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Kaolinite group minerals in the Upper Carboniferous and the Lower Permian sandstones of Pomerania area (Poland)

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Kaolinite group minerals are frequent in the Upper Carboniferous and the Lower Permian sandstones including also the Dziwna and Świniec formations. These formations lie on the Rega formation sediments (Upper Carboniferous) and are covered by the volcanogenic formation of the Wielkopolska complex (the Lower Permian). Kaolinite was observed under the polarizing microscope and scanning electron microscope (SEM). Fractions <2 µm and from 2 to 10 µm were separated from sandstone samples. They have been examined by X-ray diffraction (XRD) and infrared spectroscopy (IRS).

The amount of kaolinite ranges from 0 to 15 volume %, the average being about 3%. Kaolinite occurs as platy aggregates which in the SEM image display a pseudohexagonal crystal habit and create characteristic booklet forms. Kaolinite cements mainly fill intergranular and intragranular space. It has been altering to illite or replaced by carbonates and anhydrite. Two morphological types of kaolinite have been recognized: vermiform and blocky. The vermiform kaolinite is more coarse grained than the blocky one. Both kaolinite and dickite have blocky morphology. XRD and IRS were used to identify the studied kaolinite and dickite.

XRD analyses show the presence of kaolinite and dickite in two analysed fractions in the Upper Carboniferous sandstones. IRS analyses show the presence of kaolinite amongst the dickite, with kaolinite content decreasing from 60 to 20%, generally at depths below 3000 m. In the sandstones of the Dziwna and Świniec formations, XRD analyses show mainly the presence of kaolinite with a local appearance of dickite in the <2 µm fraction. However, IRS analyses show the presence of dickite and kaolinite mixtures. The content of dickite amongst the kaolinite varies from 20 to 50%. These results suggest that the onset of transformation of kaolinite to dickite can be observed in the studied sandstones with increasing burial depth.

The vermiform kaolinite crystallized during early diagenesis and the blocky kaolinite and dickite formed in the later diagenesis. A temperature range of about 25-80ºC is most probable for the studied kaolinite precipitation, whereas dickite forms at about 120ºC.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Sorption properties of naturals and modified clay minerals

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The sorption capacity of smectites (montmorillonites) is smaller than that of standard sorbents. It is easy, however, to modify the structure and properties of smectite-rich rocks, the raw materials for the production of sorbents, bleaching earths, and catalysts. Mixed sorbents, obtained from two or more highly dispersed components (‘nanocomposites’) can show a synergetic effect, and hold out prospects for various applications. An example of a mixed-sorbent system is an aluminosilicate containing interlayer carbon structures or inorganic gels. Such sorbents are good carriers of catalysts used in reducing NO_x to N_2 (GRZYBEK, 2007), and deactivating toxic SO_2 in exhaust gases.

Here we report the results of our studies on the sorptive properties of a mixed Na-montmorillonite-silicic acid gel sorbent. The sorption of water vapor increases after gel modification due to an increase in the number of polar sorption centers (OH groups in particular). In the case of benzene vapor, the enhanced sorption capacity can largely be ascribed to extension of the mesoporous structure having a high thermal stability. Benzene sorption is reversible at high relative pressures. Montmorillonite modified with silica acid gel is potentially useful for removing benzene contaminants from chemical laboratories.

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***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
www.Mineralogia.pl

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Mineralogical composition of test brick samples from illite and chlorite rich clay with pore forming additives (Tiszavasvári, Hungary)

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The physical and chemical stability of newly formed phases has major influence on the microstructure of products. By the addition of pore forming (PFA) materials to the raw clay, the transformations are presumably changed.

Frequently used PFA are of mineral or organic origin. Beyond the increase of porosity in brick products, PFA has the role to intake additional heat during firing. This led to the use of materials which decompose by oxidation - high carbon content in organic or inorganic form.

This investigation deals with the results of experiments made on illite and chlorite rich brick clay from east Hungary (Tiszavasvári). As PFA-s sawdust, sunflower seeds hull, rice husks, lignite and fuel grade coke (petrol-coke) were used. The mineralogical composition of test samples was investigated by X-ray Powder Diffraction (XPD) for each series. The standardless semi-quantitative composition of samples was calculated by Full Pattern Matching method (with pseudo-Voigt fitting algorithm) of Diffrac*Plus* Eva software package.

The changes in mineralogical composition of fired samples are correlated with two basic properties of PFA-s:

1. the heat produced by oxidation, determined by derivative thermal analysis,
2. pore forming capacity, deduced from the apparent porosity of test samples.

Two types of the same clay were used, with similar mineralogical and chemical composition. After firing quartz, K-feldspars and albitic plagioclase are the main phases. Hematite, gehlenite and spinell (all <5 wt.%) phases are newly formed components. Variation of K-feldspar type and percent with the PFA type and added quantity is observed. Illite and muscovite are transformed into the spinell phase and K-feldspar. Quantity of hematite is dependent on the clinochlore presence, without variation with porosity. This shows that closed pores are dominant in the microstructure. Gehlenite is formed on the expense of calcite from raw clay. Presence of amorphous phase is not observed, in spite of that previous studies showed the amorphous state of PFA grains remnants.

A brick sample from the production facility was analyzed. The mineralogical composition is differing from those of test samples.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Clay mineralogy, geochemistry and pollen of the Ričice clay deposit, Croatia, a paleo-environmental reconstruction

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The Ričice deposit, as well as the whole of the Crna Mlaka Basin, is mostly composed of Quaternary clay beds, intercalated with layers and lenses of sands and fine-grained conglomerates, developed in the Pliocene-Pleistocene period.

The Rečica clay deposit is represented by a seried of sub-parallel and gently inclined, almost horizontal, layers of silty clay, which are laterally continuous. The major part of the clays is represented by the alternation of brown and grey, sometimes yellow clays that are underlain by greenish-grey and grey-blue clays. The clay deposits are 8-12 m thick.

Clays from the Rečica deposit can be classified as a montmorillonite-illite variety, in accordance with their genetic type. The main mineral constituents are quartz, 10 Å phyllosilicate (illite and/or mica) and smectite group minerals, while goethite, kaolinite, chlorite, feldspars and dolomite are subordinate to accessory minerals. The Rečica deposit can be classified as a montmorillonite-illite variety, in accordance with their genetic type. The main mineral constituents are quartz, 10 Å phyllosilicate (illite and/or mica) and smectite group minerals, while goethite, kaolinite, chlorite, feldspars and dolomite are subordinate to accessory minerals.

The clay deposit is of an allochthonous fluviatile-swamp type. The sediments with clay were deposited during the Holocene under fluviatile conditions, as well as in areas in which ponds, swamps and small lakes prevailed.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Investigation of clay fraction (<2 μm) composition for the understanding of the changes in sedimentary environments in the Arctic Ocean during Cenozoic time (IODP Leg 302 data)

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Bottom sediments between 20 and 300 m were taken from the Lomonosov Ridge (Arctic Ocean) during the Arctic Core Expedition – Integrated Ocean Deep Sea Program (ACEX-IODP). These sediments accumulated during approximately the last 50 Ma (Moran et al., 2006). The composition of the clay fraction (<2 μm) was investigated by IR and XRD methods. Semi-quantitative evaluations of the clay minerals assemblages were based on the Biscaye XRD method. The IR spectra were mathematically simulated in order to study the composition of the amorphous and crystalline phases. Peculiarities of the sedimentation environments and climatic changes in the Arctic Ocean for the last several tens of million years ago can be reconstructed.

The warm and humid climates similar to the modern tropics existed at the 50 Ma. Bentonite residual soils were formed. Then, sediments with amorphous material and silica micro-fossils were deposited in lakes or swamped areas. The content of amorphous material from the level of 45 Ma is decreased and content of clay minerals is increased in the clay fraction. A hiatus occurred from 44.5 to 18.2 Ma. After that sedimentary environments were closely related to glacial and interglacial periods in the Arctic Ocean. Modern Transpolar Drift has been changed about 13 Ma. From that time the perennial sea ice covering the Arctic Ocean has been the main source of terrigenous material.

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MINERALOGIA - ***SPECIAL PAPERS****, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Kaolinites from NW Portugal: composition, structure and properties (materials from the EUROCLAY 2007 field trip)

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During the European Clay Conference (EUROCLAY 2007) field trip, samples from three kaolin sedimentary deposits were taken: kaolinites Alvarães, Vila Chã and Barqueiros. These samples were investigated using grain size analysis, microaggregates grain size analysis, X-ray diffraction (XRD) analysis, thermal analysis and scanning electron microscopy (SEM). Physical-mechanical and physical-chemical properties were also estimated. Oriented and non-oriented samples were analysed by the XRD and quantitative analysis carried out by the RIR method. The average thickness of individual particles was calculated from XRD and the average value of basal surface was estimated from SEM. The Hinckley index was also obtained by XRD for all the samples.

Samples were taken from the sedimentary part of deposits and contain kaolinite (40 to 70%), muscovite (13-29%) and quartz (8-31%). Crystallomorphological properties of kaolinite are similar for all studied kaolinites and d(001) ranged from 7.19 to 7.22 Å. The isometric shape of kaolinite particles is hexagonal and all samples contain halloysite which can be studied by thermal analysis.

The density of solid components, hygroscopic humidity, humidity of upper and lower limits of plasticity and cation exchange capacity were estimated for all samples. From these, the plasticity index and the index of colloidal activity were calculated.

The studied kaolinite clays have poly-component compositions and different dispersion of individual particles and big aggregates. All these factors influence the physical-chemical and physical-mechanical properties. From these detailed investigations of the mineralogical composition and crystal-morphological features of the clay minerals from the kaolins of the Portugal deposits, the main factors influencing the physical-chemical and physical-mechanical properties have been deduced.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Adobe construction: examination of mineralogically different clays of Austria regarding their use as construction building materials

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The aim of this project is to find out if mineralogical patterns are correlated with physical parameters such as strength tensile, fluid and shrinking limits etc. The investigation of the material shows properties and advantages of this renewable raw building material and also point out the sustainability of adobe construction. Loam was used as a traditional construction material for more than 10.000 years and nowadays the advantages of this material are used again in many different ways.

The applications of loam range from the preservation of ancient monuments and historical buildings, to sealing compounds and low-energy housing - the so-called passive house. Loam is a sustainable, renewable material that can be recycled and therefore harmonises with nature.

Loam, a fine structured material, consists of sand, silt and clay in similar proportions. Clay as the binding agent with its typical characteristics such as swelling and shrinking, the ability to regulate air humidity, as well as its typical plasticity properties, and adsorption capacity provides reasons for finding out more about this resource.

The question beyond this project is to estimate which analysis can measure the typical properties. Also examined is whether study of the mineralogical composition can reveal the physical properties.

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

MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Changes in the porous structure of acid-activated mixed sorbent (montmorillonite – silica gel)

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More and more common use of the chemical technologies based on interfacial phenomena gives impact to search for new sorbents and new catalysts of improved parameters, that at the same time are cheap and may be produced from easily accessible, natural raw materials. Smectites (montmorillonites), forming the main component (clayey) of the bentonite rocks have moderate sorptive properties and show some instability of structure caused by swelling. On the other hand, their structure and properties may be easily modified. In addition to the known and already applied methods of modification (acid activation and intercalation), one of the more interesting and perspective methods is the formation of mixed systems (based on two or more highly dispersed components). When the size of the components approaches the dimensions typical for colloids (such systems are often called nanocomposites), the synergetic effect appears whereby the properties of the resulting mixture are no longer a sum of the properties of its individual components. A bi-component, mixed mineral sorbent (montmorillonite – silica gel) (Krzyżanowski & Łysik, 2004) was obtained from montmorillonite (separated by sedimentation from the Milowice bentonite (Poland)). The changes in the sorptive properties of the formed system were studied measuring the low-temperature sorption of argon. The changes in the porous structure were analysed by the densimetric and porosimetric studies. The small quantity of gel modifies the primary texture of montmorillonite (cp. the increase of the interpacket spaces moved away by the globular particles of silica gel) and adds adsorption centra. Both factors cause advantageous changes of the sorptive properties of the studied system. On the other hand, the globules of the silicic acid gel move away the mineral packets in a stable way, thus enhancing the interlayer space, which facilitates the acid activation process.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Silica gel modified montmorillonite as catalytic supports in deNOx reaction

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The selective catalytic reduction of nitric oxide with ammonia is used on an industrial scale to clean stack gases from stationary sources. The industrial catalyst $V_2O_5/WO_3/TiO_2$ used for this reaction, operates at a medium temperature range. Catalysis at low temperatures (413–523 K) is being actively investigated.

There has been growing interest in the use of cationic and anionic clays as catalysts or catalytic precursors for the deNOx reaction with ammonia (SERWICKA, 2001). These clays may be modified in many different ways, such as acid pretreatment and surface deposition of carbon particles, to produce materials with varying textures, structures and acidic properties (CHMIELARZ et al, 2000; GRZYBEK et al, 2001; SERWICKA, 2001).

Here we report on the performance of a silica gel-modified montmorillonite, impregnated with transition metal (Mn, Cu, Fe) oxides, in catalyzing the deNOx reaction.

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The investigation of influence of replaceable cations stabilization process on proprieties of received intercalates

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Application of chemical technologies utilising interfacial phenomena into research and into the design and optimisation of industrial processes prompts us to search for new sorbents and catalysing agents. Smectites (montmorrilonites), which are major constituents of bentonite rocks, exhibit rather poor sorptive properties and structural instability due to swelling. On the other hand, they are susceptible to processes that change their structure and properties. The search is merited for new modification methods aimed to transform the structure of those minerals through the changes of their porosity, chemical character, surface, sorptive and catalytic properties. The purpose of the research program was to establish how partial stabilisation of interpack cations should influence the intercalation process and the properties of thus obtained intercalates. Since the intercalation mechanism involves the ionic exchange, the amount of admitted oligocations should depend on their charge and the ion exchange capacity of the mineral. Controlling the amount of admitted oligocations and their size, one controls the column/support height and spacing as the parameters determining the size of micropores. The resultant form of smectite is obtained from bentonite clay from Chmielnik, by sedimentation. Li^+ ions were thermally stabilised in the sodium-lithium form of smectite with variable molar ratio Na/Li. Stabilised samples are transformed into the intercalate form by the Vaughan method. The influence of those modifications on the texture of thus obtained samples was investigated on the basis of XRD data and argon sorption measurements (77.5 K). Lasting retention of a proportion of exchangeable cations in the smectite structure causes its ion exchange capacity to decrease. It is reasonable to suppose that this modification and the intercalation process should produce systems having various numbers of oligocations between the ion packs. Such system should be characterised by an increased volume of micropores. Two tendencies become apparent: the decrease of the specific surface value with an increased proportion of lithium in the ion composition of the interpack structure and a decrease of the specific surface with the increased temperature of calcination.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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K-Ar and Rb-Sr isotope systems are indicators of the transformation of Vendian-Riphean clayey rocks of the Russian Platform.

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The paper considers geochemical behavior of K–Ar and Rb–Sr systems in Vendian-Riphean samples of clayey rocks and clayey component of sandstones from boreholes: Yarenskaya (Mezenskaya syneclise), Morsovskaya, Vorona-9 and Vorona-10 (Pachelmskiy avlakogene). Earlier on data from boreholes Gavrilov Yam, Soligalitch, Nevel, Kepina were published. The studied rocks belong to different facies, such as marine, coastal-marine or continental deposits.

The K-Ar data of Yarenskaya borehole are approximated on the straight line in the coordinate system Ar – K. That line displays the age 640 Ma and passes above the zero of coordinate system. It demonstrates presence of excess argon. The Rb-Sr isotope systems of same samples show age of 915±90 Ma that agrees with K-Ar calculated age (950±50 Ma). The part of point is approximated on the straight line, which displays age 640±80 Ma. Combined with earlier measurements, these date suggest that the studied deposits experienced several stages of epigenetic alteration. Two of these stages are registered by K-Ar and Rb-Sr geochronometers (~950 and ~650 Ma).

The K-Ar results of Morsovskaya borehole give very large dispersion. Ages lie in interval 780-1170 Ma. Rb-Sr data are calculated in six points from the lower part of the profile and show 1100±90 Ma.

All samples from Vorona boreholes can divide two groups: 1070–1080 Ma in the upper part of the profile and 1110–1370 Ma in lower part. An errorchron relationship of Rb-Sr data show 1020 Ma. We can speak about two pre-vendian events of the transformation of rocks: 1100 and 1250 Ma. Last age has isotope mark of the source rocks.

We believe that clayey rocks were lesser modified in Morsovskaya and Vorona boreholes then in Yarenskaya because their isotope systems fix earlier events.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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Specificity of phyllosilicates transformation in shallow soils on massive rocks

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The rare formation of shallow (<5-10 cm) stony soils developed on the fine earth derived from hard rocks with no admixture of extraneous material was studied in mountainous tundra and north taiga zones (Russia). These rocks are represented by alkaline (nepheline syenites) and basic (amphibolites and metamorphosed gabbro-diabase) rocks in East Fennoscandia and ultrabasic (harzburgite – peridotite with orthopyroxene) ones in the Polar Ural. The soils are classified as Leptosol s(WRB, 2006). Soils on alkaline and basic substrates are formed under conditions of good drainage. Recent pedogenic processes (transformation of soil organic matter *in situ*, formation and migration of R_2O_3-organic complexes and mineral disintegration) are combined in one soil horizon as there is not enough depth and fine earth to form a proper soil profile. In the case of nepheline syenites, the phyllosilicates in sola are only due to their presence in the substrates as a result of epigenic metamorphism. “Pre-pedogenic” alteration of amphibolites did not result in the formation of phyllosilicates which are also absent in the sola. In contrast, the pre-pedogenic alteration of metamorphosed gabbro-diabases resulted in a considerable accumulation of phyllosilicates and chlorite, micas, kaolinite, and mixed layered chlorite-vermiculite (smectite) occur in the sola. The proportion of vermiculitic (smectitic) layers in the mixed layered minerals increases in the shallow mineral horizon under litter.

Soils on ultrabasic substrates are characterized by a color indicative of gleying which takes place under alkaline conditions and with no removal of iron. The abundance of magnesium in the ultrabasic rocks enhances substrate dispersion and leads to the alkaline reaction of the soils, even though they are developed on a non-calcareous substrate under humid climate condition. The fine earth is enriched by chlorites, talc and smectites. The content of smectite increases in the clay size fraction in comparison with the silt as a result of phyllosilicate degradation and decreases in the upper horizon simultaneously with pH value.

Thus the presence of phyllosilicates in sola over basic and alkaline rocks is only due to epigenic (“pre-pedogenic”) alteration. In contrast, ultrabasic rocks are a source of easyily weatherable minerals leading to soil formation on a matrix enriched in phyllosilicates.

MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Uptake of As by 4-Na-mica and their mechanical treatment product

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Removal of As from water has been tested with materials of low cost, in which the presence of Fe and Al seems to be important. Synthetic 4-Na-mica obtained from kaolin (high cationic exchange capacity) and product of its mechanical treatment (4-Na-micaMT) – where the alteration of the crystalline structure puts in evidence the structural Fe and Al ions – are postulated as competitive materials for As uptake.

Materials were characterized by means of XRD, SEM, specific surface area and isoelectric point determination. As adsorption capacity was evaluated in both samples at pH of 7.5, adsorptions kinetics and adsorption isotherms were also determined.

The results showed that As adsorption behavior was different for each material. The As adsorption by 4-Na-micaMT was higher than that determined for its precursor, but this material requires longer contact time (six days against two hours) to reach the maximum removal capacity. This was assigned to a higher quantity of negatively charged edge sites in 4-Na-micaMT – which leads to increase of the solution pH caused by adsorption of protons.

Having in mind that at the experimental pH used – the As species are negatively charged – it was understandable that 4-Na-mica gives the biggest As uptake per a unit mass at shorter times (<6 hours). The surface charge of 4-Na-micaMT decreases when the contact time increases and consequently the electrostatic repulsion also decreases, which allows for adsorption of a higher quantity of As species. The uptake capacities were 60.7% and 96.5% for 4-Na-mica and 4-Na-micaMT, respectively, showing their potentiality in the treatment of As polluted waters.

MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Clay minerals in soil derived from phonolite of Opolno-Zdrój area, Sudety Mts., SW Poland

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Phonolites are igneous volcanic rocks with low silica content and an aphanitic to porphyritic texture. Main minerals are usually feldspathoids (nepheline, sodalite, hauyne, leucite and analcite) and alkali feldspar (sanidine, anorthoclase or orthoclase), with sporadic sodic plagioclase. Minor minerals are biotite, sodium rich amphiboles and pyroxenes along with iron rich olivine. Phonolites occur in very few localities, mainly in Scotland, Brazil, Kenya and New Zealand. Locally there are occurrences in Cornwall and Bohemia. Knowledge concerning phonolites, especially their weathering processes and products of weathering, is still scanty.

The aim of this paper was to determine the clay minerals derived during weathering of phonolites in Lower Silesia, Sudety Mts, SW Poland. X-ray diffractograms of clay fractions separated from different horizons of a cambic soil developed from phonolites will be presented and discussed at the poster.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Dewatering and neutralization of waste drilling muds

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Method for dewatering of used drilling fluids (01 05) is presented and its efficiency is evaluated in the paper. The method includes processing of liquid drilling mud waste (with the solids content from 1 to 35 wt %) into solid material having mechanical properties approaching those of ground. The solids content in the resulting waste usually constitutes 40 to 60 wt %. The dewatering process was performed using inorganic coagulants such as aluminum and iron salts as well as organic flocculants. The waste was dehydrated employing a mobile dehydration tank station. The authors show the ways of the treated waste utilisation.

INERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Studies of acid-treated clay minerals by near-infrared spectroscopy

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The potential of near-infrared (NIR) spectroscopy in characterizing acid-treated smectites is demonstrated. We have investigated the effect of clay mineral composition, content of non-swelling layers, and the presence of alkylammonium cations in the smectite interlayers, on acid dissolution rate. Detailed analysis of the NIR region is performed by comparing the first overtone (2ν) and combination ($\nu+\delta$) bands of XH groups (X = O, C) with the fundamental stretching (ν) and bending (ν) vibrations in the mid-IR region. Spectra of acid-treated samples show a gradual decrease in intensity of the structural OH overtone (near 7100 cm^{-1}) and combination (4600–4300 cm^{-1}) bands, reflecting a reduction in octahedral atoms content. The first SiO-H overtones of terminal SiOH and geminal (OH)SiOH groups near 7315 cm^{-1} and 7130 cm^{-1}, respectively, are indicatative of a partly protonated silica phase that forms during clay mineral dissolution. NIR spectroscopy confirms that trioctahedral hectorite is much more susceptible to acid attack than dioctahedral smectites. The accessibility of the interlayers to protons significantly influences the stability of smectite clay minerals in HCl. A mixed-layered illite/smectite, containging 30% swelling interlayers, dissolves more slowly than smectite of similar chemical composition. The solubility of smectites in HCl is altered if their inorganic exchangeable cations are replaced by alkylammonium cations. NIR spectroscopy confirms that small TMA$^+$ cations cause only a slight reduction in the dissolution rate of montmorillonite whereas long-chain HDTMA$^+$ cations significantly protect the clay layers from acid attack.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Effect of montmorillonite on the association constants of supramolecular complexes with fluorescence dyes

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Inclusion complexes between α-, β-, γ- cyclodextrins (CD) and fluorescent dyes (e.g., coumarin) represent confined host/guest associations showing certain spectral and fluorescence properties (Angelova et al., 1999). Here we determine thermodynamic equilibrium constants to assess the conditions under which such complexes are formed in aqueous media. We then investigate the effect of montmorillonite on the formation of host/guest complexes in solution. This was important to prepare functionalised thin layered nanocomposites with fluorescent properties. Changes in the equilibrium constants of host/guest complex formation were investigated with static fluorescence spectrometry. The thin layered nanocomposites were further characterized by FTIR and far-IR spectroscopy to assess the effect of changing the nature of the interlayer material. In agreement with Sen et al. (2005), an increase in β-cyclodextrin concentration causes coumarin fluorescence intensity to increase. This may be ascribed to the complete or partial desolvation of the guest molecule during complexation. The loss of hydration water causes a decrease in nonradiant relaxation.which, in turn, led to an increase in the population of electronic excited states. The Benesi-Hildebrand method was used to determine equilibrium constants. Fluorescence spectra of coumarin-C522 was measured at an excitation light wavelenght λ_{ex}= 415 nm. For example, the equilibrium constant for the β-cyclodextrin/coumarin-C522 complex, obtained from the linear regression of the change in fluorescence intensity with β-cyclodextrin concentration was: $K_{C522:\beta-CD}^{20^\circ C}$ = 2747.9±163.8 $dm^3.mol^{-1}$.

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Aluminosilicate nanotubes derived from kaolinite group minerals

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Chemical modifications of clay minerals have wide potential for scientific and industrial applications. The ability to combine the properties of inorganic matrix and organic molecules at a molecular level opens the way to design improved nanocomposites. Nanotubular materials have received much attention due to interesting catalytic properties. Therefore the objective of this study was to investigate the possibility of delamination and rolling of kaolinite layers using intercalation/deintercalation method.

For the experiments kaolinites with different crystallinity and halloysite from polish deposits were used. The experimental procedure followed the synthetic route proposed by Gardolinski & Lagaly (2005a,b) and consisted of four following stages: (1) preparation of dimethyl sulphoxide precursor complex, (2) interlayer grafting with 1,3 butanediol (3) hexylamine intercalation and (4) deintercalation using toluene as solvent. Structural perturbations and morphology changes of minerals were examined by XRD, FTIR and high resolution SEM coupled with TEM mode.

The particle size of minerals subjected to modifications decreased considerably, which indicates partial delamination. Kaolinite particles which exhibit tubular morphology or show rolling effects were observed using TEM. The obtained nanotubes have mean diameter ~30 nm and are on average 150 nm long.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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Clay minerals and slope stability in Quaternary sediments in landslide areas of the Wienerwald Flysch Zone (Vienna Forest/Lower Austria)

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The Rhenodanubian Flysch of the northern Vienna Forest is composed of various layers of sandstones, marly shales, calcareous marls and clay schists which are covered by Quaternary periglacial cover beds and loess deposits. This area at the margin of the eastern Alps represents an undulating landscape of the Austrian low mountain regions.

The Vienna Forest Flysch region is considered to be susceptible to landslides. The alternating sequences of permeable and impermeable layers influence the stability of slopes negatively. Therefore slope stability is mainly dependant on the distribution of Quaternary layers and its specific clay mineralogy of clayey and marly layers.

In general, Quaternary sediments are situated on top of flysch sandstone. The base of the Quaternary deposits derives from periglacial solifluction processes, namely the Basal Periglacial Cover Bed, and consists of clays and marls mainly which have a high content of the swellable clay mineral smectite. Therefore the Basal Periglacial Cover Bed is characterized by a high plasticity and impermeability. These features are responsible for the formation of potential slip surfaces in the study area. The hanging layer is composed of up to four metres of permeable loess, which was deposited during the Würmian period. The top of the sequence is characterised by a further periglacial cover bed, composed of a mixture of loess and sandstones, which originates from the Late Glacial (Upper Periglacial Cover Bed).

On the basis of field surveys, sedimentology, mineralogy and slope stability modelling, the results from investigations on recent landslides are demonstrated.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Mineral analysis and energy industry applications

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Recent developments in diffraction and spectroscopic techniques, computing, and methodology at Chevron have resulted in: (1) a faster and more accurate means of quantitative mineral analysis of clay-bearing sedimentary rocks, (2) a more comprehensive means of structural analysis and characterization of mixed-layer clays, and (3) a way to evaluate the chemical composition of individual species that coexist in complex mineral assemblages.

Comprehensive mineral characterization is of primary importance to the energy industry in understanding the geological relationships of reservoir and seal formations, mineral influences on porosity and permeability, reactivity with drilling fluids, and the high sensitivity of the rock matrix on wireline logs and log modelling. The clay content in sedimentary rocks is a critical variable that is used to calculate fluid saturation and determine reserves.

Quantitative phase analysis (QPA) of sedimentary rocks is a significant challenge because of the presence of clay minerals. Even "clean" sandstones can have significant clays of different types, 15 to 25 % clay or more and require special consideration in reservoir characterization and formation evaluation. It is well known that such mineralogy is difficult to quantify because clay minerals have fine particle size, platy shape, and chemical and structural variability.

A new technique for QPA by X-ray diffraction (QXRD) resulting in the genetic algorithm based program QUANTA greatly increases the accuracy and speed in mineral quantification of clay bearing sedimentary rocks. In addition to the QPA of whole rock samples, analysis of clay separations by simulation of diffraction patterns from oriented specimens provides important information about the actual structure of mixed-layer clays, their origin and transformation.

In addition to XRD methods, thermal analysis studies on rocks and mineral standards are underway to gain additional structural information as well as to gain understanding of surface properties that may have important implication in the production of hydrocarbons. Demonstrations and case studies will be presented and discussed.

MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Biological processes during clay maturation

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Clay maturation to ameliorate plasticity and workability of the raw material is a process employed since ancient times. The scientific knowledge is sparse, even so it could be important for new technological applications.

There are no detectable changes in mineral phases and bulk chemistry during clay maturation, but changes within the soluble fraction, especially soluble salts and pH were observed. Bacterial metabolism interacts with the chemical milieu, so biological processes could contribute to the observed change in plasticity.

We show, for two industrially used clays from *Westerwald*, Germany, that also the indigenous bacterial population of the raw material is altered during the clay maturation.

Over 80 days of experimental period, we found changes in the number of micro organisms (*colony forming units cfu*) and their activity (*esterase activity*), which correlate with changes in pH. There are also changes in bacterial community composition, shown by DNA fingerprints (*Denaturing Gradient Gel Electrophoresis DGGE*).

There are many possible interactions between micro organisms and clay minerals. Whether micro organisms or biological factors drive the change in properties of the raw material, or whether they just react to the altered milieu, remains to be elucidated.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Layered sodium disilicates as precursors of mesoporous silicas: hydration of δ-$Na_2Si_2o_5$ and α-$Na_2Si_2O_5$

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Among various crystalline polymorphs of layered anhydrous $Na_2Si_2O_5$ of particular significance is δ-$Na_2Si_2O_5$, which can react with water to yield a hydrated layered silicate known as mineral kanemite $NaHSi_2O_5 \cdot 3H_2O$, precursor of mesoporous FSM-type silicas. Hydration of other disilicates has not been studied in detail. The aim of the present work was to get more insight into the structural transformation accompanying the hydration of α-$Na_2Si_2O_5$ phase and to compare it with the hydration of δ-$Na_2Si_2O_5$. Reaction of δ-$Na_2Si_2O_5$ and α-$Na_2Si_2O_5$ with water at ambient conditions leads in the first case to kanemite, with basal spacing d=1.025 nm, in the other to a crystalline solid, assumed to be the layered hydrated α phase of yet unsolved structure, with basal reflection corresponding to d=0.96 nm. Important differences have been observed in the kinetics of δ-$Na_2Si_2O_5$ and α-$Na_2Si_2O_5$ reaction with water. The former substrate undergoes hydration very swiftly (5 min), the latter is distinctly slower to transform, but the process is eventually completed after 8 h treatment. The difference in the hydration behaviour is assigned to the different structural properties of both disilicates. Larger six-member rings in the δ-phase facilitate cation exchange required for the phase transformation. The interlayer water trapped between the layers of hydrated α-$Na_2Si_2O_5$ is more strongly bound than in kanemite. The observed weight loss can be explained by assuming the presence of two water molecules per chemical formula of the hydrated α-phase ($NaHSi_2O_5 \cdot 2H_2O$). In view of this the lower basal spacing observed for hydrated α phase may be attributed to the lesser amount of water of hydration trapped between the layers. It is likely that smaller interlayer distances contribute to the stronger binding of water in this material.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Origin of clayey materials deposited during Aptian/Albian emersion in Istria, Croatia

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The subject of this study are clayey materials deposited during Late Aptian / Early Albian long-lasting emersion phase in Istria (period of 11-19 million years). When they show indication of subaerial exposure and pedogenesis they are considered paleosols. The goal was to estimate the provenance of clayey materials. Investigations were based on detailed sedimentological, geochemical, and mineralogical analyses of clayey materials and undissolved limestone residue from the bottom of clayey horizons. Considering isolation of Adriatic carbonate platform during Aptian/Albian, there are three possible sources of material forming investigated clayey materials: (1) undissolved limestone residue; (2) volcanic material; and (3) aeolian material. Signs of vadose zone (geopetal structure, crystal silt) and small depths of palaeokarstification in limestone, as well as, low weight content of indissoluble limestone residue indicate small contribution of undissolved limestone residue in formation of investigated clayey materials. There are signs (immobile chemical elements proportions; negative europium anomaly; fragments of pyroclasts with altered volcanic glass; zircon, feldspars, pyroxene and amphibole grains in sand fraction; smectite in undissolved limestone residue) of volcanic material contribution in formation of clayey materials. Volcanic material probably came after resedimentation because during Aptian and Albian there is no known calcium-alkaline volcanism in neighbouring areas. Irregular and rounded forms of volcanic minerals in clayey materials are also in favour of resedimentation. Aeolian dust is probably the most important component of source material. Significant atmospheric circulation and accumulation of great amount of aeolian material during Aptian and Albian due to arid climate on the land; domination of smectite (formed by alteration of great amount of volcanic material widespread due to strong volcanic activity and formed by authigenesis in soils as a consequence of hot climate with contrasted seasons); very fine grain size of investigated clayey matrix which could enable long transport; and presence of metamorphous minerals (tourmaline, garnet) are indications of aeolian origin.

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The redox properties of iron- and copper-impregnated montmorillonites: effect on DeNOx activity

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Selective catalytic reduction (SRO) of NO with ammonia is still the only realistic industrial process for removing nitrogen oxides from stack gases. Many different materials have been suggested as possible catalysts for this reaction. In this regard, layer silicates are especially interesting because they are cheap, natural materials whose texture and chemical properties may be modified. Here we investigate the redox properties of some natural and surface-modified montmorillonites that have been impregnated with copper and iron nitrate in relation to SCR.

The following layer silicates and their modified forms were used: a commercial bentonite from Fluka(B), montmorillonite separated from Milowice bentonite (Mt), B and Mt treated with acid (BH and MtH), a commercial acid montmorillonite (K5), and montmorillonites intercalated with hydroxy-Al cations (BAl, MtAl, K5Al). All of the above materials were then loaded with 5 wt % Cu and Fe using the incipient wetness technique and aqueous solutions of copper(II) nitrate and iron(III) nitrate.

The samples were characterized by argon sorption (specific surface area) and X-ray photoelectron spectroscopy (surface composition), while their reductive properties were assessed by temperature programmed reduction (TPR) and N_2O reduction with H_2. The latter reaction was chosen because N_2O, like NO, is rather difficult to reduce. We also tested selected samples for their capacity to reduce NO with ammonia under the following conditions: 800 ppm NO, 800 ppm NH_3, 3% O_2, He; mass of catalyst 200 mg; flow 100 ml/min.

The results show that the redox properties of montmorillonites are related to the origin of the materials and chemical modifications, of which acid pretreatment is the most important. These properties influence SCR activity and the formation of N_2O as a by-product.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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The removal of nitrogen oxides by modified montmorillonites

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The application of layered aluminosilicate minerals as catalysts in both industrial and environmental protection processes has been intensively investigated for a couple of years. Selective catalytic reduction (SCR) of nitrogen oxides by ammonia, hydrocarbons and alcohols is now among the most thoroughly studied catalytic reactions.

The goal of the present work is to determine the influence of the synthesis route of the catalysts, including the structure of catalysts obtained from modified aluminosilicates promoted with copper, iron, and silver ions, upon their catalytic properties in SCR reaction. Our catalysts were obtained from different starting materials *e.g.* montmorillonite originated from bentonite from Milovice, commercially available montmorillonite (Fluka), commercially available bentonite (Fluka), and commercially available acidic montmorillonite K5 (Fluka). These starting materials were modified by acidic activation and intercalation with hydroxoalumium species (with the use of Chlorohydrol). Then the active copper, iron and silver ions were deposited on both modified and unmodified montmorillonite. Metal cations were introduced from nitrate solutions using the wetness impregnation method. The content of active species was estimated as 5 wt%.

Thus prepared catalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, and the temperature - programmed reduction was performed. The textural properties were determined from low temperature argon adsorption. Moreover, the catalytic activity and selectivity of our catalysts were tested for SCR reaction.

Our results indicate that some of the modified montmorillonite – based catalysts show conversion higher than 90% and the amount of N_2O formed in side reaction is very small. Furthermore, the catalytic activity of our catalysts strongly depends on the synthesis route and the amount of deposited active species.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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Variation of mineralogy during the beneficiation of kaolin from Rio Capim, Pará, Brazil

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Kaolin mined from the Ipixuna deposit of Pará Pigmentos SA in the Capim River area in northern Brazil has been studied at various stages of beneficiation to determine the behaviour of Fe- and Ti-bearing minerals, which can be deleterious to the brightness of the product and consequently its use for paper coating.

Chemical analyses of the raw ore, the intermediate products of beneficiation, and the final product demonstrate a moderate but distinct reduction of the total Fe content through the removal of Fe oxides in the course of beneficiation. XRD and Mössbauer spectroscopy showed the principal pigmenting minerals to be hematite and goethite. However, an assortment of techniques proved necessary for a comprehensive characterization of the sample mineralogy. Thus, while XRD tentatively indicated the presence of gibbsite, IR spectroscopy provided conclusive evidence for this mineral. In particular the reject of a magnetic separation stage, being enriched in Fe and Ti, offered good possibilities for the study of the mineralogical speciations of these elements.

The Ti contents were primarily reduced due to the removal of anatase during particle size fractionation and dithionite reduction. While the Fe content of the final product is structurally bound in kaolinite, Raman spectroscopy indicated that Ti in the form of anatase have been only partly eliminated. The remnant Ti to be bound both structurally in kaolinite and anatase. Mössbauer spectroscopy confirmed chemical analyses indicating the final sample to contain ~ 0.7 % structural Fe^{3+}.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Palladium bentonites as catalysts

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Clay rocks in their natural and chemically treated forms are widely used as catalysts. Different cation-exchanged clays are also useful in this regard. Since the cation-exchanged forms occur under natural, geological conditions, both clay rock and cation type can profoundly influence the transformation of organic matter in nature. Noble metals, including silver and palladium in different oxidation states, are widely applied as catalysts. For example, palladium is used for hydrogenation, while silver is an important catalyst in photochemistry. We have prepared palladium- and silver-bentonites, and determined their properties by X-ray fluorescence spectroscopy, X-ray diffraction, thermal analysis, redox potential measurements, and scanning electron microscopy.

The sorption of palladium(II) ion by sodium-bentonite was studied. To avoid Pd(II) hydrolysis and acid decomposition of the clay, Pd(II) was applied as positively charged $[Pd(NH_3)_2]^{2+}$ and $[Pd(en)_2]^{2+}$ complexes. X-ray diffraction and thermal analysis showed little, if any, interlayer penetration by palladium(II) ions; that is, these ions were largely sorbed on deprotonated silanol sites on the surface of montmorillonite.particles. The sorbed quantity of palladium(II) ions was in fairly good agreement with the concentration of surface silanol sites. Thermal analysis showed that the palladium(II) sorbed on clay mineral surface can be reduced to Pd(0). By applying palladium as a complex to bentonite, catalysts containing Pd with two or zero oxidation state can be produced. An increase in the concentration of amorphous phases in bentonite, induced by thermal treatment, favoured catalytic activity.

MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Crystalline morphological peculiarities of kaolinites from the lateritic weathering crust of South Vietnam granites

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Evolution of the crystalline morphological properties of kaolinite in the zonal weathering crust of granites in the South Vietnam was investigated by the complex methods: scan electron microscopy, X-Ray diffraction, electron paramagnetic resonance, infra-red spectroscopy, thermal analysis. Samples were taken by the profile of weathering crust (WC) from the bottom to the upper part from the kaolinite zone and bauxite zone. Natural samples and fractions (< 63 mkm) were separated for this study.

Kaolinite has vermiculite-like aggregates (up to 10-20 mkm by C axis). In the central part (CP) of kaolinite zone aggregates composed ordered kaolinite particles with hexagonal shape and smooth basal surface up to 3-5 mkm. To the upper and bottom part of this zone aggregates come smaller, and value of basal surface is decrease and content of halluasite is increase. D (001) and average particles thickness is changing in the similar directions.

Intensities of reflections on the first (02*l*, 11*l*)) and second (20*l*, 13*l)* ellipses were investigated by the electronographes from the textures. Structural ordering varied in different part of WC. Changes of structure by the EPR are connected with three line groups: 1- Fe^{3+} in tetrahedral layers, 2- exchangeable cations in octahedral positions (with reduction of the positive charge under replacement $Mg^{2+} \rightarrow A1^{3+}$) and 3- Fe-rich magnetic phases. Degree of the resolution fluctuation bands of the hydroxylic groups, ratios of D3620/D3692 and band 1095 sm^{-1} in the field of Si-O fluctuations were studied by the WC. The characteristics of kaolinite are connected with physical, chemical and hydrodynamical conditions of the formation of the zonal lateral section of the lateritic WC of the granites in the South Vietnam.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Stability of smectite in the presence of metal iron

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To predict the long-term properties of bentonite barriers in high-level nuclear waste repositories, it is essential to study interactions between smectite and metal iron. Studies of iron-clay interactions have shown the systematic destabilization of the initial clay material and the subsequent crystallization of reaction products. The aim of the present work was to investigate smectite stability in the presence of metal Fe.

In our experiments the <2 μm fractions of Na-saturated smectites were used. The mixtures of smectite/iron powder/distilled water = 1.5 g/1.5 g/70 ml were prepared in an glove-box (N_2 atmosphere). A batch experiment was performed at 75°C for 35 days in an oxygen-free system. The reaction products were examined by XRD, FTIR, HRTEM, BWA (Bertraud-Warren-Averbach) technique.

In all reacted samples residual metal Fe was present together with newly-formed magnetite. Also small amounts of 1:1 phyllosilicates and lepidocrocite were formed. All diffraction peaks of smectite decreased significantly. Significant changes were observed in the octahedral sheet of smectites. These spectral changes are consistent with dehydroxylation and changes in bonding between tetrahedral and octahedral sheets. Fe oxides and oxyhydroxides were formed consequently from OH groups. BWA technique reveals decreasing of crystallite thickness of smectites after experiments. The same result was confirmed by HRTEM. The layer charge was determined by methylene blue method. During experiments the layer charge of all smectites decreased as proved by an increased quantity of monomers and H-dimers.

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Loess and paleosols from Aschet, Austria – clay minerals as indicators of weathering intensity

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Loess/paleosol sequences of the Upper Pleistocene from Aschet in Upper Austria were studied by an interdisciplinary group of scientists. One part of the investigation focused on the clay mineralogical composition of the <2 µm clay fraction and on granulometric analyses.

The paleosols have been formed during interglacial paleoenviromental conditions of different age as well as during interstadial conditions, characterised by variable pedogentic processes corrresponding to the paleoclimatic change.

The Pleistocene environments of glacial and interglacial origin generally relate to alternation of more physically and more chemically altered clay assemblages, respectively. In cold periods sediments are enriched in well-crystallized illites, chlorites and feldspars, whereas warm periods correspond to enhanced amounts of kaolinite and expandable minerals such as smectites, vermiculites and mixed layer minerals.

The paleosols in the Aschet profile are characterized by the occurrence of vermiculites, mixed layered minerals like chlorite/vermiculite and illite/chlorite/vermiculite as products of clay transformation during pedogenesis. In the loess sequences illitic material and vermiculites are dominant.

The grade of weathering intensity of palesols can be used as a record for the intensity of pedochemical processes and is therefore a helpful tool for reconstruction of paleoclimates. However, clay minerals basically express the intensity of weathering, and especially of hydrolysis, in the land masses adjacent to sedimentary basins. The information provided by pedogenic minerals fundamentally integrates the combined effects of temperature and precipitation, with sometimes additional data on the rainfall seasonality or drainage conditions. The climatic interpretation of pedogenetically formed clay minerals is based on the variations of illite and chlorite crystallinity and on the relative abundance of smectite and other expandable clay minerals.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Acid sites developed on aluminated PCH derived from Laponite

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Al-containing porous clay heterostructures (PCH) have been derived from Laponite via two methods: direct and post-synthesis alumination using aluminium isopropoxide as Al source. The surface acidity of the samples was studied by means of the temperature programmed desorption of ammonia and pyridine adsorption. TPD-NH_3 showed that the lowest amount of ammonia was adsorbed on non-aluminated sample PCH-Lap and desorption peak was centred at 220°C. For both the directly and the post-synthesis aluminated samples the desorption maxima shifted to higher temperatures indicating increasing strength of acidic sites available for ammonia adsorption. Relative intensities of profiles showed that higher amount of ammonia was adsorbed on post-synthesis aluminated samples, indicating that this method of alumination was particularly efficient in developing surface acidity. Within the samples aluminated by the same procedure the acidity increased with increasing amount of aluminium used for preparation of sample (Si:Al = 40 or 10). The nature of acid centres was assessed by using IR spectroscopy to monitor the characteristic vibrational modes of adsorbed pyridine. Non-aluminated PCH-Lap exhibited only weak Lewis acid sites, which disappeared completely after heating at 200°C. In contrast, the IR spectra of aluminated samples clearly showed the presence of the absorption band at 1546 cm^{-1} characteristic for pyridinium cations and indicative of Brønsted acidity. In the directly aluminated samples this band disappeared already after heating at 200°C, while post-synthesis aluminated samples had to be heated to 300°C to achieve this effect. This shows that post-synthesis alumination yields acid sites of higher strength. Acidic protons generated by alumination are exchangeable, which allows for further modification of PCHs. In the present study the samples were functionalized by cation exchange with catalytically active metalloporphyrin (MnTMPyP) species. Near infrared spectra revealed that the exchange was accompanied by the disappearance of Si-OH overtone (~7320 cm^{-1}).

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Acid dissolution of differently ordered kaolinites

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The influence of kaolinite structure ordering and the mineral composition of kaolin samples on their stability in HCl was investigated. Three kaolins Gold Field (GF) from Pugu Hills (Tanzania), Vyšný Petrovec (VP) from Slovakia and KGa-2 (KGa) from Georgia (USA) were studied. In addition to kaolinite, the XRD analysis of the original samples revealed a minor (<5 %) content of quartz and anatase in GF and KGa, respectively. A major (~50 %) content of accessory minerals such as quartz, feldspars, muscovite, (or illite) and smectite were identified in VP. The structural ordering of the kaolinites was determined by AGFI index, measured using the 02*l* and 11*l* reflections (APARICIO et al., 1999). GF and VP samples contained well-ordered kaolinites ($AGFI_{GF}$ = 1.6; $AGFI_{VP}$ = 1.3) whereas the structure of KGa kaolinite was less-ordered ($AGFI_{KGa}$ = 0.8). Dissolution of the samples was performed in 6 M HCl at 95°C for 4 to 36 hours and the solid reaction products were investigated by XRD, SEM and IR spectroscopy. The gradual dissolution of kaolins in HCl was monitored by IR spectroscopy in both the middle and near regions of the spectra. The dissolution rates of kaolins were found to be different. GF kaolin was the most stable in HCl due to a high degree of kaolinite ordering and low content of admixtures. On the other hand, the dissolution rate of KGa was higher because of lower ordering of the kaolinite structure. The VP kaolin was the most soluble clay in spite of the relative high AGFI index of the kaolinite present in this sample. The presence of a high content of admixtures more soluble than kaolinite (e.g. smectite or muscovite) influenced the total dissolution rate of this clay.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Characterization of structural changes in redox-modified smectite using near-infrared reflectance spectroscopy

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Structural changes in smectites due to redox reactions have been characterized by various methods, including mid-range (600 to 4000 cm^{-1}) infrared spectroscopy (FTIR), and have revealed extensive structural alterations in highly reduced, Fe-rich smectites; but, the magnitude of structural change depends on the extent of reduction. For example, reduction levels below about 1.0 mmole Fe(II)/g clay apparently evoked only minor, if any, irreversible changes in the clay structure. Some controversy exists, however, as to the extent of irreversible alteration that occurs, suggesting that further inquiry is needed. The objective of the present study was to apply near-infrared (NIR) reflectance spectroscopy to further probe high- and low-Fe smectites after various redox treatments. Three NIR spectral regions can be identified: (1) the region between 6400 and 7400 cm^{-1}, attributed to the first overtone of the hydroxyl stretching mode; (2) the 4800-5400 cm^{-1} region, attributed to H_2O stretching and bending combination modes; and (3) the 4000–4800 cm^{-1} region, attributed to the combination of the stretching and deformation modes of the M1M2-OH units in smectites (M1 and M2 represent dioctahedral cations). In the present study, smectites low (Upton) and high (SWa-1) in Fe were investigated over the 8000–4000 cm^{-1} frequency interval before and after reduction. Results indicated that the most intense bands were due to the first overtones of stretching vibrations due to structural AlFeOH and FeFeOH and much broader adsorbed HOH, occurring at about 7070-7105 cm^{-1}, 6930-7010 cm^{-1}, and 6812-6855 cm^{-1}, respectively. Upon reduction of Fe(III) to Fe(II), structural OH stretching overtone bands shifted to greater frequency and lost intensity, indicating that the bonding and/or symmetry properties in the octahedral sheets changed. Significant shifts in peak position and intensities also occurred in the structural OH combination bands. Shifts in bands for adsorbed water were mixed. These observations reveal that shifts in the mid-IR region are amplified in the NIR region and may prove useful for discerning various subtle effects of Fe redox treatments on structural properties of the smectite.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Effect of sonication on the redox state of vermiculites

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Recently, we have proposed the use of sonication in H_2O/H_2O_2 (30%) mixture (volume ratio 1:1) as a soft method for particle size reduction of vermiculites. And indeed repeated sonication causes a particle size reduction to about 70 nm for the Santa Olalla and to 45 nm for the Ojén vermiculite, and a concomitant rise of the S_{BET} from the initial value of about 1 m^2/g for the raw samples to 36 and 54 m^2/g for the Santa Olalla and Ojén samples, respectively. The crystal structure of Santa Olalla vermiculite is almost unaffected by sonication, whereas the Ojén vermiculite shows some broadening of the diffractions peaks, probably due to the stronger reduction of the particle size. Apart from particle size reduction sonication produces delamination in both vermiculites, and in addition it initiates scrolling up of the Ojén vermiculite particles.

However, the question arises whether the effects described have been enforced by the strong oxidation effect of the hydrogenperoxide. Therefore, Fe^{2+}/Fe^{3+} ratio has been determined by means of Mössbauer spectroscopy. Whereas this ratio remains almost constant in the Santa Olalla vermiculite, it decreases significantly from 0.30 to 0.08 in case of the Ojén sample. This is accompanied with a decrease of the layer charge, which is indicated in the infrared spectrum of a sonicated and ammonium saturated sample by the appearance of the NH_4^+ bending band at 1400 cm^{-1} together with the absorption band at 1430 cm^{-1}. In the non-sonicated sample only the absorption band at 1430 cm^{-1} is shown. The increase of the absorption band intensity at 3650 cm^{-1} suggests an increase of Fe^{3+} .

Sonication in pure water leads also to an effect on the Fe^{2+}/Fe^{3+} ratio of the Ojén vermiculite, but now in the opposite direction: the fraction of Fe^{2+} is roughly twice as high as without sonication. Again the Santa Olalla Fe^{2+}/Fe^{+3} ratio remains unchanged. The surface area S_{BET} of the reduced Ojén amounts to 50 m^2/g, thus it is in the same order as in the presence of hydrogenperoxide.

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Study of the Hofmann-Klemen effect on synthetic Zn-Stevensite

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In this study, we planed to synthesize stevensite-like sauconite having the general composition : $Si_4 (Zn_{3-x}\ \ _x) O_{10} (OH)_2 R^+_{2x}$, where   is a vacant site. Our objective is then to study the possible migration of Li^+ and Zn^{2+}cations within such trioctahedral smectites under heating following the so called Hofmann-Klemen (HK) – effect (HOFMANN & KLEMEN, 1950). The initial gel was distributed in 5 aliquots into teflon coated hydrothermal reactors with distilled water which were hydrothermally treated at 80, 100, 120,150, and 200 °C during 30 days. From X-ray diffraction the synthesized samples are clearly smectites. The number of vacant sites (x) per half unit cell ($O_{10}(OH)_2$) ranges from nearly 0 to 0.23 but no simple relationship between x and temperature of synthesis can be drawn. Samples were then Li^+- and Zn^{2+}- saturated, and overnight heated at 300°C (HK treatment). Cation exchange capacity measurements were made by FTIR spectroscopy on NH_4^+-saturated samples. After LiHK treatment, the structural formula of samples can actually be expressed as: $Si_4\, Zn_{(3-x)}Li_x\, O_{10}\, (OH)_2\, NH_4{}^+_x$, while after ZnHK treatment, it can actually be expressed as : $Si_4\, Zn_3\, O_{10}\, (OH)_2$. Concurrently, XRD and FTIR data showed that the samples moved from Zn-stevensite-like structure to Zn-talc-like structure after ZnHK-treatment. These results are interpreted as evidence that Zn^{2+} (and Li^+) migrated into the previous vacant sites under HK treatment.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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Why do two apparently similar German ceramic clays display different rheological properties during maturation?

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Maturation of clays is an important processing step to adjust rheological properties for diverse industrial applications. To elucidate the maturation process two clays (W1, W2) from different deposits (Westerwald, Germany) have been investigated over a period of three month. The phase content of each clay was determined for both bulk material and several grain sizes by means of XRD measurement and Rietveld analysis. Kaolinite, illite, quartz, K-feldspar, plagioclase, rutile, smectite, and illite/smectite mixed layer minerals were identified. The proportion of less than 10% smectite in the mixed layer minerals was estimated from simulations of pattern using NEWMOD. The quantitative phase content was crosschecked with the chemical composition measured by XRF. Deviations of ~1.5% Fe_2O_3 were assigned (a) to the presence of Fe-bearing phases detected by electron microscopy and (b) to Fe-bearing strongly disordered kaolinite. PA-curves from STA-measurements and application of the Hinckley index confirmed structural disorder.

The samples W1 and W2 showed different rheological behavior although having nearly identical chemical and mineralogical composition. Our results indicate no mineralogical changes during maturation process, but variations in pH, conductivity and release of soluble salts after a time of 10 days. Differences between W1 and W2 were observed in grain size distribution and in the presence of Fe-bearing phases: additionally to Fe(hydr)oxides, marcasite and siderite were found in W1. Whether micro organisms or biological factors drive the change in properties of clays remains to be elucidated.

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Shale - inhibiting fluids for HDD applications

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Within the scope of HDD projects there is always a risk of significant problems especially in formations containing shales. The changed tension and the input of drilling fluid into formation may cause destabilization of the near wellbore area.

To assure a reliable and cost-effective performance of drilling projects in shales a careful selection of adequate shale inhibiting fluids is necessary both before and during the drilling process. And drilling fluid parameters must be continually adjusted due to the needs of the current drilling situation.

To simulate this phenomenon lab investigation was undertaken using shale material(s) in contact with different shale inhibiting muds. The aim of our study was to develop a method of classification inhibitive properties of drilling fluids under conditions similar to those in the wellbore and to create the potential for drilling fluid optimization.

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Ammonium bearing illites in Carboniferous shales of the North German Basin

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The North German Basin (NGB), as a part of the Central European Basin CEB, represents a key area for the investigation of nitrogen accumulation in natural gas reservoirs. Especially in the eastern part of this basin, gases of Rotliegend reservoirs are nitrogen-rich with up to 90% N_2. Our studies focus on the processes of the ammonium (NH_4^+) fixation in clay minerals, the deep burial and storage, and the release and migration of nitrogen on the example of Namurian and Westphalian shales.

The principal source of nitrogen in sediments is the decomposition of organic material during diagenesis that results in inorganic nitrogen compounds such as ammonium. This NH_4^+ may be substituted for K^+ on the interlayer sites in clay-minerals. Mineralogical and element geochemical examinations and K-Ar dating on NH_4^+-bearing illites indicate a mixture between detrital and diagenetic origin which was formed or affected during burial diagenesis and during interaction with brines. The detrital components are characterized by low NH_4^+-N contents <1000 ppm whereas more than 2000 ppm nitrogen was detected in diagenetic illites formed during burial. Namurian shales and associated illites from one well of the central part of the NGB are characterized by a depletion of nitrogen connected with an isotopic shift suggesting a release of nitrogen during fluid rock interaction (Mingram et al. 2005) which is probably associated with NH_4^+ or K^+ exchange processes. Intensive fluid/rock interaction events are evidenced by fluid inclusion data (Lüders et al. 2005).

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Hydrotalcite-derived Cu-Zn-Al-Zr mixed oxide catalysts for CO_2 to methanol conversion

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Hydrotalcite-like compounds (HTlc) can accommodate a number of different M^{2+} and M^{3+} cations in different proportions and can be relatively easily synthesised. Mixed oxides obtained after calcination of HTlc posses unique properties, such as high specific surface area and homogeneous dispersion of metal ions, which makes them attractive materials for catalytic applications.

Two series of CuZnAlZr-HTlc type precursors were prepared by coprecipitation method at pH 7 and 9. The atomic ratio of the reference samples without zirconium was Cu:Zn:Al = 2,60:1:0,74. In Zr doped materials 33, 50 or 66 at.% of Al was substituted with Zr (Zr:Al ratio 1:2, 1:1 and 2:1 respectively). All materials were calcined at 550°C for 3 hours.).

XRD shows that at both pH values coprecipitation results in the formation of HTlc structure, the better crystallinity being observed for pH=9. Insertion of zirconium leads to a gradual worsening of the structural order. This effect is reflected also in the results of EGA-MS experiments, where particular steps of thermal decomposition become blurred as the amount of zirconium increases. pH of synthesis influences significantly the phase composition of calcined materials. In samples obtained at lower pH crystalline ZnO is clearly visible next to CuO. The crystallinity of the latter is also slightly better than in the samples prepared at pH=9. For both pH values the increase of zirconium content enhances growth of CuO crystals. Improved crystallinity of CuO and ZnO correlates with decreasing specific surface area. Crystalline ZrO_2 is observed only in calcined materials with the highest content of Zr.

TPR experiments suggest that the reducibility of samples obtained at pH = 7 is poorer than reducibility of the reference sample without zirconium. The differences were confirmed by *in situ* XRD study of reduction, in which crystalline copper in Zr-containing samples is observed at higher temperature than in samples without Zr (300 and 200°C, respectively).

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Diagnostic intercalation in clay minerals – use of Guanidine carbonate

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The characteristic basal (00l) spacings of clay minerals in oriented specimens were commonly used for qualitative X-ray diffraction analysis. Diagnose will be performed by a number of different cation saturations, solvations and heatings. For identification purposes the intercalated complexes should be readily formed from hydrated clay, should be stable and provide an unequivocal spacing. For innercrystalline swellable clay minerals, several organic complexes as intercalation compounds were applied, e.g. polyhydric alcohol complexes. The intercalation of these complexes takes place storing the specimens for some hours at elevated temperatures. After exchange the specimens have to measure fast, because of the evaporation within some hours. A faster and simpler application is 1,3-propanediol, an other polyalcohol, which gives a basal spacing for montmorillonite of 18.7 Å. The intercalation takes place very fast at room temperature and is longer stable. However, all these intercalations of polyalcohols have the disadvantage to be reversible. The polyalcohols evaporate, giving unequivocal and relative humidity dependent basal spacings.

For analytic evaluation the cationic compound guanidine carbonate worked satisfactorily. It can be easily and fast prepared by simple mixing with saturated solution as a paste at room temperature. Directly after mixing the sample and drying of the specimen the XRD-measurement gives a basal spacing of 13.0 Å for vermiculite and 12.5 Å for smectite. The basal spacing is long term stable and independent from relative humidity, which offers the possibility to create a defined sample for quantitative Rietveld analysis.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

An influence of different Fe-species on the rheological properties of bentonite suspensions

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Series of bentonite clays with different Fe-content, their monomineral and homoionic forms and also hydrogen peroxide-, dithionit- and hydrogen chloride-treated forms were investigated using XDR, EPR, IR and DTA technics and different Fe forms distribution in the samples were obtained. Green-Kelly test along with methylene blue adsorption technic provided information about charge density distribution in layers and its influence on the rheological behavior of clay suspensions. It was shown that Fe-species on the edges of silicate platelets influence bonding between silicate particles and determine rheological properties of clay suspensions. Appearance of Fe-species incorporated in the crystalline structure and chemically bonded to the silicate edges increase yield point of suspensions at equal cation exchange capacity. The presence of substantial thetraedral charfe and increes in cation exchange capasity also lead to higher rheological properties.

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Molecular modeling of montmorillonite (Wyoming, Cheto) surface covered by methylene blue cations

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Because of its unique properties, montmorillonite has found many industrial applications. The surface properties of montmorillonite can be modified by intercalation or sorption of organic species. The intercalation of optically active species has been widely investigated since montmorillonite layers are transparent in the visible region of the spectrum. We have intercalated methylene blue cations into montmorillonite by ion exchange, and modeled the reaction (KLIKA et al., 2007). Some of the methylene blue cations were adsorbed on the external surface of montmorillonite particles. These cations can influence the optical properties of the resultant material. Thus, the arrangement of methylene blue cations on the montmorillonite surface is an important factor affecting the photoluminescence of intercalated montmorillonite.

Molecular simulations show differences between the Wyoming- and Cheto-type montmorillonites as to the surface and interlayer arrangement of methylene blue cations. In Wyoming montmorillonite with a relatively low layer charge, the methylene blue cations lie parallel to the silicate layers, while in the high-charge Cheto montmorillonite, the methylene blue cations adopt a tilted arrangement with respect to the silicate layers. Accordingly, the luminescence behavior of the materials is different. Molecular simulations were carried out using the Cerius^2 model.

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Preparation of silver-montmorillonite nanocomposites

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Silver nanocomposites are useful for many industrial applications. A variety of conventional sol-gel preparative methods exist for the fabrication of Ag nanocomposites in the form of either a bulk powder or thin film. Another type of Ag nanocomposite is formed by depositing silver nanoparticles on the surface of inorganic supports (e.g., Al_2O_3, SiO_2, TiO_2) and phyllosilicates (e.g., montmorillonite and kaolinite) (PATAKFALVI et al., 2003; PRAUS et al., 2008). In this study we prepared silver nanoparticles supported on a Na-rich Wyoming-type montmorillonite (MMT).

The montmorillonite was initially intercalated with silver cations. The adsorption data fitted the Langmuir isotherm, indicating that Ag^+ formed a monolayer in the interlayer space. With increasing content of Ag^+ the MMT layer structure gradually decomposed and exfoliated.

The intercalated silver cations were then reduced with sodium borohydride ($NaBH_4$) or formaldehyde (CH_2O). For the CH_2O reduction various alkaline additives were required. Here we used NaOH, $NaHCO_3$, and triethanolamine, Silver reduction was assessed by measuring the silver plasmon absorption bands around λ_{max}= 410 nm, using UV-VIS spectrometry. The resultant nanoparticles were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Both the shape of the absorption bands and the electron micrographs show that reduction with $NaBH_4$ gave rise to silver nanoparticles of narrow polydispersity and a mean diameter of about 7 nm. This is in good agreement with the value of 8.5 nm, calculated from XRD patterns (PRAUS et al., 2008). On the other hand, reduction with CH_2O produces aggregates of up to 70 nm in diameter.

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Physicochemical conditions of formation of the epithermal dickite from Nowa Ruda, Poland

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Geochemical analyses for trace vanadium (V) and chromium (Cr) have been undertaken on a representative sample of a typical dickite filling vein at Nowa Ruda, Lower Silesia. The mineralogy of the Nowa Ruda sample is comparatively simple, dickite being the principal component (>95 % of total sample), with lesser amounts of gypsum ($CaSO_4 \times 2H_2O$) and/or anhydrite ($CaSO_4$). Geochemical fractionation and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) indicate that most (>90% of total metal) of V (190 ppm) and Cr (435 ppm) reside in the dickite. Electron Spin Resonance (ESR) shows that most (>70%) of V in the dickite structure is in the form of vanadyl (VO^{2+}) ions. A high concentration of Cr^{3+} is also detected in this structure by ESR. The V (and VO^{2+}) and Cr (Cr^{3+}) enrichments of Nowa Ruda dickite were probably occurred its formation by an invasive epithermal (acid-sulfate) solution. The ultimate source of V and Cr in Nowa Ruda dickite was probably the surrounding volcanic rocks (enriched with minerals olivines, pyroxenes, Fe-oxides) of gabbros massifs of Nowa Ruda Basin. V and Cr were leached by the hydrothermal (acid-sulfate) fluids before their mixing with the groundwaters, forming the epithermal solutions in Nowa Ruda Basin. From geochemistry of VO^{2+} and Cr^{3+}, it is deduced that the oxidation potential (Eh) and H^+ concentration (pH) of the epithermal solution were approximately 0.6-1.0 V (highly oxidizing) and 2.8-4.0 (highly acidic), respectively, during the formation of dickite from the Nowa Ruda Basin.

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Diagenetic changes in sandstones and shales from the Podhale Basin

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The original composition of rocks deposited in sedimentary basins is modified in the course of chemical processes associated with burial diagenesis. The nature of diagenetic processes in different lithologies may be different. Podhale Basin because of a monotonous original mineral composition of its rocks and simple tectonics was selected for a study of simultaneous diagenesis of sandstones and shales.

For shale and sandstone samples from this region the following analyses were made: XRD analysis of quantitative mineral composition of whole rocks using QUANTA software, assay of the smectite content in mixed-layer illite-smectite minerals using <0.2 µm fraction, chemical composition assay of the whole rocks samples (performed by Actlabs, Canada), measurement of cation exchange capacity (CEC), measurement of EGME sorption and calculation of total specific surface area (TSSA).

The following variations in the vertical profile of the basin were detected:

- The amount of quartz in sandstones does not increase with depth as it happens in the case of shales;
- Sandstones contain less potassium feldspar than shales;
- The amount of plagioclase is higher in sandstones and, like in shales gently increases with depth (albitization);
- Kaolinite is less abundant in sandstones than in shales and its quantity is decreasing down the profile;
- The sum of clay minerals both in shales and in sandstones shows no clear trend with depth;
- Similar %S in mixed-layered illite-smectite from shales and from sandstones at similar depths indicate the same degree of diagenesis in both types of rocks.
- Calcite is the dominant carbonate (order of 10% in shales and 20% in sandstones) and it follows similar trend in shales and sandstones: a slight general decrease with depth, with local minimum zone between 1500m to 2500m. In both lithologies dolomite is present at a stable level of 3-4%.

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Climato-environmental controls on clay mineralogy of the Lower Toarcian black shale succession of the Mecsek Mountains, Hungary: a possible evidence for extreme continental weathering during the early Toarcian oceanic anoxic event

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In the Mecsek zone (Hungary), the clay-mineral assemblages of the Lower Jurassic siliciclastic rocks and upsection dominantly marly lithologies suggest a climatic regime with fluctuating humidity and supply of terrigenous clastics to the basin. Towards the Toarcian, kaolinite becomes the dominant clay mineral (kao/ill>1) suggesting a humid climate and very intense continental weathering. Based on the high-resolution clay mineralogical composition, a stratigraphic pattern in the distribution of clay minerals with three distinct peaks of kaolinite/illite ratio (up to 5.3) is apparent. In the lower part of the black shale section studied, paper laminated black shale intervals are relatively enriched in kaolinite, whereas some thin-bedded black shale horizon contain more illite. Upsection, an interval characterized by a rapid increase in the proportion of kaolinite (up to 80% of the clay fraction) can be recognized. In the upper part of the section, the proportion of illite increases upward, while kaolinite decreases. Additionally, the total organic carbon contents and the isolated kerogen carbon stable isotope data fluctuations show a coincident pattern.

The dominance of kaolinite with very high kaolinite/illite ratios may be associated with the degree of drainage in the continental areas. Similar explanation based on Os isotope data was also proposed for the Lower Toarcian organic-rich mudrocks from Yorkshire, England, where the magnitude of the Os isotope excursion indicates an increase of ~400-800% in the continental weathering flux. Additionally, relatively high proportions (20-25%) of kaolinite occur in the Toarcian pelagic sediments in southern Switzerland, equally suggestive of enhanced continental weathering. Therefore, our result provides a clay-mineralogical evidence for the extreme continental weathering rate during the Toarcian oceanic anoxic event.

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Comparisons of structural iron reduction in smectites by bacteria and dithionite: a variable-temperature Mössbauer spectroscopic study

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The reduction of structural Fe in smectite may be mediated either abiotically, by reaction with dithionite, or biotically, by reaction with *Shewanella oneidensis* strain MR-1, a dissimilatory Fe-reducing bacterium. The effects of abiotic reduction on clay surface chemistry are much better known than the effects of biotic reduction. Because bacteria are likely the principal agent for mediating redox processes in natural soils and sediments, further study is needed to ascertain the differences between biotic and abiotic reduction processes. The purpose of the present study was to compare the effects of dithionite (abiotic) and bacteria (biotic) reduction of structural Fe in smectites on the clay structure as observed by variable-temperature Mössbauer spectroscopy. Three reference smectites, namely, Garfield nontronite, ferruginous smectite (SWa-1), and Upton, Wyoming, montmorillonite, were reduced to similar levels by either *Shewanella oneidensis* or by pH-buffered sodium dithionite, then each sample was analyzed by Mössbauer spectroscopy. Parallel samples were reoxidized by bubbling O_2 gas through the reduced suspension at room temperature prior to Mössbauer analysis. Redox states were quantified by chemical analysis, using 1,10-phenanthroline. The reduction level achieved by dithionite was controlled to equal that of the bacterial reduction treatment so that valid comparisons could be made between the two treatments. Bacterial reduction was achieved by incubating the Na-saturated smectites with *S. oneidensis* strain MR-1 in a minimal medium including 20 mM lactate.

The spectra from bacteria- and dithionite-reduced samples, with similar Fe(II) contents at about 1 mmole Fe(II)/g clay or less, were similar at 77 K but at 4 K large differences were noticed between the bacteria- and dithionite-reduced samples. These differences revealed that the point of attack by the reducing agent and the resulting distribution of structural Fe(II) in the octahedral sheet are different depending on the method of reduction. Spectra of reoxidized samples were similar to the unaltered states, indicating that reduction, regardless of which method is chosen, is largely reversible with respect to structural changes in the smectite.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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Relationships between fine layer structure and hydration of compensating cations in TOT phyllosilicates

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The nature of the interlayer cation, the layer charge and its location have been recognized as important factors controlling the swelling properties of smectites. The fine layer structure also seems to play a major role.

A series of synthetic TOT phyllosilicates, prepared at 400°C, 1 kbar PH_2O, with the structural formula: $Na_x(Mg_{3-y}Al_y)(Si_{4-x-y}Al_{x+y})O_{10}(OH)_2.nH_2O$, with $0.3 \leq x \leq 1$, for $y = 0$ and $0 \leq y \leq 1$, for $x = 1$ has been investigated by XRD under controlled humidity conditions (85%). The series with $y = 0$ and variable x values corresponds to saponites, derived from talc by the substitution $^{[12]}\square$, $^{[4]}Si^{4+} \rightarrow {}^{[12]}Na^+$, $^{[4]}Al^{3+}$. For $x = 1$ and $y > 0$, the layer charge remains 1, but both [4] and [6] compositions are modified by the substitution $^{[6]}Mg^{2+}$, $^{[4]}Si^{4+}$ $^{[6]}Al^{3+}$, $^{[4]}Al^{3+}$.

In saponites, the basal spacing d_{001} is ≈ 15 Å, whatever the charge, up to $x = 0.9$. It corresponds to a two-layer hydrate, with $5H_2O$ per Na^+. For $x = 1$, trace amounts of one-layer hydrate, with $2H_2O$ per Na^+ ($d_{001} \approx 12$ Å) and of a non-swelling phase ($d_{001} \approx 10$ Å) are observed. In the series with $x = 1$ and $y > 0$, the 15 Å phase remains dominant up to $y = 0.2$ Beyond this value the one-layer hydrate (12 Å) and the non-hydrate (10 Å) are the major phases. The two-layer hydrate disappears for $y > 0.5$, and the one-layer form beyond $y = 0.75$.

We have developed a model based on the effective coordination number, i.e. EcoN (WEISS et al., 1992), to explain these observations in contradiction with admitted rules. Along the two series, the rotation angle of tetrahedra (α) increases, from 5° in low-charge saponite ($x = 0.35$), to 19°, for $x = y = 1$. Low α values mean a twelve-fold coordination of Na^+, which rattles in its too large interlayer site, and traps water molecules. The amount of interlayer water decreases with the EcoN. The EcoN of Na^+ reaches [6], for $\alpha = 16°$, which corresponds to $x = 1$ and $y = 0.75$, for this composition and for $y > 0.75$, only a 10 Å phase is observed.

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Paleoenvironmental Evolution of Estuarine Systems based on Clay Minerals - the Case of Minho Estuary (NW Portugal)

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The Minho estuary is located in the northwestern Portuguese coast, north of Oporto. It is elongated almost NNE-SSW, and is partially sheltered from the ocean by a sand spit, rooted in the southern margin. This is a common feature of all northern Portuguese estuaries (Douro, Ave, Cávado, Lima), with the barrier differing in length and resulting from local reversal of littoral drift. Aiming the paleoenvironmental reconstruction of Minho Estuary based on clay minerals associations, two cores were drilled in the barrier, aligned normal to coastline with a distance of 200m between them. Mineralogical analysis of both the fine (<63 µm) and clay (<2 µm) fractions was carried out using X- Ray Diffraction (XRD). The semiquantitative determination of minerals by XRD, in disaggregated material (<63 m) and in oriented aggregates (<2 m), followed criteria recommended by GALHANO et al. (1999) and OLIVEIRA et al. (2002). For the fraction <63 m, 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 m), illite, chlorite, kaolinite and smectite contents and the kaolinite/illite ratio were compared. The obtained results allowed to define unformal units along the studied log as well as to put forward paleoenvironmental and paleogeographical considerations. 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.

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Removal of disturbing substances from paper furnishes by hydrotalcite materials

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Paper describes results of laboratory testing of hydrotalcite-type Anionic Clay (Layered Double Hydroxide) as an adsorbent of anionic, organic disturbing substances such as pitch and stickies, which are present in different types of paper pulps and furnishes. Synthetic hydrotalcite (HTC) used here consist of Mg-brucite layers modified by the presence of Al (III). The MgO/Al_2O_3 ratio R is ~4. This product is commercially available from Akzo Nobel. Commercial pitch talc was used as reference in most of the tests.

Test methods used in this investigation include measurement of microstickies – i.e. as Total Organic Carbon (TOC), as well as testing of turbidity, UV-visual light absorbance, tackiness and Chemical Oxygen Demand (COD).

De-Inked Pulps (DIP) and the paper machine White Waters (WW) were treated both with hydrotalcite and talc. In all cases the performance of hydrotalcite was significantly different and better from that of the commercial pitch talc.

Hydrotalcite, which at its high specific surface (~ 180 m^2/g) carries the positive charge, can adsorb the negatively charged disturbing substances such as pitch and stickies. On the other hand talc, which carries no charge at its slightly hydrophobic surface, might be attracted to the hydrophobic surfaces of disturbing substances.

The nature of those two different mechanisms of neutralization and removal of disturbing substances from paper pulps and furnishes will be discussed.

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How to make loam bricks more stable

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Over the last few years ecologic building materials, such as loam bricks, became of greater economic importance. Studies of the mineralogy, granulometry, chemistry and cation exchange capacity of the raw materials are necessary for the optimisation of load capacity, robustness and the resistance of loam bricks against air humidity.

Four different types of loam provided by an Austrian brick company have been analysed: A1, A2, B and C. These four samples were analysed by means of X-ray powder diffraction to characterize their bulk mineralogical composition and clay mineralogy. The X-ray data show that samples A1 and A2 are similar in composition, containing quartz and feldspar; whereas samples B and C also contain calcite and dolomite.

Their clay mineral content ranges between 50 and 70%. Chlorite, vermiculite, illite and kaolinite constitute the clay fraction of samples A1 and A2. Smectite could only be found in samples B and C.

Samples A1 and A2 showed an ideal grain size distribution and an absence of expandable clay minerals, thus they were used for further studies of burst strength and bending tensile strength.

Different additives like finely ground trass, kieselgur, brick-dust, slagstar, Acronal S650, wood shavings and a clay mineral rich loam where added to the loam and homogenised.

Little loam bricks were prepared to quantify the burst strength and bending tensile strength. A brick series were coated with a hydrophobic impregnation fluid. The bricks were stored in boxes for 20 days with air humidities of 100% and 75%, respectively. After 1, 5 and 20 days the burst strength and bending tensile strength were measured to identify the humidity level which will be critical for brick's stability.

The initial strength of loam A1 with Acronal S650 is higher than that of the other types. However, it looses strength under the influence of high air humidity. Despite the comparatively small initial strength, loam A1 with slagstar shows the smallest losses after exposure to high air humidity.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Hydrogen bonding and vibrational spectra in kaolinite-dimethylsulfoxide and -dimethylselenoxide intercalates – a solid-state computational study

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Intercalates of phyllosilicates and organic compounds are of great interest in many fields due to the increasing number of their applications. Unfortunately, structural research of the phyllosilicates of interest is hampered by the large variability of their chemical composition and especially by the frustrating lack of well-ordered single crystals of a sufficient size. Absence of relevant structural information on phyllosilicates directly obtainable from diffraction or spectral experiments led to the use of the various computational methods also to the field of structural mineralogy. The accuracy of the current computational methods has reached such a high level that they can compete with neutron diffraction experiments in obtaining accurate geometries of hydrogen bonds. The additional benefit brought by the theoretical calculations is that they not only provide accurate atomic coordinates, but they can also routinely supply vibrational density of states or even vibrational spectra as well.

Accurate positions of all the atoms in the structures of DMSO- and DMSeO-intercalated kaolinites have been obtained by the total energy minimization in the solid state at a DFT level of theory. The bond distances and angles in the constituent polyhedra are in good agreement with those reported in the most recent single-crystal refinement of kaolinite. The organic molecules are fixed in the interlayer space by three moderately strong O-H…O hydrogen bonds of different strengths, while the weak C-H…O and O-H…S(Se) contacts play a minor role. The optimized atomic coordinates were used to calculate the individual vibrational modes within 0-4000 cm^{-1}. The impact of formation of hydrogen bonds on the energies of the OH stretching and Al-O-H bending modes is documented with the help of calculated partial vibrational densities of states (Scholtzová & Smrčok, 2008).

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The role of minor components in the fixation of Cu^{2+} cations by bentonites after saturation with Cu^{2+} solutions and thermal treatment

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The fixation of cations by bentonites has largely been studied using size-fractionated (< 2 µm) materials. Raw bentonite, however, usually contains several minor components (e.g. quartz, carbonate, sulphate). Here we investigate the role of these components and preparation conditions in the fixation of Cu^{2+} by two bentonites, Volclay (Wyoming) and Calcigel (Bavaria), differing in cation exchange capacity (CEC) and mineral composition. The raw and fractionated samples were saturated with Cu^{2+} by treating 1 g of bentonite with 25 ml of 0.02 M $CuCl_2$ or $CuSO_4$ solutions for 2 h (5 times). The Cu^{2+}- exchanged materials were heated for 24 h at temperatures between 300 and 450°C, and their CECs were determined. The chemical and mineralogical compositions of the raw and fractionated bentonites were also determined by XRD analysis and FTIR spectroscopy.

After treatment with $CuCl_2$ or $CuSO_4$ solutions, the Cu^{2+} content of the raw (technical) bentonite was markedly higher than that of the fractionated (< 2 µm) material. This may be ascribed to the formation of copper phases (e.g., malachite or posnjakite) in raw bentonite as indicated by XRD as well as the interlayer sorption of Cu^{2+} cations.

On heating, the Cu^{2+} cations moved from the interlayer space into the layer structure. This irreversible migration also occurred in the < 2 µm fraction. As a result, there was a collapse of the interlayers (demonstrated by XRD) and a change in Si-O and OH vibrations (indicated by FTIR analysis). The release of Cu^{2+} from bentonite was influenced by the nature of the extracting solution and interim thermal treatment. Copper carbonate phases are not modified by heating but will dissolve in ammonium solutions.

In studying the fixation of Cu^{2+} ions by technical bentonites, attention should be paid to the generation of copper phases, and the movement of interlayer Cu^{2+} into the clay mineral structure.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Illitization in hypersaline environment of the Pliocene-Pleistocene Sedom Lagoon, Dead Sea valley

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The origin of illite found within rock salt of the Pliocene-Pleistocene Sedom Formation was studied using XRD, FT-IR spectroscopy, SEM and chemical analysis. The rock salt of the Sedom Formation was deposited in hypersaline evaporitic environment of the Sedom Lagoon. These rocks are exposed in the Mount Sedom which is located in the Dead Sea valley.

The mineral assemblage in the rock salt includes halite and accessory minerals: mainly anhydrite, illite, dolomite, some kaolinite and quartz. Presence of quartz grains demonstrates that detrital minerals were transported to the Sedom Lagoon. The precursor detrital minerals were illite/smectite, kaolinite, calcite and quartz, which are the common minerals in the alluvium of the area. The appearance of illite, as the main clay mineral within the rock salt, indicates that illitization process took place in the Sedom Lagoon. The illite was formed by illitization of the detrital illite/smectite transported to the Sedom Lagoon. The illitization took place due to relative high potassium concentration of the hypersaline evaporitic environment.

FT-IR spectroscopy demonstrates that the lagoonal illite is rich with magnesium in dioctahedral sites of their structure. The substitution of aluminum with magnesium in the octahedral sheet of the illite structure took place due to relative high magnesium concentration of the hypersaline evaporitic environment. As a result, isomorphous substitution of aluminum with magnesium took place in dioctahedral sites.

The appearance of dolomite as the main carbonate mineral indicates that dolomitization process also took place in the Sedom Lagoon. The calcite in the lagoon was transformed to dolomite by this process. Dolomitization process requires elevated magnesium/calcium, which is related to deposition of anhydrite that had removed calcium from the brines of the Lagoon.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

The ceramic technology used in the manufacture of Early Bronze Age pottery from the Canaan area

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The ceramic technology used in the manufacture of Early Bronze Age (EBA) pottery from the Canaan area was studied using petrography, X-ray diffraction, infrared spectroscopy and chemical analyses. Analyses were performed on 'Metallic' Ceramic Ware and on Brown Hole-Mouth Cooking Ware.

Analyses of the fired clay within the ceramic matrix by Fourier transform infrared (FTIR) spectroscopy demonstrate that the 'Metallic' Ceramic Ware was produced from kaolinitic raw material, whereas the brown cooking ware was produced from smectitic raw material. The amounts of Al_2O_3 and SiO_2 within the fired clay are in accordance with kaolinitic and smectitic raw material, respectively.

Kaolinitic raw material is more suitable for ceramic production. However, this raw material is not widespread in the Canaan region. The presence of quartz grains within the ceramic material indicates that the 'Metallic' Ceramic Ware was manufactured from kaolinitic raw material taken from sediment containing these grains. Such raw material is exposed at the Hermon Mountain foothill in the sandstones of the Lower Cretaceous. The production from kaolinitic raw material requires firing at high temperature.

Smectitic raw material was necessary for the manufacture of the Brown Cooking Ware in order to produce ceramics stable in cooking directly over fire and able to withstand repeated heating and cooling. The presence of basalt fragments within the ceramic material indicates that the Brown Hole-Mouth Cooking Ware was manufactured from smectitic raw material taken from basaltic soil.

The results demonstrate that the potters in the EBA had knowledge of raw materials and firing technology thus enabling them to select suitable ones, according to the advantages of each, for the manufacture of 'Metallic' Ceramic Ware and for cooking ware.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Transformation of soil clay minerals under anthropogenic salinization

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The objects of our investigation are the podzolic soils from the Seriogovo salt plug territory (Russian platform) where salt mineral waters deposits are situated.

Samples were obtained from 7 soil uncontaminated (background) and saline cross sections near the Seryogovo salt deposit from 0 to 103 cm depth..

X-ray analysis indicates that almost all clay samples of the background sections contain smectite, illite, chlorite, kaolinite with smectite being dominant. The clay fractions of the saline soils contain chlorite, vermiculite, interstratified chlorite/vermiculite, kaolinite and illite, with chlorite being dominant.

The smectite of the uncontaminated soils is not well ordered, as is evident by incomplete collapse to 1.0 nm when heated to 550°C. Small amounts of disordered chlorite are also found in these samples. In the lower parts of saline cross sections smectite almost disappears, while the most abundant minerals are pedogenic dioctahedral chlorite and interstratified minerals.

The comparison of the ”*d*(060)” value on the XRD patterns of clays from the uncontaminated and contaminated soils show that both trioctahedral and dioctahedral minerals are present but the intensity of the 060 peak for the dioctahedral mineral of saline soils is proportionally larger than that of the uncontaminated clay.

The investigations show that there are differences between the clay minerals of saline and background soil samples of Seriogovo deposits because of their transformation under the environmental changes. The expandable layer silicates typical of the background soils transformed to non-expanding dioctahedral soil chlorite. Transformation reactions involved the introduction of non-exchangable hydroxy polymers into the interlamellar space of pre-existing smectite or vermiculite (WILSON, 1999). Interlayer hydroxide layers are therefore more stable than exchangeable cations of clay mineral crystal structure in the saline environment.

The results presented suggest that chlorite was formed diagenetically by prolonged periodic percolation of salt brines through pervious layer silicates.

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Inelastic neutron scattering (INS) study of hydrogen bonds in kaolinite-dimethylsulfoxide intercalate

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The study reported here is part of a project focused on obtaining an accurate description of hydrogen bonding in selected sheet silicates using a combination of spectroscopic methods with quantum chemistry calculations. Inelastic neutron scattering spectra (INS) taken within 0-4000 cm^{-1} are applied to obtain the information on the dynamics of the hydrogen atoms in the structure. The main advantage of the INS is that it represents, due to large differences in scattering abilities of main constituting elements (Si, Al, O vs. H), actually a "hydrogen" spectrum. The INS spectroscopy is hence an attractive alternative to conventional vibrational spectroscopic methods as the INS intensity is directly proportional to displacements of hydrogen atoms. Even though negligible contributions from all but H atoms make an INS spectrum, compared to IR/Raman spectra, more readable, its interpretation is best accomplished by first analysing theoretically calculated spectra followed by judicious assignment of peaks in a measured spectrum. The spectra of kaolinite-DMSO-intercalates were taken with the TOSCA (ISIS) and IN1BeF (ILL) spectrometers. Both “normal” DMSO and deuterated DMSO were used to separate the contributions of CH and OH hydrogen atoms. The contributions of the individual H atoms were unambiguously identified by comparison of the experimental spectra with the vibrational spectra calculated by the harmonic approximation and also molecular dynamics calculation, which are free of such limitations.

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Natural silica-smectite mixed phases as new clayey material in industrial applications

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Süd-Chemie has identified a new type of clay which can be assigned as natural mixture of a natural silica gel and a smectite. Without any treatment the material exhibits a high specific surface area ($\geq$190 m²/g) and a high porosity. Due to the fixation of the smectite in the silica network, the clay does not exhibit the typical swelling behaviour of smectites in aqueous solution. Various industrial applications of the new clay are discussed:

- Bleaching earth for edible oil refining,
- Bioseparation processes (protein purification),
- Carrier for liquids (e.g. feed additives).

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Layer silicates from selected boreholes on Fore Sudetic Monocline (Western Poland)

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Composition of volcanic rocks from Bolewice-1 and Jeniniec-2 boreholes is close to andesite. They are highly altered under prehnite-pumpellyite metamorphic facie conditions. Primary textures are visible but primary minerals are scarce. They are represented by clinopyroxenes and spinels. Secondary minerals are represented by: albite, pumpellyite, prehnite, carbonates, epidotes, zeolites, hematite and layer silicates. XRD results indicate that major layer silicates are mixed layer chlorite/vermiculite phases; both corrensite and irregularly interstratified phases, and vermiculite. Studied samples contain also minor amount of celadonite, occasionally rich in Cr. Underlying sedimentary rocks contain chlorite veinlets.

FWHM (Full Width Half Maximum) parameter of layer silicates from studied samples is variable ranging from 0.20 to >0.35 for phases displaying best crystallinity. These values indicate that temperatures of metamorphism correspond to from subgreenschist-greenschist facies metamorphism. The temperature of layer silicate formation is consistent with temperature of formation of Ca-silicates present in the studied rocks (Himmelberg et al. 1995; Merriman & Frey, 1999). FWHM parameter of layer silicates from underlying sedimentary rocks is similar to those of layer silicates from metavolcanic rocks Jeniniec-2 borehole, and it is lower that those for layer silicates from samples coming from Bolewice-1 borehole. The mixed layer chloritic phases are interpreted as being a result of metamorphic retrogression. They are very poor in iron, Mg# > 0.7.

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Mixed-layer illite-smectite in Kinnekulle K-bentonite, Baltic Paleobasin

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The composition and morphology of the diagenetic illite-smectite (I/S) of the Ordovician Kinnekulle K-bentonite was studied to understand the illitization of the clay minerals in the Baltic Paleobasin. The same K-bentonite bed from 9 different locations in the basin was sampled and analyzed by means of XRD, AFM methods and K-Ar dating.

Illite-smectite in studied samples is a highly illitic three-component mixed-layer mineral with illitic layers content of 63-77%, 16-26% of low-charge smectite and 3-14% of high-charge smectite (vermiculite-like) layers. The thickness of the particles remains in all samples very low – in average 3 ± 1.5 nm. Typically the particles are isometrical with aspect ratio of 1.2-2. However the population of lath shaped particles with the aspect ratio (L/W) higher than 4 was observed in less illitic samples. The content of illitic layers in northern part of the basin decreases with increasing burial depth and is accompanied with morphological transformation from euhedral to lath shape particles that is opposite to a conventional illitization trend. Geological reasons for these trends are unknown at present state of knowledge but it may indicate the localized higher heat and/or fluid flow events in the northern part of Baltic Paleobasin. K-Ar dating shows widely scattering variation of digenetic ages from 390-448 Ma. Shallower samples in northern part of the basin are isotopically younger, which agrees with the lower illite content in mixed-layer mineral in these samples.

The structural composition as well as the morphological parameters of I/S indicate a mixed dissolution-crystallization (DC) and solid-state-transformation (SST) mechanism in the Kinnekulle K-bentonites. The DC mechanism is suggested by the (1) regular euhedral-lath shape particles, (2) morphological evolution along with the structural rearrangement. SST mechanism is suggested by (1) very low and constant thickness of I/S particles and (2) (vermiculitization) the formation of the high-charge crystal interfaces from the original low-charge montmorillonite. It seems that illitization mechanism is mainly controlled by SST, but this evolution has been overprinted with DC mechanism that was triggered by a fluid flow event(-s) during Caledonian formation in northern part of the basin. However a “normal” burial diagenetic illitization can be suggested in central/ southern part of the basin.

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Anhydrite dissolution kinetics

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CO_2 sequestration in deep saline reservoirs may be combined with the exploitation of geothermal energy. The injection of cooled and CO_2-enriched brines into the reservoir may, however, induce substantial redistribution of anhydrite, which has a retrograde solubility with temperature. For modeling this potential redistribution, the rate laws of dissolution need to be known. In our investigation we measured the dissolution kinetics of anhydrite from the Zechstein at low saturations in batch experiments and at high saturations with mixed-flow reactor (MFR) experiments. We used pure H_2O, which allowed us to monitor the (relatively fast) reactions by measuring the electrical conductivity. Temperatures varied between 10 and 80°C.

Although the reproducibility of the dissolution rates measured in batch experiments was very high, the rates were not consistent with the MFR rates and they depended on the solid-solution ratio. This indicates that the batch rates were probably not steady-state rates. Furthermore, the form of the rate law extracted from the low-saturation measurements was not compatible with the dissolution behaviour near equilibrium measured in the MFR. The results will be discussed in terms of recent dissolution models suggested by Lasaga and coworkers.

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Measuring the cation exchange capacity of vermiculite

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The inorganic cations balancing the negative layer charge of swelling clay minerals, such as smectite and vermiculite, can be exchanged for other cations. Ammonium acetate is often used to measure the cation exchange capacity (CEC) of these minerals. The method consists of several steps, and hence is very time consuming (MACKENZIE, 1951). On the other hand, the Cu-triethylentetramine (Cu-trien) method for determining the CEC of smectite minerals, is a rapid process (MEIER & KAHR 1999).

Here we investigate the feasibility of using the Cu-trien method to measure the CEC of a vermiculite from Russia. The material was dry-ground in a mill (CGS 10, Netzsch) to produce a powder with a particle size of less than 10 µm. Coexisting phases in the sample were removed by a series of purification steps. The CEC of the material obtained after each step was measured, and compared with the CEC of the untreated (original) verrmiculite. Portions of the purified material were then saturated with different cations (Na^+, Li^+, Mg^{2+}, Ca^{2+}, Cu^{2+}). Since Cu-trien can fully replace monovalent cations (Na^+, Li^+), the method can provide a good estimate of the (total) CEC. Divalent cations (Mg^{2+}, Ca^{2+}, Cu^{2+}), on the other hand, can only partially be exchanged for Cu-trien.

The results show that purification and chemical pretreatment of vermiculite influence CEC measurements by the Cu-trien method.

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On the significance of parent mineral structure and the immediate environment for kaolinite formation

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The relation of parent mineral structure and the chemical and physical properties of the immediate environment on kaolinite formation, its structural perfection and morphology was studied in two examples: 1) diagenetic kaolinization in Santonian fluvial sandy-cleyey sediments (North Sudetic Trough), and 2) kaolinite of metasomatic processes origin in Tertiary weathering crust on gneisses (Wyszonowice, Lower Silesia).

Kaolinite in Santonian sediments is distinguished by an unusual number of well-shaped pseudohexagonal crystals, as well as vermicular aggregates of plates. It has a high degree of crystallinity and very well ordered structure. The content of Ti and Fe impurities is very low. A considerable part of the well-shaped kaolinite represents a rare variety called ”kaolinite 700^0”. Its dehydroxylation temperature (680^0C) is about 100^0 higher that normal Tc kaolinite (580^0C). This property is a consequence of perfection of the internal structure and coarse crystalline form (>2 μm), and can be explained by a “sealed box model” of intra structure dissociation of solid. Detail SEM/EDS study revealed that these coarse, perfect structure kaolinite crystals are formed inside muscovite plates by rebuilding of mica structure, according to the equation: $2KAl_2[Si_3AlO_{10}](OH)_2 + 2H^+ + 3H_2O = 1.5\ Al_4[Si_4O_{10}](OH)_8 + 2K^+$. To form kaolinite from muscovite it is necessary to exchange K^+ by H_3O^+ ion which next transforms in the structure into OH groups. Si and Al change the position but their content is not changed. In this way three layers of kaolinite are formed from two layers of mica with a small increase of volume of set of new formed layers. Ti and Fe are removed to the outside of the mica plate forming anatase and iron oxide. Muscovite kaolinitization is a slow process. Weathering of feldspars is faster by incongruent dissolution and kaolinite plates grow perpendicular to the feldspar surface forming vermicular aggregates. Only a trace of feldspar remains in the sediments. The processes of kaolinite formation described occur in sediments permeable to water and in intensive leaching conditions. The content of dissolved elements in pore water was low.

Large scale kaolinitization takes place in weathering crusts on gneisses where mica transformation is accompanied by incongruent dissolution of feldspars and kaolinite formation, with leaching of K, Al and Si. The content of the dissolved elements in pore solution is high, modifying the mica rebuilding process. Muscovite transforms first into mixed-layer mica-montmorillonite and kaolinite is the product of the degradation of montmorillonite. In the bottom zone of the weathering profile where the content of dissolved ions is higher, Mg and Fe in the biotite structure are substituted by Al and it transforms at first into a dioctahedral, muscovite-like mica. The influence of the original mineral structure and thermodynamic and kinetic factors of the kaolinitization process on the form, size and perfection of the kaolinite crystals are discussed.

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Investigations of shale inhibiting properties of drilling fluids by transient permeability measurements under triaxial stress conditions

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Wellbore instability is one of the most substantial technical problems in drilling and a major source of trouble and additional costs. The pressure within the formation changes during drilling process. This geomechanical impact and other processes based on chemical and physical interaction between the drilling fluid and the formation lead to significant problems especially in shales. The changed pressure and the inflow of drilling fluid into the formation may cause changing pore pressure result in destabilisation phenomena within the near wellbore region. To simulate these phenomena laboratory investigations were undertaken using original core material. The shale was characterised, porosity and pore size distribution were determined. Transient permeability tests under different tension conditions were carried out using an HP/HT-triaxial-apparatus. Accompanying standardised and self developed index trials including micro hardness tests were conducted to support the investigation.

As a result of the study a promising method of classifying the inhibitive properties of different drilling muds under conditions similar to those in the wellbore was developed and experimental data for drilling fluid selection were provided. The imperative of a complex characterization of both shales and shale – drilling fluid interaction can be established. Suggestions to efficiently improve cuttings and wellbore stabilization in shales can be given.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
www.Mineralogia.pl

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Gamma-irradiation effects on smectite properties

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Bentonite, consisting primarily of smectite, is a common choice for barrier materials in high-level nuclear waste disposals. The conditions in the near field of the waste are severe in terms of radiation and temperature.

The effect of heavy doses (up to 1 MGy) of gamma-radiation on the structural and mineralogical parameters (crystal size distribution, specific surface area, cation exchange capacity, layer charge, etc.) of smectite was investigated.

Two clay fractions of Slovak bentonites were used for this study. The first, originated by the alteration of ryolite tuffs, is composed mostly of Al-Mg-montmorillonite. The second one is the alteration product of andesitic volcanism and composed of Fe-montmorillonite. Series of samples (dried at 105°C, water saturated and mixed with 10 % powdered elementary iron) were packed in closed glass containers and irradiated at room temperature by a ^{60}Co gamma-source. The dose rate was 0.21 kGy/h and the integrated doses were 0.2; 0.7 and 1 MGy.

The mineralogical composition and the crystal structure of the samples were investigated by X-ray diffraction and infrared spectroscopy. The cation exchange capacity was determined using the complexes of copper (II) ion (MEIER & KAHR, 1999), layer charge by the Rhodamine 6G technique and total surface area by EGME technique.

No changes of smectite were observed using above mentioned analyses. Mineral composition as well as the structure of the main mineral - smectite seems to be stable even under at highest gamma-irradiation doses. Some previous studies have indicated possible effects of the high water content and high iron content on the smectite stability exposed to gamma irradiation. Results of this study do not show such effects.

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MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
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Montmorillonite-derived porous clay heterostructures (PCHs): A study of structure evolution

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Porous clay heterostructures (PCH) represent a link between the microporous pillared clay materials and the mesoporous molecular sieves synthesized with the use of surfactants as structure directing agents. PCH are formed by intragallery *in situ* assembly process of surfactant-inorganic precursor nanostructures.

The starting material for PCH synthesis was the Na-montmorillonite (clays of different origin were used). The preparation procedure consisted of three steps:

- opening of the clay interlayer by intercalation of a long chain quaternary ammonium cationic surfactant (hexadecyltrimethylammonium – HDTMA),
- introduction of a silicon source (tetraethylorthosilicate – TEOS) and a neutral amine as a co-surfactant directing the formation of silica nanaostructures in the interlayer region,
- removal of the organic template by calcination at 600-650^{o}C.

The evolution of the PCH structure and the role of synthesis conditions were studied with XRD (including *in situ* high temperature study), FTIR, ^{29}Si MAS NMR, SEM, nitrogen adsorption isotherm at -196^{o}C, and thermal analysis. It was found that the physico-chemical characteristics of porous clay heterostructures strongly depend on:

- the origin of clay: smectites with lower CEC show higher surface area and more uniform pore size distribution in comparison to smectites with higher CEC
- the carbon chain length of surfactant used for organoclay preparation: the longer chain length the better developed pore volume and specific surface areas
- the carbon chain length of neutral amine co-surfactant: the longer the chain the larger pore volume and pore diameter.
- the co-surfactant/organoclay ratio: the higher the amount of amine the larger pore size.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Natural and synthetic ammonium illites: a review

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The ammonium cation has similar properties to potassium, and therefore often can be found in the mica interlayers as a cation compensating permanent mica layer charge. Trace concentrations of ammonium can always be detected in mica structures but in this paper only illites and illite-smectites where tobelitic part represent at least a few percent are being considered. The paper summarizes data on ammonium illites from different geological environments of the Western Carpathians published in the last 10 years and brings new data on sites with new occurences. It describes as well the ammonium illite formation through the hydrothermal and wetting and drying experiments.

Hydrothermal environment

Tobelite with the ammonium representing up to 85 % of the interlayer fixed cations was found in the hydrothermal environment of Vihorlat Mts. The presence of ammonium bearing illite-smectite with a R1 ordering and composition close to rectorite (both sodium and potassium is fixed in the illite interlayers) was determined in hydrothermally altered rocks of Cervena Studna formation in Banska Stiavnica Mts.

Burial environment

The clear relation between ammonium and organic matter explains the abundant occurrence of NH_4 in the structure of sedimentary micas connected with organic matter of all stages of maturation either as a major element or as a trace cation. It has been described in buried sediments of the anchimetamorphic burial history in Zemplinicum, Hronicum, and Gemericum geological units, respectively. Ammonium bearing illite was identified in diagenetic sediments of Dukla Formation as the consequence of interaction between clays and oil fluids at elevated temperature.

Weathering environment

One site with the presence of ammonium in the illite structure was described from hypergene environment of weathering profile developed on the illite-smectite deposit Dolna Ves.

Laboratory experiments

Hydrothermal synthesis of the gel of illitic composition at 300°C led to the formation of pure non expandable ammonium illite. The same experiment conducted with the glass of the same composition produced mixed-layer illite-smectite with the ammonium as a fixed cation of illite layers. Wetting and drying experiments of ammonium saturated smectites led to irreversible fixation of ammonium in the smectite interlayers.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Clay mineral composition of different horizons of soils derived from granites in the Sudety Mts and Foresudetic Block, SW Poland

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Granite, as a most common granitoid, occurs in many areas in south-western Poland, although soil profiles derived from this parent rock do not appear over big areas. There are, however, many papers dealing with weathering processes and formation of clay minerals in soils derived from this parent rock.

The aim of this work was to determine the composition of the clay minerals formed in soil profiles developed from granites located in the Sudety Mts. and Foresudetic Block in Lower Silesia, SW Poland, and to find to what extent soil-forming processes affect the composition of mineral colloids derived during weathering.

The objects of the investigation were shallow cambic soils located in the upper parts of hills formed from granite intrusions of the Luzycki and Strzegom-Sobotka Massifs.

Soil samples were collected from different genetic horizons and prepared for X-ray diffraction analyses by dispersing in distilled water. Clay fractions were obtained by separation using a centrifuge. No additional treatments were made, with the exception of saturation with glycol and heating at a temperature of 550 ^{O}C.

X-ray diffractograms of soil horizons from the humus horizon through to parent rock indicate a diversity mineral composition in the various horizons. Illite was dominant in all horizons, while vermiculite was most frequently observed in the shallower horizons. Minor amounts of kaolinite were detected in all horizons.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Extraction of diagenetic and detrital ages and of $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio from K-Ar dates of clay fractions

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The illite age analysis (IAA) is a classic method of diagenetic and detrital age extraction from mixed ages measured by K-Ar. This approach is based on measuring masses of diagenetic and detrital illitic components in a few different grain size fractions and on measuring mixed ages of these fractions. A plot of the function: exp(λt) - 1 (where t is time and λ is the decay constant) vs. weight percent of the detrital fraction is constructed. On the basis of linear extrapolation to end-member fractions, the diagenetic and the detrital age is obtained. This approach does not take into account various contents of potassium in different polytypes ($\%K_{detrital}$ and $\%K_{diagenetic}$). In order to do that, the detrital mass fraction ($wt.\%_{detrital}$) should be recalculated into the percent of detrital potassium ($\%I_{d(K)}$):

$$\%I_{d(K)} = \frac{wt.\%_{\det rital} \times \%K_{\det rital}}{wt.\%_{\det rital} \times \%K_{\det rital} + wt.\%_{diagenetic} \times \%K_{diagenetic}} \times 100$$

It is very difficult to constrain analytically the potassium content of different polytypes. Therefore, a new approach to this problem has been developed. It was observed that the plot of $^{40}Ar^{*}/^{40}K$ vs. $\%I_{d(K)}$ for exactly determined ratio of $^{40}K_{detrital}/^{40}K_{diagenetic}$ is linear. On the basis of this observation a computer program was written in Java. It takes as an input a few measured detrital illite mass fractions along with the mixed K-Ar ages of the relevant grain fractions, and calculates the end-member ages and the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio, using genetic algorithms.

The errors in diagenetic and detrital illite mass fraction determination cause that the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio and the end-member ages can be evaluated only with some uncertainty. The best results are obtained if the measured mass fractions represent a relatively broad range. Also constraining one of the unknowns (particularly the $^{40}K_{detrital}/^{40}K_{diagenetic}$ ratio) significantly improves the results.

Evaluation of data obtained from literature with the proposed approach leads to conclusion that $^{40}K_{detrital/}{}^{40}K_{diagenetic}$ ratio is often higher than 1.00, and some of 1*M*d illite polytype can be of detrital origin. If this is not the case and if a broad range of mass fractions is covered and differences between end-member ages are relatively small, IAA analysis still gives proper results even if true $^{40}K_{detrital/}{}^{40}K_{diagenetic}$ ratio is different from 1.00.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Fe oxyhydroxides in the hydrothermal deeps of the Red Sea

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The submarine hydrothermal fluids that discharge into the Red Sea Deeps had reacted with hot magmatic rocks, Miocene evaporites and organic rich shales prior to their discharge. Various iron oxides form mono-mineralic layers that reflect fluctuation in brine discharge into the deeps rather than a diagenetic pattern. Mn-Fe oxyhydroxides were crystallized either in the margins of the deeps or close to the interface between the hydrothermal brines and the overlying aerobic Red-Sea Deep Water.

Thetis Deep Fe-oxides are associated with Fe-chlorite (chamosite). Magnetite and co-precipitated goethite and chlorite are enriched with V, P, S and Ti that originate from the leached rocks underneath. Mn rich goethite and hematite were probably crystallized at the uppermost part of the hydrothermal brine or as the hydrothermal activity ceased and Red-Sea Deep Water reached the deep bottom. Authigenic Mn-oxihydroxides (todorokite and woodruffite) co-precipitated with Fe-oxihydroxides.

In the southern Atlantis-II - Chain - Discovery Deeps complex, Fe- oxihydroxides are frequently associated with allochtonous particulate material and authigenic Fe rich clays, short-range ordered Si-Fe phases (singerite) and Mn oxyhydroxides. Crystallization of Si-rich goethite, lepidocrocite and ferrihydrite found in Chain and Discovery Deeps, occurred at the upper part of the hydrothermal water column that over-flows from the southern part of the Atlantis II Deep into the Chain and Discovery Deeps. Mn-oxihydroxides and Mn-Fe-oxihydroxides were both crystallized either close to the interface between the hydrothermal brine and Red-Sea Deep Water or at marginal facies.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

New data on sepiolite-falcondoite in garnierite veins from Falcondo Ni-laterite deposit (Dominican Republic)

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New chemical and structural data on sepiolite-falcondoite solid solution in garnierite veins from Falcondo Ni-laterite deposits (Central Dominican Republic) are reported. The samples were investigated using XRD, DTA-TG, SEM, TEM and EMPA. Garnierite veins are spatially associated to lower horizon of laterite profiles. The mineralogy of garnierite veins is highly variable. However, sepiolite-rich and falcondoite-rich garnierites can be distinguished in the different garnierite veins. In hand samples, falcondoite-rich garnierite displays a whitish green color, whereas sepiolite-rich garnierite shows a white color and slightly schistose texture.

Powder diffraction profile refinement confirmed the structure type for both sepiolite and falcondoite, with refined cell parameters of 13.385(4), 26.955(9), 5.271(3) Å and 13.33(1), 27.03(2), 5.250(4) Å and space group Pncn. Estimated crystallinity for sepiolite (average size 14 nm) is much better than that observed in falcondoite (average size 9 nm).

TEM images of sepiolite display aggregates with a characteristic fibrous morphology. The fibers are > 3μm long and 0.02 μm wide.

Chemical compositions of Central Dominican Republic analyzed samples cover a large interval of falcondoite-sepiolite solid solution (Fal_3 and Fal_{70}). These compositions suggest a complete miscibility along the sepiolite-falcondoite join. The maximum NiO content is 30.42 wt% and the (Ni+Mg)/Si ratio vary from 0.6 to 0.73, to compare with the expected value of 0.66. The amounts of Fe, Al, Cr, Ti, Ca, Na and K are very low or below the detection limit. The tetrahedral cations exceed 12 atoms per formula unit in several analyses. These deviations are consistent with the presence of quartz intergrown with sepiolite and falcondoite.

In summary, our results show that Ni-rich sepiolite and falcondoite are important ore mineral in the Dominican Republic saprolites.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Reservoir quality of Louisiana Miocene shelf sandstones: clays are the key

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Miocene reservoirs were deposited in a variety of shelf environments ranging from distributary channels, fluvial point bars, to upper/middle shoreface. These reservoirs are found today at >150C, increasing geologic risk due to porosity reduction. A set of seven wells were assessed for reservoir quality variability using basin modeling methods, sandstone petrographic methods, and diagenesis modeling methods (Touchstone).

Diagenetic trends reveal that there is a negative correlation between porosity and quartz cement over the depth range of 11K to 23K feet. Additionally, chloritic coatings are found to exist over the same interval in varying quantities, and where present inhibit quartz cementation. Two significant wells penetrating highly bioturbated lower shoreface environments contain chlorite coatings which range from 40% to 65% grain coat completeness. These coatings are more complete than those found in other adjacent non-bioturbated deltaic environments. These two reservoirs have significantly lower quartz cement volumes than their nearshore equivalents and consequently better reservoir quality present day.

The origin of the higher chloritic grain coat completeness in the distal shoreface sands is not clear, but is thought to be related to interaction between the sediments and bioturbating organisms in the depositional system. Clay mineralogical detail reveals the coatings contain dominantly R1 illite/smectite/vermiculite and an R0 chlorite/serpentine with 5% serpentine layers. These clays are similar to clays described in Ryan and Hillier (2002) and may represent part of a green clay alteration pathway.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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The impact of clay minerals on mass movements

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The main reason for the occurrence of mass movements and landslides are mostly expandable clay minerals contained in sedimentary rocks. Due to their small grain size and other specific properties they influence the mechanical behaviour of rocks very strongly. Their decreasing the stability through water absorption causes the initially mentioned problems.

In Austria, flysch sediments are widely spread from Vienna in the East to Vorarlberg in the West. Flysch consists of very stable sandstones on the one hand and soft, unstable clay marls on the other. For a long time, these marls have been known responsible for mass movements in this geological zone.

This project deals with the classifiaction of mass movements and the characteristics of clay minerals in general whereas special attention is paid to how clay minerals influence landslides. Within this project it is analysed to what extent the distribution of the different types of clay minerals contribute to the formation of gliding layers.

This question is applied on two sites in Upper and Lower Austria where slope instability is a problem. One of the main problems are buildings situated on such unstable slopes. Very often, buildings are affected and sometimes even destroyed by those mass movements. Since this is also an economic issue, counteraction must be taken.

On the purpose of determining the mineralogy and especially the clay content of those geological units, samples were taken from drill cores, prospectings, and probes and were examined by means of bulk and clay mineral analysis. High amounts of mixed layer minerals, smectite, and illite were found. There seems to be a correlation between the occurrence of those minerals and the gliding tendency of the observed slopes.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Cretaceous/Paleogene boundary (KBP) Fish Clay at Højerup (Stevns Klint, Denmark): Ni, Co and Zn in the carbonate and smectite of the black marl

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The black marl of the Fish Clay is made up mainly from biogenic calcite and cheto-Mg-smectite.

The biogenic calcite and cheto-Mg-smectite of this marl shows enhanced concentration of Ni, Co and Zn. The predominant source of these metals was probably the impact-ejecta fallout deposited on the top of nearby soil which was leached by the impact-induced-acid? surface waters.

Most of Ni and Co in the smectite is derived from chondritic component of the fallout but the ultimate origin of Zn may have been the impact-target rocks. The incorporation of these three metals into the smectite occurred during the KPB but before its redeposition to the Fish Clay site.

The enrichments of Ni in the biogenic calcite-rich/smectite fractions of black marl represent the metal sudden/rapid input into the seawater at the KBP.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Characterization of two commercial nanoclays and the morphology modification of the PHB obtained

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To minimize the environmental problems generated by the conventional plastics, major worldwide chemical companies are moving towards partly replacing traditional petrochemical commodity polymers with biopolymers which would allow for the reduction of xenobiotics in the environment and in landfill loads. The biodegradable polymers, polyhydroxyalkanoates (PHAs), emerge as possible palliatives, being poly (3-hydroxybutyrate) (PHB) – the most widespread and thoroughly characterized PHAs. The use of commercial nanoclays (5-10% by weight) for the preparation of nanocomposites have received special attention because of their improved properties as compared to conventional filler composites (GARCIA-LOPEZ et al. 2003).

In this work, the effect of the process conditions (5% nanoclays, 165ºC, 50 rpm and 30 min stirring) on the structure of the final material was studied for the mixtures preparation of PHB with commercial nanoclays (Cloisite Na^+ and Cloisite 30B – both from Southern Clay Products).

The nanoclays and products were characterized by means of XRD, TEM and DTA and DSC. The specific surface area (by means of water vapor adsorption) of the nanoclays was also measured.

DTA analyses of Cloisite Na^+ and Cloisite 30B indicate that the organic anions have a key impact on thermal stability of organoclays – which is in agreement with results obtained by CERVANTES-UC et al. (2007) - using the thermogravimetric method.

An increase in the crystallization temperature and smaller size of spherulite was found for the mixtures of the clays with the PHB.

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MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Submicroscopic accessory minerals overprinting clay mineral REE patterns

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The REE concentration of clay minerals, widely used in genetic interpretation of sedimentary formations, is generally analysed on bulk samples (INAA, ICP-MS). Among clay minerals, granular (typical size range: 60–1000 μm) glauconites offer a unique possibility for the application of local methods, e.g. LA-ICP-MS. Own LA-ICP-MS data of density-separated glauconite series, the GL-O glauconite standard and a phosphorite-derived glauconite were compared to data obtained by bulk methods (INAA, solution ICP-MS). LA-ICP-MS data often gave smaller (up to two orders of magnitude!) concentrations for REEs than bulk methods.

Apatite was detected by EDX in glauconite where phosphate was below detection limit by bulk methods. Already 0.2 % apatite present may cause a 100% contribution (error) in the REE content of glauconites. The effect of REE-phosphates is more dramatic. An unknown Ca-REE-phosphate ($Ca_{0.3-0.4}(Ce_{0.4}La_{0.1-0.2}Nd_{0.1})PO_4$) was identified by EDX in a Hungarian glauconite population, precipitating in the few-μm-size pores of glauconite. LA-ICP-MS analyses of these grains yielded total REE concentrations up to 5000 mg/kg. Model calculations showed that 0.0006 % monazite in glauconite may cause 100% error in the determination of the "glauconite" REE content.

The true REE content of glauconites was found to be low (0.5–0.01 PAAS; total REE content usually < 100 ppm), and decreasing with ongoing glauconitisation, but the own REE content is often camouflaged by REE-concentrating accessory phases, a problem surely of importance in the study of sedimentary rocks, too. These results showed that our data on clay mineral REE patterns may often be erroneous and that local analytical methods are necessary to reveal the true REE content of clay minerals.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Rietveld phase quantification of mixed-layered structures

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Phase quantification of clay minerals and similar layered structures by X-ray powder diffraction and the Rietveld method is hampered by several kinds of disorder in layer stacking. Such structures can consist (a) of stacks of layers with identical atomic arrangement and basal spacing, stacked with several translation vectors in a kind of “polytype-like” displacement, (b) of stacks of completely irregularly (turbostratic) arranged layers of the same type, or (c) of stacks of different kinds of layers with any kind of displacement, even turbostratical orientation. Outside the Rietveld method, several approaches for modelling of diffraction patterns of disordered layered structures do exist (DRITS & TCHOUBAR, 1990; TREACY et al., 1991). Although even automatic refinement procedures of one of these approaches were developed (LEONI et al., 2004), the refinement of mineral mixtures similar to sedimentary rocks is not yet possible.

Recently a powerful Rietveld-compatible solution has been developed for case (b) “turbostratic disorder”; however, the problem of mixed layering of different kinds of layers was still incompatible with the existing models. This problem can be overcome using the recursive method. The aim of the talk is to show that the recursive method can be implemented in a Rietveld model using a supercell approach in combination with a complex manipulation of the structure factor calculation. The consistency of the models is demonstrated by a refinement of measured patterns of clay minerals, which contain different kinds of stacking disorder.

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***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Clay mineral formation in acid soils in the area of an abandoned pyrite mine in Wieściszowice (Rudawy Janowickie Mts., SW Poland)

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Acid sulfate soils developed on mine dumps as well as on rock outcrops in the area of an abandoned pyrite mine in Wieściszowice (Rudawy Janowickie Mts., Western Sudetes, SW Poland) were investigated using XRD, FTIR and SEM-EDS methods. A low level of weathering (soil-forming) processes as well as low pH_{H2O} (from 2.8 to 4.4) in whole profiles is characteristic for studied soils.

Chlorite-sericite, pyrite-bearing schists of the Leszczyniec Unit (part of Karkonosze-Izera Massif) are the bedrocks of the soils. Primary phyllosilicates occurring in the bedrock are trioctahedral chlorites (brunsvigite, according to chemical composition) and dioctahedral micas (muscovite and paragonite).

Predominant minerals in clay fraction (<2 μm) of soils are chlorites and micas (‘illitic material’ represented by K-mica and Na-mica). In the clay fractions of the soil kaolinite and smectite are also present, minerals that do not occur in the parent rock. A mixed-layered illite/smectite mineral occurs in smaller amounts (presence of broad peaks ~8,6Å and ~5,6Å on XRD patterns). Smectite and illite/smectite mixed-layered minerals are more abundant (compared with other phyllosilicates) in fine clay fraction (<0.2 μm). Minor amounts of quartz and albite are also present in clay fractions of the soils.

Kaolinite occurs in each of investigated soil profiles as evidenced by the presence of characteristic peaks (7.18Å, 3.58Å, and sometimes others) on XRD patterns and absorption bands (e.g. near 3700 cm^{-1}) on IR spectra. The largest amounts of this mineral are observed in soil developed on sericite schists (containing mainly micas, quartz and pyrite). Kaolinite seems to be more abundant also in A or A/B horizons (comparing with other horizons) of some soil profiles.

It is difficult to determine whether vermiculite is present in investigated soils, because of possible overlapping of vermiculite and chlorite peaks on XRD patterns and/or probably very low content of vermiculite.

Results of this preliminary study suggest the formation of smectites and kaolinite in the acid sulfate soils investigated.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Synthesis of multiwall carbon nanotubes catalysed by smectite type of clays

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The chemical deposition growth of multiwall carbon nanotubes (MWCNT) was studied on nontronite particles used as catalyst. Particles were deposited as thin layer film on the silicone substrate either as sodium or iron exchanged form. Upon drying, the substrate was used for catalyst activation in an electrically heated oven at 700°C followed with carobn nanotubes growth phase. The synthesis total flow rate for argon used as an inert gas and acetylene used as synthesis gas varied (73 and 140 ml·min^{-1}), also the flow rate ratios (7, 11). Any of the selected conditions resulted in a growth of carbon nanotubes, however, with differences in their quantity and quality. The MWCNT´s were proved by transmission electron microscopy (TEM). Quantitative aspect of synthesized MWCNT´s growth was comparable by the density of the surface coverage using scanning electron microscopy and qualitative aspect was observable from TEM and micro-raman measurements in the raman shift range of 100-2000 cm^{-1}.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Mineralogy of red clays in SE Transdanubia, Hungary: comparison with similar Carpathian and Dinaric formations

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Quantitative XRD analyses were made on 181 red clay samples and compared with published data from the Carpathian and Dinaric area. The red clays on the limestone surfaces can be regarded as *terra rossa* in the same sense as in N. Hungary, the Carpathians and in the Dinaric range. They cannot be derived from the insoluble residue of the underlying limestone but their composition reflects climatic conditions of weathering.

Terrestrial red clays filling fissures and recently existing caves in limestone of the Villány Mts. are called *Tengelic Red Clay Formation* (Middle Pliocene to Lower Pleistocene). They occur in two types. A third type appears on the base of the Middle Pleistocene *Paks Loess Formation.*

(1) The older type of the *Tengelic Fm.* corresponds to the *Beremend Member* and to the *Csarnótan* biostratigraphic stage. It is red kaolinitic clay containing typically disordered kaolinite, mixed-layer smectite/kaolinite, smectite and little gibbsite. It was formed in the local subaerial weathering crust in warm, humid, subtropical or monsoon climate. Products of similar weathering, mineralogy and age occur on Mt. Esztramos, N. Hungary, in the Poltár Formation, S. Slovakia and on the Susak Island, Croatia.

(2) The younger member of the *Tengelic Fm.* called *Tengelic Member* contains red (or “reddish”) clay beds. It can be found not only on the karst surfaces but also in wide hilly areas of SE Transdanubia. It contains relatively fresh material (illite, chlorite), the weathering products are predominantly smectite and goethite formed under warm and dry climate in environmental conditions of savannah and steppe or forest steppe.

(3) The basal red clay layers of the *Paks Loess Fm.* contain similar material as the underlying red clays belonging to the *Tengelic Member* of the *Tengelic Fm.* The slightly but significantly lesser degree of weathering (more illite and chlorite, less smectite) indicates cooling of the climate.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Reductive transformation of nitrobenzene using bio-reduced Fe-clays: progress towards the development of *in-situ* groundwater remediation technology

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Clay minerals have numerous applications in industry, agriculture and the environment although currently, the Fe-bearing varieties are not widely exploited. Fe-rich smectites, e.g. nontronite, can contain up to 20wt% of structural Fe^{3+} and if a suitable electron donor is available, this structural Fe^{3+} can be utilized by Fe-reducing bacteria as a terminal electron acceptor. When reduced and in contact with fluid, the overall reactivity of Fe-clays changes, especially where interactions with water and various organic compounds are involved. Moreover, the presence of reduced Fe-clays has been found to induce the degradation of certain organic contaminants, e.g. chlorinated aliphatics and nitroaromatics.

The goal of this study is to develop an *in-situ* groundwater remediation technology targeting redox-sensitive organics, in the form of a permeable Bio Fe-clay barrier. To achieve this, the reductive capabilities of several iron-reducing bacteria have been tested using the structural Fe^{3+} in <2μm fractions of a Fe-rich smectite (nontronite, NAu-2) and a Fe-bearing bentonite (Speeton Clay Formation, Yorkshire, UK) as terminal electron acceptors. Of the bacteria tested, *Shewanella algae* BrY was able to bio-reduce structural Fe^{3+} within these clays most rapidly and to the greatest extent, giving $Fe^{2+}/Fe^{2+}+Fe^{3+}$ ratios of 0.34 and 0.19 for the nontronite and Speeton bentonite, respectively. These results are novel because the capability of *S. algae* BrY to reduce structural Fe^{3+} in clays has not previously been tested. Nitrobenzene was selected as the test redox-sensitive organic compound as it is a common subsurface contaminant and is of global toxicological concern. To test the capability of bio-reduced Fe-clay to transform nitrobenzene to aniline, the less toxic and more stable degradation product of nitrobenzene, nontronite suspensions with 20% and 30% structural Fe^{2+} were spiked with various concentrations of nitrobenzene and monitored for 5 days. Results showed that in all cases where reduced clay, *S. algae* BrY and the electron shuttle, AQDS, were present, 100% of the nitrobenzene had been transformed to aniline within 24 hours. Future column experiments will investigate the adsorption and degradation rates of nitrobenzene in contact with the Fe-clays. Results to date will be presented.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Crystall-chemical classification of smectites within the unified system of projection of chemical compositions of phyllosilicates

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Smectites are discussed in relation to the first crystall-chemical classification of phyllosilicates based on the unified system of projection of chemical composition (WIEWIÓRA, 1990). Three-dimensional plots are constructed, illustrating the relation of smectite to other 2:1 end member phyllosilicates. In dioctahedral sub-group, montmorillonite is the member of the theoretical solid solution series pyrophyllite – leucophyllite, and the layer charge is due to octahedral substitution. Beidellite is the intermediate member of a series pyrophyllite-muscovite. In trioctahedral subgroup, the major smectites are saponite and hectorite. Both are derived from talc, the former by tetrahedral substitution (talc-phlogopite series), the latter by octahedral substitution of Li for Mg (talc - tainiolite) series.

The XY projection field for smectites, derived from the above-mentioned 3D classification diagrams, is similar to micas and differs only by translation of the origin of the oblique axes. A sample is plotted using Si^{4+} and R^{2+} chemical data along orthogonal axes. If the layer charge is known, one can read out the values of vacancy and R^{3+}. For dioctahedral smectites with the charge located in the octahedral sheet (montmorillonites), a simple orthogonal classification diagram is proposed, based on Fe^{3+}-Al ratio and the value of layer charge (WIEWIÓRA et al., 2000).

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MINERALOGIA* - *SPECIAL PAPERS, *33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Swelling and dispersibility of shales in water based drilling fluids

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The vast majority of drilling problems occur in shales. Borehole instability leads to such problems as tight hole, differentially stuck pipe, sloughing and wash out incidents, all incurring significant costs associated with delays during drilling. Expandable clay minerals like smectites and mixed layer clays have long been considered to be responsible for these problems, which in the past could be effectively addressed by the use of oil-based fluids. However, these fluids cause environmental pollution and research is now focused on efficient inhibitive water based fluids which are able to solve the shale instability problem with least damage to the environment.

In this study the swelling and dispersion behaviour of three shale types in various water-based drilling fluids were compared in the context of their clay mineralogy and presumed reactivity. Low reactive shales should have an insignificant content of expandable clays, moderately reactive shales should have either larger clay content or contain clays of higher expandability than shales of low reactivity, and highly reactive shale should have large amounts of highly swelling clays. The studied shales were characterized by mineralogical analysis, cation exchange capacity and linear swelling tests in various salt solutions such as NaCl, NaBr, NaCOOH, KCl, KCOOH and mixed salt solutions, and in different drilling fluids based on gypsum, polyol/polymer, KCl/polymer, complexed aluminium and soluble silicates. Results showed that low reactive shales from the Mediterranean area proved to be a problem from another point of view in that they were exceedingly dispersive. This behaviour was not much influenced by salt solution treatment. In contrast highly reactive shales from Denmark, were stabilized by using certain concentrations of KCl in combination with other salts. From an assessment of the overall results, it was concluded that efficient inhibitive drilling fluid design in shale formations needs to take into account shale dispersibility in addition to clay mineralogy and swelling properties.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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Shale instability and clay mineralogy: a review

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Shale instability in well bores has long been, and still is, a major cause of concern in the oil industry. It is manifested through a variety of effects, the principal ones being sloughing and washout of shale into the well bore, swelling and dispersion of cuttings. Shale instability gives rise to a variety of problems including bit balling, adherence of clay material to the drill pipe, hole enlargement and poor cement jobs. Drill pipes may also become completely stuck, forcing abandonment of the hole. The causes of shale instability are generally recognized to be of a combined physico-chemical nature. Although some authorities place a greater emphasis on purely physical aspects, for the most part the interactions between drilling fluids and the clay minerals in shales are considered to be of primary importance.

It was early recognized that problem shales could be stabilized by the use of potassium-based drilling fluids (O'Brien & Chenevert, 1973). Here the K^+ ion was thought to reduce the swelling, hydration and dispersive tendencies of water-senstitive clay minerals, which were identified as montmorillonite, illite and mixed layer illite-smectite. These clay minerals are still considered to be especially reactive with respect to water-based drilling muds, with kaolinite and chlorite being considered as relatively unreactive. Opinion is not unanimous on this grouping, however, nor on the nature of shale destabilization and its inhibition. For example, Santarelli & Carminati (1995) questioned whether shales did actually swell in situ, irrespective of their active clay mineral content, preferring to interpret the instability observed in the laboratory to capillary effects on dried samples. Furthermore, they suggested that a water-based KCl mud could mineralogically transform kaolinite close to the well bore, leading to a weakening of the shale. Recent work by Carpacho et al. (2004) on kaolinitic shales in South America suggests that their instability is associated with the rapid illitization of kaolinite in the highly alkaline conditions close to the well bore. Use of drilling fluids based upon an aluminium organic complex stabilized these shales. Also controversial at the present time is the extent to which shale instability can be attributed to osmotic effects between the drilling fluids and the fluids present in the shale pores, with subsequent interactions with sensitive clay minerals. These and other controversial questions will be briefly reviewed and the scope for further research involving the role of clay mineralogy in shale instability will be discussed.

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Clay mineralogy of geophagic materials from Tanzania and other countries

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Geophagy is the deliberate and regular consumption of soils, clays and related materials by animals, including man. Various hypotheses have been advanced to explain this unusual behaviour, the main ones being to alleviate hunger pangs, to counteract deficiencies in micronutrients such as iron, zinc and calcium, and to reduce gastro-intestinal distress following exposure to toxins or pathogens. Geophagic materials have often been found to be rich in minerals of the kaolin group, which have in many cases been specifically identified as halloysite (Aufreiter *et al* 1997; Mahaney *et al* 1999). Wilson (2003) reviewed this and other work and concluded that the identification of the kaolin mineral in these geophagic materials required further characterization, as it was considered to be unlikely that animals have some extraordinary capacity to select halloysitic materials for their consumption.

We have investigated the clay mineralogy of 11 different geophagic materials from Zanzibar, Tanzania, that are regularly consumed by pregnant women. These materials are mainly from decomposed rocks (saprolites) that occur at depth in weathering profiles and are of various colours and clay contents. They are invariably poor in iron, zinc and calcium and their clay fractions are always dominated by a kaolin mineral. XRD examination, with supplementary ethylene glycol, formamide and heat treatments reveal that the clay fractions of five of the geophagic materials are dominated by kaolinite, two are dominated by halloysite and three consist of a mixture of kaolinite and halloysite. One sample consists mainly of a kaolin-rich mixed-layer structure, the nature of which is being further investigated. Also currently being further researched is the clay mineralogy of a collection of geophagic materials consumed by humans in other countries, including Kenya, Uganda, Rwanda, India, Turkey, Kyrgyzstan and Ukraine, the results from which will be presented in full and discussed in the context of the various explicative hypotheses.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Scientific study of the artwork at Nako, India

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Nako is a remote Tibetan village high up in the Western Himalayas of the Indian state Himachal Pradesh, where a compound of four earthen early period Buddhist temples with unique interior decorations has survived from the 12th century AD to the present day. The deterioration suffered at the site resulted in an urgent need for a conservation programme and a three-year scientific study funded by the Austrian Science Fund (FWF).

The study on the interior earthen support materials for sculptures and wall paintings in the four temples focuses on the chemical and mineralogical composition, and physical and mechanical properties – parameters that characterize the original substrate materials and also indicate their behaviour in the changing environmental conditions. Necessary therefore is not only the examination of the present state of the internal earthen supports, but also mapping and further condition assessment together with a selection of suitable sampling areas for analyses.

A substantial part of the research is carried out as analytical work with samples of adobe, mortars and plasters from defined sample locations. Instrumental techniques include optical microscopy, scanning electron microscopy with energy dispersive X-ray analysis, X-ray diffraction, pycnometry, mercury porosimetry, ion chromatography, particle size analysis, and measuring of the plasticity according to Atterberg. All sample and analysis information is stored in a digital sample database. The analyses results of samples taken from the temple building materials will not only serve for the scientific documentation of the temple architectural structures but will also exemplify the visible state of the supports for the interior decorations, show the actual impact of environmental effects, give an explanation of deterioration patterns and can also help to outline suitable and sustainable future preservation strategies.

Besides the study of the temple support materials, identification and analyses of local earthen materials still being used as traditional building materials for village housing have been undertaken and results are being compared with the original construction material of the temple. The acquisition of this knowledge, which can further help in conservation procedures and recommendations for the long-term care and maintenance planned by the villagers for their temples and artwork, will be an additional and very important goal of the research project.

MINERALOGIA - ***SPECIAL PAPERS****, 33, 2008*
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Rheological model for drilling fluids using generalized yield power law

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Drilling muds used for oil drilling are described with various rheological models (Newtonian, Bingham, Ostwald de Waele, Herschel-Bulkley). The Herschel-Bulkley model (Yield Power Law) which best describes the rheological parameters of drilling fluids requires modification. Principles of determining rheological parameters of drilling mud described with a model of Generalized Yield Power Law (GYPL) fluid were presented in the paper. The functions of shear stresses and shear rate are given. Then the conditions of laboratory measurement of rheological parameters of Generalized Yield Power Law fluids were introduced and corresponding mathematical dependences derived. Based on this the rheological model parameters were determined. When elaborating the block diagrams, the numerical methods for solving the dependences were introduced. Rheological parameters of an exemplary drilling mud were calculated using the methods.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
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POLSKIE TOWARZYSTWO MINERALOGICZNE

The computer method for determining a rheological model of drilling fluid

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Various types of fluids are used in a number of the above-mentioned methods, e.g. drilling fluids, lubrication fluids or sealing fluids. The properties of the used fluids depend, among others, on their rheological parameters. For describing the cause-and-effect relations between the rheological properties of fluids and the technology of its application, rheological models are constructed. The accuracy of fit of the rheological model to the real fluid minimizes error of the calculated parameters, e.g. character of fluid's flow, pressure losses in a circulation system, diameter of drilling tool or reamer nozzles, mechanic and hydraulic parameters of drilling, particle sedimentation and efficiency of cuttings removal, radius of technology of injection (flow volume, pressure and time of injection), power consumption during mixing operations, efficiency of mixing as well as thermal conductivity problems encountered during flow and mixing. A method of optimal selection of rheological model of drilling fluid worked out at the Department of Drilling and Geoengineering, Faculty of Drilling, Oil and Gas AGH-UST is presented in the paper. Relevant mathematical equations have been derived along with analytical and numerical methods of their solution. On this basis software RheoSolution has been elaborated. It helps the process of rheological model selection. The applicability of the proposed methodology has been exemplified.

MINERALOGIA - **_SPECIAL PAPERS_**, _33, 2008_
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

A comparison of paleosoils in different loess deposits

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Paleosoils in loess deposits give information on past soil-forming environments. Clay minerals, soil organic matter and carbonate content are indicators of former climate conditions and pedogenesis (BAJNÓCZI et al., 2006; KARLSTROM et al., 2008).

Different paleosoils from Wolkersdorf (Austria), Dolni Vestonice (Czech Republic) and Mexico were studied. Clay minerals were identified using X-ray diffraction. In the samples from Wolkersdorf and Dolni Vestonice, chlorite, illite, and smectite dominated, while in the Mexican soils high amounts of poorly crystallized kaolinite were found.

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. Also particle size analyses were performed.

The composition of soil organic matter was characterised using Fourier transform infrared (FT-IR) spectroscopy, thermogravimetry and differential scanning calorimetry.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Polish clayey raw materials for the production of ceramic tiles

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The ceramic industry is one of the fastest developing industries in Poland during the last years. In its production value structure, tiles lead (ca. 26%), while the share of tableware is ca. 18%, and sanitaryware – 7%. The tile sector has reported the largest growth compared to other ceramic branches. Its output in the last 15 years increased sevenfold, whereas the production of sanitaryware – fivefold. As a result, consumption of the basic ceramic raw materials has increased very fast, especially of white-firing clays, as well as red-firing ones.

For the production of white-body ceramic tiles (especially *gres porcellanato*) white-firing clays are the main clayey component. Currently these raw minerals are exclusively obtained as a result of processing sandy kaolinite-illite clays as well as kaolinite sands and/or sandstones. For this purpose some Cretaceous clays in the Bolesławiec region (SW Poland) and Jurassic clays in the Opoczno area (central Poland) are used. Kaolinite of the Cretaceous clays is well ordered, whereas of the Jurassic ones – mainly disordered. The Polish white-firing clays (especially the Cretaceous ones) are relatively coarse (median 1.9-2.5 μm, fraction <2 μm ca. 50%). It results in different ceramic properties: the Cretaceous clays are medium plastic and weakly sintering (bending strength after drying <2 MPa, water absorption after firing >10%). However, taking into account the volume of the Polish production of ceramic tiles, the domestic resources of clayey raw materials are insufficient which requires importing, especially from Ukraine and – to a lesser extent - from Germany.

In Poland for the production of colour-body ceramic tiles the Triassic red clays are commonly used. They are mainly mined in the N margin of the Holy Cross Mts in central Poland and – to a lesser extent – on the Cracow-Silesian monocline. Their mineral composition is similar. Clay minerals are represented first of all by illite which is accompanied by kaolinite, smectite, chlorite and mixed layered minerals (mainly illite/smectite). Non-clay minerals are as follows: quartz, hematite and – sometimes – feldspars. Generally, the currently exploited Triassic clays are calcite-free, representing their most valuable in ceramic industry, well-sintering variety.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

5-fluorouracil-intercalated layered double hydroxide as carrier for efficient cellular delivery

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A kind of inorganic layered host materials, layered double hydroxide (LDH) is widely known as hydrotalcite-like compound and often called anionic clay. LDH is endowed with potential for vector, since its layers lead to safe reservation of biofunctional molecules such as drug molecules or biomolecules. Therefore, LDH is focused the synthesis of new biocompatible nanohybrid materials. In this study, in order to develop a new type biocompatible nanohybrid material, we investigated an intercalation of anticancer drug, 5-Fluorouracil (5-FU), into Mg-Al LDH both by ion-exchange reaction and coprecipitation reaction. It is well-known that Mg-Al LDH itself is non-toxic and the NO_3/Mg-Al LDH (d_{003}=0.89 nm) and Cl/Mg-Al LDH (d_{003} = 0.78 nm) can be used as precursor materials for ion-exchange reaction. The synthesized nanohybrid materials (5-FU/LDH) were characterized by various methods such as XRD, FT-IR and SEM that verified the successful intercalation of 5-FU and provided information regarding the interlayer structure of the nanohybrids. The anticancer efficacy of 5-FU/LDH was estimated in vitro by WST-8 bioassay with the cell culture lines (L929).

The observed basal spacings of the 5-FU/LDH-cop by coprecipitation method, 0.8 and 1.1nm, resulted from the horizontal (parallel to the layer) or monolayer vertical (perpendicular to the layer) orientation of the incorporated 5-FU. In addition, the basal spacing (003) of the 5-FU/LDH-ie-NO_3 and 5-FU/LDH-ie-Cl by ion-exchange method were expanded to 1.10 nm. In addition, the crystallinity of the 5-FU/LDH-ie was higher than that of the 5-FU/LDH-cop.

In vitro activation of the 5-FU/LDH for L929, 5-FU shows 70% of cell viability at 1.0×10^4 ng/ml dosage, whereas the 5-FU/LDH-ie-NO_3, 5-FU/LDH-ie-Cl and 5-FU/LDH-cop at about 6.0×10^2, 3.0×10^2 and 6.0×10^2 ng/ml, respectively. Such a concentration gap is surely due to the fact that the 5-FU/LDH could permeate the cell membrane much more effectively than 5-FU itself. The obtained results show these drug-inorganic nanohybrids can be used as a potential drug delivery system.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Preparation of novel inorganic-organic nanocomposites from „host-guest“ intercalates of kaoline and halloysite

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Novel hybrid systems of kaolinite and halloysite can be prepared by intercalating suitable guest molecules between successive kaolin layers within a single particle. Dimethylsulfoxide (DMSO) is a typical guest molecule that can intercalate directly into 1:1 type clay minerals, through hydrogen bonding and dipole interactions. DMSO can be displaced by other guest molecules, giving rise to novel supramolecular hybrid systems. Here we report that inorganic-organic layered hybrid material based on kaolinite can be prepared by intercalation of coumarin C522 through the guest displacement reaction. The resultant material was characterized by X-ray diffraction and Fourier transform infrared spectroscopy. FTIR showed intense perturbation of the AlAlOH stretching vibrations of kaolinite in the 3700–3600 cm–^{1} region for both the DMSO and coumarin C522 intercalates. XRD indicated ~100% intercalation of DMSO into kaolinite. The basal (*d(001))* spacing of the starting kaolinite increased from 0.72 nm to 1.12 nm on intercalation of DMSO, a value typical for DMSO- intercalated kaolinites. Displacement of DMSO by coumarin C522 decreased the basal spacing to 0.84 nm, indicating that the coumarine molecules adopted a parallel orientation with respect to the kaolinite layers.

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MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Preliminary mineralogical characteristics of soils developed from Lower Triassic clay deposits (Buntsandstein) in the Holy Cross Mts. (S Poland)

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Soils developed from red clay deposits of different stratigraphic-facies units of the Lower Triassic (Buntsandstein) have been subject to investigations. Due to the specific character of the parent rock, it is difficult to determine the influence of pedogenic processes on the formation of the physical, chemical, and exploitation properties of these soils.

The study was focused on the mineralogical characteristics of the assemblage of clay minerals, so as to determine the relation between the processes of litho- and pedogenesis during the formation of the soil substrate. XRD and SEM methods were applied in the analysis.

XRD studies pointed to the domination of illite or kaolinite in the soil substrate of the genetic horizons of all studied soils; these minerals are accompanied by a variable volume of chlorite or vermiculite. Detailed analysis of the diffractograms shows that features of these minerals are very similar to the features of minerals from the Triassic rocks lying beyond the influence of pedogenic processes. This testifies to the lithogenic origin of the minerals.

A low content of mixed-layer minerals e.g. illite-smectite type or vermiculite type HIV has been noted in the sub-surface ochric and mollic horizons. Their presence should be linked with the direct influence of the soil environment on the lithogenic soil substrate.

SEM analysis showed the variable structural properties of the clay substrate within the soil horizons. In the middle and lower part (below ca. 50 cm), structures built of intact packets of kaolinite or illite have been observed in pores between grains, as well as independent units. According to literature data they represent diagenetic structures typical of the Lower Triassic clay deposits (Barczuk 1979). In the surface horizons the structural features are strongly transformed towards dispersion, followed by secondary aggregation.

The obtained results indicate the dominance of lithogenic features of the soil substrate in the studied soils. Influence of pedogenic processes is restricted to the surface horizons and is reflected in physical destruction, whereas chemical influence leading to the transformation of minerals and formation of new pedogenic minerals is poorly marked. The poor development of pedogenic processes in the studied soils may result from their 'young' age (erosion of soil profiles) and from the distinct resistance of the clay soil substrate developed from Lower Triassic rocks to pedogenic factors.

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MINERALOGIA - SPECIAL PAPERS, 33, 2008
www.Mineralogia.pl

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Two illite generations in a Vendian shale: the K-Ar and O-isotope evidence

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Six clay subfractions (SFs) in narrow size-ranges from 1-2 μm down to 0.1-0.2 and <0.1 μm have been separated from shale of the Basa Formation (The Vendian, southern Urals) and studied by the XRD, K-Ar and O-isotope methods. All the SFs are dominated by illite, an admixture of chlorite is no more than 5-10 per cent. The coarser SFs include some $2M_1$ illite as well as the usual 1M polytype. The finer SFs contain only $1M_d$ illite. The characteristics of clay particles vary unidirectionally with their sizes. As the size decreases from 1-2 μm to 0.1-0.2 and <0.1 μm: (1) The I_{002}/I_{001} ratio tends to increase from 0.20-0.25 to 0.30-0.50; (2) Illite crystallinity index shows a rise from 0.28° to 1.06°Δ2θ; (3) The content of K also increases from 3.92 to 5.20 per cent; (4) The K-Ar dates are diminished from 920 to 582 Ma; (5) There is a negative correlation between the contents of K and ^{40}Ar in the SFs. The δ^{18}O value is 12.39-12.36‰ V-SMOW in the coarsest 1-2 μm SF and rises to 15.07-15.71‰ in the 0.6-1 μm SF. Yet then it drops drastically with reduction of the particle sizes to 11.71-11.85‰ in 0.3-0.6 μm SF and to 8.93‰ in 0.1-0.2 μm SF.

All the evidences together suggest that the SFs consist of two non-cogenetic illite generations and contain them in various proportions. It is obvious that the $2M_1$ and 1M illites of the first generation in coarser SFs with low crystallinity indices are of detrital origin because their K-Ar dates far exceed those corresponding to stratigraphic position of the Basa Formation. On the contrary, the K-Ar date of 582 Ma for the second $1M_d$ illite generation in the finest <0.1 μm SF is in good agreement with this position and appears to correspond with the time of burial diagenesis of the Basa sediments.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

The cation distribution in glauconite structure: the model conception and Mössbauer data

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Practice of using of glauconite 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 glauconites enables to estimate, whether the cation distribution is primary or resulted from post-diagenetic transformation of the mineral structure. Moreover, it is possible to specify the chemical peculiarity of these processes. The efficiency of the approach under consideration has been demonstrated previously (see bibliography in Zaitseva et al., 2008).

This method was used to assess structure peculiarities of the glauconites from the sandstones of the Khaipakh Formation, Olenek Uplift, Northern Siberia. It was shown that the Rb-Sr (1170±16 Ma) and K-Ar (1175±44 Ma) dates established for glauconites correspond to the time of early diagenesis in their host sediments, being suitable for age assessment of the Khaipakh Formation.

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MINERALOGIA - **_SPECIAL PAPERS_**, _33, 2008_
www.Mineralogia.pl

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POLSKIE TOWARZYSTWO MINERALOGICZNE

State-of-the-art of the quantitative mineral analysis of clay-bearing rocks as revealed by the 4th Reynolds Cup contest

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The Reynolds Cup contest is a biennial competition on quantifying the mineral composition of three known clay-bearing artificial mixtures as accurately as possible. In 2008 the 4th competition was organized. Detailed information on the artificial mixtures, the results of the competition and successful methods and techniques used by the top-contenders will be presented.

***MINERALOGIA** - **SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Modification of FSM-16 mesoporous materials structure – preliminary results

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FSM-16 (folded sheet materials) is an ordered mesoporous silica with hexagonal arrangement of uniform pores in the range 2-5 nm. It can be synthesized from the crystalline single-layered polysilicate kanemite ($NaHSi_2O_5.3H_2O$) via templating with ***aqueous solutions of organic surfactant molecules. The aim of the present study was to obtain FSM-16 materials of potential interest for catalytic applications, by doping*** the solids with Al(III) and Fe(III) in order to develop acid or redox functions. The metal cations were introduced into the FSM-16 materials by means of direct synthesis, at the stage of kanemite preparation. The samples with Si/Al and Si/Fe ratio of ∞, 60, 40 and 20 have been prepared. XRD confirmed the formation of a typical FSM-16 structure in all investigated materials. The pore size distribution showed the presence of uniform pores of ca 2.3 nm width. ^{27}Al MAS NMR spectra revealed that all Al existed in tetrahedral sites, indicating that the incorporation of Al into the silica framework of the FSM structure was complete in the whole range of investigated Si/Al ratios. The results of Mössbauer spectroscopy used to study the oxidation state and local environment of Fe showed the presence of tetrahedrally coordinated Fe^{3+} centres in all studied samples. ESR spectroscopy revealed the presence of several signals. One, at $g \approx 4.3$, indicated the presence of isolated Fe sites in strongly distorted tetrahedral environment. Other signals, appearing at $g \approx 2.0$, could point both to the tetrahedral and octahedral Fe centres. In the Si/Fe=20 material with the highest Fe content a signal contribution from magnetically interacting Fe species was detected, which might point to the presence of amorphous, extra-lattice FeO_x clusters.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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Synthesis, physicochemical characterisation and catalytic properties of hydrotalcite-like Cu-Mn-Al compounds

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The aim of this study was to obtain mixed oxides containing Cu, Mn and Al from hydrotalcite-like precursors and determine their activity in the total oxidation of volatile organic compounds (VOCs). Carbonate forms of HTlcs were obtained by coprecipitation method at a constant pH. The synthesized series included ternary Cu-Mn-Al solids with different Cu:Mn:Al ratios, as well as binary oxides Cu-Al (2:1) and Mn-Al (2:1). Precursors were converted into the mixed oxides via calcination at 450°C for 3h. No HTlc structure forms in the binary Cu-Mn system. However, addition of Al allows for the precipitation of HTlcs. In the present study the lowest Al content at which HT-like structure can still be observed is ca. 5 at.% (sample Cu:Mn:Al = 12:5:1). The second factor determining the nature of the precipitate is the pH value of the synthesis. Carbonate forms of HTlc structures incorporating both Cu and Mn are formed at pH 9-10. High pH enhances also the crystallinity of obtained HTlcs. Al lower pH values Mn incorporation is incomplete and crystalline phase of layered $Cu_2(OH)_3(NO_3)$ appears together with nitrate forms of Cu-Mn-Al-HTlc of low crystallinity, and, occasionally $MnCO_3$ (rhodochrosite). Crystallinity of the HTlc precursors depends also on the sample composition. Growing relative Cu content results in improved HTlc crystallinity, while increase of Mn content leads to the less crystalline material. Mixed oxides formed by calcination of HTlcs at 450°C are very active in the catalytic combustion of toluene. On the basis of XRD, TPR, HRTEM and XPS studies it is suggested that $CuMn_2O_4$ spinel phase, whose formation is favoured in the Mn rich Cu-Mn-Al samples, is responsible for enhanced activity.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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Mineral composition and petrophysical parameters evaluation from well logging data: Carpathian Foredeep example

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Knowledge of mineral composition is helpful in the interpretation of log data, where the hydrocarbon saturation is expected as the final result. In the shale-sand lithology, where the rock matrix can conduct the electric current, the Waxman- Smits formula should be applied. This formula combines the rock porosity, water saturation, water resistivity and CEC with the whole rock resistivity. The cation exchange capacity (CEC) is introduced to this formula as a parameter determining the shale ability to conduct electricity. Typically CEC is controlled by the smectite content of the rock. Porosity is the second important parameter calculated from the log data, using its direct relation with the bulk density and the matrix density. Matrix (mineralogical, grain) density can be calculated precisely only when the mineral composition is known.

Extended mineralogical (quantitative mineral composition, CEC, TSSA) and chemical (major, trace and REE) analyses were made for over 300 core samples obtained from four gas fields in the Miocene formation of the Carpathian Foredeep. The analysis allowed to quantify the most important clay components: mixed-layer illite/smectite and discrete illite.

Statistical multivariate analysis of all data helped to set up a comprehensive petrophysical model. Finally we could establish a reliable correlation ($r^2 = 0.95$) of thermal neutron absorption cross section Σa and total natural radioactivity GR with CEC, with boron and rare earth elements (the two most important Σa contributors) in the rock matrix. Correlation increases to $r^2 = 0.98$ when Si, Ca and Fe contents are included to model. These good correlations permit a continuous on-line CEC determination and therefore a reliable application of the Waxman-Smits water saturation model.

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Applicability of selected clays from NE Slovenia

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Samples of selected clays from NE Slovenia were analysed in order to determine the possibility for their use. Analysis of particle size distribution, plasticity index determination as well as detailed mineral composition determined by means of X-ray powder diffraction, were carried out.

Clays from genetically similar layers exhibit differences in mineral composition as well as mechanical and PSD properties.

Among the clay minerals illite, illite/smectite mixed layer mineral and clinochlore prevail. Quartz, iron oxide and feldspar are present in all samples. Silt fraction reaches 80-89% and plasticity index is in the range of 19 to 59.

There is an excellent correlation between mineral composition of clays and their mechanical properties.

Results show that investigated clays are suitable for production of ceramics – thin walled hollow bricks, and also for liners and barriers.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Impact of clay minerals and some drilling mud additives on microbial life

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Biological processes taking place in mixtures of soil and drilling mud were investigated. The consumption of oxygen and production of CO_2 were accepted as indicators of metabolic processes. For this purpose a flow respirometer Micro-Oxymax was used by Columbus Instruments. These parameters were measured in different reclaimed drilling muds with brown soil as a reference. Different variables were considered:

- enrichment of substrata with organic matter, e.g. straw or sawdust,
- concentration of nutrients in varying proportions, especially N:P:C,
- inoculation by fungus *Pezicula malicorticis*.

Fungi were used as a source of effective enzymes for plant tissue decay and possible decay of other artificial organic compounds dissolved in drilling muds.

The results showed that high montmorillonite content in drilling muds was rather useful for the microbial community. Reclaimed soils had two to three times greater metabolism than the control arable soils. The obtained results confirmed the clay containing drilling fluids can be treated and advantageously used in environmentally friendly conditions. The respirometric method can be used for analysis and interpretation of the reclaimed systems.

AUTHOR‘S INDEX

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ABSTRACTS - *ERRATUM*

ZAKOPANE, POLAND, SEPTEMBER 22-27, 2008

***MINERALOGIA** - **SPECIAL PAPERS**, 33, 2008*
www.Mineralogia.pl

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Clay mineral assemblages and diagenesis in Ordovician shale of Iraq

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In the Ordovician succession of Iraq, shale alternates with sandstones and generally forms about 60% of the succession in the Khabour Formation. X-ray diffraction analysis of the Khabour shale revealed the presence of illite, chlorite and kaolinite, in addition to mixed layers of illite-smectite and non-clay quartz, feldspars and mica. Scanning electron microscopic study has revealed the presence of randomly interstratified illite-smectite and neoformed iron-rich chlorite (Figure 1A,C). The presence of the later mineral is indicated also through the EDAX analysis, which shows higher content of Fe in the studied chlorite. The mixed illite-smectite layer is observed in not well–developed honeycomb structure with the incipient development of illite fibers (Figure 1B), an indication of random interstratifications of illite-smectite at a depth of 2,400 m in the Khabour shale of well Akkas-1, western Iraq. Below this depth the randomly interstratified illite-smectite is changed to a regular or well developed one (orderly interstratified OI). Other minerals observed are the illite fibers and illite flakes that present as a pore-throat between detrital components and fill the pores partly or as flakes covered the grains. Chlorite in disc shapes also present as pore filings in addition to hexagonal shape plates of Kaolinite (Figure 1C). In deeper buried shales of the studied section, mica is commonly observed in these shale which are generally fissile with dominant irregular pyrite bloches (AL-JUBOURY & AL-HADIDY, 2008). The enrichment with mica and common presence of illite plates and thick hexagonal platy kaolinite (dickite) are observed. Generally, the gradual conversion of smectite into mixed-layer illite-smectite (I-S) with increasing burial depth and increasing temperature is common in shales deposited in subsiding basin (EBERL, 1984).

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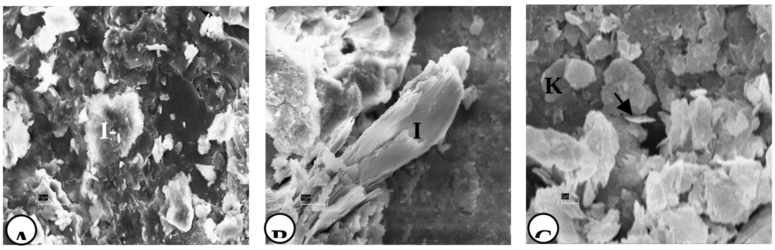

Figure 1: A, SEM image of illite-smectite (I-S), B, illite (I), and C, disc-shaped chlorite (arrow) and hexagonal kaolinite (K). Khabour shale, well Akkas-1, western Iraq.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
www.Mineralogia.pl

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Clay mineral composition of the seafloor sediments from the Gulf of Thailand, South China Sea

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This paper presents selected results of multidisciplinary research performed to characterize seabed morphology, features of sediments and quaternary geology of the Gulf of Thailand. This gulf is a part of the South China Sea and it has a maximum water depth of 86 m below the mean sea level. The thickness of Holocene marine sediments ranges from 20 to 0.50 m.

The major stratigraphic boundary for shallow sediments within the central part of the Gulf of Thailand is the unconformity separating Holocene marine soft clays and stiff silts/clays from the underlying Pleistocene alluvial-fluvial-deltaic complex. The seafloor sediments of the central part of the Gulf of Thailand can be correlated with lithostratigraphic units of Lower Central Plain of Thailand.

The samples for this study were collected from marine deposits of the Holocene-Pleistocene period. The upper part of sea sediment (unit A) is greenish grey, very soft, silty clay, highly saturated with water, and contains marine fossils. Kaolinite is the major component of the clay fraction. Minor amounts of illite and I/S mixed layers have been detected. The lower part (unit B) consists of cohesive stiff to very stiff sediment, which varies from clayey silt to sandy silt. Clay fractions consist of kaolinite, illite, I/S mixed layer and chlorite. Unit C are comprise of a series of stiff to hard clays interbedded with minor horizons of silt or sand. They may contain silt partings, ferrous stains, shell fragments and organic pockets.

The clay mineral assemblages in samples from the investigated area is similar to the clay minerals assemblages from Lower Central Plain of Thailand. Kaolinite- rich soils are most common for the upland soils in the north-eastern peninsular Thailand, covering nowadays about 47% of the country (YOOTHONG el al., 1997). Kaolinite is the major clay mineral observed in the unit A of the seabed sediments. Clay minerals spectrum found in the unit B comprises of kaolinite, smectite (mixed layer I/S), chlorite and illite. Kaolinite-smectite-illite assemblage is related to the northern part of the Central Plain and to the valleys of the northern region, whereas the smectite-illite and less kaolinite assemblage occurs mostly in deltaic plains and former tidal plains.

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Formation of clay minerals in a depleted gas reservoir, Molasse Zone, Austria

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Sandstones of the studied Miocene gas reservoir are resedimented deposits from the southern slope of the Austrian Alpine Molasse Basin. Reservoir rocks are heterogeneous medium- to coarse grained sandstones containing large clasts of shales and carbonates. The gas reservoir has been produced and is now used for underground gas storage. To better understand the mineralogy of the reservoir sandstones with respect to the different zones (gas-, water- and transition zone) and the effect of drilling fluids to the formation, multiple analyses were carried out.

Diagenetic alterations in the sandstones are feldspar overgrowths on detrital K-feldspar grains; authigenic quartz overgrowths; framboidal pyrite formation, later dissolution and octahedral pyrite formation; calcite- and dolomite cementation; authigenic clay mineral formation and an early formation of glauconite.

The focus was to characterise the authigenic clay fraction (excluding shale clasts) in the different zones. Samples of the gas-bearing, the transition, the secondary watered and the initial water zone were analysed.

X-ray diffraction analyses of the clay fractions showed that there are clear zone-dependent differences. Increasing crystallinity of smectite, chlorite and illite from the gas-bearing to the initial water zone and an increase in the clay mineral content could be observed. Most important is the fact, that there are no expandable clay minerals in the gas-bearing zone. This changes in the transition zone where smectites are developing.

There is a considerable effect of the rising water level (due to gas production) on the authigenesis of clay minerals in the pore space. Within a few years of the start of water infiltration new clay minerals are forming. Existing ones start to recrystallise and expandable clays appear in the transition zone where primarily none were present.

The drilling mud had little interaction with the reservoir rocks. Expandable clay minerals showed different behavior from the outer rim (about 1cm) of the cores towards the center. Smectites absorbed potassium from the drilling mud which resulted in a decrease of the interlayer spacing.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
www.Mineralogia.pl

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The adsorption of heavy metal ions by clay minerals

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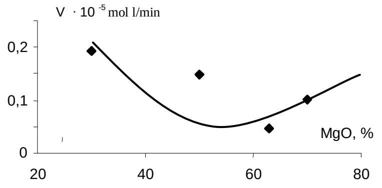
This work deals with the investigation of sorption of heavy metals from water phase by clay minerals of different composition. Layered double hydroxides are the most known clay minerals with anion-exchange properties.

The ion-exchange procedure is the most effective method of heavy metals adsorption from liquid phase. The widely used sorbents are the active carbons of different modifications, but the use of active carbons is limited by their high cost. As well, the sorption of heavy metals by active carbons is a physical process; there is no bond between the ions and the matrix, so the equilibrium process is possible. So the investigation of new alternative sorbents for heavy metal ions is very important.

The aim of our work was to investigate new sorbents and to create a new technology for ions adsorption from liquid phase.

We have studied the adsorption of heavy metal anions (CrO_4^{2-}, $Cr_2O_7^{2-}$ etc.) by layered double hydroxides with general formula $Mg_xAl_y(OH)_z$ with different degree of the isomorphouse substitution (MgO: 1 – 30, 2 – 50, 3 – 63, 4 – 70 %). The sorption has been studied in dynamic regime in neutral phase. The concentration of chromium ions was determinated by spectrophotometric method using the diphenylhydrazine as indicator.

The dependence of a reaction rate on the mineral composition is shown in the picture.



The dynamic anion-exchange capacity of studied sorbents is as: «30» - $6{,}9\cdot10^{-2}$, «50» - $7{,}7\cdot10^{-2}$, «63» - $1{,}05\cdot10^{-2}$, «70» - $2{,}2\cdot10^{-2}$ meq/g. One can conclude that the adsorption rate has the direct correlation with the anion-exchange capacity. The most effective sorbent is the sample with MgO — 60%, the degree of chromium adsorption is about 90%.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008
www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

The comparison of heavy metal adsorption by natural and synthetic takovites

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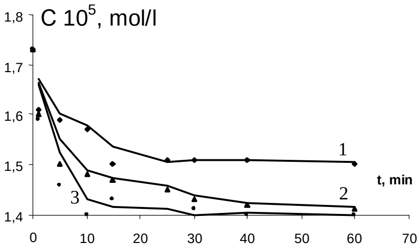
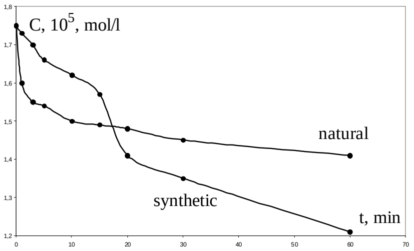
Heavy metal ions adsorption from water phase with active carbon has been studied earlier. But the use of active carbons is limited by their very high cost. So it is very important to create and investigate the new classes of alternative sorbents with high capacities and low costs.

The mineral takovite, $Ni_2Al(OH)_{16}CO_3 \cdot 4H_2O$, occurs in karstic bauxites togather with minerals such as nepouite, gaspeite, and carrboydite in weathering nickel sulfide deposits. The structure of takovite consist of brucite like layers. Two-dimensional layers have the positive charge due to the isomorphous substitution of layer cations by cations with higher positive charge. The carbonate-ions and water molecules are in the inner interlayer space. The earlier experiments have shown that acid treatment did not cause the structure destruction.



The synthetic takovite has been obtained by the reaction of Ni^{2+} and Al^{3+} concentrated solution with hydroxide-carbonate solution. After that takovite was crystallized at 60–325 ^{0}C and dried.

The composition of takovites has been determined: (natural: Al_2O_3 - 67 %; NiO - 23 %; TiO_2 - 4,4 %; SiO_2 - 3,7 %; Fe - 0,6 % . synthetic: Al_2O_3 - 73 %; NiO - 22 %; TiO_2 < 0,1 %; SiO_2 < 0,1 %; Fe < 0,1 %). X-ray podwer pattern analysis has shown the next inner space dimension d_{001} (synthetic takovite d_{001} = 7,51 – 7,55 A, natural takovite d_{001} = 7,6 A). Also X-ray podwer pattern analysis has shown, that natural takovite has additional phase with lines 14.50, 28.30, 34.40. One can conclude that it is reevesite.



The sorption of heavy metal anions by synthetic and natural takovites has been studied in dynamic regimes in neutral phase. The concentration of chromium ions was determinated by spectrophotometric method using the diphenylhydrazine as indicator. The figures show the results of the experiments (the amount of takovites: 1 – 0,05; 2 – 0,0686; 3 – 0,1 g).

MINERALOGIA *-* ***SPECIAL PAPERS****, 33, 2008*
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Clay mineralogy of the Late Miocene successions of north part of the Aktoprak Basin (Central Turkey)

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Three profiles representing alluvial fan and lacustrine facies in the north-east part Aktoprak Basin have been investigated. messinian alluvial fan, lacustrine sediments, the so-called Kızılbayır Formation of Aktoprak basin (Central Turkey) consists of conglomerate, sandstone, claystone, limestone, marl and dolomite. Dolomite, limestone and marl are white or beige-cream colored and fine grained. Conglomerate, sandstone and claystone are typical with red colors. Red claystones cropping out at the lower part of the sequence is alternated with sandstone and lenses of conglomerate. Dolomite, limestone and marl are observed only at the middle part to top of the profile of lacustrine sediments. The most significant results are as follows: (1) Feldspar, quartz, calcite, and dolomite minerals are dominant in the study area. They are accompanied by chlorite, smectite, illite and palygorskite; (2) SEM studies indicated that calcite and dolomite are hexagonal and rhombic crystal types. The minerals show meteoric type cement which characterizes a meteoric-vadose zone. Cement is mainly calcite and occurs as fine- and coarse-grained calcite; (3) Chlorite, smectite, and illite are products of alteration of the underlying Güney Formation and then transported by the local streams into the Kızılbayır Formation, thus these are considered as reworked materials; (4) Authigenic palygorskite is as a result of the precipitation of carbonate units in alkaline conditions, high Si and Mg activity and low Al.

***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

An investigation into the influence of the stabilization process of replaceable cations on the proprieties of obtained intercalcates

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Application of chemical technologies utilising interfacial phenomena in research and in design and optimisation of industrial processes prompts us to search for new sorbents and catalysing agents. Smectites (montmorrilonites), which are major constituents of bentonite rocks, exhibit rather poor sorptive properties and structural instability due to swelling. On the other hand, they are susceptible to processes that change their structure and properties. The search for new modification methods aimed to transform the structure of these minerals through the changes of their porosity, chemical character, surface, sorptive and catalytic properties is well merited. The purpose of the research program was to establish how partial stabilisation of interpack cations influence the intercalation process and the properties of thus obtained intercalates. Since the intercalation mechanism involves ionic exchange, the amount of admitted oligocations should depend on their charge and the ion exchange capacity of the mineral. Controlling the amount of admitted oligocations and their size, controls the column/support height and spacing as the parameters determining the size of micropores. The resultant form of smectite was obtained from bentonite clay from Chmielnik, by sedimentation. Li^+ ions were thermally stabilised in the sodium-lithium form of smectite with variable molar ratio Na/Li. Stabilised samples were transformed into intercalate form by the Vaughan method. The influence of these modifications on the texture of thus obtained samples was investigated on the basis of XRD data and argon sorption measurements (77.5 K). Lasting retention of a proportion of exchangeable cations in the smectite structure causes its ion exchange capacity to decrease. It is reasonable to suppose that this modification and the intercalation process should produce systems having various numbers of oligocations between the ion packs. Such a system should be characterised by an increased volume of micropores. Two tendencies become apparent: a decrease of the specific surface value with an increased proportion of lithium in the ion composition of the interpack structure and a decrease of the specific surface with the increased temperature of calcination.

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***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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Changes in the porous structure of acid-activated mixed sorbent (montmorillonite – silica gel)

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More and more common use of chemical technologies based on interfacial phenomena gives a boost in seeking out new sorbents and new catalysts of improved parameters, that at the same time are cheap and may be produced from easily accessible, natural raw materials. Smectites (montmorillonites), forming the main component (clayey) of bentonite rocks have moderate sorptive properties and show some instability of structure caused by swelling. On the other hand, their structure and properties can be easily modified. In addition to the known and already applied methods of modification (acid activation and intercalation), one of the more interesting and perspective methods is the formation of mixed systems (based on two or more highly dispersed components). When the size of the components approaches the dimensions typical for colloids (such systems are often called nanocomposites), the synergetic effect appears whereby the properties of the resulting mixture are no longer a sum of the properties of its individual components. A bi-component, mixed mineral sorbent (montmorillonite – silica gel) (KRZYŻANOWSKI & ŁYSIK, 2004) was obtained from montmorillonite (separated by sedimentation from the Milowice bentonite (Poland)). The changes in the sorptive properties of the formed system were studied measuring the low-temperature sorption of argon. The changes in the porous structure were analysed by densimetric and porosimetric studies. The small quantity of gel modifies the primary texture of montmorillonite (cp. the increase of the interpacket spaces moved away by the globular particles of silica gel) and adds adsorption centra. Both factors cause advantageous changes of the sorptive properties of the studied system. On the other hand, the globules of the silicic acid gel move away the mineral packets in a stable way, thus enhancing the interlayer space, which facilitates the acid activation process.

Acknowledgements. Financial support for this study was provided by AGH framework no: 10.10.210.52.

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***MINERALOGIA - SPECIAL PAPERS**, 33, 2008*
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POLSKIE TOWARZYSTWO MINERALOGICZNE

Possible illite polytypes in the glacigenic sediments

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Traditional clay studies mostly are addressed to massif and homogenous sediments and rocks and only some of them gave detailed mineralogy of clay minerals from geochemical active environments. Clay mineral evolutions from different stages of primary sediment diagenesis are well known, however, the knowledge is very limited to past glacial environments.

In particular X-ray diffraction analysis of clay minerals and studies of structure modifications in the illite crystal lattice can provide new information regarding processes under different geological conditions and be useful to understand changes associated with sedimentation and weathering peculiarities.

The objectives of the study are to carry out quantitative X-ray phase analysis of the clayey sediments from till and basin sediment contact zones, quantify the clay mineral phases in the samples and analyze illite polytypes. An effort is undertaken to explain an impact of glacier geological activity accumulating subglacial material on the illite structures or clayey fraction transport.

Study demonstrate, that identification of minerals is complicated due to a large number of phases present in samples and diffraction maxima for some phases are overlapped in XRD powder patterns. Modifications of illite structures are studied for samples containing fractions of size <2 μm and illite structure modifications are determined in the range from 22.0° to 35.5° 2θ CuK radiation (30kV, 40mA).

Besides reflections of illite, strong maxima of quartz, albite, hematite and other phase can be observed in the samples for studied region. There are several more overlaps of illite reflections, these overlapping reflections are not used in determination of illite structures. Differences in the illite polytypes are semi-quantitatively obtained from X-ray powder diffraction data. Study demonstrates various proportions of 1M*cv* and 1M*tv* polytypes structures. Several more 2M_1 reflections are detected in samples of lacustrine basin and glacigenic sediments. With regard to previous studies an individual approach in the samples bearing many phases for quantitative comparison of illite polytypes and the data processing profile simulation computer program should be applied. However, this cannot be always recognised as ultimate solution for possible polytypes quantitative evaluation.

MINERALOGIA* - *SPECIAL PAPERS*, *33, 2008

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POLSKIE TOWARZYSTWO MINERALOGICZNE

Possible raw material for manufacture of helenistic pottery on the island of Vis, Croatia

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The ancient Issa, one of the oldest urban nucleus in Croatia, is situated on the island of Vis. Archaeological excavations have yielded many artefacts (pottery kilns, moulds, fragments of pottery waste, vessels with distinctive shapes and decoration) which indicate local pottery production within the settlement during the Hellenistic and Early Roman periods.

The subject of this study is possible raw material of local origin for its production. Clayey material, as well as possible temper material were sampled from several locations on the island. Different types of sampled clayey materials include: relatively pure clays found in the vertical cracks within Cretaceous limestones and in some other restricted areas on the island; terra rossa, Pleistocene paleosol rich in clay; and material formed by weathering of volcanic rocks. Possible temper materials sampled are: Quaternary quartz sands, probably of aeolian origin and Albian quartz sediments of unknown origin.

Current investigations are based on detailed mineralogical analyses of ceramic fragments and possible raw materials. Mineralogical analyses include powder XRD analyses of bulk samples, as well as XRD analyses of random and oriented samples of the clay fraction of clayey material.

***MINERALOGIA* - *SPECIAL PAPERS*, 33, 2008**
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MINERALOGICAL SOCIETY OF POLAND
POLSKIE TOWARZYSTWO MINERALOGICZNE

Clay minerals of Lake Hovsgol (Mongolia) bottom sediments as indicators of paleoclimate changes in Central Asia

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The study of clay mineral assemblages and crystallochemical characteristics of individual mineral phases is a powerful tool for understanding the processes of lacustrine sedimentation. Theirs compositional and structural variations in sedimentary sequences depend directly on the climatic and environmental evolution in the region.

Lake Hovsgol, located in Mongolia, occupies an area of 2760 km^2 with a maximum depth up to 262 m. The Holocene-Pleistocene bottom sediments recovered by borehole HDP-04 (core length 81.2 m) have an age of 1 Ma. The bottom sediments are represented by fine silty clays with intercalations of carbonate-free diatom oozes. Samples were studied by the X-ray powder diffraction and IR-spectroscopy methods. Analyses were performed on bulk non-fractionated samples. It was established that the mineral association in lake sediments includes layer silicates, carbonates, quartz, plagioclase and amphibole.

Comparative analysis of layered silicate assemblages and their crystal chemistry was carried out using author's XRD modeling. The method is based on the calculation of the interference function of the one-dimensional disordered crystals with finite thickness. The modeling includes fitting of theoretical to observed patterns and optimization of the modeled parameters by non-linear programming. The association of layer minerals is include mixed-layer illite-smectite, muscovite, illite, chlorite, chlorite-smectite, and kaolinite.

Warm and humid interglacial intervals are characterized by high content of fine illite and great amounts of smectite layers in the illite-smectite. In contrast, during cold glacial intervals sedimentation of well-crystallized muscovite and illite-smectite with low smectite layers content is predominated. Our conclusions are consistent with results of study of carbonate minerals distribution in the HDP-04 core and other indexes of biological paleoproductivity.

Information recorded in mineral assemblages, composition, structure, and crystallochemical parameters of clay minerals in sediment can serve as independent criterion of paleoclimatic reconstructions in Central Asia.

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Smectitisation of volcanoclastic materials in soil from the Swabian volcano pipes

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In the Swabian Volcano around Kirchheim and Urach about 300 volcanic pipes of Miocene age occur in an area of 40 km diameter. These volcanic materials are basaltic (Melilithit-Ankarutit) in origin and often admix with neighboring sediments.

A sequence of 4 soils with different admixtures has been analyzed. The soils are Calcaric Regosols, rendzic Leptosol and Phaeozems.

Micromorphological and XRD observations showed that carbonatisation of parts of the volcanic material could be detected, along with the development of clay minerals and a strong tendency for smectite (saponite) formation. Other minerals were partially inherited from adjacent Jurassic limestones. The mineral an assemblage will be explained and the properties of the smectite described in detail.

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New formation of zeolite in a volcanic pumice of Hegau, SW Germany

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Zeolite was discovered as a new formation by micromorphologic observation in a Ranker (Eutric Leptosol) from basic saprolised volcanic bomb pumice. The pH of the topsoil was recorded at 6.5 and in the subsoil 7.2. The clay fraction included 90% smectite, a new mineral formation, and the rest as illite and kaolinite.

As a result of the weathering of volcanic material, carbonate was formed. This carbonate was identified with the polarization microscope and the X-ray diffraction analysis. 1% of the soil is transformed into carbonates. The existence of zeolite was proved by a polarization microscope and X-ray diffraction analysis. The formation, shape, and morphological structure of zeolite minerals were described with scanning electron microscope. The zeolite crystals are different species and all idiomorphic. Pedogenic formation of these rare minerals can be proved by morphological observation and explained with the specific physico-chemical properties of the soil.