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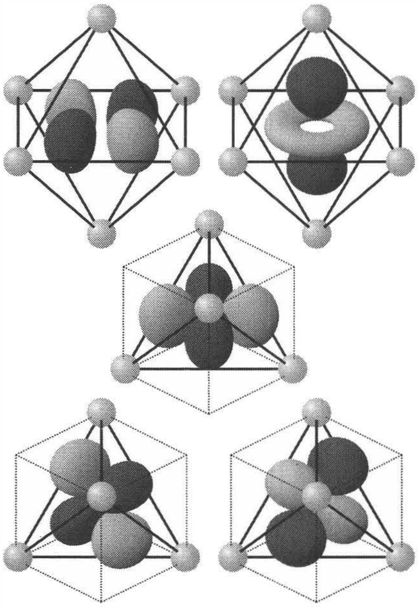
Abstracts



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SHORT-RANGE ORDER OF Fe(II) IN SPHALERITE BY MAGNETIC SUSCEPTIBILITY AND ^{57}Fe MÖSSBAUER SPECTROSCOPY

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Several physical properties of sphalerite, which propose cubic ZnS as "tunable" material with non-linear magnetic and magneto-optic properties, are associated to the most common substitutions of Zn by paramagnetic cations (Fe and Mn) thus defining the class of the Diluted Magnetic Semiconductors (DMS). The replacement of Fe and Mn for Zn in sphalerite, where no structural constraints are present, is assumed to occur with a statistical metal distribution. However, the possible presence of short-range ordering phenomena cannot be ruled out, thus affecting the fine electronic properties of this material, which may significantly change as a function of the short-range distribution.

An extensive study of natural and synthetic Fe-bearing sphalerites (Fe-content ranging between 0.005 and 0.250 afu) has been carried out through the combined characterisation of the temperature dependence of the magnetic susceptibility (investigated from 300 to 2 K) and of the room-temperature ^{57}Fe Mössbauer spectroscopic features.

Magnetic susceptibility measurements evidence, in the low temperature range, the presence of clustered Fe(II) even in the most diluted samples, whereas in the high temperature range magnetic data account for the molar contribution in the standard Curie-Weiss model.

All the Mössbauer spectra (may be) are described in terms of variable proportions of three components, namely one singlet and two doublets absorptions, centered at the same isomer shift, relative to isolated Fe(II) ions and different Fe(II) clusters, respectively.

The comparison of all the experimental results points out a self-affinity of Fe(II) ions in sphalerite favoured by the superexchange interaction, which stabilises the formation of clusters even in the relatively diluted samples.

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A CALIBRATION CURVE FOR THE OH CONTENT OF VESUVIANITE: A POLARIZED SINGLE-CRYSTAL FTIR STUDY

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A well-characterized suite of vesuvianite samples from the volcanic ejecta of Latium (Italy) was studied by SREF (single-crystal X-ray refinement), EMPA, SIMS (Secondary-Ion Mass Spectrometry) and single-crystal, polarized radiation, FTIR spectroscopy in the OH-stretching region. Light elements in particular were analyzed by SIMS using an ion microprobe (Cameca IMS 4f) at CNR-Istituto di Geoscienze e Georisorse (Pavia). A $^{16}O^-$ primary ion beam accelerated at 12.5 kV, with a beam intensity of 3 nA and a beam diameter ≤ 5 μm was employed. The SiO_2 (wt%) content (from EMPA) was selected as an internal reference for H, Li, Be and B (OTTOLINI et al., 2002; OTTOLINI & OBERTI, 2000). Most samples are B- (up to 3.67 wt%) and F-rich (up to 2.38 wt%). All IR spectra consist of a rather well-defined triplet of broad bands at higher frequency (3700-3300 cm^{-1}), and a very broad, composite absorption below 3300 cm^{-1} These spectra are characteristic of B-rich and F-rich vesuvianites (GROAT et al., 1995). Measurements with **E**//c or **E**⊥c show that all bands are strongly polarized with maximum absorption for **E**//c, and agree with previous band assignment to the two O(11)-H(1) and O(10)-H(2) groups in the structure (GROAT et al., 1995). Pleochroic measurements with changing direction of the **E** vector of the incident radiation shows that the orientation of the O(11)-H(1) dipole is OH^c ~ 35°, in excellent agreement with the neutron data of LAGER et al. (1999). A calibration curve, based on SIMS data on the same crystals used for FTIR analysis is presented. The integrated molar absorption coefficient for vesuvianite is $\varepsilon_i = 97.000 \pm 2000$ l mol^{-1} cm^{-2} This value is in good agreement with the calibration curve for minerals established by LIBOWITZKY & ROSSMAN (1997). Preliminary data show that a quantitative determination of water in vesuvianites is also possible using powder IR spectroscopy, provided the sample is prepared in a well-standardized way.

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EPR, HF²EPR SPECTROSCOPY AND SQUID STUDY OF NATURAL BORNITE: PRELIMINARY RESULTS

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Bornite (Cu_5FeS_4) is a copper ore mineral of considerable economic relevance, playing an important role in the solar cells, as a composite superconductor, or as a DMS. In order to study its magnetic structure, the metal ions valence distribution and their interactions, X-band and high frequency EPR and magnetisation measurements were performed on a natural bornite sample of the Natural History Museum of Florence University.

The obtained magnetic data show a magnetic phase transition from a paramagnetic to an antiferromagnetic state with a Néel temperature $T_N \sim 75$ K and other discontinuities in the full investigated range (0 - 300 K). The evidence of a further magnetic phase transition was also observable near 30 K.

The experimental Curie constant value found in the high temperature regime is lower than the theoretical value for spin-only Fe(III) ions and suggests a high Fe(II) content. This observation suggest the hypothesis of bornite as a mixed valence system, with electron hopping taking place both between Fe(II) $\leftrightarrow$ Fe(III) and Cu(I) $\leftrightarrow$ Cu(II), the latter being required by charge neutrality. The observed EPR spectra, however, are different both from the typical Cu(II) and Fe(III) spectra. The 300 K and 5 K data show the same very intense peak centred at $g \sim 2.02$, the linewidth of which increases by decreasing temperature. This behaviour is characteristic of a concentrated system, where the exchange interaction prevents the determination of the single ion features. This is in line with a transient redox mechanism between adjacent ions.

Due to the peculiar electronic structure of this semiconductor, paramagnetic resonance experiments have been performed also on powders aged under pressure (1350 atm). The pressed sample, studied at X-band, shows a superposition of two lines, the former at $g \sim 2.02$ and a second, very narrow, at $g \sim 2.00$, thus pointing to an evident pressure influence. In the EPR measurements, performed at 95 and 190 GHz, the narrow line is always observed, whereas the broader X-band EPR line is not detectable.

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SPECTROSCOPIC EXAMINATIONS OF THE STRUCTURE AND ALKALI SORPTION OF HIGHLY POLYMERIZED C-S-H PHASES

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Cement is an inorganic hydraulic binder widely used in civil engineering, etc. By the reaction of cement with water Calcium-Silicate-Hydrate (C-S-H) gel is the principal hydration product (TAYLOR, 1964). For example, building materials based on Portland cement could contain up to 70 wt% C-S-H gel. Therefore, the structure of the C-S-H gel is responsible for the mechanical properties of the hardened cement paste.

The composition of the C-S-H gels within the $CaO-SiO_2-H_2O$ system varies over a large molar CaO/SiO_2 (C/S) range: from about 0.5 in older and partly carbonated hardened cement pastes up to 2.2 in fresh ones. Even lower C/S are probable due to weathering of hardened cement pastes and deteriorative reactions like alkali-silica-reaction (ASR). The latter leads to the formation of highly polymerized, alkali bearing C-S-H gels. The formation processes and the structure of these gels are widely unknown.

The existing models for the structure of C-S-H gel, mainly based on the structures of the crystalline C-S-H phases tobermorite and jennite, are suitable only for C-S-H gels with C/S ratios between 2/3 and 3/2. Despite the widespread occurrence of highly polymerized C-S-H gels there is still no proposal for a structural model for C-S-H gels with a C/S ratio $< 2/3$.

Due to the lack of long range order, spectroscopic methods such as FT-IR, XAFS and NMR are of great relevancy for structural investigations of the C-S-H gels. First results from these spectroscopic methods will be discussed and gain an insight in the structure and formation processes of alkali bearing highly polymerized C-S-H gels.

IR spectra of several C-S-H gels with C/S ratios varying between 0.2-1.5 and different alkali concentrations have been recorded at the IR-Beamline at ANKA (Angströmquelle Karlsruhe). The IR spectra of our samples clearly demonstrate systematical high frequency shifts of the Si-O-Si stretching vibrations with decreasing C/S ratio, thus indicating an increasing of the polymerization of the silicate structure (YU et al., 1999). In the OH stretching region a systematical shift of the broad absorption band provides useful information about changes of the H_2O environment upon varying C/S ratios. Additionally to the IR data, XAFS measurements at the Ca absorption edge provide detailed informations about the local environment around the Ca atom. ^{29}Si NMR data provide informations about the degree of polymerization of the SiO_4-tetrahedra in the gel structure.

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VESUVIANITE: IR AND MÖSSBAUER SPECTROSCOPY DATA

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Vesuvianite is chemically and structurally one of the most complicated rock-forming minerals. Vesuvianite can crystallize in three space groups: *P4/nnc* (high vesuvianites), *P4/n* and *P4nc* (low vesuvianites) in dependence on string ordering in structural channels. The circumstance that the space group of vesuvianite depends on ordering of only 4 atoms in the unit cell makes it difficult to distinguish these "rod" polytypes by diffraction methods. Spectroscopic methods are more sensible to local structure and therefore we used IR and Mössbauer spectroscopy to investigate these samples.

We recorded the infrared spectra of high and low vesuvianite samples in the region of Si-O and B-O fundamental vibrations and also in the OH stretching region. It was revealed that by means of factor group analysis it is possible to predict the number of infrared active internal modes of SiO_4 ions and hydroxyl in different positions and to explain the differences of the spectra due to symmetry and composition of these varieties. Thus, IR spectra gave us the possibility to immediately differentiate between high and low vesuvianites. In addition, also the IR spectra of partly ordered vesuvianite samples were described: they have the characteristic features of both varieties in the OH stretching region.

It is considered that high vesuvianite forms at high temperature (> 400 °C) and low vesuvianite is characteristic for rocks formed at low temperatures (< 300 °C). But we have found in our collection some samples which do not obey this rule. The fact that temperature is not the only factor leading to one or another space group is of great importance from a petrological point of view.

We assigned the absorption bands in low vesuvianites spectra to MgAlOH, AlAlOH, AlTiOH, $AlFe^{3+}OH$. These cations are ordered in the inequivalent Y(3a) and Y(3b) octahedra of the low vesuvianite structure. IR spectra of boron-bearing samples have shown that boron occurs only in triangular positions of the low vesuvianite structure and in both, triangular and tetrahedral positions of the high vesuvianite structure. A diffuse character of the IR spectra and the presence of a band at 1110 cm^{-1} are prominent features of wiluite.

A Mössbauer spectroscopy study has been carried out with the purpose to determine the valence and structural conditions of iron atoms and also to investigate isomorphic substitutions in the vesuvianite structure. It was shown that Fe^{2+} and Fe^{3+} ions occupy both octahedral and 5-coordinated sites with a slight preference for the latter. Concerning the relative content of Fe^{2+} and Fe^{3+} ions, Mössbauer data allowed to establish two main schemes of isovalent substitutions in the investigated collection of vesuvianite samples: $Mg^{2+} \Leftrightarrow Fe^{2+}$ and $Fe^{3+} \Leftrightarrow Al^{3+}$ It is shown that along with isovalent schemes, two schemes of heterovalent substitutions occur: $B^{3+} + Mg^{2+} \Leftrightarrow 2H^{+} + (Fe^{3+}, Al^{3+})$ and $Ti^{4+} + O^{2-} \Leftrightarrow (Al^{3+}, Fe^{3+}) + OH^{-}$. The case of replacement including Fe^{3+} ions is preferable for the first mechanism of heterovalent substitution, and the second scheme involves predominantly Al ions.

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PHEROMONES ANALYSIS BY VIBRATIONAL SPECTROSCOPY

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The application of Infrared and Raman spectroscopies with a view to determine the structure of some pheromone components is presented. The pheromones are used in horticulture, to prevent the sickness of the forest, and in agriculture for pest control (SIMIONESCU & MIHALACHE, 2000). The studied pheromones have unsaturated long linear or branched chains (8-23 carbon atoms), functionalized with various groups like carbonyl, ester, hydroxyl. The IR and Raman spectra give information about the qualitative aspects of the pheromonal cocktail. We used both above mentioned vibrational spectroscopies since these methods are non destructive and complementary techniques (ILIESCU et al., 2002; COLTHUP et al., 1964). These spectroscopic methods allowed us to study the structure of these natural compounds and made also possible the identification of its E (965 cm^{-1}) and Z isomers (Fig. 1).

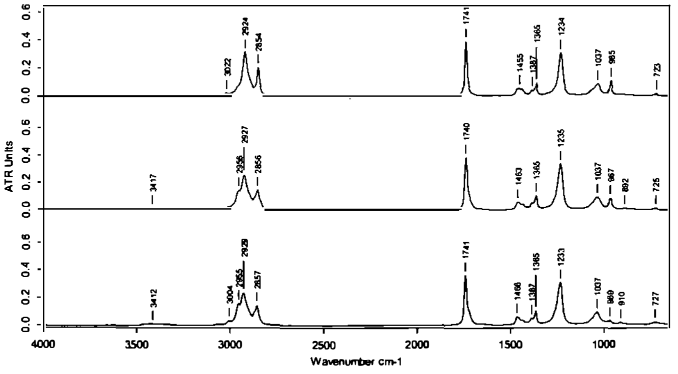

Fig. 1. Similarities and differences between E and Z isomers at E – 10,12OAc, E – 8,12OAc, Z – 7,12OAc

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EPR STUDY AND MAGNETIC INVESTIGATION OF SYNTHETIC HEMATITE, α-Fe_2O_3

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Hematite (α-Fe_2O_3) belongs to the iron oxides group and is widely distributed in nature. The hematite structure can be described as corundum type, and consists of an arrangement of Fe^{3+} ions in octahedral coordination with oxygens in hexagonal close-packing.

Hematite is an antiferromagnetic mineral with Néel temperature $T_N = 960$ K and presents a first-order magnetic transition at $T_M = 265$ K, called Morin transition. Below this temperature the spins are aligned along the *c*-axis and hematite is antiferromagnetic; above T_M the spins lie in the basal plane of the crystal and show a weak ferromagnetism due to a slight spin canting out of the basal plane (DUNLOP & ÖZDEMIR, 1997). Despite its complex magnetic behaviour has been widely investigated, some questions, such as the origin of memory effect when it is thermally cycled through T_M, are still matter of debate (DE BOER et al., 2001).

In this contribution we present a thorough magnetic study on a fine powdered sample of synthetic hematite using a superconducting quantum interference device (SQUID) magnetometer and electron paramagnetic resonance (EPR) at different frequencies (from 9.25 GHz up to 285 GHz). The structural characterisation of this sample was performed through powder XRD and TEM.

The use of multifrequency EPR to characterise nanostructured metal oxide based material is a novel approach that can provide new and unique insights of the properties of these minerals. The Morin Transition was observed by EPR, as well as its strong dependence on the applied field, which was confirmed by magnetisation measurements.

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SPECTROSCOPIC CHARACTERIZATION OF Fe-OXIDES AND -OXYHYDROXIDES ASSEMBLAGES RELATED TO ARD PROCESSES (LIBIOLA MINE, ITALY)

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The Libiola Fe-, Cu-sulfide mine (Eastern Liguria, Italy) represents one of the most important Italian exploited sulfide-ores. The ore deposit was mined from 1864 to 1962 either through open pits and underground excavations, in an area comprising 18 galleries, 7 open pits, and over 30 vertical shafts. Mine wastes were deposited in five major piles and in several minor waste-rock and tailings dumps, placed throughout the mining area.

In the Libiola Mine area numerous evidences of active ARD processes are present, occurring where the water-sulfides interactions are strongly favoured by the mining activities. The major mineral phases, resulting from these processes are the Fe-oxides and -oxyhydroxides occurring within ochreous to reddish crusts or within ochreous unconsolidated muds (MARESCOTTI & CARBONE, 2003).

An accurate characterization of the nanocrystalline Fe-oxides and -oxyhydroxides has been undertaken using X-ray powder diffraction (through the Rietveld quantitative interpretation), several spectroscopic techniques (Diffuse Reflectance Spectroscopy, IR, μ-Raman, EPR) and magnetic measurements (performed using a SQUID magnetometer).

The experimental evidences of XRPD, DRS and IR point to the presence of hematite and goethite as the main constituents of the crusts, with rare minor associations of quartz. The complex banded pattern of the samples has been related to different stages of the evolution of the precipitate. Thus, most of the macroscopic features of the assemblages arise from the intergrowth of these two main components. Moreover, both the IR and μ-Raman investigations revealed the presence of some accessory phases, namely lepidocrocite and schwertmannite, which represent "relics" of the pristine deposition of the precipitates and of the early stages of their evolution.

EPR spectra present features which can not be simply related to bulk hematite and goethite and to their relative proportions. In fact the reduced size of the grains substantially modifies the magnetic behavior of both minerals as indeed shown by magnetic measurements, which show for all the investigated samples, the characteristic behavior of superparamagnetic assemblies of particles.

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INTERLAYER CATION CHARACTERIZATION IN PHYLLOSILICATES: A XANES INVESTIGATION

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Micas are the most common group of phyllosilicates, minerals that are among the least studied by XAS although being interesting for their two-dimensional structure properties. Micas are structural systems made up of infinite, parallel sheets two-dimensionally extending along the ***a*** and ***b*** axes and stacked on ***c****. The three-dimensional mica structure consists of a composite M module made up of an octahedral sheet sandwiched between two facing tetrahedral T sheets, plus a pseudo-hexagonal planar network of cations, again extending along the ***a*** and ***b*** axes, which form the interlayer A. This latter layer is bound to the facing T sheets of two opposite TMT layers by weak ionic forces. Potassium, present in micas only as interlayer cation, is surrounded by two facing distorted hexagonal networks of O atoms belonging to two opposite tetrahedral sheets, with Al, Si and Fe atoms being the tetrahedral centres. In this study we tried to identify and reconstruct, using XANES spectroscopy, the local distortions of the tetrahedral sheets induced by the presence of Fe in both the tetrahedral and octahedral sites, by means of a systematic comparison of powder and single-crystal polarized XANES spectra taken at the potassium *K* edge. Previous XANES investigations performed at the Al, Mg, and Fe *K* edges have already demonstrated correlation between the total Fe content in the octahedral sheet and the overall structural modifications occurring in trioctahedral micas (TOMBOLINI et al., 2002a, b). In this work, using the MXAN code to fit the XANES spectra, we discuss the correlation existing between distortions at the interlayer cation sites and the experimental features at the potassium *K* edge in micas having different Fe concentrations. In these layered structures, the fitting method shows that multiple scattering calculations succeed in measuring the distortions induced by Fe; moreover, the quality of the data greatly depends upon sample orientation with respect to the incident beam direction, so that in-plane and out-of-plane orientations can also be determined. A general reconstruction of the structural environment of the interlayer cations in micas will be presented and discussed.

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COMPARATIVE SPECTROSCOPIC STUDY OF CARBONATE ROCKS FROM WESTERN MACEDONIA IN GREECE

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Naturally occurring carbonate rocks are extremely important natural resources finding widespread applications (TULYAGANOV et al., 2002; MA et al., 2000), thus being placed among the most important raw materials and their study is the subject of the work of many researchers (DEER et al., 1992). Samples were collected from the broader Kozani area (northwestern Macedonia, Greece), which geotectonically belongs to the Pelagonian zone. The Pelagonian zone consists of a crystalline pre-Carboniferous basement, which includes a series of metamorphic rocks intruded by large masses of Upper Carboniferous granites. The samples in powder form, with major components in different proportions of calcite $CaCO_3$, the most stable phase of calcium carbonate, and dolomite $CaMg(CO_3)_2$ were studied, aiming in the determination of the calcite/dolomite ratio. Other minerals (quartz, feldspars, micas, etc.) were participating in minor quantities in their mineralogical composition. The samples were also analyzed by XRD and other methods. The particle size was the same for all studied samples.
For the quantitative characterization, a FTIR based method is used (ZORBA 2003, 2004). FTIR spectroscopy is an established experimental technique for qualitative mineral identification (McMILLAN & HOFMEISTER, 1988; WHITE, 1974) and is also being developed for quantitative mineralogy. FTIR relies on the detection of vibrational modes and mineral identification is possible because minerals have characteristic absorption bands in the mid infrared.
In the present study the qualitative determination is based on the frequency shifts in the vibrational frequencies of functional groups due to chemical composition and the quantitative analysis of mineral sample is extracted from the FTIR spectrum through the use of appropriate peak analysis software employed for the calculation of the constituents' ratio. Comparison of the results with those received from XRD leads to the examination of the accuracy of the method used.

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THE $P2_1/m \Leftrightarrow C2/m$ PHASE-TRANSITION OF SYNTHETIC AMPHIBOLES IN THE SYSTEM Na_2O-Li_2O-MgO-SiO_2-H_2O: AN *HT*-FTIR STUDY

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In the last few years a series of experimental studies has renewed the interest in the $Na(NaMg)Mg_5Si_8O_{22}(OH)_2$ amphibole end-member, studied long ago by GIBBS et al. (1962) and MARESCH & LANGER (1976). $Na(NaMg)Mg_5Si_8O_{22}(OH)_2$ has the $P2_1/m$ space group at room temperature (IEZZI et al., 2004), and undergoes a displacive $P2_1/m \Leftrightarrow C2/m$ phase-transition at 257 °C (CÁMARA et al., 2003). The room-*T* OH-stretching IR spectrum of $Na(NaMg)Mg_5Si_8O_{22}(OH)_2$ is characterised by two distinct groups of bands, which can be assigned to the two non-equivalent O-H dipoles in the $P2_1/m$ structure; this implies that the IR OH-spectrum of these amphiboles is a powerful tool for a fast detection of $P2_1/m$ symmetry.
We present here a powder high-*T* FTIR study of amphiboles synthesised in the Na_2O-Li_2O-MgO-SiO_2-H_2O system. Spectra were collected in the *T* range 25-380 °C on KBr disks, using a Linkam THS600 heating stage mounted on a NicPlan microscope at the University of Roma Tre. At 800 °C and 0.4 GPa, the $^BNa \Rightarrow {}^BLi$ exchange is complete along the $Na(NaMg)Mg_5Si_8O_{22}(OH)_2$ – $Na(LiMg)Mg_5Si_8O_{22}(OH)_2$ join. Both XRD and FTIR spectroscopy show that all solid-solution terms have $P2_1/m$ symmetry at room-*T*. In particular, the IR spectra consist of two main bands around 3740 and 3715 cm^{-1}, the exact position of which being a function of ^BLi (NNN effect), and two minor bands at 3690 and 3667 cm^{-1} At the transition temperature, the two main bands merge into one single absorption around 3720 cm^{-1} No significant change is observed beyond this *T*. The behaviour of the IR OH-stretching bands is in agreement with the second-order character of the $P2_1/m \Leftrightarrow C2/m$ phase-transition, which was obtained by single-crystal XRD studies of $Na(NaMg)Mg_5Si_8O_{22}(OH)_2$. The IR spectra show that the T_C of the phase-transition is linearly dependent on the amphibole composition: for $^BLi = 0$ apfu it is close to 250 °C (in agreement with CÁMARA et al., 2003), whereas for $^BLi = 1.0$ apfu it is close to 340 °C; this latter value is coherent with preliminary powder-XRD synchrotron data on the same sample. Therefore, in this system where the composition of the A and C-group sites is virtually constant, the $P2_1/m \Leftrightarrow C2/m$ phase-transition is determined by the aggregate mean ionic radius at the B-group sites.

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SPECTROSCOPIC CHARACTERISATION OF TRAVERTINES BY EPR TECHNIQUES: A MULTIFREQUENCY STUDY

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The EPR characterisation of paramagnetic metal cations, *e.g.* Mn(II), Fe(III), in calcite-based materials has attracted many studies, because of the very informative experimental spectra and the peculiar crystal field of the Ca site in this mineral. Recently, EPR spectroscopy has been also applied to the travertine characterisation, appearing a promising tool for the understanding of the physico-chemical condition of its genesis.

Mn(II), occurring as an ubiquitary trace substituent of Ca, may be considered as an ideal tool for the systematic investigation of travertines of different localities and origins, because the EPR spectrum depends on the local ionic crystal field. Several parameters (zero-field and hyperfine structure, linewidth, isorientation) appear to be promising criteria to distinguish and classify different travertines. A significant variability of the EPR spectral parameters, in fact, can justify their use as minero-chemical and geochemical markers. Nevertheless, a very accurate knowledge of the dependence of the spectrum on all the Hamiltonian interactions is required. A multifrequency approach, therefore, has been undertaken, in order to refine and clarify the informations contained in the very complex X-band spectrum.

The study has been carried out on a sample, coming from Papigno (Terni, central Italy), a very recent deposit (60 ka), inactive nowadays. At present, a meteogene travertine is being deposited near the village of Marmore and the isotopic $\delta^{13}C$ composition of the two deposits is very similar (from -1.9 to 1.0 ‰ PDB at Papigno and from -0.8 to 0.5 ‰ PDB at Marmore). Room temperature 9.5, 95, 190 and 285 GHz EPR spectra were recorded at very low scan speed. While the 9.5 spectrum consists of the well-known sextet, characterised by a splitting of each major peak in positive and negative portions and by the forbidden lines, the high frequency spectra are simplified, being constituted only by the six m_S $-1/2 \Rightarrow +1/2$ allowed transitions. The multifrequency approach evidences a reduction of the linewidth passing from X band to 95 GHz and the presence of a field independent splitting of the transitions. The latter must be due to either fine or hyperfine structure or both. An interpretation of the multifrequency spectra in terms of the fine structure including third order perturbation terms is presented.

UV-VISIBLE-NIR SPECTROSCOPY AND XRPD OF RUTILE PIGMENTS DOPED WITH CHROMOPHORES (Cr, Mn, Ni, V) AND COUNTERIONS (Mo, Nb, Sb, W)

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The high refractive indices and melting point of TiO_2 make it a valuable pigment for ceramic applications, where anatase is progressively converted to rutile on heating. The capacity of the rutile structure to host a number of the first row transition elements allows to get a rather wide colour palette: orange (Cr), brown (Mn), yellow (Ni) and gray (V). Together with the chromophore, a high field strength ion (so-called *counterion*) is added in the industrial practice to achieve the desired colour and improve the technological properties of pigments.
The colouring mechanisms have been not thoroughly investigated, being generally attributed to crystal field transitions, with some role played by a Ti-O charge transfer (EPPLER, 1987; ISHIDA et al., 1990; SORLÍ et al., 2004).
The aim of this work is to understand better these mechanisms on typical industrial co-doped rutile pigments having the stoichiometry $Ti_{1-2x}A_xB_xO_2$, where A = Cr, Mn, Ni, V (chromophore ion) and B = Mo, Nb, Sb, W (counterion), with x=0.03. Samples were prepared by conventional ceramic process (firing from 700 to 1100 °C). A combination of UV-visible-NIR spectroscopy (diffuse reflectance, Perkin Elmer λ35, 200-1100 nm, integrating sphere, $BaSO_4$ as reference, standard illuminant D_{65} and observer 10°) and X-ray powder diffraction (Philips PW 1820/00, monochromated-$CuK_{\alpha1,2}$ radiation, 15-130°2θ, 0.02°2θ/10s) with Rietveld refinement (GSAS-EXPGUI) was used for pigment characterization.
The colour of rutile pigments is determined by both charge transfer (CT) and crystal field (CF) effects: a Ti^{4+}-O^{2-} CT band shifts from the UV to the visible region with the anatase-to-rutile transformation, contributing to get an intense coloration. A progressive incorporation of chromophore into the rutile lattice produces CF d-d transitions, partially overlapped with the CT band, and complex spectra very difficult to be quantitatively interpreted. Moreover, there are clues that the valence of some transition elements changes during the synthesis: the cell volume is correlated with the weighed cationic radius assuming the following valence, coherent with optical spectroscopic data: Cr^{3+}, Mn^{3+}, Ni^{2+}/Ni^{3+},V^{4+}, Mo^{5+}, Nb^{5+}, Sb^{5+}/Sb^{3+}, W^{5+} The cell dimensions *a* and *c* are mainly affected by the ionic radii of chromophores and counterions, respectively, according to the sequences: V<Cr<Mn<Ni and Mo~W<Nb<Sb.

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THE ESTIMATION OF VOLCANIC GLASS CONTENT IN NATURAL MATERIALS USING PXRD AND FTIR TECHNIQUES

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One of the basic constituents of the industrial rocks is the volcanic glass. Therefore, the calculation of its percentage in a sample is important in Economic Geology. Volcanic glass is usually observed in PXRD as a broad background hump starting at approximately 10° 2θ. Five standard sample mixtures were used with the following weight percent ratios of amorphous and crystalline phases: 100-0 %, 75-25 %, 50-50 %, 25-75 % and 0-100 %, respectively. The 100 % volcanic glass used as standard material, is obsidian from the island of Santorini (KANTIRANIS et al., 1999). Crystalline materials chosen for the preparation of the sample mixtures were quartz, calcite, muscovite, montmorillonite and heulandite. The five constituents of the crystalline phases in the samples were present in equal quantities. The conditions for the preparation and analysis of the samples were identical.

PXRD analysis was performed on randomly oriented samples, which were scanned over the interval 3-63° 2θ, using a Philips PW1710 diffractometer, Ni-filtered CuK_α radiation and PCAPD v.3.6 (1994) software. The PXRD patterns were studied by two methods. For the first method, the area of the broad background hump of each sample was compared with the corresponding area of the broad background hump of the 100 % volcanic glass. For the second method, which calculates the crystallinity of the sample, each individual peak of the PXRD patterns of the samples was analyzed using exponential shape functions (pseudo-Voigt function), including those for amorphous material (STERGIOU, 1995). The results of the two methods were used providing that the variance of values of volcanic glass were ±3 %.

FTIR measurements were performed using the KBr pellet technique. The transmission spectra were recorded using a Bruker IFS113v spectrometer under vacuum in the MIR region, with a resolution of 2 cm^{-1} The presence and characteristics of each band is due to vibrations related to sites with corresponding symmetry. Any structural change taking place influences characteristic bands and this gives direct information on the crystallinity. The development of these bands through the increase of volcanic glass participation is used for the quantitative analysis of the studied samples.

The results indicate that the two techniques could constitute a reliable procedure for the accurate estimation of the amount of volcanic glass contained in a natural rock sample.

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XPS STUDIES OF BINARY Cu-Sn ALLOYS AGED IN CLIMATIC CHAMBER

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During the last few decades great interest has arisen concerning conservation problems of metal artefacts exposed in an open environment due to the formation of alteration products. Alteration patinas have greatly increased as a result of the increase in pollutants produced by human activity. In recent years, non-destructive surface analytical probes, such as PIXE, LIPS, and XPS have been applied to this problem. X-ray Photoemission Spectroscopy (XPS) is not always suitable for natural patinas which are often quite thick, but it can be applied to studies of patina onset obtained by ageing materials in a climatic chamber. The characteristics of this technique, in fact, make it especially suitable for studies of the initial alteration mechanisms for a large range of materials. During the initial alteration step, the corrosion products formed are usually extremely thin so that XPS may be used to detect the presence and determine the chemistry of alteration products, produced at this stage.

XPS has previously been used to detect initial corrosion products formed on metals and alloy surfaces (in particular copper, bronzes and brasses) exposed to pollutant gases such as SO_2, NO_x and Cl_2. These include phases such as Cu_2O, CuO, CuCl, which correspond to the minerals cuprite, tenorite, nantokite. Here, a new XPS imaging instrument has been used to detect the formation of copper carbonates, sulphates and chlorides and tin sulphides on the surfaces of binary Cu-Sn alloys aged in a climatic chamber with SO_2 as a pollutant. Parallel XPS imaging has been used to acquire a wide energy spectrum at each pixel, which coupled with PCA analysis has been employed to obtain enhanced image contrast between elemental and chemical speciation at the alloy surface.

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CRYSTAL CHEMISTRY OF THE STANNITE-GROUP COMPOUNDS (EPMA, EPR, SQUID, MÖSSBAUER SPECTROSCOPY)

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In order to check the model of complex isomorphous replacement "Cu → Fe" (EVSTIGNEEVA et al., 2003), and to determine the metal valence states, EPMA, EPR, SQUID, and Mössbauer spectroscopy were performed on 10 synthetic analogues of the kuramite - stannite series, $Cu_{3-x}Fe_xSnS_4$ ($0 < x < 1$). The Cu valence and the character of chemical bond were studied with EPMA on the base of self-absorption of the measured copper X-ray emission. According to the first results the contribution of Cu 3*d* electrons to the chemical bond increases if the Fe content increases from 0 to 0.5 afu. It is caused by the Cu–Fe interaction due to the short Cu-Fe distance between Cu_{Tetr} and Fe_{Oct}. The general dependency of experimental magnetic susceptibility on the temperature corresponds to the theoretical high-temperature limit of the Curie constants calculated on the base of the proposed model of isomorphism (EVSTIGNEEVA et al., 2003). The magnetic susceptibility line is bent at [Fe] ~0.5 afu, and consists of two positive linear trends. The Curie constant values are located below the theoretical line at [Fe] < 0.5 afu, while above 0.5 Fe afu they plot slightly above this line. The first trend should be explained by the intermediate spin state of Fe^{3+}, the best fit agrees with $S = 3/2$. The second trend, parallel to the theoretical one, but shifted to higher emu/mol values, corresponds to the Fe^{3+}/ Fe^{2+} exchange model considering that a small spin-orbit interaction increases the Fe^{2+} contribution in comparison with stannite, 3.15 in spite of 3 emu/mol., as was shown by BERNARDINI et al. (2000). These results can prove the Fe spin transition between 0.5 – 0.6 Fe afu. The Fe spin state and antiferromagnetic interactions like those established for natural and synthetic stannites (BERNARDINI et al., 2000) are discussed. The data obtained are in good agreement with results of Mössbauer spectroscopy, but the schemes of isomorphism in stannite family compounds proposed earlier need to be precised.

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STRUCTURE AND COLOR OF THE JACK CREEK DUMORTIERITE (MONTANA, USA) USING SPECTROSCOPIC APPROACHES

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A blue dumortierite sample from the Jack Creek hydrothermal system (Boulder Basin, Montana, USA) (FOIT et al., 1989) was studied using Fourier-transform infrared spectroscopy (FTIR), electron paramagnetic resonance (EPR) spectroscopy, near UV-visible-near Infrared spectroscopy, X-ray absorption near edge spectroscopy (XANES) and Mössbauer spectroscopy.

FTIR spectroscopy shows for the OH groups the existence of various environments, which are related to substitutions and/or vacancies in the M1 octahedral site. Mössbauer spectroscopy consistently reveals the presence of Fe^{2+} and Fe^{3+} in octahedral sites, Fe^{3+} being dominantly represented. The strong and sharp signal observed at 0.113 T in the EPR spectra of pink dumortierite samples with low Fe content (Lincoln Hill and Louvincourt) (FUCHS et al., 2004) and related to a site with a pure axial distortion, [i. e., a site symmetry with a n-fold ($n \geq 3$) rotation axis, corresponding to the Al1 site in dumortierite] is not present in the Jack Creek sample. In contrast, the signals observed at 0.16 T correspond to more distorted sites (ABRAGAM & BLEANEY, 1970). This rhombic signal can be related to Fe^{3+} ions located in tetrahedral or in distorted octahedral sites (Al2, Al3 or Al4).

EPR and XANES also indicate that a fraction of the Fe atoms are not isolated but concentrated in magnetic domains. Optical spectroscopy indicates an important contribution of intervalence charge transfer transitions (IVCT), the most important between Fe^{2+} and Fe^{3+} and a smaller contribution between Fe^{2+} and Ti^{4+} These transitions are responsible for the blue color of the Jack Creek Dumortierite sample.

Based on the XANES study of the Jack Creek (Montana) sample Ti seems to be mainly restricted to the M1 site (95%). Ab initio XANES (using FEFF) calculations at the Fe K-edge suggest that Fe is located mainly in the Al2, Al3 and Al4 sites (having the highest energy and shorter average Al-O distances). Thermodynamically, Fe would preferentially partition toward the Al1 site. But, a temperature dependence of different site distortion could explain this apparent discrepancy as for Fe in olivine.

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ELECTRONIC STATE OF SULFUR IN TETRAHEDRITE-TENNANTITE SERIES: A MICRO-XANES STUDY

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Tetrahedrites (*s.l.*) are an important group of economically valuable sulphosalt minerals with ideal simplified formula (WU & PETERSEN, 1977), $(M^{1+})_{10}\,(M^{2+})_2\,(M^{3+})_4\,[S_{13}]$, where M^{1+} ions are mainly Cu with some Ag, divalent ions being Cu, Zn, Fe, Hg, Cd, Pb, and trivalent ions Sb, As, Bi. The cubic crystal structure of tetrahedrite (*s.l.*) contains two formula units per unit cell. The atomic array derives from the arrangement in sphalerite - the prototype of so-called "tetrahedral structures" where each one of the constituting ions (Zn^{2+} and S^{2-}) is surrounded by a tetrahedron of species with opposite sign, by leaving unoccupied (vacant) four out of sixteen cubic closest-packing anion positions, and further replacing this tetrahedral cluster of vacancies by one sole S-atom. This replacement process provides pyramidal and triangular coordinations to some of the metal ions, and gives rise to a peculiar coordination and binding situation for one out of thirteen sulphur atoms in the formula unit. The S-atom replacing a tetrahedral cluster of packing vacancies becomes octahedrally coordinated by six close Cu/Ag and additionally by four Sb/As (themselves in pyramidal coordination by S^{2-}) with the lone electron pair probably oriented towards that peculiar central S-atom.

X-ray absorption experiments at the sulphur *K*-edge were performed using the instrumental set-up of beam line ID-21 (SUSINI et al., 2000) at the ESRF* with the purpose of disclosing the influence of the environment (geometry and nature of metal ions coordinating sulphur) and of eventual bonding effects upon details of S 1*s* XANES spectra.

Samples of minerals belonging to the tetrahedrites-tennantite series with varied chemical composition and geologic provenance (Neves-Corvo mine in Portugal and Atacocha mine in Perú), plus synthetics with established composition within the systems Cu-As-Sb-S were studied.

The general trend of S *K*-edge XANES spectra from tetrahedrites, compared to prototype minerals (e.g. chalcopyrite), is similar but the white line does not occur with similar intensity and some post-edge features display different relative intensity, being sometimes split.

Theoretical calculations and XANES spectra modelling with FEFF8.10 code (ANKUNDINOV et al., 2000) were performed with the purpose of interpreting the observed details, either for the model minerals or the tetrahedrite-tennantite series, both minerals and synthetics.

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CRYSTAL CHEMICAL BASES FOR A DATA BANK ON SULPHUR *K*-EDGE *XANES* SPECTRA IN SULPHIDE AND SULPHOSALT MINERALS

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The general trend of the X-ray absorption spectrum close to an edge – either *K* for low atomic number elements or *L* for heavier ones – is known to respond to the electronic state of the absorber, allowing for deducing the formal valence of this element mainly through the energy shift observed for the discontinuity.

The atomic vicinity of the absorbing species within the host condensed-phase (that is, the chemical binding) also affects the energy region close to an edge. Beyond depending on the nature of coordinating species, the particular features of pre- and post-edge regions in XANES spectra also reflect the joint influence of geometry and symmetry of the coordination polyhedron – features that are well established in solids with known crystal structure.

Minerals are then suitable model compounds for interpreting XANES data, both through the direct comparison of collected spectra and via theoretical modeling using any of the available calculation codes – e.g. FEFF (ANKUNDINOV et al., 1998), WINXAS (RESSLER et al., 1999). A crystal chemical approach to the mineral crystal structures therefore becomes most useful for disclosing true cause-effect relations.

Sulphur-containing minerals are essentially sulphates with SO_4^{2-} tetrahedra as anionic groups linked to a diversity of cations and not seldom to water molecules, sulphides (isolated S^{2-} anions), disulphides (S_2^{2-} dimers) and sulphosalts where various situations may coexist, including a high coordination number for peculiar S-atoms – e.g. in tetrahedrites (FIGUEIREDO & FERREIRA, 2002). Coordination environments of S^{2-} by metal ions in sulphides range from tetrahedral in sphalerite-type to octahedral in galena-type sulphides, being less regular in sulphosalts (FIGUEIREDO et al., 1988). Both cubic crystal structure types, $Zn^{t}[S^{t}]$ and $Pb^{o}[S^{o}]$, as well as the cubic disulphides typified by pyrite $Fe^{o}[|S_2|^{t}]$, display wide morphotropic domains. Accordingly, it is possible to find suitable examples for modeling different bonding situations.

If the electronic state of the metal(s) is also studied, the success of theoretically modeling the S *K*-edge XANES spectra is highly enhanced. The building up of a data bank could then be envisaged, under the requisite of strictly quoting the provenance of mineral samples and their physical characteristics. The aim of this work is just to settle the crystal chemical bases for such a data bank, starting with a small illustrative group of sulphide and sulphosalt minerals.

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AN X-RAY ABSORPTION SPECTROSCOPY STUDY AT SULFUR *K*-EDGE OF HAÜYNE FROM SAINT ANTÃO ISLAND (CAPE VERDE)

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Haüyne is an aluminosilicate first described by Brunn-Neergard in 1807 (quoting Dana, 6th ed., p. 431). The crystal structure was determined by MACHATSCHKI (1934) and received the SB symbol S6$_9$. Since then various isotypical minerals were identified, namely sodalite, nosean and lazurite – the latter being sulphur-enriched and used as a natural and valuable blue pigment named ultramarine. The cubic framework of Al and Si tetrahedra forms large cages identical to those found in zeolites, where a large anion (mainly sulphate, but also chlorine) is hosted, surrounded by alkali cations (mainly Na with minor K and Ca).

Despite being known for almost two centuries, haüyne is still nowadays a subject of intense structural and chemical study (TAUSON et al., 1998) and its occurrence in mantle rocks has been reported for the first time only a few years ago (WULFF-PEDERSEN et al., 2000).

Recently, haüyne was identified in tephritic and phonolitic rocks from Santo Antão Island, Cape Verde Arquipelago, and a peculiar microstructure was remarked (SILVA & MENDES, in preparation). A chemical study with synchrotron radiation X-ray fluorescence (SRXRF) was subsequently undertaken using the photon microprobe of the LURE* (line D-15A at DCI), aiming at understanding the chemical variations that could be associated to fluctuations in the bluish colour. A systematic presence of Sr and Mo as trace elements was noticed by SRXRF analysis in all haüyne samples from Santo Antão.

In parallel, an X-ray absorption study at the sulphur K-edge was undertaken at the ESRF* using beam line ID-21 in order to ascertain the speciation state of that element in relation to colouring. XANES spectra clearly denoted the presence of oxidised sulphur in the form of sulphate through the characteristic sharp white line at 2482 eV. *Ab-initio* simulations based on the multiple scattering approximation implemented in the FEFF code (ANKUNDINOV et al., 1998) were carried out to model S *K*-edge XANES spectra. Observed post-edge features and other details are discussed taking into account SRXRF data and theoretical spectra modelling.

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OH DEFECTS IN SPODUMENE: A COMPARATIVE STUDY OF SPODUMENE OF VARIOUS GENETIC TYPES

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Lithium-bearing pyroxene, spodumene (ideally $LiAlSi_2O_6$), is a nominally anhydrous mineral (NAM). As recent research shows, many of NAMs (including pyroxenes) contain various concentrations of incorporated OH defects (ROSSMAN, 1996). Polarised FTIR absorption spectra of spodumene single-crystals were measured to compare the water contents in spodumenes of four genetic types (magmatic, hydrothermal, secondary – after petalite, and metamorphic) with other pyroxenes. Well developed spodumene crystals of hydrothermal origin (kunzite and hiddenite) were studied to understand the OH bonding system in spodumene. Sections parallel to (100), (010) and (110) were measured. On the basis of these measurements and due to the excellent cleavage of spodumene crystals, only polished cleavage plates parallel to (110) were used in cases of spodumenes of other genetic types. OH defect concentrations were calculated using the Lambert-Beer's law (for details see LIBOWITZKY & ROSSMAN, 1997).

FTIR spectra of all samples are characterized by pleochroic absorption bands in the 3400 to 3500 cm^{-1} spectral region (predominantly two bands at around 3409 and 3423 cm^{-1}). From the pleochroic behaviour of these spectra it seems that the OH dipole direction is oriented approximately parallel to n_γ in the spodumene structure, as observed for other pyroxenes (BERAN & LIBOWITZKY, 2003). Small variations of water content in spodumenes of various genetic types were detected: magmatic spodumenes contain <0.1 to 3.3 wt. ppm H_2O, hydrothermal spodumenes 0.1 to 0.2 wt. ppm H_2O, spodumene after petalite contains up to 0.6 wt. ppm H_2O and metamorphic spodumene contains up to 2.0 wt. ppm H_2O. Heterogenous distribution of OH defects within one single crystal was observed.

Water content calculations from sections or cleavage plates parallel to (110) produce slightly overestimated values (< +10 % rel.). Therefore, and because of high background from fluid inclusions and interference fringes, the calculated concentrations of OH defects have relatively large errors. In comparison with other pyroxenes (usually 1200 to 20 wt. ppm H_2O, depending on geological environment; SKOGBY et al., 1990), all spodumenes contain significantly lower contents of OH in the structure.

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NATURE OF BENITOITE $BaTiSi_3O_9$ LUMINESCENCE

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Three broad bands and one narrow line have been detected in laser-induced luminescence spectra of benitoite. At 300 K the first band has λ_{max} = 420 nm, Δ = 80 nm and τ = 2.6 μs. The excitation spectrum consists of a narrow band peaking at 290 nm with a shoulder at 245 nm. At lower temperatures luminescence intensity and band shape remain practically the same, but τ becomes substantially longer, up to 1.1 ms at 40 K. It is proved that this blue band is connected with intrinsic isolated TiO_6 octahedra. The metastable level $^3T_{1u}$ is the emitting level at low temperatures with long τ. At higher temperatures an energy level with higher radiation probability must be involved in the emission process, and this level is situated at 0.06 eV higher than the lowest level. These two levels may be connected with $^3T_{1u}$ level splitting or with closely spaced $^3T_{1u}$ and $^3T_{2u}$ levels. Decay time shortening and thermal quenching are connected with non-radiative decay within the TiO_6 luminescence center, while energy migration does not take place at least up to room temperature.

At 300 K the second band has λ_{max} = 660 nm, Δ = 135 nm and τ = 1.1 μs. The excitation spectrum consists of an asymmetric band peaking at 350 nm. At lower temperatures the luminescence intensity is 10 times stronger and the emission band becomes narrower with longer τ (100 nm and 25 μs at 40 K, respectively). Such behavior may be connected with an intrinsic Ti^{3+} luminescence center. Excitation peaking at 355 nm is connected with the $^2T_2$-^2E transition, while the splitting of the ^2E state is a reason of the two shoulders present in the excitation spectrum. At lower temperature the opposite transition generates an intensive luminescence band peaking at 660 nm with τ = 20 μs. Thermal quenching and drastically reduced decay time with increasing temperature result from a non-radiative transition from excited to ground state.

At 300 K the third band has λ_{max} = 725 nm, Δ = 125 nm and τ = 100 μs. It is accompanied by a narrow line at 682 nm with similar τ. At lower temperatures the broad band is much weaker, while the narrow line becomes substantially stronger with longer τ, reaching 1.1 ms at 40 K. Such behavior is suitable for a d^3 luminescence center, possibly Mn^{4+} or Cr^{3+}

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SINGLE-CRYSTAL RAMAN SPECTROSCOPY OF VESUVIANITE GROUP MINERALS IN THE OH REGION

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Minerals of the vesuvianite group with formulae $X(1\text{-}3)_{18}X'(4)Y'(1)Y(2,3)_{12}T(1,2)_5[Z(1,2)O_4]_{10}[Z(3)_2O_7]_4W_9O_{1\text{-}2}$ (Z = 2) are presented by "rod" polytypes: *P*4/*nnc*, *P*4/*n*, *P*4*nc* (ARMBRUSTER & GNOS, 2000). Symmetry of vesuvianite is defined by string ordering of 4 cations at 8 channel positions (Y', X'). Character and the number of IR and Raman bands poorly depend on the symmetry of the polytype and in general will be assigned by local site arrangement. Principle of the local site arrangement analysis was before used by GROAT et al. (1995) for interpretation of vesuvianite IR spectra in OH region. The cation composition of $Y(3)$ sites, presence of B, Al at $T(1)$, OH → F substitution at O(11) and hydrogarnet defects at $Z(1,2)$ have principal influence on position and character of OH-bands of the Raman spectra in the region 3300-3700 cm^{-1} (Fig. 1, Table 1). The bands of OH groups taking part in formation of strong H-bonds (<3300 cm^{-1}) will be defined by cation composition at $Y'(1)$, presence of B at $T(2)$ and OH → F, Cl substitution at O(10)H(2) (Fig. 1, Table 1).

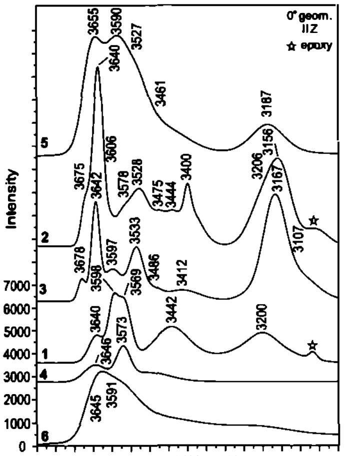

Fig. 1. Raman spectra of vesuvianite

Table 1. Symmetry and site occupation of investigated vesuvianite group minerals

		Y(1)	Y(3)	W [O(10)+O(11)]	T	Z
1.	*P*4/*nnc*	1Fe	6.1Al + 1.2Mg + 0.4Ti + 0.3Fe	4.5OH + 3.1F + 0.4Cl	0	18
2.	*P*4/*n*	0.6Fe + 0.4Mg	7.2Al + 0.8Mg	9OH	0	18
3.	*P*4/*n*	1Fe	5Al + 2Mg + 1Fe	~9OH	0	18
4.	*P*4/*nnc*	0.6Fe + 0.4Mg	4.3Mg + 3Al + 0.6Fe + 0.1Ti	0.3F + 0.nOH	4.2B	17.6Si + ?
5.	*P*4*nc*	1Fe (+Mg?)	3.7Al + 3.1Mg + 1.2Fe	~5OH + 0.5F + 0.3Cl	1.4B + 0.5Al	17.5Si + 2OH
6.	*P*4/*nnc*	0.5Fe + 0.5Mg	7.8Al + 0.2Fe	~6.3OH + 0.4F + 0.1Cl	0.6B	16.25Si + 7OH

1 – vesuvianite-F, Polar Yakutia, Russia (GALUSKIN et al., 2003a); 2 – vesuvianite-Al-OH, Kazakhstan; 3 – vesuvianite-OH, Ural, Russia; 4 – wiluite, Wiluy, Yakutia, Russia; 5 – vesuvianite-B, Wiluy, Yakutia, Russia; 6 – Si-deficient vesuvianite ("hydrovesuvianite"), Wiluy, Yakutia, Russia (GALUSKIN et al., 2003b).

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THE INFRARED MICRO-SPECTROSCOPY FACILITY AT THE SYNCHROTRON ANKA: MINERALOGICAL APPLICATIONS

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ANKA is a new synchrotron at the Forschungszentrum Karlsruhe. It has been in user operation since March 2003 and it is running routinely at 2.5 GeV beam energy and 200 mA current.

At the infrared (IR) beamline, we have been developing mineralogical applications based on Fourier transform IR micro-spectroscopy. Our aim is to address the need for more sophisticated investigations by using the advantages of the synchrotron radiation compared to laboratory sources such as higher flux in the far IR and higher spatial resolution because of the higher brilliance in the complete IR spectral range. The infrared beamline ANKA-IR uses a bending magnet edge as a source and covers a spectral range from 4 to 10000 cm^{-1} (0.5 meV - 1.24 eV; 2.5 mm - 1 µm). Its end is coupled with two experimental stations centered around two Bruker IFS66v/s spectrometers. One of them is equipped with an infrared microscope (Bruker IRscopeII) covering the far-, mid- and near-IR ranges. Set-ups for studies at low/high temperatures as well as at high pressure are under construction.

Our research directions include the study of new and not fully understood mineral crystal structures, transitions from semi-amorphous to crystalline state, mechanisms of incorporation of toxic ions into crystal structures, etc.

In many mineralogical applications there is a need for spatially resolved studies at the microscale. IR and Raman microscopy combines the rich crystallochemical specificity for samples even in amorphous state associated with vibrational spectroscopy. Compared to the spatial resolution achieved by Raman micro-spectroscopy the spatial resolution, which can be achieved by infrared micro-spectroscopy, is diffraction limited and of the order of a few tens of micrometers. Using a conventional infrared thermal source, the resolution cannot be made as low as the diffraction limit would. This is because of the lack of energy at the sample position when measuring samples smaller than 20 µm. High brilliance is desirable for any measurement with a limited "throughput" By using synchrotron-based IR micro-spectroscopy we can investigate samples down to the diffraction limit.

In this presentation two different examples of synchrotron based infrared studies combined with Raman spectroscopy with application to cement mineralogy, e.g. mechanisms of incorporation of Zn and the reaction of the crystal structure of synthetic Ca-gyrolite upon heating, and characterization of hydrocarbon bearing small sized fluid inclusions in minerals, that demonstrate the power of this technique will be given.

INFRARED AND RAMAN SPECTROSCOPIC STUDY ON GYROLITE-GROUP MINERALS

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Gyrolite, $Ca_{16}[Si_8O_{20}]_3(OH)_8.14H_2O$, is a member of the large family of the calcium-silicate-hydrate (C-S-H) phases, which are of great importance in cement chemistry. It occurs in hydrothermally-treated cement systems with low CaO/SiO_2-ratios.

The mechanisms of incorporation of Zn and the reaction of the crystal structure of synthetic Ca-gyrolite upon heating in air at temperatures greater than 400 °C were investigated.

After our X-ray analysis Zn substitutes Ca in the so-called X octahedral layer consisting of isolated octahedra. The maximum substitution corresponds to Zn/(Zn+Ca) = 1/6. In this case the X layer is fully occupied by Zn: $Zn_3Ca_{14}[Si_8O_{20}]_3O_2(OH)_6 \cdot 14H_2O$. Results from infrared spectroscopic investigations of a series of Zn substituted gyrolites between Zn/(Zn+Ca) = 0 up to 1/6 will be presented. Incorporation of Zn causes a disorder in the positions of the OH groups pointing towards the X octahedral layer as shown by the disappearing of a well defined OH stretching band at 3615 cm^{-1} characteristic for the pure Ca-gyrolite and the broadening of the main OH stretching band at 3638 cm^{-1} The two crystallographically different positions of H_2O molecules (coordinating Ca and free water molecules) are reflected in the two bending bands at about 1633 and 1670 cm^{-1} Increasing Zn content changes the crystallographical environment of the water molecules shown by the "smearing" of the bending bands. In the case of a fully occupied X octahedral layer by Zn, the former free water molecules coordinate Zn octahedra. Correspondingly to that the higher frequency bending peak disappears. The intensity of the asymmetrical Q^3 $Ca_X - O - Si_{S2}$ bond stretching at about 1134 cm^{-1} decreases relatively to the intensity of the 1148 cm^{-1} peak with increasing Zn doping.

Synthetic Ca-gyrolite (consisting of single silicate sheets) transforms to a truscottite-like phase (single + double silicate sheets) upon heating at 400-600 °C in air as evidenced by XRD, IR and Raman spectroscopy. The trigger for the gyrolite – truscottite phase transition is the loss of the water molecules at 400 °C. There exists a correlation in the IR spectra between the decrease in the intensity of the main H_2O bending band at 1633 cm^{-1}, the disappearance of the shoulders at 1595 and 1666 cm^{-1}, and the appearance of two additional OH stretching bands at about 3697 and 3740 cm^{-1} after heating at 400 °C. We suppose that the new OH groups giving rise to the higher frequency bands at 3697 cm^{-1}, appearing also in the Raman spectra are coordinated only by one Ca atom in the interstices of the truscottite-like structure. The FIR spectra of gyrolite heated at 400 and 500 °C support the idea that the main changes in the Ca structure occur during the gyrolite – truscottite phase transition at 400 °C. These are related to the transformation of two of the water molecules coordinating Ca_X cations into OH groups thus provoking the breakdown of the Ca X-sheet. At the same time, two S_2 silicate sheets condense forming new 180° Si-O-Si bonds and giving rise to new symmetrical and asymmetrical Si-O-Si (Q^4) stretching bands at about 806 and 1253 cm^{-1} (IR) and 1182 cm^{-1} (Raman).

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SYNTHESIS, STEREOCHEMISTRY AND REACTIVITY OF SOME 2-METHYL-2-(3'-NITROPHENYL)-4-HYDROXYMETHYL-1,3-DIOXOLANES

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The efficient synthesis (SOLOMONS & GRAHAM, 1996) of new dioxolane compounds used in treatment of contaminated water with heavy metals like mercury, cadmium or lead was performed. Two stereoisomers were identified using ^{1}H and ^{13}C NMR (MAGER et al., 1996; SILVERSTEIN, 1997) and X-ray diffraction techniques.

The ^{1}H-NMR spectra showed major differences in aliphatic area (McCLELLAND et al., 1993), differences which lead to the separation of two pure stereoisomers. Only the *anti* stereoisomer was used in the further steps of the synthesis due to the π stacking interactions (STEED & ATWOOD, 2000) observed, which influenced the final conformation of the structure.

The ORTEP plot of the *anti* stereoisomer crystals (Fig. 1) highlighted π stacking interactions that confirm in this way the NMR data (STENBERG & KILIK, 1974).

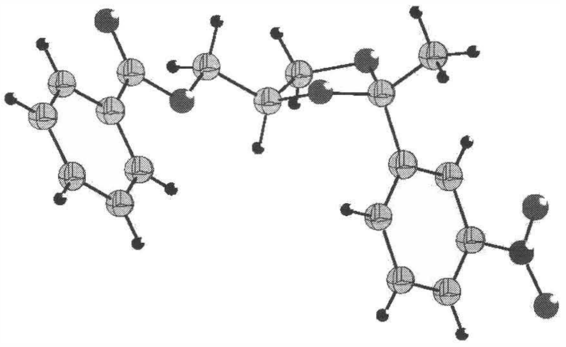

Fig. 1. ORTEP plot for anti 2-methyl-2-(3'-nitrophenyl)-4-hydroxymethyl-1,3-dioxolane

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CHEMICAL AND MINERALOGICAL CHARACTERIZATION OF SOME RAW CERAMIC MATERIALS AND THEIR TRANSFORMATIONS DURING THE THERMAL TREATMENT

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Various types of kaoline, feldspar and sand as representative raw materials for electrical ceramics were investigated in order to determine their effect on ceramic properties and microstructure.

The mineralogical composition and structural particular features of the samples of raw materials were tested by X-ray diffraction (XRD), Differential Thermal Analysis (DTA), and Infrared Spectroscopy (IR). The chemical composition of four kaoline samples, a sample of feldspar and one of sand was also determined.

IR spectra present the characteristic bands of raw and thermally treated kaoline; the variations of the intensities in the 3690-3620 cm^{-1} region are related to the crystallization degree (from well- or poorly-crystalline kaolinite). The mullite formation as ceramic phase is strongly influenced by the type or crystallization degree of the clay minerals.

A mixture of these raw materials following the recipe and the specific technology of an usual electroceramic composition was prepared. The thermal treatment of the ceramic mixture and respectively of the raw material was carried out at 1300 °C for 1 hour.

The firing transformations in the mixture and the final microstructure of the ceramics were studied by optical and electron microscopy. The chemical composition of the crystalline and amorphous phases determined by EDX indicated the presence of a certain degree of heterogeneity in the ceramic body's microstructure.

It is concluded that the final microstructure and properties of ceramic products are influenced by chemical and mineralogical composition of the raw materials. Impurities (such as Fe and Ti oxides) have a great influence on the electrical properties. The mineral components, especially those of the kaoline, play an important role during wet preparing of ceramic masses (the presence of smectites increases the plasticity but also the fired shrinkage) and crystalline phase formation during thermal treatment (poorly- or well-crystallized mullite and cristobalite).

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PREHNITE – A NEW LAPIDARY MATERIAL

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For more than three years pale green jewellery enters the mineral and gem markets under the erroneous name of garnet with tourmaline inclusions. XRD analyses have identified the material as prehnite. The spectacular green and brown bacillary inclusions were detected by EDS as epidote and amphibole. The prehnite locality is Diakon, Nioro du Sahel, Diakon Arrondissement, Kayes Region, Mali, Africa and it was disposed in Hong Kong.

The orthorhombic rock-forming mineral prehnite was named after the Dutch colonel *Hendrik von Prehn* (*1733 – †1785), who discovered this mineral near the Cape of Good Hope as the first type mineral of the African continent. The ideal formula of this combined sheet and chain silicate is $Ca_2(Al,Fe)[AlSi_3O_{10}](OH)_2$. The EDS analysis gave SiO_2 48.0 wt%, Al_2O_3 26.3 wt%, CaO 23.2 wt%, FeO 1.41 wt%.

Prehnite from Mali has pale grey green colour. Other localities as the Australian ones produce prehnite with a more yellow tint. Good quality prehnite can be semitransparent to translucent in some cases. The physical properties of the semiprecious prehnite from Mali are concordant with the properties from single crystal prehnite given in literature from other localities. The average refractive index n = 1.627, dependent of epidote and amphibole inclusions. Prehnite from Mali has a specific gravity of 2.86-2.98 g/cm^3 and a hardness of about 6-6.5.

Distinct single crystals of prehnite are relatively rare but known from alpine fissures like the famous "Prehnitinsel" in the Austrian Habachtal. More commonly, prehnite occurs as seconddary mineral filling in volcanic cavities, like the amygdales of more than 10 cm at Hall's Creek in Western Australia.

As the prehnite of the new find of the Kayes Region in Mali is characterised by numerous inclusions of epidote, dispersed amphibole needles, small idiomorphic garnet and magnetite, the development of this prehnite could be given as low grade metamorphic.

Prehnite is also used as a simulant for jade. It can be distinguished from jadeitites by means of CL-microphotography and CL-microspectrography. Similar textures, which can quickly be made visible by CL, have never been found in all jadeitites investigated so far. Careful measurements of CL spectra might also help. In spite of the close proximity of maxima of CL bands of both species, prehnites can be energized at far lower energies than jadeitites. Both methods are non-destructive.

SYNCHROTRON INFRARED SPECTROSCOPY OF SYNTHETIC $P2_1/m$ AMPHIBOLES AT HIGH PRESSURE

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The $Na(NaMg)Mg_5Si_8O_{22}(OH)_2$ amphibole represents a key double-chain silicate to model the $P2_1/m$ – $C2/m$ phase-transition in A-site filled amphiboles (IEZZI et al., 2004). It has $P2_1/m$ symmetry at room-*T*, and reverses to the usual $C2/m$ space-group of monoclinic amphiboles at ~257 °C (CAMARA et al., 2003). Della Ventura et al. (this volume) found that the aggregate B-site dimension has a strong influence on the transition temperature (Tc) based on high temperature infrared (HTIR) studies of the OH stretching vibrations. We report here an IR study of the same samples studied by Della Ventura et al. (this volume) at high pressure up to 30 GPa using synchrotron radiation.

The experiments were carried out at U2A beamline on the VUV ring of the National Synchrotron Light Source, Brookhaven National Laboratory. The fine amphibole powder was loaded into a symmetric diamond anvil cell (DAC) together with some ruby chips as pressure gauge. High-pressure IR absorption spectra of the synthetic amphiboles were collected using a Bruker IFS 66v/S vacuum Fourier transform interferometer, Bruker IRscope II microscope equipped with a HgCdTe type-A detector.

The spectrum of the Na end-member shows three bands: (A) at 3740 cm^{-1}, (B) at 3715 cm^{-1} and (C) at 3667 cm^{-1}, respectively (IEZZI et al., 2004). The higher-frequency bands are assigned to two non equivalent H atoms interacting with ^{A}Na; this pattern is typical of an amphibole with a *P*-lattice. The ^{B}Li-bearing amphiboles show in addition a fourth, minor band at 3690 cm^{-1} The bulk intensity of the A and B bands is > 95%, suggesting that the analysed amphiboles have virtually full A-sites. With increasing *P*, we observe two main modifications of the spectra: 1) all bands linearly shift toward higher frequency. At 20.8 Gpa, the peak centroid of the main (A) band is > 3800 cm^{-1} 2) the A and B bands merge into a single, broad absorption, and the *P* value at which the A-B doublet disappear is a function of the B-site occupancy. For the ^{B}Na end-member the A and B bands merge at around 18 GPa; for sample 406, with nominal B-site composition ($Na_{0.2}Li_{0.8}Mg_1$), the A and B bands merge around 13 GPa. These results show that the $Na(NaMg)Mg_5Si_8O_{22}(OH)_2$ amphibole undergoes a $P2_1/m$ – $C2/m$ phase transition at high *P*, and that the transition pressure, P_C, is a function of the aggregate dimension of the B-site, in a fashion similar to that observed by Della Ventura et al. (this volume) for increasing *T*. However, while for decreasing $<^{B}r>$ (increasing ^{B}Li in solid-solution) Della Ventura et al. observe an increase in the *Tc*, the results presented here show that the reverse is true for *Pc*, in a fashion similar to what occurs in clinopyroxenes.

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CO_2 AND H_2O IN CORDIERITE FROM THIN-SECTIONS: A RAMAN-SPECTROSCOPIC APPROACH

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Cordierite is a common metamorphic mineral in aluminous, medium- to high-grade crustal rocks. In equilibrium with other Fe-Mg-silicates, cordierite changes its Fe-Mg-ratio comprehensible with temperature and may therefore be used as geothermometer in e.g. granulite-facies rocks (DEIBL et al., 2003a). However, molecular CO_2 and H_2O can be incorporated in the channels and cavities of cordierite, greatly influencing its stability field and distorting the geothermometric calculations. CO_2 and H_2O in natural Mg- and Fe-rich cordierite single crystals were previously studied and quantified by combined Raman and IR-spectroscopy (e.g. KOLESOV & GEIGER, 2000). In this study, we tried to estimate the CO_2 and H_2O content of natural Mg-rich cordierite in a thin section from a granulite-facies metapelite (Grt + Sp + Crd + Sill + Bt + Fsp + Qtz) from the Sauwald (Southern Bohemian Massif). The *P-T* conditions of this rock were determined to be 750 – 800 °C and 4 – 6 GPa (DEIBL et al., 2003b).

Spectra were obtained by a JOBIN-YVON™ LabRAM-HR800 Raman spectrometer, a He-Ne 633nm laser and an OLYMPUS™ 100x objective (n.a. 0.9). The laser spot on the surface had a diameter of approx. 1 µm. All spectra were recorded at parallel orientation of the incident laser beam and the scattered light. Nine natural and synthetic cordierite single-crystals of known CO_2- and H_2O-concentration (colorimetric titration; BERTOLDI et al., 2004) were measured for calibration purposes. The x-axes of the single crystals were oriented parallel to the polarization of the incident laser beam and the x-parallel CO_2-molecule in the structure. Fitting of relative intensity ratios of the CO_2 stretching mode at 1383 cm^{-1} and two cordierite lattice vibration modes at 973 and 1185 cm^{-1} against CO_2-concentration resulted in a linear calibration curve. This curve can be used to calculate the CO_2-content with a precision around 0.1wt%. It was applied to a natural cordierite of 600 µm diameter in an uncovered thin-section from the Sauwald. The x-axis of the grain laid approximately in the thin-section plane and was oriented parallel to the polarization of the incident laser beam. Fifteen spots across the grain were measured, showing a complex variation in CO_2-content from core to rim. A non-linear relation between H_2O intensity ratios and concentration indicate complex orienttation and bonding of the H_2O-molecule in cordierite and prevented quantification.

Polarized micro Raman spectroscopy of cordierite in thin sections provides information about CO_2-content down to 0.1wt% at a spatial resolution of about 2 μm^3 Further research is necessary for the Raman-spectroscopic determination of the H_2O-content.

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INFRARED ABSORPTION AS A USEFUL TOOL TO SEPARATE NATURAL FROM SYNTHETIC AMETHYSTS

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The study presents results of investigations made for a representative series of samples that consisted of natural and synthetic amethysts. The investigations have been conducted in a parallel and vertical direction to the optical axis (*c*) of the stones. Infrared absorption has been used for testing and developing analytical methods useful for detection of differences between these two categories of stones. We were able to reject several criteria of selection proposed by authors of previous publications - SMAALI (1998), ZECCHINI et al. (1999) - who claimed that the absorption peak at 3595 cm^{-1} should only appear in the case of natural amethysts. Furthermore, we were able to contradict their claim that the absorption peak at 3543 cm^{-1} is only observed for synthetic amethysts. The deconvolution of the spectra allows the determination of the band widths. This value (important or feeble) will be criteria of differentiation between the natural and the synthetic amethysts. Moreover, for the synthetic "prismatic" amethysts, only the absorption bands at 3543, 3585, 3614 cm^{-1} have been revealed, whereas the bands at 3589 cm^{-1} and 3595 cm^{-1}, as observed by NOTARI et al. (2001), were not detectable in the case of using the same stones. In addition, the investigations of peaks at 3575 cm^{-1} in amethyst of Bolivia (Altiplano) and at 3630 cm^{-1} in some amethysts from Madagascar, Mexico (Vera Cruz) and Russia (Ural), allows us to suggest that there are specific properties originating in these countries' amethysts. It should be taken under account, which further measurements taken for a larger number of amethyst samples are needed in order to prove this claim. Finally we were able to say that with the orientation only the intensity of the peaks changes, but none of them disappeared. By inference, the significant infrared absorption of amethysts can be measured in any direction.

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ON A MODE OF Fe^+, OH^- OCCURRENCE IN OLIVINE (MÖSSBAUER, IR, EELS COMBINED WITH TEM)

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Traces of Fe^{3+} or OH^- detected by spectroscopic methods in olivine samples can either be incorporated in the olivine lattice (intrinsic mode) or form their own phases included in the olivine host (extrinsic mode). We used the combination of TEM, Mössbauer spectroscopy, IR, EELS and *ab initio* methods to elucidate the intrinsic and extrinsic mode of Fe^{3+} and OH^- occurrence in olivine samples from mantle xenoliths in kimberlites.

We found that ***intrinsic*** $\boldsymbol{H^+}$ is incorporated in the olivine structure via formation of M1 vacancies. ***Intrinsic*** $\boldsymbol{H^+}$ can occur in olivine as (i) OH^--bearing point defects homogeneously distributed in the olivine matrix (isolated point defects) and (ii) OH^--bearing point defects arranged into planar defects parallel to either (100) or (001) and (101). ***Extrinsic*** $\boldsymbol{OH^-}$ occurs as nano-inclusions of OH^--bearing phases such as hydrous olivine, 10Å-Phase, serpentine and talc precipitated at planar defects and dislocations. The planar defects are distributed in the olivine matrix either randomly or regularly; in the latter case they produce the 2***a***, 3***a***, 3***c*** and $3d_{101}$ superperiodicity with respect to the olivine structure by formation of hydrous olivine structures. *Ab initio* methods were used to predict the H^+ location and hydrogen bonds parameters for the 2***a***-hydrous olivine structure.

From IR and TEM data we conclude that protonation of olivine occurred during crystallization in the mantle and is not a result of a later metasomatic hydration.

The ***intrinsic*** $\boldsymbol{Fe^{3+}}$ ions are incorporated in the olivine structure via formation of M1 vacancies which form planar defects parallel to (001) of olivine under low-temperature oxidation. Periodic arrangement of such kind of planar defects results in the laihunite (or, the same, ferriolivine) formation. Low-temperature oxidation of olivine which contains OH^--bearing nano-inclusions results in transformation of precursor hydrous olivine phases to a mixture of nanometer-sized FeOOH, $Fe(OH)_3$ and SiO_2 due to interaction between Fe^{3+} and OH^- defects (***extrinsic*** $\boldsymbol{Fe^{3+}}$ ***and*** $\boldsymbol{OH^-}$).

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MOLECULES OF CARBON OXIDES IN CORDIERITE CHANNELS: A SPECTROSCOPIC STUDY

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The spectroscopic micro-FTIR technique has been used to examine a series of natural cordierite samples of different geological environments and chemical composition. Polarized single-crystal spectra were measured in the range 3000-2000 cm^{-1} on oriented polished platelets (100), (010) and (001). The behaviour of CO_2 and CO molecules, as well as other minor volatile components trapped in the structural channels of the cordierites, was studied in the temperature range 80-700 K. An experiment on degassing was performed by heating a cordierite sample at a temperature of 1250 K during 10 hours. Location and orientation of $^{12}CO_2$, $^{13}CO_2$ and CO molecules in structural channels, as well as the character of CO_2 libration were determined. Polarization-dependent complex sets of valence vibrations were identified for CO_2 molecules. Most intense bands were measured in *a*-polarization at 2348 and 2283 cm^{-1}, the latter was assigned to $^{13}CO_2$. $\delta^{13}C$ values were calculated for different samples from the A_{2283}/A_{2348} band intensities ratio and compared with published data. A weak CO band at 2135 cm^{-1} is detected in samples of CO_2-enriched cordierites from granulites. The main *a*-polarized $^{12}CO_2$ band at 2348 cm^{-1} becomes narrower and exhibits fine structure at LN_2 temperature: an additional band at 2330 cm^{-1} and a shoulder at 2352 cm^{-1} appear in the spectra. The molecular axes of the CO_2 and CO molecules are parallel to the *a*-axis of cordierite crystals. Only trace amounts of CO_2 oriented parallel to the *c*-axis were found in some samples. This confirms recent results of KOLESOV & GEIGER (2000). The complex spectral shape of CO_2 band envelopes in *a*- and *b*-polarizations is very likely due to a rotational motion of the carbon oxides molecules. Repeating spectral measurements after heating confirm the weak mobility of CO_2 and CO molecules in the channel sites at temperatures below 700 K and the full degassing of cordierite after heating at 1250 K. Differences in the carbon oxides spectra observed in cordierites from genetically different environments, including variations in CO/CO_2 ratio and in the $\delta^{13}C$ of captured carbon dioxide molecules, are discussed.

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NEW RAMAN SPECTROSCOPIC OBSERVATIONS OF HYDRATED TRANSITION ZONE SPINEL/SPINELLOID PHASES

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Wadsleyite [β-$(Mg,Fe)_2SiO_4$, spinelloid III] and ringwoodite [γ-$(Mg,Fe)_2SiO_4$,spinel], the nominally anhydrous high pressure polymorphs of olivine are thought to be the most abundant minerals in the Earth's mantle transition zone between 410 and 660 km depth. They can incorporate respectively up to 3.3 and 2.5 wt% H_2O in form of OH into their crystal structure. While the Fe-content of wadsleyite and ringwoodite with an assumed natural amount of ~11% Fe influences transition zone properties (e.g., elasticity) globally the OH content may be more important within and adjacent to cool subducting slabs. Wadsleyite II (spinelloid IV) is a hydrous, Fe-bearing silicate phase that might occur between the stability regions of wadsleyite and ringwoodite.

We present Raman spectra from ~50 to 4000 cm^{-1} of high-quality single-crystals of hydrous Mg-endmember and hydrous Fe-bearing wadsleyite, wadsleyite II, and ringwoodite. The transition zone phases were synthesized in a multi-anvil apparatus at the Bayerische Geoinstitut, Germany and high-pressure Raman spectra were obtained up to 60 GPa using a diamond-anvil cell and solid helium as pressure-transmitting medium.

The Raman spectra of wadsleyite and wadsleyite II are similar as would be expected from their closely related structures. In the OH stretching region the spectrum of wadsleyite II appears more complex than the spectrum of wadsleyite consisting of at least 6 modes. The most interesting observation of the high-pressure study of wadsleyite II is the appearance of Raman bands (not detectable/resolvable at 1 bar) in the region 450-650 cm^{-1} above ~35 GPa. For ringwoodite, the Raman spectrum of Fo_{100} composition shows all five characteristic spinel modes whereas the hydrous Fo_{89} composition exhibits additional modes in the range 709-939 and 100-250 cm^{-1} In both phases the SiO_4 stretching modes shift continuously up to 60 GPa; additional bands emerge in the region 550-580 cm^{-1} near 40 GPa in the Fo_{89} sample.

Comparisons of Raman spectra of hydrated transition zone phases with varying iron content reveal that pure protonation has only a minor effect on the lattice dynamics while coupled iron and proton substitution leads to additional levels of transformation complexity reflected in reversible, pressure–induced modifications in the Raman spectra of hydrous Fo_{89} ringwoodite and wadsleyite II. The present observations could provide additional insight into the existence of new protonated, iron-bearing, unquenchable phases in cool, wet regions near subducted material.

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IMPORTANCE OF WEATHERED METEORITES FOR MARS: DATA ON VNIR REFLECTANCE-SPECTROSCOPY, RAMAN-SPECTROSCOPY AND MÖSSBAUER-SPECTROSCOPY

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With respect to global tectonics the present day Mars is considered as a single plated planet. Due to the lack of consumptive plate tectonics, the Martian sedimentary record represents a long-term archive of exogenic processes. The compositions and mixing relationships of three principal components, which may be inherent in Martian soil, were derived from APXS-Pathfinder and XRFS-Viking chemical data (KOLB et al., 2003). The principal soil components were chosen to represent Pathfinder Soil Free Rock, physical weathering products of Pathfinder andesites and meteoritic material with CI-chondrite composition. Correlation trends of the available chemical data in the ternary composition space of the principal components corroborate the existence of a Global Dust Unit and provide constraints on its composition. Evidence from spectroscopic data, returned by numerous Mars missions, has to be found to strengthen the argument of substantial meteoritic contribution to the Martian soil. VNIR reflectance spectroscopy has been used from the beginning of spectroscopic Mars research, because of the strong ferric absorption edge of Martian soil materials and easy achievement of space-flight proven hardware and telescopic observation. Mössbauer-spectroscopy is used for in-situ soil science in the frame of the Mars Exploration Rover mission (SQUYRES et al., 2003). Future mars missions will involve Raman-spectroscopy due to its capability in phase identification among intimate phase mixtures (ELLERY et al., 2003). We investigated meteoritic finds by means of VNIR reflectance-spectroscopy, Raman-spectroscopy and Mössbauer-spectroscopy. Current focus is given on meteoritic finds from Omani desert. Future investigations will consider chondritic finds from Antarctica, too.

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A RAMAN SPECTROSCOPIC STUDY OF Fe-Mg OLIVINES

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End-member synthetic fayalite and forsterite and a natural solid-solution composition crystal of composition (Mg$_{1.80}$,Fe$_{0.20}$)SiO$_4$ as well as polycrystalline forsterite and fayalite isotopically enriched in ^{26}Mg and ^{57}Fe, respectively, were synthesized and their Raman spectra were measured. The observed isotopic shift of vibrational modes permits the assignment of spectra, especially in low-frequency region, to be improved. The low wavenumber Raman modes in olivine are best described as lattice modes consisting to a large degree of mixed vibrations of M(2) cation translations and external vibrations of the SiO$_4$ tetrahedra. The polarized single-crystal spectra of forsterite and Fo$_{90}$Fa$_{10}$ were recorded at a number of temperatures from room temperature to about 1200 °C. From these data, the microscopic Grüneisen parameters for three different A$_g$ modes for both compositions were calculated, and also the structural state of the solid solution crystal was investigated. The difference in the measured mode wavenumbers between the heating and cooling is due to hysteresis effect. The spectra of the Fo$_{90}$Fa$_{10}$ crystal, unlike the spectra of forsterite, show a discontinuity in the wavenumber behavior for the mode at ~220 cm^{-1} at 700-1000 °C upon heating and cooling (Fig. 1). Both these observations are discussed taking into account the various crystalline effects, i.e. annealing of the point defects, structural transformation, rigid rotation of the SiO$_4$ tetrahedra, changing of the oxygen-oxygen interaction. The discontinuity in the wavenumber behavior of the mixed Mg/T(SiO$_4$) mode (Fig. 1) may be related to variations in the Fe-Mg intracrystalline partitioning behavior in the Fo$_{90}$Fa$_{10}$ crystal, i.e. to some decrease in the concentration of Fe^{2+} at M(2).

The mode wavenumber and intensity behavior of internal SiO$_4$ vibrations as a function of temperature are discussed in terms of crystal field and dynamic splitting and also ν_1 and ν_3 coupling. Crystal field splitting increases very slightly with temperature, whereas dynamical field splitting is temperature dependent. The degree of ν_1-ν_3 coupling decreases with increasing temperature.

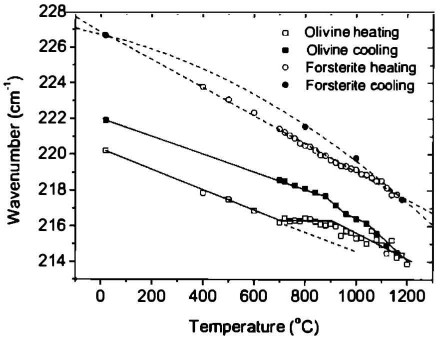

Fig. 1. Temperature dependence of the wavenumber of the A$_g$ mode at 220 cm^{-1} in Fo$_{100}$ and Fo$_{90}$Fa$_{10}$.

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MOLECULE-MINERAL INNER SURFACE INTERACTIONS IN NANOPOROUS SILICATES: A RAMAN SPECTROSCOPIC INVESTIGATION

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We have undertaken single-crystal Raman measurements of zeolites (bikitaite, natrolite), SiO_2-clathrates (melanophlogite) and other silicate structure types with small nanopores (beryl, cordierite, hemimorphite) at different temperatures. The goal is to investigate the nature of inner surface molecule-crystal interactions and the role of hydrogen bonding in minerals. The angular dependencies of the OH-mode scattering intensities in single-crystal measurements, made at low and ambient temperatures, permit the direction of the molecular bonds and the main molecular polarizabilities for different O-H bonds to be obtained.

In bikitaite, H_2O molecules occur in infinite [010] channel ways and build a hydrogen-bonded H_2O chain termed 'one-dimensional ice' The molecules are ordered, whereby one H atom per molecule is unbonded and the other is hydrogen-bonded to a neighboring H_2O molecule. They show little interaction with the framework. The hydrogen-bonded O-H stretching bands in the Raman spectra show little line broadening, which is not typical for many hydrogen-bonded systems. With increasing temperature, the hydrogen bonding weakens continuously until the chain 'breaks' and isolated H_2O molecules are present.

The Raman spectrum of melanophlogite shows the presence of quasi-free N_2, CO_2 and CH_4, but no H_2O molecules. Most of the CH_4 is partitioned into the smaller nearly spherical [5^{12}] cage, while CO_2 and N_2 appear to prefer the larger more oblate [$5^{12}6^2$] cage. The difference in wavenumber for their stretching modes between room temperature and 4 K is minimal. The molecules are orientationally disordered in the cavities and they have only weak dispersion interactions with the SiO_2-crystal framework. However the incorporation of molecules is necessary to allow the SiO_2 framework to condense.

Cordierite and beryl contain quasi-free CO_2 molecules, as well as H_2O in small cavities. The CO_2 molecules are orientated parallel to the crystallographic *x*-axis. The H_2O molecules have their H-H vector parallel to the *z*-axis in alkali-free crystals and are dynamically disordered about the *z*-axis. They show little hydrogen bonding with their frameworks.

It is noteworthy that the polar H_2O molecule can be found in these two 'zeolite-like phases', but not in melanophlogite. Melanophlogite is hydrophobic, while nearly all other nanoporous silicates are hydrophilic. The incorporation of the polar H_2O molecule may be related to the nature of the electronic charge distribution within the crystal framework.

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$Fe_3(PO_4)_2(OH)_3 \cdot 5H_2O$, A NEW MONOCLINIC FERRIC IRON PHOSPHATE MINERAL FROM GERMANY: CRYSTAL STRUCTURE, SINGLE-CRYSTAL RAMAN SPECTRA AND CLOSE RELATION TO WAVELLITE

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A new monoclinic ferric iron phosphate mineral has been found at the abandoned Grube Mark near Essershausen, Taunus, Hesse, Germany (BLAß, 2002). The mineral forms pale brown-yellow, translucent to transparent, acicular crystals (rarely up to 1.5 mm in length) which are always intergrown to form bundles of subparallel crystals. These are associated with beraunite (reddish "oxiberaunite" variety) and cacoxenite.

All acicular crystals studied were twinned by non-merohedry. The crystal structure has been determined using single-crystal intensity data (Mo$K\alpha$ X-radiation, CCD area detector, 293 K) collected from a twin. The model was refined in space group $P2_1/n$ (a = 9.777(3), b = 7.358(2), c = 17.830(5) Å, β = 92.19(4)°, V = 1281.7(6) Å^3, Z = 4) to $R1$ = 13.3 % and $wR2_{all}$ = 35.3 % from 2045 'observed' reflections with $F_o > 4\sigma(F_o)$. The relatively high residuals are due to the twinning and weak intensity data. The chemical formula obtained from the refinement is $Fe_3(PO_4)_2(OH)_3 \cdot 5H_2O$, which was confirmed by quantitative electron microprobe analyses. Single-crystal laser-Raman spectra (Renishaw M1000 MicroRaman Imaging System) show, in the region > 1500 cm^{-1}, several bands (s = strong; sh = shoulder) due to OH stretching vibrations (at ~3567, 3412(s), ~3197(s), ~3060 to ~3052(sh) cm^{-1}) and H-O-H bending vibrations of water molecules (~1625 cm^{-1}).

Chemically, the new mineral is the Fe^{3+}-analogue of wavellite ($Al_3(PO_4)_2(OH,F)_3 \cdot 5H_2O$, orthorhombic, space group *Pcmn*; ARAKI & ZOLTAI, 1968). Structurally, however, it is not isotypic with wavellite, but crystallises in a monoclinically distorted variant ($P2_1/n$; subgroup of *Pcmn*) of the wavellite structure type. Details of the structure and its hydrogen bonding scheme will be discussed.

The title compound has the same chemical formula as the amorphous species santabarbaraite (PRATESI et al., 2003) which forms, however, exclusively on in-situ oxidative alteration of vivianite, $Fe^{2+}_3(PO_4)_2 \cdot 8H_2O$.

Mr. Michael Legner is thanked for providing the studied samples. Financial support by the Austrian Science Foundation (FWF) (Grant P15220-N06) is gratefully acknowledged.

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RAMAN SPECTRA OF TITANOSILICATE MELTS

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Titanium is a minor element in most rock-forming silicate melts. Nevertheless, this element is petrologically significant (MYSEN et al., 1980). Titanium is in six-fold coordination by oxygen in the majority of natural silicates, and titanium can replace silicon in four-fold coordination in alkaline minerals. A structural feature of titanosilicate glasses is that titanium can be both in six-fold coordination, and in four-fold coordination. Structure of melts of systems: 33%Na_2O·67%SiO_2-x%TiO_2, 40%Na_2O·60%SiO_2-x%TiO_2, 50%Na_2O·50%SiO_2-x%TiO_2 (x=1, 5, 10, 20 %) have been investigated by Raman high-temperature spectroscopy. The pulse laser was used for excitation of spectra and a synchronized system of account of photons was used for the registration. It is necessary to discriminate a thermal background from the heating furnace and melt.

As an example, Raman spectra of the compound with 50%Na_2O-45%SiO_2-5%TiO_2 are shown in Fig. 1 at temperatures of 293-1389 K. Bands in the range of 1050-1075 cm^{-1}, 940-970 cm^{-1}, 860-880 cm^{-1} and 570-625 cm^{-1} are observed in the spectra of titanosilicate glasses and melts. Bands at 1050-1075 cm^{-1} and 940-970 cm^{-1} are attributed to the highly localized symmetric Si-nonbridging O stretching vibrations of Q^3 and Q^2 species, respectively (MYSEN & NEUVILLE, 1995). The low frequency bands are associated with stretching vibrations of Si-O-Si linkages. The band at 860-880 cm^{-1} is assigned to vibrations of TiO_4 units (FURUKAWA & WHITE, 1979). Raman spectra of crystalline phases which are formed at heat treatment of glasses at temperatures of 800-1000 K were obtained too. Systematics of the band behavior in Raman spectra depending on composition (SiO_2 and TiO_2 content) and temperature are established.

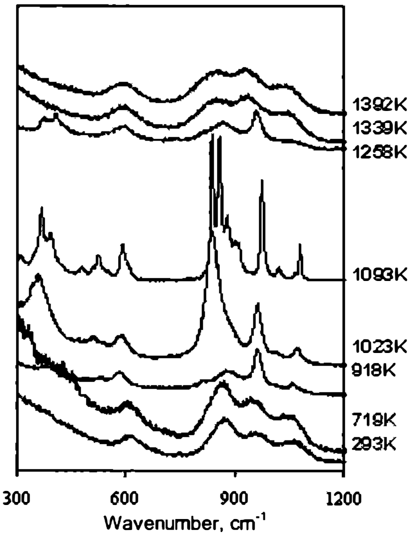

Fig. 1. Raman spectra of the compound with 50%Na_2O-45%SiO_2-5%TiO_2 at different temperatures

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TEMPERATURE-INDUCED STRUCTURAL TRANSFORMATIONS OF LAYERED TITANOSILICATE JDF-L1

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The efforts to produce new materials with industrially useful properties in the past years resulted in the synthesis of a number of microporous titanosilicates with potential applications in catalysis, ion exchange, separation processes. Some of these materials do not have mineral analogues and their comprehensive characterization may contribute significantly to understand their nature and properties as well as to optimize the preparation of titanosilicates having desired structural topology.

Layered titanosilicate JDF-L1 is synthesized in a Na_2O-TiO_2-SiO_2-H_2O system, applying a rapid procedure without using organic additives in the synthesis mixture. The thermal evolution of the JDF-L1 structure is studied by thermogravimetric-differential thermal analysis, powder X-ray diffraction and Raman spectroscopy. It is shown that on heating JDF-L1 undergoes a sequence of structural rearrangements causing formation of non-crystalline alkali titanate-titanosilicate phases, defect-rich microcrystalline silica and crystalline titanosilicate narsarsukite, the latter becoming the dominant phase at high temperatures. Upon thermal treatment JDF-L1 undergoes reconstructive phase transitions involving order-disorder-order processes and resulting in formation of narsarsukite as a final dominant phase. According to XRD and Raman spectroscopic data, the thermal evolution of the JDF-L1 structure consists of three main stages:

(i) below 550 °C - a gradual decrease in the interlayer spacing caused by H_2O removal, accompanied by topological changes in the Si-O entities and layer undulation;

(ii) near 580 °C - total collapse of the JDF-L1 structure, providing material for formation of X-ray amorphous Ti-rich phases, microcrystalline silica of opal CT-type, and nucleation of narsarsukite;

(iii) above 600 °C - atomic rearrangements in the matrix of non-crystalline alkali titanate-titanosilicate phases and opaline silica resulting in enhanced crystallization of narsarsukite.

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RESULTS OF AN ESR-STUDY OF QUARTZ FROM THE ARCHAEAN METAMORPHIC COMPLEXES IN THE KOLA SUPERDEEP BOREHOLE SECTION

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The researches were made within IGCP Project 408 (UNESCO). The main tasks of the Project are to compare properties of rocks in the section of the Kola Superdeep Borehole SG-3 (0-12262 m) and their homologues as well as geological correlation of the rocks in the SG-3 section with Precambrian formations of the Pechenga structure frame.

Present results are mainly based on a spectroscopic study of the extensive collection of samples of quartz (ca. 150) from the core SG-3 material and supposed rocks-homologues of the borehole area. ESR (electron spin resonance) was a main method for the study of quartz from the rocks. This method allows a selective registration of different atomic defects in the mineral structure. We used a multistage procedure of radiation-thermal influence on the mineral in order to reveal the highest possible diversity of atomic defects in quartz and facilitate their concentration evaluation. This procedure includes annealing at temperatures of 320, 530, and 1000 °C, and γ-irradiation of the samples by doses of 0.5 and 30 Mrad. ESR spectra of the powder samples of quartz were recorded at room temperature and boiling-point of liquid nitrogen with the commercial radiospectrometer SE/X 2547 (RadioPAN, Poland). The investigations were made on vacancy defects (E_1-centres) and defects associated with isomorphous incorporation of Al-, Ge-, Ti-ions into the lattice of rock-forming quartz.

The dependence of impurity-related Al-, Ge-, Ti-centres, and proper structural defects in the quartz along the SG-3 section on the bedding depth and petrogenesis of the Precambrian host rocks were estimated. Concentration shifts (vacancy defects) and redistribution of defects according to the structural positions (lithium and proton species of Ti-centres, Al-centres in regular and irregular positions) are evident.

The investigations carried out show that the impurities and structural defects in the rock-forming quartz can serve as a genetic mark for metamorphic rocks of the Precambrian formation complexes and as one of the criteria for typification and correlation of deep strata of the early Precambrian, exposed by the SG-3 section.

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HYDROXYL IONS IN SYNTHETIC CRYSTALS: DO THEY DIFFER FROM THOSE IN MINERALS?

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Synthetic crystals are produced for practical applications where the presence of hydroxyl ions in the material may be either desirable or undesirable. In any case a small amount of OH^- ions in *as-grown* anhydrous crystals (alkali halides, fluoroperovskites, oxides etc.) can easily be detected by the high resolution FTIR absorption technique, if the crystals are grown at high temperatures (600 – 1600 °C) from melt or solution in air atmosphere. Unlike to many cases of minerals, the relatively large single crystal samples do not require special microsampling methods or FTIR microscopes. The information obtained from the vibrational frequency of the OH^- ions, and from the pleochroism of the absorption bands are in general very similar and can be used to determine the structural site of the hydroxyl defect in the crystal lattice.

Two review papers have recently been published on OH^- defects in minerals and synthetic oxide crystals by BERAN & LIBOWITZKY (2003) and WÖHLECKE & KOVÁCS (2001), respectively, which present the main similarities and differences between the two classes of materials. In the present work, the anharmonicity of the stretching mode characteristic for all O-H vibrations, the weak coupling to phonon bands in some complex oxides derived from the temperature dependence of the OH^- bands, and the effect of a structural phase transitions on the O-H vibrational frequency in $LaGaO_3$ crystals will be surveyed. The role of hydroxyl ions in the thermal fixing of holographic gratings in photorefractive materials is also shown, and how the composition of some niobates and tantalates can be characterized by the shape of the OH^- bands.

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FTIR SPECTROSCOPY OF OH^- IONS IN $Pb_5(GeO_4)(VO_4)_2$ APATITE

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Lead germanate vanadate – $Pb_5(GeO_4)(VO_4)_2$ (PGV) – is a promising acousto-optical material, which can be grown from melt by the Czochralski method (YANO et al., 1971). PGV crystallizes in a hexagonal structure characterized by the space group $P6_3/m$ (IVANOV & ZAVODNIK, 1989). It belongs to the general $A_4B_6(XO_4)_6Y_2$ apatite structure, where lead occupies both A and B positions, germanium and vanadium are randomly located in tetrahedral sites, X, and the anionic position, Y, remains empty. In hydroxyapatites Y denotes the OH group. In oxide crystals grown in air atmosphere, however, hydroxyl ions are usually present as impurities occupying oxygen sites (WÖHLECKE & KOVÁCS, 2001). The aim of this paper is to study the vibrational properties of hydroxyl ions possibly incorporated in synthetic $Pb_5(GeO_4)(VO_4)_2$ single crystals, using the Fourier Transform InfraRed (FTIR) absorption technique.

The presence of hydroxyl ions in *as-grown* $Pb_5(GeO_4)(VO_4)_2$ crystals has been confirmed by detecting an absorption band related to the stretching vibration of OH^- ions at $\nu = 3558\ cm^{-1}$ wavenumber at 300 K, $\Delta\nu \approx 20\ cm^{-1}$ These values are in relatively good agreement with those reported for $Ca_{10}(PO_4)_6(OH)_2$ hydroxylapatites, $\nu \approx 3572\ cm^{-1}$, $\Delta\nu \approx 10\ cm^{-1}$ (CANT et al., 1971). The OD^- isotopic replica at $2625\ cm^{-1}$ wavenumber has appeared in the crystal after a high temperature treatment at 1073 K in D_2O vapour atmosphere. The anharmonicity of the stretching mode calculated from the frequencies of the OH^-/OD^- ions is $x_e \approx 0.024$, in excellent agreement with those found for hydroxyl ions in other oxides (WÖHLECKE & KOVÁCS, 2001). The stretching mode frequency has shifted to higher energies, while the halfwidth of the slightly asymmetric band has shown an anomalous increase for decreasing temperatures ($\nu = 3561.5\ cm^{-1}$, $\Delta\nu = 24\ cm^{-1}$ at 9 K). Anomalous behaviour has also been observed for the halfwidth of the absorption band using polarized light. At 300 K for light propagating along the *c* axis (ordinary polarization) $\Delta\nu$ is about $20\ cm^{-1}$, while for extra-ordinary polarization $\Delta\nu = 13\ cm^{-1}$ The band intensity, however, shows only a slight change for *o* and *eo* polarization directions. The anomalous temperature and polarization behaviour of the OH^- absorption band and the possible lattice sites of the hydroxyl ions in synthetic $Pb_5(GeO_4)(VO_4)_2$ apatite single crystals will be discussed.

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NMR AND DIFFRACTION STUDY OF ACETONE INTERCALATED IN THE LAYER SILICATE RUB-18

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Interaction of organic molecules with inorganic surfaces is of interest because of a variety of technical applications and because of the environmental impact (OGAWA & KURODA, 1995). In order to study these processes intercalates are used as model system. In particular the analysis of the hydrogen bond network established between guest-molecules and the host-compound are of interest. As simplest molecule for the study of the interaction, acetone has been used (BOROVKOV et al., 1982).

The synthesis of Acetone-Rub-18 was carried out starting from H-Rub-18, a derivative of the Na-form (BOROWSKI et al., 2002), by treatment with acetone or D6-acetone at room temperature. The level of intercalation is about 95%. The sample was stored at room temperature in D_2O atmosphere to avoid D-H exchange. DTA, TGA investigations (measured with a BÄHR STH 503, T=293-463 K, heat rate 3 K/min) show two weak signals at 318 and 382 K which are explained as processes involving the intercalated acetone molecule. In the ^{1}H MAS NMR spectra (spectrometer: Bruker ASX-400, spinning rate - 12 kHz, dwell time - 4 μs, D1 10 s) there are two signals at 2.0 ppm (methyl group) and 6.0 ppm (silanol group). The high temperature (temperature range 298-430 K) ^{1}H MAS NMR spectra show the splitting of the two main signals into 5 and 6 signals with greater amplitude than at room temperature, respectively. The chemical shift values of the two signals in a ^{29}Si MAS NMR spectroscopy experiment (spinning rate-3.5 kHz, dwell time- 25 μs, D1- 60 s) are typical for Q^3 ($Si(-OSi)_3(-OH)$) and Q^4 ($Si(-OSi)_4$)-connected silicate tetrahedra, respectively. Powder neutron diffraction data were used to investigate the crystal structure of the composite. The data were collected on the high-resolution powder diffractometer HRPT (PSI Villigen, Swiss) at λ=1.886 Å from 5-163° 2Θ with step width 0.1° The symmetry of the structure of D6-Acetone-Rub-18 was determined as $P4_12_12$. Unit cell parameters were refined with least square methods: a_0=7.479(7), c_0=37.334(9) Å. The location of intercalated guest molecules was determined using Fourier syntheses maps. The geometric parameters of the silicate layers shifted only slightly upon the intercalation. The acetone molecules are located in the "semi cages" between silicate layers and stabilize the structure (Fig. 1).

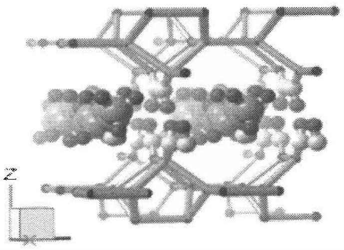

Fig. 1. Fragment of the crystal structure of H-Rub-18 intercalated with D6-Acetone

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THE REVELATION OF TYPOMORPHIC PROPERTIES OF METAMORPHIC CARBONATE ROCKS.

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To determine the belonging of marble to a certain deposit, these laboratory methods of testing can be used: spectrophotometry, luminescence analyses and X-ray diffraction. Marble specimens from Karelia (Tivdia, Juven, Ruskeala), Middle Ural (Polevskoe, Ufaley), Greece and Italy (Carrara Mountains) were investigated using these methods. The age and formation condition of these rocks differ considerably and thus influenced the composition and structural features of the composing minerals. This is confirmed by the chemical analysis (Table 1).

Table 1. Chemical composition of marbles in ppm

Sample	Mg	Fe	Mn	Pb	Ce	Σ REE
Polevskoe	6488	111	44,1	0,8	0,5	5,9
Carrara Mount.	9958	287	102,8	1,1	1,5	6,4
Juven	1900	321	47,1	1,4	2,9	10,5

X-ray analysis revealed a significant difference in phase composition. Marbles from Juven (white-grey, coarse-grained) and Greece (white, fine-grained) proved to be the most similar to pure calcite. They contained only a little amount of quartz. Ural marbles (grey and white) contained a considerable dolomite and quartz mixture, and pink Tivdia marble consisted almost completely of dolomite with small amount of quartz. Lattice parameters of the investigated carbonates varied within the range a_0 = 4.804-4.981, c_0 = 15.996-17.028 Å; c/a = 3.33-3.44. Photoluminescence (PL) of marbles was investigated in visible and ultraviolet range. The intensive blue-violet luminescence is typical for white coarse-grained marbles. It is related to cerium impurities and is typical for Iceland spar. Other sorts of marble have different colors and variable luminescence in sample volumes. To obtain more extensive spectroscopic data, some samples were dissolved in hydrochloric acid. The optical absorption and the PL of their solution were investigated. We also investigated carbonates, used in the construction of Saint Isaac's Cathedral (architect Rinaldi, 18 c., Saint Petersburg) and Queen's pavilion in Peterhof (19 c.). The results are shown in Table 2.

Table 2. Spectral characteristics of marbles

Sample	Color	PL, λ^{em}_{max}, nm	Solutions	
			absorp., λ^{ab}_{max}, nm	PL, λ^{em}_{max}, nm
Polevskoe	white	530	360	430
Carrara Mount.	white	340, 400 - 450	250, 330	340, 540
Juven	white - grey	430	250, 300, 360	420
Ruskeala	grey	520 - 550		
Tivdia	pink + white	520, 540	260, 335	540
Ufaley	grey	–		
ruins 18 c.	white	340, 400 - 450		

Thus, this investigation has shown that using these methods enables to determine characteristic features of marbles of a certain type and to determine its origin. The results can be used for the characterisation of the marble and during the construction and restoration works.

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APPLICATION OF MICROANALYSIS (SEM-EDS) IN THE STUDY OF HEAVY MINERALS FROM RECENT STREAM ALLUVIA IN THE TATRA MTS.

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Heavy minerals from the recent alluvia in the upper parts of valleys in the Tatra Mts. were studied. Samples of alluvia were collected from six streams in the Tatra Mts. and examined using a scanning electron microscope fitted with an energy dispersive spectrometer (JEOL 5410 and NORAN Voyager 3100). Polished thin sections of heavy mineral fractions were prepared and studied in an optical microscope in transmitting and reflected light and examined in a scanning electron microscope fitted with a dispersive energy spectrometer (SEM-EDS).

Heavy minerals assemblages from recent alluvia in the Western Tatra Mts. are composed of garnets, opaque minerals (magnetite, ilmenite), amphiboles, zircon, tourmaline, and rutile. Xenotime and monazite occur in relatively high amount. Staurolite, apatite, and sillimanite are present as minor components. In the Western Tatras a relatively high content of sulphides was noted. Garnet grains are characterised by high content of almandine end-member (Alm 45-75 %); spessartite is also present in significant amount (Sps 5-55 %). Amphiboles are represented mostly by magnesio-hornblende. All sulphide grains (pyrite, Fe-Cu sulphides) are strongly oxidised. Heavy minerals assemblages from the High Tatra Mts. consist of apatite, epidote, ilmenite, magnetite, zircon, monazite, rutile, hematite, chlorite, allanite, titanite, prehnite, pumpellyite, sillimanite, pyrite, barite. Amphibole, prehnite, xenotime, allanite, barite and pyrite are scarce. Apatite grains exhibit variations in chemical composition (Mn and Cl content). Most Fe-Ti oxides exhibit complex intergrowths of very thin lamellae and lenses of Ti-ilmenite and rutile enclosed in Ti-hematite host.

Heavy mineral assemblages generally reflect the composition of accessory minerals (both primary and formed during hydrothermal alterations) present in source rocks. High abundance of crushed and irregular grains can be related to glacial transport and subsequent extraction of grains from moraines. Presence of grains with porous margins indicates intense leaching related probably to the activity of humic acids in alluvia. Scarcity of sulphide veins in the Western Tatras suggests that a relatively high content of oxidised sulphide grains in heavy mineral assemblages is related to their removal from old mine tailings present in upper parts of valleys.

Results of heavy minerals from alluvia in the Tatra Mts. can be important in the discussion on the origin of young clastic deposits in the Podhale and Orava basins (KIEBAŁA et al., 2001).

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INFRARED AND MÖSSBAUER SPECTROSCOPY OF NATURAL GLASSES

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Natural glasses have been investigated by methods of IR- and Mössbauer spectroscopy.
The ^{57}Fe Mössbauer spectra were obtained at room temperature using spectrometer MC-2201. The spectra of the studied glasses represent an asymmetrical doublet, the high-velocity peak is slightly wider and less intense in comparison with low-speed peak. The mathematical simulation of spectra was done by the program UNIVEM. At modeling of spectra the equaling of half-widths and intensities of low- and high-velocity lines of each doublet was supposed.

It is shown, that ferrous iron dominates in modern basalt glasses. The Fe^{2+} ions occupy octahedral positions in glasses, which are characterized by a different degree of distortion of the polyhedron. The Fe^{3+} ions also occupy octahedral positions. The redox ratio of iron in basalts from the East-Pacific Rise is slightly higher than the redox ratio of iron in oceanic basalts from the Mid-Atlantic Ridge. The redox ratio of iron in basalts from the Bouvet triple junction varies from 10 to 28 %. The redox ratio of Fe ions in ancient glasses considerably exceeds that of Fe ions in modern basalt glasses. It is related with secondary changes due to postmagmatic hydration.

In investigated tektites and impact glasses ferric iron is in tetrahedral positions. Its content amounts to 2-7 % of the total content of iron in glasses. The Fe^{2+} ions are in octahedral coordination and occupy structurally nonequivalent positions. This is related to the formation of tektites and impacts as a result of fast cooling from high temperatures.

The IR-spectra of investigated tektites and basalt glasses show three major absorption bands: the high-frequency region above 1000 cm^{-1} contains a strong, broad asymmetric band with a maximum near 1100 cm^{-1}; a peak is centred at 800 cm^{-1} and a strong band appears in the low-frequency region at 470 cm^{-1} The band at 1100 cm^{-1} is assigned to Si–O stretching vibrations associated with tetrahedral SiO_4 groups. The band in the region 400-500 cm^{-1} is assigned to the bending mode Si–O–Si(Al) (TAYLOR, 1990; POE et al., 1992). The band with maximum at 800 cm^{-1} is connected to vibrations of AlO_4 tetrahedra. In some samples bands in the region 580-640 cm^{-1} are observed. These bands are related to vibrations of AlO_5 and AlO_6 groups (McMILLAN et al., 1992). In some samples also a shoulder is present in the 900-1000 cm^{-1} region which is due to stretching vibrations of non-bridging Si–O bonds.

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OPTICAL SPECTROSCOPIC STUDIES IN $LiNbO_3$: Mg CRYSTALS BELOW AND ABOVE THE PHOTOREFRACTIVE THRESHOLD

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$LiNbO_3$ is a well known non-linear optical material, but in many cases its application is limited by the photorefractive effect. The optical damage resistance can be improved by doping the melt with MgO above a threshold concentration. The threshold was found at about 5 mol % MgO for the congruent composition (BRYAN et al., 1984), but it strongly depends on the stoichiometry of the crystal. Several seemingly contradictory defect structure models have been developed to interpret this phenomenon (DONNERBERG et al., 1991; IYI et al., 1995; LIU et al., 1996).

Optical absorption methods are very simple and sensitive tools for the determination of the threshold concentration. The UV absorption edge and the IR spectrum of the OH^- ion vibration have systematically been measured in $LiNbO_3$ samples for wide composition and Mg concentration ranges. The Mg content (0-9 mol %) of the crystals with congruent, stoichiometric and an intermediate composition has been determined by atomic absorption spectroscopy. At the threshold the vibrational frequency of the hydroxyl ions moves abruptly to higher energies, while the shift of the UV-edge changes its direction. Above the threshold value, however, there is a linear dependence for the UV-edge and for the halfwidth of the A_1 Raman peak at 631 cm^{-1} and an approx. square root dependence for the OH^- frequency as a function of Mg concentration. The halfwidths of the A_1 Raman peaks at 251 and 275 cm^{-1} are also influenced by the sample composition. Our results confirm the model of LIU et al. (1996), in which the number of antisite Nb_{Li} decreases and that of $Mg_{Li}V_{Li}(NbO_3)_2$ defects increases with increasing Mg content up to the threshold, and for Mg concentrations exceeding the threshold, complexes containing Mg on both Li and Nb sites are formed.

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CRYSTAL CHEMISTRY OF GAHNITE-BASED PIGMENTS: A DRS, EPR AND HF^2EPR STUDY

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The exact knowledge of the phase composition and of the crystal chemistry of the inorganic pigments, in relation to their colouring properties, represents a fundamental step to improve the quality of the final product and to lower the production costs. Spinel-based pigments are widely studied because of their stability even in drastic thermal and redox industrial treatments. The insertion of metal ion chromophores into this structure allow, not only to improve and control the relative synthesis, but also to exploit their use in ceramic applications as fast firing and in high temperature glazes.

Two synthetic Cr- and Ni- bearing gahnite ($ZnAl_2O_4$) based pigments, pink and blue, respectively, representing potential candidates in the manufacturing of coloured bulk glass-ceramics, have been investigated by different spectroscopic techniques: DRS, EPR and HF^2EPR. The two pigments were synthesised from industrial raw materials (Al_2O_3, ZnO and $Cr_2O_3/NiCO_3$) by firing at elevated temperatures with a short thermal cycle. The final products were investigated by X-ray powder diffraction (XRPD), thus revealing gahnite as major/unique phase. Rietveld refinements, performed on high-quality powder patterns, suggest the doping chromophore (Cr/Ni) to be quantitatively incorporated in the spinel structure. Nevertheless, the data do not allow to ascertain the crystal chemistry of the synthesised gahnite, and its relation to the observed colour.

Diffuse reflectance spectra were collected on both pigments, to identify the transitions in the UV and VIS range, whereas EPR and HF^2EPR spectroscopies were applied only on the Cr-bearing material, because Ni^{2+} is undetectable in room temperature experiments. The obtained results point to an octahedral coordination for both Cr^{3+} and Ni^{2+} in gahnite; a small fraction of tetrahedral Ni was determined in the blue pigment. Both ions have been found to be isolated, the spectral evidence of pairs and/or clusters being absent. In both materials, the bulk colours arise from single ion crystal field transitions of the doping chromophore, Cr and Ni, respectively. The crystal field surrounding the chromophore has been fully interpreted. Moreover, the systematic characterisation of the products of several syntheses allowed to establish the efficiency of the doping process and dependence of the crystal chemistry on the synthesis condition, thus giving relevant information on the stability of the pigment colour.

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SPECTROSCOPY OF FULGURITE GLASSES

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Fulgurites are glassy tubular bodies, which formed after the melting of rocks by the stroke of a lightning. They are relatively rare and not sufficiently enough studied geological objects. In our investigations we use several methods such as X-ray analysis, Mössbauer spectroscopy, infra-red spectroscopy, and electronic microscopy. We studied fulgurite from the area of Nigoziro in Karelia, Russia, which formed on carbon-containing aleurolits. The main component of fulgurite is alumosilicate glass; its chemical composition roughly corresponds with the composition of carbon-bearing aleurolits.

With the help of X-ray analysis we found that fulgurite glasses have quartzo-felsphatic composition. We also exposed the heterogeneity of the glasses which consist in combined presence of an amorphous glassy matrix and of crystalline formations differing in composition: orthoclase, hematite, chlorite, pyrite.

The state of iron in fulgurite was studied with the help of Mössbauer spectroscopy. In the spectrum four double-peaks of iron can be distinguished. One double-peak of trivalent iron in tetrahedral position ($\delta = 0.32$) which contains 4.1 % of all iron, and three double-peaks of divalent iron in octahedral positions. The latter differ by the extent of distortion of the octahedra ($\delta = 1.1$; 1.13; 1.05). Accordingly, the content of iron at these positions amounts to 33.9, 30.4, and 31.6 from total iron.

The infra-red spectra of fulgurites consists of absorption bands which are typical for silicate glasses and which are related to the silicon-oxygen vibrations of the glassy fulgurite matrix. We also found several narrow bands of crystalline quartz giving evidence for the presence of crystalline quartz.

Using micro-probe analysis we determined that the main mass of the glassy fulgurite substance consists of a Si-Al-Fe melt. In main parts of the melt areas of almost pure glasses are distinguished. The simultaneous appearance of fragments such as residual quartz tells that the temperature of the melt in that zone was near the temperature of quartz melting, this is about 1700 °C.

We also often found inclusions of hematite Fe_2O_3. Its grains have straight borders. The appearance of these inclusions allows us to estimate the temperature of the fusion which did not reach the temperature of hematite melting. Besides, in the glass we found inclusions of hematite with tracks of partial melting.

Appearance of a great amount of skeleton formations with the composition such as FeO (wüstite) gives evidence for a high cooling speed. Such structures form because of dissociation in the cooling stage.

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IR AND RAMAN STUDIES OF SOME MOLYBDENUM-LEAD-PHOSPHATE GLASSES

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The structure of $xMoO_3 \cdot (1-x)[2P_2O_5 \cdot PbO]$ glass system with $0 \leq x \leq 0.5$ was investigated by IR and Raman spectroscopies.

FT-IR spectra of the $xMoO_3 \cdot (1-x)[2P_2O_5 \cdot PbO]$ glasses exhibit the characteristic bands for the $2P_2O_5 \cdot PbO$ glass matrix and of MoO_3 oxide. At low concentration of MoO_3 the bands characteristic for phosphate oxide dominate. The strong bands around 900-950 cm^{-1} were assigned to the P-O-H bending and to the harmonics of P-O-P bending vibrations, whereas the 1047 cm^{-1} band is due to the stretching vibration of the PO_4^{3-} group (DAYANAND et al., 1996). The strong band around 1240 cm^{-1} is attributed to the P=O stretching vibration. The weak band around 1150 cm^{-1} is assigned to the $P\text{-}O^{(-)}$ ionic stretching vibration, whereas the 500 cm^{-1} band is due to the harmonics of the P-O bending vibration. With the increase of the molybdenum oxide content the shape of the bands is changed, and a new band around 780 cm^{-1} occurs for high concentrations of MoO_3. Other characteristic bands of MoO_3 are not present because these are overlapped by the characteristic bands for the P_2O_5.

The characteristic bands of the $2P_2O_5 \cdot PbO$ matrix are also obtained from Raman spectra. Thus, the band at 696 cm^{-1} is attributed to the P-O-P stretching vibration (ILIESCU et al., 1994). The P-O stretching vibration arises at 1068 cm^{-1}, whereas the O-P-O stretching vibration appears at 1174 cm^{-1} (SCAGLIOTTI et al., 1987). The P=O stretching vibration is present at 1220 cm^{-1}

It can be seen from the spectra that the IR and Raman bands are influenced by the presence of MoO_3 oxide in the glass matrix. This fact suggests that from low concentrations of MoO_3, structural changes occur in the $2P_2O_5 \cdot PbO$ glass matrix due to molybdenum ions that play the role of network modifiers.

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CHEMICAL INVESTIGATIONS OF INCRUSTED STONE ON HISTORICAL MONUMENTS

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The corrosion damages on natural stones of historical buildings have accelerated during the last decades. The cause of the accelerated corrosion is connected to the nature of building materials, partly with construction style, but the most important factors are environmental conditions. After some years the built stone becomes discolored or covered by aggressive incrustations/crusts and finally the stone may be totally destroyed. The knowledge of causes and mechanism of decay is necessary for the conservation of historical monuments. Especially, it is very important for the choice of appropriate ways of cleaning of incrusted stones. These problems were subject of the investigations carried out on the monument "Unknown soldier" on the Mt. Avala near Belgrade.

The monument built from 1934 to 1938 is made of blocks of gabbro (Jablanica quarries). In this monumental mausoleum, 3971.95 m^3 of stone blocks were built (ZIVANOVIC, 1962). The blocks are of different size and mortar connected with some joints filled by molten lead. At that time building contractors put sheets of lead alloy between the blocks. Today, we found relicts of these sheets and lead in empty joints. After 65 years of their exposing to atmospheric influence the stone blocks show different forms of physical-chemical and biological degradations.

A visual observation of stone blocks pointed out immediately on the very different state of the gabbro decay between the outer part (exposed to rain water) and the protected, inner one. On the outer parts of facade the most important damage types of stone are: blistering, peeling, granular disintegration and scaling. All of these pathological forms are induced by aggressive incrustations from joints (MATOVIC & ROSIC, 2004).

The two different types of incrustations were identified on stone surfaces (white and black). Using X-ray diffraction (XRD) it was possible to identify their mineral compositions responsible for the genesis of stone decay. The following associations of minerals were identified in samples of incrustations:

white sample: hydrocerussite $Pb_3(CO_3)_2(OH)_2$, X $NaPb_2(CO_3)_2OH$, plumbonacrite $Pb_{10}(CO_3)_6(OH)_6O$, calcite - $CaCO_3$;

black sample: anglesite - $PbSO_4$.

The forms of decay and obtained data show that the main causes of gabbro decay are atmospheric water, moisture, frost, hard dissolved salts, dissolution of mortar and lead in joints, thermal changes of stone etc.

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INVESTIGATION OF COLOURING MECHANISM OF REE-PEROVSKITES THROUGH COMBINING STRUCTURAL AND UV-VIS-NIR SPECTROSCOPY DATA

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The research of red ceramic pigments is a current topic in traditional ceramics since most industrial products give hues far away from the pure red. New red pigments have been developed based on the perovskite $A^{III}B^{III}O_3$ structure, with A=Y or REE and $B=Al_{1-x}Cr_x$, where $0.03<x<0.12$ (BALDI & DOLEN, 1999). Though extensively characterised from the technological viewpoint, perovskite pigments still present unsolved questions concerning the mechanisms involved in their coloration. This study was carried out through combining high resolution XRPD, performed using synchrotron radiation at the ESRF, with UV-Vis-NIR spectroscopy, performed using diffuse reflectance measurements.

Rietveld refinements of XRPD data confirmed the substitution of Cr for Al in the 6-coordinated B site and a decrease of B-O distance when the A site is filled with bigger REEs; hence an inverse correlation exists between the A-O and B-O distances.

UV-Vis-NIR spectra showed the existence of rare earth multiplets in the red region and the occurrence of peaks due to Cr^{3+} transitions $^4A_2$-^2E, but the final colour of pigments is due to a broad band absorbing the blue and green visible region never observed in the literature (WEBER & VARITIMOS, 1974). Besides, a shift of the broad band in the visible region was observed and related with the type of REE inside the site A. The origin of this broad absorption band is still unknown, but on the basis of the up to date results it can be hypothesized the following origins:

coalescence of the two Cr^{3+}peaks due to $^4A_{2g}(^4F)\rightarrow{}^4T_{2g}(^4F)$ and $^4A_{2g}(^4F)\rightarrow{}^4T_{1g}(^4F)$ transitions, but the shift of the absorption band does not follow the trend predicted by the crystal field theory;

charge transfer between Cr-O, but from literature data (POOLE & ITZEL, 1963) the absorption band for Cr^{4+} and Cr^{6+} is predicted at higher energies than those observed.

In conclusion, the red colour of (Y or REEs) $(Al_xCr_{1-x})O_3$ perovskites is due to multiple mechanisms, involving crystal field *d-d* and *f-f* spin allowed and spin forbidden transitions and particularly an absorption band, whose origin is still debated.

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SHORT-RANGE STRUCTURE OF IRON IN ANORTHITE-DIOPSIDE GLASS

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Iron is the dominant transition element in natural glasses and melts; hence an understanding of its structural behaviour is of primary importance to knowledge of physical properties such as density and viscosity, chemical properties such as redox behaviour, and dynamic processes such as magma generation and volcanism. Mössbauer spectroscopy provides a measure of the short-range structure of iron in glass, as well as a quantitative determination of $Fe^{3+}/\Sigma Fe$, which can provide information on the T-fO_2 history of natural magmas. However Mössbauer spectra reflect site-to-site distortions of iron coordination polyhedra which complicate spectral analysis. Various approaches have been suggested, and while $Fe^{3+}/\Sigma Fe$ is relatively independent of the fitting method, the hyperfine parameters that relate to the short-range structure of iron are generally not. We therefore undertook a study of a well characterised suite of glasses in order to develop a fitting approach that could be applied over a wide range of iron compositions (both Fe^{2+} and Fe^{3+}), with the goal of characterising the effect of oxygen fugacity and glass composition on the short-range structure of iron in these glasses.

The glasses comprised two series: (1) 1 wt% $^{57}Fe_2O_3$ added to $An_{42}Di_{58}$ (nominally corresponding to the eutectic composition) and equilibrated at 1409°C over a range of oxygen fugacities from $fO_2 \sim 10^5$ bars ($Fe^{3+}/\Sigma Fe=1$) to 10^{-13} bars ($Fe^{3+}/\Sigma Fe=0$); (2) increasing amounts of Fe_2O_3 (2, 4, 7, 10, 20 or 30 wt%) added to the same $An_{42}Di_{58}$ starting composition and equilibrated at 1409 °C and three different oxygen fugacities (10^0, 10^{-4} and 10^{-7} bars). The glasses were studied using XANES (BERRY et al., 2003) where Fe^{3+} concentrations were calibrated based on Mössbauer analysis using a multiple Lorentzian doublet approach (JAYASURIYA et al., 2004). The derived Fe^{3+}/Fe^{2+} values are proportional to $\log fO_2$ with a slope of 0.245 ± 0.004, in excellent agreement with the theoretical value of 0.25 predicted by thermodynamics (JAYASURIYA ET AL., 2004). The present study evaluates the degree to which structural information can be extracted from the Mössbauer data, and shows that an extended Voigt-based fitting analysis with two-dimensional distributions of isomer shift and quadrupole splitting reveals significant trends in the dataset, including the presence of four- and five-fold coordinated Fe^{2+} Variations in the structural state of iron as a function of oxygen fugacity and total iron concentration provide insight into the physical and chemical properties of the corresponding silicate melts.

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SYNTHESIS, CRYSTAL STRUCTURE, INFRARED AND RAMAN SPECTRA OF $Sr_5(As_2O_7)_2(AsO_3OH)$

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The new compound $Sr_5(As_2O_7)_2(AsO_3OH)$ was synthesized under hydrothermal conditions. It represents a previously unknown structure type and it is the first substance known to contain both $(As_2O_7)^{4-}$ and $(AsO_3OH)^{2-}$ groups.

The crystal structure of $Sr_5(As_2O_7)_2(AsO_3OH)$ was determined by single-crystal X-ray diffraction (293 K, Mo$K\alpha$, $2\theta_{max} = 60°$): space group $P2_1/n$ ($a = 7.146(1)$, $b = 7.142(1)$, $c = 32.750(1)$ Å, $\beta = 93.67(3)°$, $V = 1668.0(5)$ Å^3, $Z = 4$). It is built from five crystallographically unique SrO_{6-8} polyhedra and two $(As_2O_7)^{4-}$ groups besides a protonated $(AsO_3OH)^{2-}$ group. $(As_2O_7)^{4-}$groups involve four crystallographically non-equivalent $(AsO_4)^{3-}$ tetrahedra. The position of the hydrogen atom was located experimentally. To obtain further information on the anion groups and especially on the very short hydrogen bond length of 2.494(4) Å, where the donor and acceptor atoms are not equal due to (average) space-group symmetry, infrared and Raman spectra were acquired.

The IR spectral region between 3500 and 1000 cm^{-1} shows a peculiar increase in "background absorption", which is a typical feature of compounds with very short hydrogen bonds. It represents an extremely broad (FWHM ~ 1000 cm^{-1}) and low-energetic band that is assigned to the OH stretching mode of the $(AsO_3OH)^{2-}$ group. It is quite characteristic that this band can be observed only in one of the polarized spectra, whereas it is absent in the other polarization directions and almost invisible in powder spectra. The former is caused by the preferred orientation of the OH vectors in the structure. Because of the broad band shape, As—O tetrahedral stretching vibrations and lattice modes are superimposed in the low-energy region of the spectrum (stretching modes < 1100 cm^{-1}; bending + lattice modes < 450 cm^{-1}). The large FWHM aggravates a precise determination of the band center, which is estimated to be roughly at ~1600 ± 200 cm^{-1} According to the d—ν correlation for hydrogen bonds (NOVAK, 1974; LIBOWITZKY, 1999) this wavenumber is in excellent agreement with the refined O_h—H···O bond length. The sharp and truncated band at ~1250-1300 cm^{-1} in the IR powder spectrum is assigned to the bending mode of the OH group and it corresponds with typical bending frequencies of strongly H bonded hydroxyl groups (NOVAK, 1974; BERAN & LIBOWITZKY, 1999).

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CRYSTALLOGRAPHY, RAMAN AND IR SPECTROSCOPY OF PERHAMITE – AN INTERESTING SILICO-PHOSPHATE

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Perhamite, $Ca_3Al_7(SiO_4)_2(PO_4)_4(OH)_6 \cdot 16.5H_2O$, is an interesting silico-phosphate found in pegmatitic veins and rock phosphate deposits in the United States, Germany and Australia (MILLS, 2003). Its combination of mixed anion, hydroxyl and water units make it ideal for an integrated Raman and IR study. The crystal structure has also recently been revised giving new insight into the framework of this mineral. Perhamite morphology consists of very thin intergrown platelets that can form a variety of habits such as stalagmite-like aggregates and rosettes generally less than 40 μm across.

The structure of perhamite is related to that of the crandallite-group minerals and the chain silicate vlasovite. A disordered region of vlasovite-like $(Si,Al)_4O_{11}$ ribbons together with water molecules is sandwiched between blocks of ordered crandallite-type structure.

Raman spectroscopy of perhamite has revealed intense bands in the regions 1110–1130 and 966–996 cm^{-1} In these regions the SiO_4 and PO_4 symmetric stretching modes can be found. Other bands observed in the range 1005–1096 cm^{-1} are attributed to the ν_3 antisymmetric bending modes of PO_4. Bands in the low-wavenumber region are assigned to the ν_4 and ν_2 out-of-plane bending modes of the SiO_4 and PO_4 units.

Infrared spectroscopy in the hydroxyl-stretching region (Fig. 1) shows a number of overlapping bands which are observed in the range 3581–3078 cm^{-1} These wavenumbers enable an estimation to be made of the hydrogen bond distances and correspond to 3.176(0), 2.880(5), 2.779(6), 2.749(3), 2.668(1) and 2.599(7) Å. An arbitrary cut-off point of 2.74 Å (based upon the wavenumber 3300 cm^{-1}) was used to distinguish the weak hydrogen bonding from the strong hydrogen bonds.

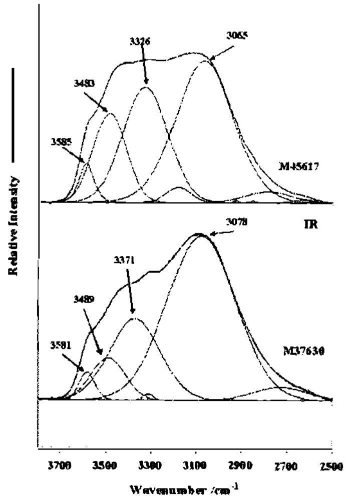

Fig. 1. Infrared spectra of perhamite samples M37630 and M45617 in the hydroxyl stretching region

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ORDERING OF PARAMAGNETIC DEFECTS IN NATURAL DIAMONDS WITH MICROTWINS.

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Up to now all paramagnetic centers observed in diamond crystals were found to align with a single coordinate system determined by crystallographic axes. In this respect, natural plastically deformed diamonds with brown and pink colours were not different from diamonds, which had not suffered any postgrowth transformation. However, the present EPR study of violet diamonds with planar deformation lamellae observed with an optical microscope has shown that the behaviour of such crystals was very unusual.

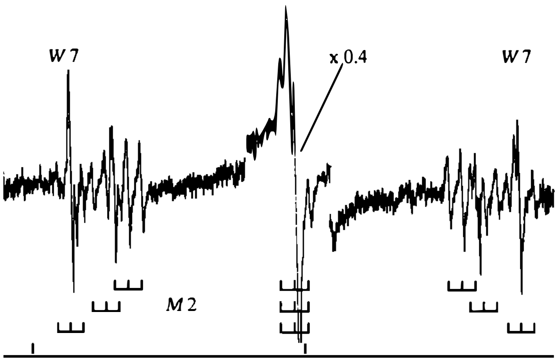

Fig. 1. X-band EPR spectrum for violet diamond containing W7 and unusually oriented M2 centers, recorded at room temperature with magnetic field along [001]

A large number of additional lines was discovered in an EPR spectrum of violet diamond recorded at standard diagnostic orientation with $H \| L_4$ (Fig. 1). There was no doubt that these lines belong to a center including two nonequivalent nitrogen atoms, as well known *N*1 and *W7* centers and recently discovered by us *M2* and *M3* centers. Analysis of the angular dependence of the spectra shows that hyperfine parameters for both nitrogen atoms are similar to those for *M2*. However, the main axes of these tensors do not coincide with the crystal axes, but correspond to {111} orientations of lamellae, which are twinned after a spinel law. Visual analysis displays that the amount of twinned lamellae in violet diamonds is not more than 1%, but all observed *M2* centers are located in them. Regarding the *W7* center, the most characteristic for plastically deformed diamonds, its content is roughly the same in the whole main part of the crystal and in the twinned lamellae.

Therefore, our investigation reveals that plastic deformation in natural violet diamonds could occur by a mechanical microtwinning. EPR gives the possibility to see this process from the inside through the analysis of paramagnetic defect transformations showing the change in the crystal structure at the level of individual atoms.

This work was supported by the Russian Foundation for Basic Research (Grant 02-05-64696).

X-RAY ABSORPTION SPECTROSCOPY AT 3*d*-METAL $L_{2,3}$ AND O *K*-EDGES IN COLUMBITES

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Columbites are economically important Nb and Ta ores typical of pegmatites. Structurally identical synthetic compounds are intensively studied due to magnetic and electronic properties that make them technologically important materials. The crystal structure of these oxide minerals is a derivative from α-PbO_2 structure, based on a hexagonal closest packing of oxygen anions with cations half-filling the octahedral interstices in a chain-pattern. Cation octahedra share edges along each zigzag chain and vertices with adjacent chains in neighbouring layers. A triple unit cell comes out from the ordering of two consecutive layer levels of pentavalent cations interleaved by one layer of transition metals (Fe,Mn). Oxygen anions display a triangular coordination by coplanar cations from which at least one is pentavalent. Cation disordering induces the mixing of three possible configurations – three (Nb,Ta), two (Nb,Ta) plus one (Fe,Mn), one (Nb,Ta) plus two (Fe,Mn) – , a quite common feature in natural compounds that is apparently precluded in synthetics.

Ordering may be attained by heating mineral fragments in air and rapidly cooling from about 1000 °C (ERCIT et al., 1995), but some discussion still prevails on the oxidation of 3*d* transition metals upon heating (ZAWISLAK et al., 1997). To ascertain the valence state of Fe and Mn, soft X-ray absorption at metal $L_{2,3}$ and O 1*s* edges was performed at BESSY* using beam line D11.1A-PM3 (SX700 monochromator with an energy resolution better than 0.2 eV). Studied columbites (from Zambezia mineralurgical province in Mozambique) cover a wide range of compositions checked by electron microprobe. The ordering state of as-collected and heated samples was monitored by X-ray diffraction.

To model O 1*s* XANES spectra, *ab-initio* simulations were carried out based on the multiple scattering approximation implemented in the FEFF code (ANKUNDINOV et al., 1998). Comparison of experimental and calculated spectra with data collected from simple oxide minerals (FIGUEIREDO & MIRÃO, 2002) allows for identifying features of O 1*s* XAS spectra explained by hybridisation of oxygen 2*p* with metal 3*d* states disturbed by chemical bonding.

Conversely, intensity variations of particular features in metal $L_{2,3}$ spectra indicates oxidation by heat treatment progressing from the surface inwards the mineral fragments.

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EQUATION OF STATE AND TRANSITION PRESSURE FOR BRUCITE DEHYDRATION: THEORETICAL APPROACH

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Brucite, $Mg(OH)_2$ is a simple crystalline hydroxide, and is an end-member for hydrous minerals that hosts H_2O in the crust and mantle of the Earth. Owing to its structural simplicity, it serves as useful prototype for layered hydrous minerals.

In order to explore the high pressure behaviour of brucite, *ab initio* total energy calculations based on local density approximation (LDA) and generalized gradient approximation (GGA) of density functional theory have been performed. Using neutron diffraction it has been observed that at high pressures, hydrogen atoms are disordered over the three 6i Wyckoff sites with one-third occupancies where as at ambient pressures they are oriented parallel to *c*-axis (2d Wyckoff site). In order to explore such order-disorder behaviour, we constructed a 3x3x1 super-cell with hydrogen occupying only one of the three 6i sites, and arranged the H atoms such that displacement of each hydrogen atoms from 2d to 6i position forms an enclosed ring. *Ab initio* structural relaxations confirm the mechanical stability, and energetic favorability, as compared with the 2d structure, of this arrangement. We determine the theoretical equation of state for brucite with K_o of 53 GPa and its pressure derivative, K_o' of 6.2, using LDA, and a K_o value of 34 GPa and K_o' of 5.8 with GGA (both corrected for zero pressure and thermal pressures at T = 300 K). We also simulate the transition pressure for the dehydration of brucite at T = 0 K, comparing the enthalpies of $Mg(OH)_2$ and sum of enthalpies of MgO and H_2O (ice-VIII). We are exploring possibilities of formation of symmetric hydrogen bonding at higher pressures. We are also exploring the elastic constants (c_{ij}) for brucite and their pressure dependence.

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NMR STUDIES OF MOLECULAR DIFFUSION AND PROTON TRANSFER IN HYDRATED MINERALS

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The physical-chemical properties of hydrated minerals in which the H_2O molecules are located in structural cavities, channels or between layers, essentially depend on the librational and translational motions of the water molecules (WINKLER, 1996; PAUKOV et al., 2002). Along with infrared-, dielectric-spectroscopy, and incoherent neutron scattering, the most often used technique to determine the low-frequency dynamics of molecular H_2O in minerals is ^{1}H-NMR spectroscopy (STEBBINS, 1988). Recently, we proposed a new wide-line ^{1}H NMR approach based on the consideration of the anisotropy of the fluctuations of the intramolecular proton-proton interaction, arising during the process of the H_2O molecular diffusion. With this approach, a number of intriguing results, such as the pressure-enhanced H_2O self-diffusion in natural zeolites (MOROZ et al., 2001), have been obtained. The ensuing development of the approach discussed enabled us to suggest a way to measure the rates of the proton-transfer reactions in water subsystems of hydrated microporous minerals (AFANASSYEV et al., 2000; AFANASSYEV & MOROZ, 2003). It has been shown that the intermolecular proton transfer is due to the interaction of water molecules with the protonic defects, presented by the acid (Brønsted) cites. As a rule, these reactions are exhibited at temperatures corresponding to the intense H_2O self-diffusion. These circumstances allow one to use water molecules as a NMR molecular probe for visualization of the active acid sites and consequently for characterization of the catalytic activity of minerals even if the site concentration is small enough that obstacle its detection with available spectroscopic techniques (MOROZ et al., 2003).

This work was supported by Russian Academy of Sciences (Program #26, Hydrogen Energetic).

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VIBRATIONAL SPECTRA OF KLADNOITE, NATURAL ANALOGUE OF PHTHALIMIDE $C_6H_4(CO)_2NH$

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Aromatic compounds occur very rarely as minerals. Kladnoite, the only mineral containing nitrogen as NH-group, was discovered on the burnt coal dumps of Kladno, Czech Republic in 1937 and more later it was found in the Chelyabinsk coal basin, Russia (ROST, 1937; CHESNOKOV & SHCHERBAKOVA, 1991). X-ray diffraction patterns of Czech and Russian kladnoite are similar and correspond to synthetic phthalimide (CHESNOKOV & SHCHERBAKOVA, 1991; ZACEK et al., 2000)]. A detailed assignment of most of the observed frequencies in vibrational infrared (IR) and Raman spectra of phthalimide (PIMH) polycrystalline and single crystal samples has been previously reported (HASE, 1978). For monoclinic phthalimide crystals symmetry (space group $P2_1/n = C_{2h}^5$, Z = 4), all vibrational A_g and B_g (A_u, B_u) fundamentals are Raman (IR) active (MOROZ, 1998). Main PIMH modes are observed in the Fourier transformed (FT) IR (Fig. 1a) and FT-Raman (1064 nm exitation, Fig. 1b) spectra of kladnoite from Russia. As against a Raman spectrum of synthetic PIMH (HASE, 1978; AROCA & CLAVIJO, 1988), attempts to record Raman spectra using 514.5 nm excitation were unsuccessful due to strong fluorescence with maximum at 568.6 nm shown by the samples with this laser line. An analysis of NIR FT-Raman, FT-IR spectra and fluorescence of both Russian and Czech kladnoites is presented.

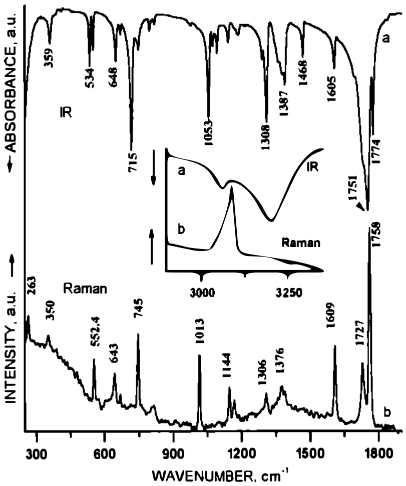

Fig. 1. FT-IR (a) and NIR FT-Raman (b) spectra of Russian kladnoite

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RAMAN MICROSCPECTROSCOPY: THE KEY ROLE IN THE RECONSTRUCTION OF PT-PATHS OF HP-METAMORPHISM

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Raman microspectroscopy was applied to determine Al_2SiO_5 polymorphs situated in high-AlMg sapphirine-bearing metamorphic rocks from shear zones in the Central-Kola terrain (Kola Peninsula, Russia). Rocks consist predominantly of cordierite, biotite, orthopyroxene, sapphirine, spinel and sillimanite. The rocks also contain very small acicular crystals and ultra fine-grained orthopyroxene-Al_2SiO_5 intergrowths that replace cordierite and biotite. These aggregates mark a late rock alteration. Previous investigators considered the aluminosilicate as sillimanite (fibrolite). Hence, the rock alteration was interpreted as retrograde branch of the granulitic metamorphism.

Previously reported Raman spectra of Al_2SiO_5 polymorphs allow a clear identification of the mineral observed. Polarized Raman spectra were taken at room temperature from polished thin sections using the microscope-based DILOR XY Raman spectrometer equipped with 514.5 nm Ar^+ ion laser, backscattering geometry, lateral resolution ≤ 12 μm, spectral resolution 1 cm^{-1} To control the anisotropy of crystals, the spectra were registered for two crystal orientations for each measured point (the polarization plane of incident light was oriented parallel and perpendicular to the crystal elongation [001] or to the cleavage {010}).

Most of the Raman band positions and intensities from the studied acicular aggregates are in full conformity with the Raman spectrum of kyanite. In some measured points up to 15 additional bands in the spectrum of acicular aggregates have been revealed. Most of them exactly correspond to the Raman spectrum of cordierite. One can conclude, Raman microprobe undoubtedly reveals the presence of kyanite both in its intergrowths with orthopyroxene and (for most long needle-shaped grains) in the surrounding rock matrix represented by early cordierite.

The kyanite-orthopyroxene paragenesis is an extremely rare one world-wide and the Central-Kola terrain is the second proved granulitic locality of it. Reaction textures and thermodynamic considerations suggest that this assemblage was prograde and formed at a new HP metamorphic event (ca. 700 °C and 8-9 kbar) which followed another HP-HT metamorphism (peak at ca. 920 °C and 9.5 kbar). Both these HP events overprinted metamorphic rocks locally within long-lived shear zones.

This work was supported by RFBR (grant № 01-05-65174), Russian Ministry of Industry and Science (grant for the support of scientific schools SS-615.2003.5), Austrian Exchange Service (ÖAD), Russian Ministry of Education (grants № PD02-1.5-361 and E02-2.0-58), Administration of St.-Petersburg (Russia) (grant № PD03-1.5-55), CRDF (grants № Y1-G-15-01 and Y1-G-15-04) and Russian Science Support Foundation.

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RAMAN SPECTROSCOPY OF ROCKS IN THIN SECTIONS: ANALYTICAL CONSTRAINTS

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Raman spectroscopy is a well-known technique used for the fingerprinting of mineral substances. The Raman technique can be well adapted for studies of thin sections of rocks and minerals. If the Raman spectroscopic determination of minerals in thin sections is made as a routine procedure, both sample properties and individual characteristics of studied crystals constrain the resulting information. The main constraints are discussed below.

1. Constraints caused by properties of minerals and mineral aggregates.

1a. Some characteristic Raman bands of minerals reveal strong depolarization ratios. In this case the effectiveness of the Raman fingerprinting strongly depends on the spatial orientation of crystallographic axes in a grain of the studied mineral. In case of textured samples (in many metamorphic, some magmatic rocks and also vein aggregates) the Raman fingerprinting will depend on the orientation of the rock by which the thin section was produced. The effect of crystal orientation cannot be fully eliminated. It can be reduced by measuring of depolarized scattered light.

1b. The topology of the Raman spectrum can differ according to the retardation of the crystal. Birefringence causes the rotation of polarization plane of the scattered light. It is especially important for structural studies (order/disorder phenomena, phase transformations). If crystals are zoned with the variable retardation in different zones, false conclusions about the breaking of symmetry selection rules can be made. To avoid such artefacts the observation in depolarized light can be used. By the polarized exciting light the measurement with the crystal in position of optical extinction can be used.

1c. Luminescence from the studied mineral and from the surrounding matrix causes the common constraints by Raman fingerprinting. This phenomenon is well-known and will be not considered here.

2. Constraints caused by the nature of sample. Rock thin sections are mounted on glass plates using special types of organic glue (Canadian balsam etc.). The excitation area when using conventional non-confocal microscope-based Raman systems can be large enough to partially include the glue layer. It can result in strong background luminescence, heating and evaporation of glue, which makes Raman observation impossible.

The outlined analytical problems demonstrate that a careful mineralogical examination of a thin section must be made before the Raman investigation can be carried out. The microscope attached to the Raman spectrometer must be equipped with a transmitted light illumination system, rotating stage and a set of polarizers for visible light. Confocal microscope geometry is desirable. A depolarizer (i.e., $\lambda/4$ plate) for the scattered laser light is required.

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RAMAN BAROMETRY OF MINERAL INCLUSIONS IN DIAMOND CRYSTALS

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Inclusions of high-pressure minerals trapped inside diamond crystals may provide valuable information about the conditions under which their diamond host was formed. A "minimum value" for the pressure in the source region is determined through the estimation of fossilised pressures of inclusions. Note that the observed pressure will always be lower than the formation pressure, especially if pressure has been released partially through the formation of fractures in the diamond host (Fig. 1). Such remnant pressures can be determined *in situ* from shifts of vibrational modes. The application of this technique to an inclusion, however, requires the availability of a precise pressure-calibration of band shifts, which are for instance determined in diamond anvil experiments, for the respective phase. The remnant pressure on included minerals for which such pressure-calibration has not been done can nevertheless be estimated. Raman maps of the diamond LO=TO mode reveal not only the strain distribution in the host diamond (NASDALA et al., 2003) but can also be used to locate the diamond micro-area with the strongest compression and, with that, the highest preserved pressure.

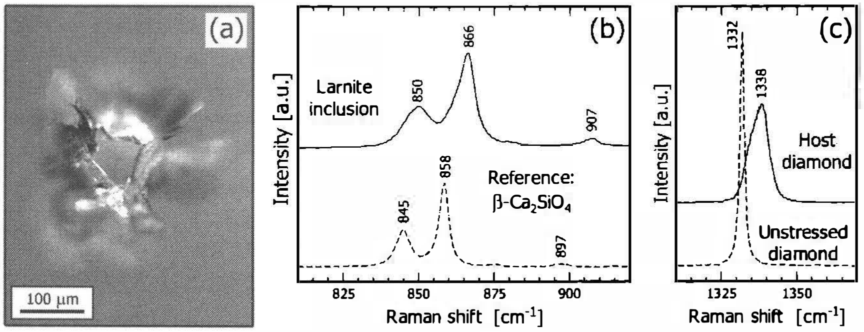

Fig. 1. The Raman spectrum of a larnite inclusion (a) inside a large diamond crystal from the Kankan district, Guinea, is shifted with respect to that of unpressurised β-Ca_2SiO_4 (b) due to significant remnant pressure acting on the inclusion. The fossilised pressure can be determined from the frequency of the LO=TO mode of the neighbouring diamond host. An up-shift of ~6 Δcm^{-1} (c) corresponds to ~2.7 GPa (e.g., HANFLAND et al., 1985)

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INFRARED SPECTROSCOPY OF NATURAL AND SYNTHETIC TOBERMORITES

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IR-sectra of natural and synthetic tobermorites show many similarities, but there are some obvious differences between natural and synthetic phases and also between the single phases (MERLINO et al., 1999; HOCHLEITNER, 2000). An important influence on the form of the spectra has the ratio calcium/silicon of each sample, but also the quality of the cystals. The ratio is mainly responsible for the position of each band and the quality is responsible for the sharpness of the bands (Fig. 1).

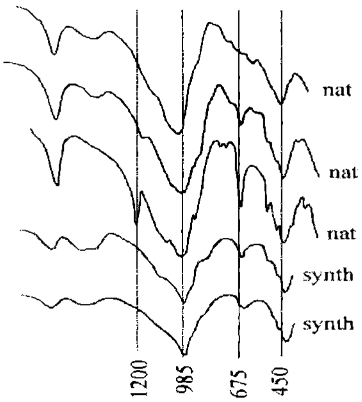

Fig. 1. IR-spectra of natural and synthetic tobermorite.
1200 = Si-O-stretching vibrations of Q^3-places,
985 = Si-O-stretching vibrations of Q^2-places,
675 = Si-O-Si bending vibrations,
450 = internal deformation of SiO_4-tetrahedron

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A POLARIZED SINGLE-CRYSTAL STUDY OF SYNTHETIC WATER-POOR BERYL

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Beryl typically contains extraframework alkali-ions, H_2O and/or CO_2 molecules in the structural channel. The water molecules occur in two different orientations: type I , having their two-fold axis perpendicular to the *c* axis of beryl, and type II, typically adjacent to alkali ions, having their two-fold symmetry axis parallel to [100] (e.g., WOOD & NASSAU, 1968). The OH-stretching IR spectra of beryl have been extensively studied (see KOLESOV & GEIGER, 2000 and references therein). However there is no general consensus on the assignment of the observed bands to structural configurations. Much confusion probably arises from the fact that most beryls contain simultaneously both types of water, and there is no knowledge on the effect of a possible interaction between them. We present here a single-crystal, polarized-light FTIR study (done on a NicPlan microscope, equipped with a MCT detector and a gold-wire polarizer) on oriented polished sections of a flux-grown emerald. Contrary to the synthesis conditions, the emerald was found to contain low amounts of type II water exclusively, possibly associated with trace alkali ions in the channels (detected by EMPA). On the (100) section, the **E**$\perp$c spectrum shows a unique sharp and intense band at 3643 cm^{-1}, while the **E**//c spectrum consists of two low-intensity bands at 3643 and 3587 cm^{-1}, respectively. Based on this pleochroic behavior, the 3643 cm^{-1} band is assigned to the ν_3 antisymmetric stretching of type II water. The second, minor band at 3587 cm^{-1} has maximum absorbance for **E**//*c*; it is assigned to the ν_1 symmetric stretching of type II water, as also suggested by the intensity ratio I_{3643} I_{3587} close to 1:20. The polarization of the observed bands definitely indicates that type II water has its molecular axis //*c* with its H...H vector $\perp$*c*. The integrated molar absorbance for beryl, never calibrated so far, has been determined from the curve of LIBOWITZKY & ROSSMAN (1997) to be ε_I at 3643 cm^{-1} = 27126 l mol^{-1} cm^{-2} This value allows to calculate a water content of 30 ppm for our synthetic, nominally anhydrous, beryl.

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PHASE-CONTROLLED PENTACENE THIN FILMS AND THEIR CHARACTERISTICS IN ORGANIC TRANSISTORS

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Pentacene is an organic molecule consisting of five fused aromatic rings and there are at least four known crystalline phases in pentacene thin films. By variation of different parameters such as substrate temperature and by choosing the right substrate the portion of each phase can be controlled in a defined manner.

One of the two main phases, the so called thin film phase, is of high importance in thin-film transistors, because of its high mobility, which is similar to those in amorphous silicon TFTs. The second main phase is the bulk phase and there are strong indications that the intrinsic mobility is much lower compared to the thin film phase (BOUCHOMS et al., 1999; GUNDLACH et al., 1999).

In the present work we grow and analyse polycrystalline pentacene films on different substrate materials. These films were treated either by immersion in an organic liquid or by temperature treatment to cause phase conversion between the thin film- and the bulk phase of pentacene. The films were analysed with optical microscopy, Atomic Force Microscopy and by X-ray diffraction. Based on these techniques we could observe the change of the morphology of the polycrystalline films with respect to their ratio between the phases. The characteristics of pentacene based thin film transistors were measured in dependence on the different phases.

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INFLUENCE OF Ca-Mg SUBSTITUTION ON THE Cr^{3+} CRYSTAL FIELD PARAMETERS IN NATURAL GARNET SOLID SOLUTIONS

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Electronic absorption spectra of a series (19 samples) of natural Mg,Ca-garnets with constant amount of octahedral Cr^{3+}, $^{[8]}(Mg_{1-x}Ca_x)_3{}^{[6]}(Al_{0.67}Cr_{0.33})_2{}^{[4]}Si_3O_{12}$, from deep-seated xenoliths in kimberlite pipes of Siberia and South Africa were measured and evaluated. It was established that increasing of x_{Ca} from 0.02 to 0.745 results in decreasing of: (i) $10Dq_{Cr^{3+}}$ from 17800 cm^{-1} to 16580 cm^{-1}, (ii) β parameter, reflecting the ionicity of the Cr-O bond, from 0.714 to 0.682, and (iii) FWHM values of ν_1 and ν_2 absorption bands of Cr^{3+} The above dependences are represented by two distinct linear trends (a) ($x_{Ca}<x_{Cr}$) ($10Dq = 17845 - 2469.5 \cdot x_{Ca}$, r=0.992) and (b) ($x_{Ca}>x_{Cr}$) ($10Dq = 17583.3 - 1361.1 \cdot x_{Ca}$, r=0.995) with the boundary between these trends that corresponds to the composition $x_{Ca} = x_{Cr}$.

The observed character of variation of the Cr^{3+} crystal field parameters along the garnet solid solution studied reflects, most probably, different stages of the Ca and Cr^{3+} ordering in the shared X- and Y-sites of the structure, respectively. Such ordering is caused by the mechanism of the optimization of Ca and Cr^{3+} local environment (BOSENICK et al., 2000). The presence of large Cr^{3+}-centered octahedra in the pyrope host structure is energetically favourable when Ca replaces Mg if Ca and Cr^{3+} are placed in adjacent (shared) X and Y sites, respectively (UNGARETTI et al., 1995).

In garnets with ratio $x_{Ca}<x_{Cr}$ two types of Cr^{3+}-centers occur: (i) Cr^{3+}- ions in a pure pyrope matrix, that is octahedral Cr^{3+} surrounded by six next-next-neighbour Mg atoms (Mg_6-Cr^{3+}); (ii) Cr^{3+}-ions in "mixed" X-cation surrounding, that is $(Mg_{6-x}Ca_x)$-Cr^{3+}, where $\lim(x) \rightarrow 6$.

In garnets with $x_{Ca}>x_{Cr}$ ratio only Ca_6-Cr^{3+} centers ("uvarovite like" clusters) exist.

In both cases the mentioned change of Cr^{3+} crystal field parameters is caused by an increase of the Ca amount and as result of increasing Cr–O distances and their covalency. However, in the first case (trend (a)) Ca atoms replace Mg in local environment of Cr^{3+} and in the second one (trend (b)) – in the Cr-free parts of the garnet structure.

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ASTEROMINERALOGY OF CIRCUMSTELLAR OXIDE DUST

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Within asteromineralogy – the research field dealing with the mineralogical composition of solids in space – substantial progress has been achieved during the past few years by *spectroscopic* and *microanalytic* methods (see, e.g., HENNING, 2003). In the infrared spectra of circumstellar shells and other dust-forming environments, several emission and absorption bands produced by sub-micron-sized dust particles could be identified.

While substantial efforts have been taken to detect the signatures of silicates (such as olivine), carbon and carbon compounds (such as diamond and silicon carbide) in the infrared spectra of astronomical objects, *oxides* have been more or less neglected as potential components of cosmic dust. No systematic investigation of these solids, combining astronomical and mineralogical information, has been carried out. The present contribution tries to fill this gap.

As first shown by POSCH et al. (1999), spinels can be detected in the IR spectra of circumstellar shells of red giant stars. It is noteworthy that terrestrial spinels, unless exposed to temperatures in the order of 1000 K, have different IR properties than their cosmic counterparts. By annealing experiments and subsequent FTIR spectroscopy, FABIAN et al. (2001) have been able to reproduce the emission features of the latter. We will deliver further evidence for this feature carrier identification.

Furthermore, Mg-Fe-oxides with stoichiometries close to that of wustite are shown to be the carriers of a strong, comparatively broad emission feature located at 19.4-19.6 μm, which is observed in the spectra of red giant stars as well (POSCH et al., 2002, 2004). This mineral species is also characterized by a temperature-dependence of its IR spectra, especially at low temperatures (~100 K), at which the widths of the main band decreases. We show that there are both cold and warm cosmic environments in which magnesiowustites are able to form and survive. Other potential components of circumstellar dust are titanium oxides (POSCH et al., 2003), but for their formation, no spectroscopic evidence is available as yet.

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SITE PREFERENCE AND PARTITIONING OF SCANDIUM IN SILICATE GARNETS

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Incorporation and site preference of Sc (~ 5 %) in four synthetic garnets (Py, $Py_{60}Gr_{40}$, $Py_{20}Gr_{80}$, and Gr) along the join pyrope-grossular were investigated by a multi-disciplinary experimental–theoretical approach, which combines EMPA, SC and powder XRD, and Sc K-edge XAFS. The XAFS experiments were performed at ID26 (ESRF). The XANES spectra clearly show significant differences in the spectral features of grossular and pyrope, suggesting different local environments for Sc. This finding is supported by the results of the multi-shell fit of the EXAFS signals: Sc is incorporated into the dodecahedral X site in the pyrope-type structure, but in the octahedral Y site in the grossular-type structure. Moreover, a different site-partitioning behaviour is observed for Sc in the solid-solution terms. The first shells contributions of the $Py_{60}Gr_{40}$ EXAFS signal could be obtained by a weighted combination of Sc in tetrahedral (T) and X site, while the first shells fit of $Py_{20}Gr_{80}$ EXAFS signal could be fitted by a weighted combination of single scattering paths calculated for Sc in both Y and T site. In this last case, however, a minor partitioning of Sc also in X site cannot be ruled out. These results are fully compatible with those of the structure refinement of the end-members, which showed (i) higher site-scattering (ss) and ADP values at the X site and lower ss at T in Py; (ii) higher ss and longer mean bond lengths at Y (and T) in Gr. The site partitioning and preference of Sc in garnets is thus dramatically detennined by the matrix.

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^{57}Fe MÖSSBAUER SPECTROSCOPIC INVESTIGATIONS ON THE BROWNMILLERITE SOLID SOLUTION SERIES $Ca_2(Fe_{2-x}Al_x)O_5$

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Brownmillerite Ca_2FeAlO_5 is one of the four main components of portland cement clinkers. For $Ca_2(Fe_{2-x}Al_x)O_5$, there is a complete solid solution between $Ca_2Fe_2O_5$ (mineral name srebredolskite) and $Ca_2Al_2O_5$ up to x = 1.36 at ambient conditions (REDHAMMER et al., 2004 and references therein). Using ceramic sintering and slow cooling of the melt, 32 different samples between x = 0.00 and 1.36 have been synthesized. Besides the investigation by powder and single crystal X-ray diffraction, most of the samples were investigated by ^{57}Fe Mössbauer spectra at room and elevated temperatures also.

At room temperature pure $Ca_2Fe_2O_5$ exhibits two magnetically ordered subspectra, which can be assigned to ferric iron on both the octahedral (O) and the tetrahedral (T) sites. The ratio O : T corresponds to the ideal 1 1 ratio. Both sites show unusual large quadrupole splittings of -1.471(5) mm/s for the tetrahedral and +1.514 mm/s the octahedral site respectively. The internal magnetic field at the probe nucleus is 42.8(1) and 50.4(1) Tesla, values typical for ferric iron. The main component V_{zz} of the electric field gradient at the octahedral site spans up an angle of 85° with the direction of the internal magnetic field, whereas it is oriented at 90° to V_{zz} at the tetrahedral site. In situ heating experiments have shown that the Néel - temperature in pure $Ca_2Fe_2O_5$ is 450 °C. Exchanging ferric iron by aluminum causes an increasing complexity of the spectra. Besides one spectrum for ferric iron on (O), two subspectra for tetrahedrally coordinated ferric iron can be resolved, which only differ in the size of the internal magnetic field. Additionally, the incorporation of aluminum causes the spectra to become successively more relaxed and data evaluation becomes highly difficult. Increasing aluminum content causes the Néel temperature to decrease. For samples with x = 1.10 only paramagnetic two line spectra are revealed at room temperature. The Al/Fe distribution has been determined both, from the Mössbauer data and the single crystal intensity data. For low aluminum contents, they show a distinct preference of aluminum for the tetrahedral site. Above a $^2/_3$ filling of the tetrahedral site with aluminum, additional Al is equally distributed over both sites. Within the complete solid solution series, the quadrupole splitting for both the (O) and the (T) sites slightly increases linearly, suggesting somewhat more distorted crystallographic sites in the high aluminum containing samples.

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MAGNETIC ORDERING IN THE QUASI-1D COMPOUND $Cu_2Fe_2Ge_4O_{13}$ AS MONITORED BY ^{57}Fe MÖSSBAUER SPECTROSCOPY AND SQUID MAGNETOMETRY

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The germanate compound $Cu_2Fe_2Ge_4O_{13}$ has been synthesized by solid state ceramic sintering techniques between 1173 K and 1423 K. The structure is isotypic with $Cu_2Sc_2Ge_4O_{13}$, described recently by REDHAMMER & ROTH (2004). The title compound is monoclinic, space group $P2_1/m$, $Z = 4$, $a = 12.134(2)$ Å, $b = 8.5153(9)$ Å, $c = 4.8795(8)$ Å, $\beta = 96.10(2)°$. The structure consists of crankshaft-like chains of edge -sharing FeO_6 octahedra running parallel to the crystallographic *b* - axis. These chains are linked laterally by $[Cu_2O_6]^{6-}$ dimers forming a sheet of metal-oxygen-polyhedra within the *a* - *b* plane. These sheets are separated along the *c* - axis by $[Ge_4O_{13}]^{10-}$ clusters. Cooling to 15 K does not alter the crystallographic symmetry of $Cu_2Fe_2Ge_4O_{13}$. SQUID magnetometric measurements at an external field above 0.1 T show two events in $\chi(T)$, one at around 100 K, and one at 40 K. The first one is characterized by a broad maximum in the temperature dependence of the magnetic susceptibility χ, the second one by a change in slope. At low external magnetic fields (0.01 T), the second event is also visible as a clearly resolved peak. The question arises, which magnetic ordering phenomena can be assigned to these two events. In situ low-temperature ^{57}Fe Mössbauer spectroscopy has been used to get a deeper insight into these ordering processes. At room temperature, the spectrum consists of a single quadrupole doublet with a large quadrupole splitting. This doublet can be assigned to the strongly distorted CuO_6 octahedron. Cooling down to liquid nitrogen temperature does not alter the general appearances of the spectrum, i.e. no magnetic ordering can be detected. However, a distinct increase of the width of the resonance absorption lines is observable between 140 K and 100 K. Thus the 100 K maximum in $\chi(T)$ is assigned to low dimensional magnetic ordering within the Cu-dimers. At 40 K full magnetic 3-dimensional ordering takes place expressed by the appearance of a magnetically split ^{57}Fe Mössbauer spectrum.

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ABSORPTION EFFICIENCIES OF STARDUST MINERALS

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Oxide and silicate minerals are not only important components of the Earth's mantle, but they form also as small solid particles ("dust grains") in the extended atmospheres of pulsating red giant stars at temperatures below 1500 K. Astronomical infrared spectroscopy, combined with measurements of "cosmic dust analogues" in the laboratory, has enabled significant progress in the identification of IR emission bands detected at wavelengths between 8 and 70 µm in the spectra of circumstellar shells. We present results of this combined laboratory and astronomical spectroscopy approach to the task of establishing a circumstellar dust mineralogy (see DORSCHNER in HENNING, 2003).

The present contribution is focused on the absorption efficiencies of astronomically relevant oxides like the TiO_2 modifications anatase (RICHTER et al., 2004) and rutile (POSCH et al., 2003) and $MgAl_2O_4$ (spinel) (FABIAN et al., 2001). Reflectance and transmittance measurements of these materials result in new refractive indices (n) and absorption indices (k) in the NIR (0.5 – 2.5 µm) & MIR (2.5 – 25 µm) range. The n and k values are not sufficient for the calculation of model spectra of dust enshrouded astronomical objects. Therefore, we derived absorption efficiencies (Q_{abs}) for different particle shapes (e.g. spheres) from the n and k values of different materials according to the numerical schemes compiled by BOHREN & HUFFMAN (1983). These Q_{abs} values are different from those derived from measurements of powder samples which contain grains of unknown shape and orientation. Only Q_{abs} can be compared with the spectra of circumstellar dust shells. We show the influence of grain shapes on Q_{abs} and compare spinel's and other minerals' Q_{abs}-profiles with astronomical emission bands.

On the basis of the absorption efficiencies it is also possible to calculate the temperature of the dust grains in circumstellar shells. For selected minerals, we demonstrate also the influence of the magnitude of k in the NIR on stardust radiative equilibrium temperature (RICHTER et al., 2004).

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APPLICATION OF RAMAN SPECTROSCOPY TO THE IDENTIFICATION OF ASBESTOS MINERALS

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The techniques normally employed in the identification of asbestos phases often require lengthy sample preparation, implying a greater risk for the creation of artefacts. Raman spectroscopy, instead, is useful in determining the mineralogical phases present in fibrous minerals because it does not require sample preparation and because it allows the Raman spectrum of a mineral to be obtained by placing the specimen directly in the path of the incident beam. If an optical microscope is coupled with the spectrometer, the Raman spectrum of a small, optically selected portion of the sample can also be obtained. The potential applications of this technique are especially promising in the case of specimens composed of different mineralogical phases, as is often the case with asbestos; moreover, the technique can also be applied to different materials, such as those used in the building industry, to determine whether they contain asbestos or not. This study demonstrates that unequivocal identification of the mineral phase can be attained by analyzing the position in the Raman spectrum of the bands related to the $[SiO_4]^{4-}$ vibrational modes. A practical application of Raman spectroscopy to a synthetic cement is also presented.

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SPECTROSCOPIC METHODS USED FOR STRUCTURE INVESTIGATION OF SOME NEW DIOXANE DERIVATIVES

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New 2-aryl-5-hydroxy-1,3 dioxane derivatives were obtained by the acetalization reaction of glycerol with several aldehydes (MURZA & SAFAROV, 1987; GARDINER et al., 2002). The compounds were investigated by X-ray diffraction techniques and high-field ^{1}H and ^{13}C NMR spectroscopy. The assignment of the signals is based on bidimensional NMR spectra. The complex NMR spectra suggest anancomeric structures.

We succeeded to isolate adequate crystals for some of these compounds which could be analyzed using X-ray diffraction techniques. The DIAMOND diagrams (Fig. 1) revealed the chair conformation of the 1,3-dioxane rings, the equatorial or axial preference of the aromatic substituents and important intramolecular and intermolecular aromatic π stacking interactions (GROSU et al., 2003; BALOG et al., 2004).

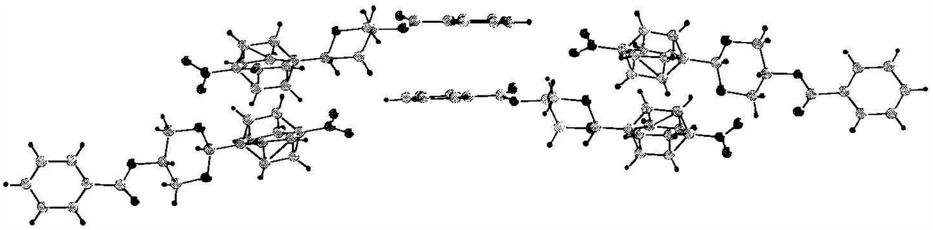

Fig. 1. DIAMOND diagram for trans–5–benzoiloxy–2(p–NO_2–phenyl)–1,3–dioxane

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AB INITIO SIMULATION OF THE ELECTRONIC STRUCTURE OF ZIRCON ($ZrSiO_4$) AND QUARTZ (SiO_2)

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Zircon, $ZrSiO_4$, is the widespread natural mineral that usually concentrates uranium and thorium. It is characterized by an extremely high resistance to chemical and physical degradation. Recently zircon has been proposed as the prospective material for the immobilization of plutonium. For the industrial applications as waste forms, it is important to develop the microscopic model of the radiation damage of zircon including the atomic and electronic structure of metamict (amorphous) and heterogeneous ($ZrSiO_4+SiO_2+ZrO_2$) areas of the mineral.

Ab initio quantum-chemical cluster calculations of $ZrSiO_4$ electronic structure were carried out using the MO LCAO discrete-variation X_α-method. Zircon was simulated by the clusters $[Si_5Zr_6O_{44}]^{44-}$ and $[Zr_5Si_6O_{44}]^{44-}$ containing the central tetrahedron SiO_4 and the central dodecahedron ZrO_8, respectively. The comparative analysis of the electronic structure of SiO_4 tetrahedra in zircon and those in alpha-quartz has been performed on the base of the cluster models $[Si_5Zr_6O_{44}]^{44-}$ (for zircon) and $[Si_5O_{16}]^{12-}$ (for quartz). When constructing the clusters, the following structural features of the minerals have been taken into account: (1) the isolated SiO_4 tetrahedra in $ZrSiO_4$ and polymerized ones in SiO_2; (2) the three-fold coordination of oxygen atoms (^{III}O) in $ZrSiO_4$ and two-fold coordination of oxygen atoms (^{II}O) in SiO_2; (3) the [001] edge-connected chains of Zr and Si polyhedra in zircon; (4) the unequivalence of the connection of ZrO_8 dodecahedra in [100] and [001] directions of zircon.

For the energy spectrum of both minerals, electronic configurations, effective charges of atoms, total and deformation electron density maps have been calculated. It was shown that the energetic and spatial electron density distributions for ^{III}O and ^{II}O atoms differed noticeably. In particular, the $^{III}O2s$, 2p spectrum is characterized by a smaller width that may be explained as the result of increasing ionicity and decreasing of the oxygen orbitals hybridization in zircon as compared with quartz. It was supposed that the higher chemical stability of zircon was due to the peculiarities of the electronic structure of ^{III}O atoms. Using the spatial integrating of the electron density in the clusters the effective charges of atoms have been calculated. Their values were the following: $Q_{Si} = 2.51\ e$, $Q_{Zr} = 2.78\text{-}2.87\ e$, $Q_O = -1.28\ e$ in zircon, $Q_{Si} = 2.57\ e$, $Q_O = -1.24\ e$ in quartz. The larger Q_{Si}-value in quartz as compared with zircon indicates the more covalent character of the Si-O bonding in the latter mineral. This is a result of increasing covalent mixing of Si3s, 3p and O2p states in isolated SiO_4 tetrahedra of zircon. It was established that the Zr-O bonding features differed in [100] and [001] directions of zircon. It was shown that the theoretical results were in the good agreement with the experimental data of optical spectroscopy and XPS.

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$MgAl_2O_4$-$MgCr_2O_4$-$FeAl_2O_4$-NATURAL SPINELS FROM THE URALS ULTRAMAFITES: MÖSSBAUER STUDY, QUANTUM-CHEMICAL SIMULATION OF THE LOCAL ATOMIC AND ELECTRONIC STRUCTURE

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Crystal chemistry of $MgAl_2O_4$-$MgCr_2O_4$-$FeAl_2O_4$ natural spinels from the Urals ultramafites has been investigatied by means of Mössbauer spectroscopy and microprobe analysis. The Urals ultramafites are represented by the main massifs of the alpine-type and dunite-clinopyroxenite-gabbro complexes. They characterize the redox state evolution of ultramafites from their formation up to the early serpentinization process. The oxidation state of the iron atoms in the minerals has been estimated and the site distributions of Fe^{3+} and Fe^{2+} ions has been analyzed. The Mössbauer parameter variations in 150 samples of the spinels have been discussed. The *ab initio* quantum-chemical cluster calculations of the short-range order structure relaxation and the electronic state spectrum for normal and partially inverse spinel solid solutions $MgAl_2O_4$-$MgCr_2O_4$-$FeAl_2O_4$ was carried out. The relaxed atomic positions were found by the cluster total-energy minimization within the GAMESS program; the electronic structure of relaxed clusters were analyzed by DVM program by discrete-variation X_α-method. Spinel was simulated by the cluster $[{}^{VI}Me_{cent}{}^{IV}(Mg,Al)_6{}^{VI}(Mg,Al)_6O_{38}]$ containing the central octahedron ${}^{VI}Me_{cent}O_6$ (Me_{cent} = Al, Mg, Fe, Cr) surrounded by six tetrahedra (${}^{IV}MgO_4$ or ${}^{IV}AlO_4$) and six octahedra (${}^{VI}MgO_6$ or ${}^{VI}AlO_6$). To find the total energy minimum, the coordinates of six oxygen atoms nearest to the central cation were varied. The equilibrium distances ${}^{VI}Me_{cent}$-O were found to be 1.93 Å for Me_{cent} = Al, 2.03 Å for Mg, 2.00 Å for Fe, and 1.97 Å for Cr, that were in satisfactory agreement with structure refinement data for natural spinels. The central octahedron was shown to be trigonally distorted. The deviations from the cubic symmetry of the nearest oxygen surrounding were obtained to increase at the substitutions Al→Cr→Fe→Mg. The local values of the oxygen parameter *u* were calculated and compared with the experimental averaged values of *u*. The electronic structure and effective atomic charges were calculated both for "idealized" clusters and those with relaxed structure. The influence of relaxation effects on the changing of the spatial distribution of electronic density and integral atomic charges was considered. In particular, effective cation charges increase as the interatomic distances decrease; the ionicity of bonding between cations and the surrounding oxygen atoms increases. The theoretical results were used for evaluation of the spectroscopic parameters of the spinel solid solutions, such as electric field gradient at the iron core (or the quadrupole splitting of Mössbauer spectra) and the transition energies of the optical absorption spectra. Comparable analysis of the data obtained on the base of "idealized" and relaxed models showed that the octahedra distortions should be taken into account when interpreting spectroscopic parameters of natural spinels.

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MÖSSBAUER SPECTROSCOPY OF Fe-CONTAINING SULFATES

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Mössbauer spectroscopy has been applied to study Fe-containing sulfates of melanterite $M^{2+}[SO_4]\cdot 7H_2O$ ($M^{2+} = Fe^{2+}$, Mn, Co, Zn, Cu), halotrichite $AR_2[SO_4]_4\cdot 22H_2O$ ($A = Fe^{2+}$, Mg, Zn, Mn, Co; R = Al, Fe^{3+}) and copiapite $AFe^{3+}{}_4[SO_4]_6(OH)_2\cdot 20H_2O$ ($A = Fe^{2+}$, Mg, Zn, Cu, Al, Fe^{3+}) groups from the various localities of the Ural, Russia.

Mössbauer spectra of melanterites may be considered as superposition of two doublets corresponding to Fe^{2+} In the spectra of melanterites having compositions most close to ideal $Fe[SO_4]\cdot 7H_2O$, the doublets are characterized by nearly equal isomer shift (δ) and various quadrupole splitting (Δ); squares of both doublets are practically equal that means uniform (1:1) distribution of Fe^{2+} between both sites. Replacement of Fe^{2+} by Cu or/and Zn leads to such effects that ratios of doublet squares are changed from 1:1 to 1:2 and more, indicating irregularity of Fe^{2+} distribution between the structural sites; the values of quadrupole splitting are increased for a site with a smaller part of Fe^{2+} and decreased for a site with a high part of Fe^{2+} The results are in excellent agreement with modern data according to those two types of Fe^{2+} octahedra, M1 and M2, existing in the structure of melanterite. Cu replacing Fe^{2+} is concentrated mainly in the M2 site (PETERSON, 2003).

As distinct from melanterites, sulfates of halotrichite and copiapite groups may contain both Fe^{2+} and Fe^{3+} For this reason, a spectrum is complicated and interpretation is getting more difficult. Mössbauer spectra of halotrichites may be characterized by three doublets at minimum, two of those with the greater values of δ and Δ correspond to Fe^{+2}, the parameters of the doublets being close to that observed for melanterite, giving evidence for the common features in the structures of these minerals (HAWTHORNE et al., 2000). The third doublet, with lower values of δ and Δ is related to Fe^{3+} The spectra of Fe^{2+}-free copiapites from the burnt dumps of coal mines close to ideal alumino- and magnesiocopiapite are characterized by two doublets referring to Fe^{3+} The ratio of doublet squares is 1:1. The spectra of most occurring copiapites containing both Fe^{2+} and Fe^{3+} are supposed as superposition of three doublets, two of those as in a previous case correspond to Fe^{3+} and the third doublet is classified as Fe^{2+}

For halotrichites and copiapites, the contents of Fe total, Fe^{2+} and Fe^{3+} have been defined by methods of wet chemistry. In addition, the contents of Fe^{2+} and Fe^{3+} have been calculated on the base of Fe^{2+}/Fe^{3+} doublet squares and total content of Fe. Differences vary from 0.01 0.43 % for Fe^{2+} and from 0.08 - 0.50 % for Fe^{3+} To calculate the formulae of these sulfates, Mössbauer data give the most satisfactory results.

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OPTICAL STUDIES OF FLUIDS IN FIBROUS DIAMONDS

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Fibrous diamonds can provide unique information about fluids from upper mantle and contribute to our understanding of diamond growth conditions. In the course of this study we applied several complementary local techniques for a comprehensive study of microinclusion chemistry and phase composition as well as distribution of carbon and nitrogen isotopes within samples cross section. This approach permitted to monitor the evolution and changes of fluids and isotopes during different growth steps. In this presentation we will discuss results of microscopic IR measurements performed on these samples. Similarly to previous investigations of fibrous diamonds (e.g., CHARETTE, 1966; CHRENKO et al., 1967; GALIMOV et al., 1979) we observe numerous infra-red (IR) absorption bands due to microinclusions. It is interesting to note that the mineral species in fibrous diamonds from different world deposits (Africa, Canada, Yakutia, Brasil) are broadly similar: Phosphates (e.g., apatite), carbonates (probably ankerite), and silicates are among the most common minerals. Shift of quartz and CO_2 absorption bands indicates that the inclusions are under confining pressure in the range 1.5-2.5 GPa. A common feature for IR spectra of many fibrous diamonds is the absorption ascribed to silicate melt phase (around 1000 and 1100 cm^{-1}).

In some stones point-by-point spectroscopic investigations (Fig. 1) clearly indicate some compositional evolution of growth medium, which is often supported by chemical and isotopic analysis. It is notable that in some cases the evolution could be observed even within single growth zone as revealed by CL.

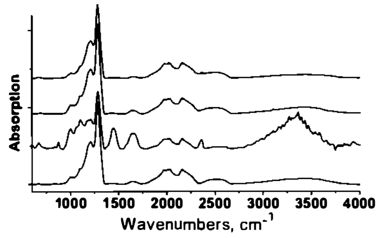

Fig. 1. IR spectra of fibrous diamonds

A remarkable feature of fibrous diamonds is that microinclusions also contain different water solutions and CO_2. In many spectra several lines in the region of OH valence vibrations are observed, indicating that minerals in inclusions contain OH groups. Possibly some of the observed lines are related to OH-groups in talc and/or serpentine. IR measurements at different temperatures will be reported. This work will give more reliable information about chemical and phase composition of microinclusions.

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COMPARING THE STRUCTURE OF LITHIUM CONTAINING GERMANATE AND SILICATE GLASSES

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The addition of alkali cations to silicate melts and glasses results in the depolymerisation of the silicate network, and formation of non-bridging oxygens (NBOs). The size of the alkali cation has recently been observed to influence the distribution of Q species (Q^3, Q^2) that exist within silicate glasses. In particular, lithium-containing glasses have higher Q^2/Q^3 ratios than equivalent Na or K containing glasses. However, this Q species dependence on alkali size appears to be different for germanate melts and glasses. We are currently investigating the Q species distribution between lithium containing silicates and germanate glasses. Silicate and germanate glasses containing from 5 to 30 mol% Li_2O have been prepared and examined using Si *K*-edge XANES/EXAFS, Si *L*-edge XANES, Raman spectroscopy, ^{29}Si NMR and ^{7}Li NMR. Our studies have revealed that lithium-containing germanate glasses appear to have a lower Q^2/Q^3 ratio than the equivalent Na- and K-containing compositions. Furthermore, with the addition of lithium, the Q^2/Q^3 ratio increases for silicate glasses, but decreases for germanate glasses. The lithium containing germanate glasses also appear to have greater amounts of Q^2 relative to Q^3 species, than comparable lithium-containing silicate glasses.

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MINERALOGY AND CHEMISTRY OF SOME GLAUCONITES FROM POLISH FLYSCH CARPATHIANS DETERMINED BY INFRARED SPECTROSCOPY, SEM-EDS ANALYSES AND X-RAY DIFFRACTION

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Four samples of glauconites from flysch deposits of the Polish Outer Carpathians were studied for characterization of their most significant mineralogical and chemical features. Samples were collected from two cross-sections (near Ropica and Folusz) which are situated in the marginal, northern part of the Magura Nappe (Siary subunit). Glauconite host-rocks are sandstones of the Magura Beds, Lower Oligocene in age.

The glauconitic grains were separated using the following methods: glauconite-bearing rocks were disaggregated, submitted to magnetic separation, acetic acid treatment, purification by ultrasonic cleaning, and finally handpicking. The main properties (morphology, mineralogy and chemistry) of the green grains were studied by applying: optical microscopy, scanning electron microscopy (SEM-EDS), X-ray diffraction and IR spectroscopy.

The polycrystalline glauconitic grains occur mainly in the 50 μm – 500 μm size range. They are dark-green in colour and exhibit considerable variety in morphology. Most frequent morphological types are (according to TRIPLEHORN, 1966): spheroidal-ovoidal with smooth surface; tabular-discoidal; irregular shapes are also observed. XRD analyses of the oriented powder samples display the characteristic (001), (003), (112), (112) peaks of glauconitic minerals (ODIN & MATTER, 1981). The chemical data of the grains such as high K_2O content (average 7 to 8 wt%) and Fe_2O_3 content (up to 19 wt%) confirm their glauconitic nature. The mineralogical and the chemical evidences indicate that glauconitic grains of each sample reflect the evolved (or even highly evolved) stage of glauconitization.

The IR spectra were interpreted from a qualitative point of view, based on the data published by WIEWIÓRA & ŁĄCKA (1980). All the bands characteristic for the glauconitic minerals can be observed. The major $Si–O_{basal}$ (990-1025 cm^{-1}) bands are shifted towards lower wavenumbers which indicates a low amount of expanding layers in the glauconitic minerals. Also the two distinct Si–O bands in the region between 990-1100 cm^{-1} are clearly divided. In the region between 450-465 cm^{-1} the bands of the samples containing more aluminium are shifted towards higher wavenumbers as compared with high-iron samples; all the samples have bands at around 3500 cm^{-1} which indicate that they represent Fe-glauconites.

The IR spectra confirm the chemical and mineralogical data that the studied material represents the last stages of glauconitic evolution. In general, the differences between samples are not significant and they represent similar types from the point of view of maturity, morphology and crystal chemistry.

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ELECTRONIC ABSORPTION SPECTROSCOPY OF NATURAL (Fe^{2+}, Fe^{3+})-BEARING SPINELS OF MAGNESIO-SPINEL-HERCYNITE AND GAHNITE-HERCYNITE SOLID SOLUTIONS AT DIFFERENT TEMPERATURES AND HIGH PRESSURES

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Natural Fe^{2+}, Fe^{3+}-bearing spinel solid solutions from the magnesiospinel-hercynite and gahnite-hercynite series were analyzed and studied by electronic absorption spectroscopy in the spectral range 30000-3500 cm^{-1} in the temperature and pressure ranges $77 \leq T_K \leq 600$ and $10^{-4} \leq P_{GPa} \leq 11.0$. Two crystals were light-violet in color (type I) and six green or bluish-green (type II). The spectra of both types of spinel are dominated by an UV-absorption edge near 28000 to 24000 cm^{-1}, depending on the iron contents, and a very intense band system in the NIR centered around 5000 cm^{-1}, which is caused by spin-allowed *dd*-transition of tetrahedral Fe^{2+}, derived from $^5E \rightarrow ^5T_2$. The strong band is split into four sub-bands, which can only be observed in very thin platelets. Between the UV-edge and the high-energy wing of the NIR-band there occur a number of very weak bands in type I spinels while the green type II spinels show some of these with significantly enhanced intensity. The intensity of the very weak bands is nearly independent on temperature. Such bands are attributed to spin-forbidden electronic transitions of $^{IV}Fe^{2+}$ Temperature and pressure dependence of the intensity enhanced bands of spinels type II indicate that they are caused by $^{IV}Fe^{2+}$ and $^{VI}Fe^{3+}$ By temperature and pressure behaviors they are attributed to spin-forbidden transitions $^6A_{1g} \rightarrow ^4A_{1g}$, ^4E_g, $\rightarrow ^4T_{2g}$ and $\rightarrow ^4T_{1g}$ of $^{VI}Fe^{3+}$, the two latter being strongly intensified by exchange-coupling interaction with adjacent $^{IV}Fe^{2+}$ The pressure dependence of $^{IV}Fe^{2+}$ *dd*-band system in the NIR caused by spin-allowed $^5E \rightarrow ^5T_2$ transition noticeably differs from that of octahedral Fe^{2+}, an effect which is attributed to a dynamic Jahn-Teller effect of $^{IV}Fe^{2+}$ in the spinel structure. In difference to $^{VI}Fe^{2+}$ in many oxygen-based minerals, the splitting of the spin-allowed bands derived from $^5E \rightarrow ^5T_2$ transition of $^{IV}Fe^{2+}$ in spinels does not decrease with pressure. On the contrary, it markedly increases showing that values of vibronic coupling coefficients of $^{IV}Fe^{2+}$ are rising. Also, the values of tetrahedral moduli of Fe^{2+} in spinel, evaluated from high-pressure spectra and X-ray diffraction structural refinements, are significantly different that again may be caused by a dynamic Jahn-Teller effect of $^{IV}Fe^{2+}$ in the spinel structure.

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RAMAN SPECTROSCOPY ON GEM-QUALITY MICROCRYSTALLINE AND AMORPHOUS SILICA VARIETIES FROM ROMANIA

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Raman spectroscopy is used as a powerful tool for mineral phase identification in geological samples, and for characterizing the crystal chemistry of heterogeneous materials. A special case is represented by mineral polymorphs, such as the SiO_2 phases. On the basis of optical microscopy, microcrystalline silica (low- or α-quartz) has been usually reported as "chalcedony", "jasper", "chert", or "flint" Previous micro-Raman investigations (KINGMA & HEMLEY, 1994) have evidenced the presence of a new tetrahedrally coordinated silica polymorph, *i.e.* moganite in virtually every studied microcrystalline silica sample.

In order to test the ubiquity of moganite in such geological materials, and for checking if a relationship between the colour/textural variations *vs.* the presence of specific polymorphs could be established, micro-Raman measurements were performed on gem-quality microcrystalline and amorphous silica varieties from several Romanian occurrences. The best studied occurrence was Gurasada (Apuseni Mts.), due to the remarkable diversity of SiO_2 varieties found in Paleocene („banatitic") pyroclastic agglomerates and tuffs: chalcedony (including agate), jasper, opal, silicified wood. Most of the samples show macroscopic and/or microscopic variations in colour (grey-red-blue-white), transparency or texture (from massive to banded). Other studied occurrences from the Apuseni Mts. were Rachiş and Techereu (both of "ophiolitic" pyroclastic origin), but also famous sites from Baia Mare area (Trestia and Oraşu Nou - related to the Neogene volcanism) were included for comparison.

The measurements were performed on a Dilor Labram system equipped with an Olympus LMPlan Fl 50 microscope objective, an 1800 lines/mm grating and an external laser with an emission wavelength of 514 nm, and additionally 632 nm. In the recording of the micro-Raman spectra a power of 100 mW on the sample has been employed. The focal length of the spectrometer is 300 mm and the slit used for all measurements was 100 µm. Thus, the spectral resolution was about 4 cm^{-1}

The Raman spectra show the presence of low-quartz in all the microcrystalline silica varieties (chalcedony, agate, jasper), but also in some areas of the studied opals. The shoulder of the 465 cm^{-1} quartz band which is noticeable at values around 500 cm^{-1} is interpreted as an evidence of an intergrowth with moganite (KINGMA & HEMLEY, 1994), thus present in small amounts in most of the studied samples (including opal). The pattern of the coloured areas could not be correlated to the presence of a specific silica polymorph; however, in some cases certain non-silica phases (such as calcite, or organic carbon sp2-containing phases) may be responsible for the observed colour and/or transparency variations.

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LOCAL STRUCTURAL STATE OF ZIRCON FROM METAGRANITES – A RAMAN SPECTROSCOPIC STUDY

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Zircon from amphibolite facies metagranites (Ograzhden Mountain, Serbo-Macedonian massif, Bulgaria) exhibits complex internal structures visible in cathodoluminescence (CL) and backscattered electrons (BSE) microscope images. Different processes, such as metamictization, annealing, diffusion and recrystallization, cause alteration of the protolith, magmatic zonation and form secondary internal features. The determination of the process governing the formation of a particular internal area is of a great importance for geochronological reconstructions. We have applied Raman spectroscopy, CL and electron microprobe to analyze the correlation between the local structural peculiarities and the radioactive element content of natural inhomogeneous zircon. The Raman spectroscopic data reveal different degree of structural disorder that can be estimated by the following spectral features: a) the position and the width of the peak near 1008 cm^{-1}, generated by the $\nu_3(SiO_4)$, which is sensitive to point defects and distribution in the Si-O bond lengths; b) the relative intensity of the same peak, indicating disruption of the translation symmetry in the zircon lattice; c) additional Raman signals between 150 and 650 cm^{-1} indicating a formation of ZrO_2 phases as a consequence of the zircon structure damage on nanometric scale; d) existence of a halo between 1000-1200 cm^{-1}, due to diffuse light scattering from dislocations and related defects resulting from the accumulations of point defects such as vacancies and broken Si-O-Zr linkages; e) additional well-pronounced peaks in the range 1100-1250 cm^{-1} that do not depend on the excitation light wavelength, pointing to occurrence of chain-like clusters of linked SiO_4 tetrahedra. Zircon separated from equigranular metagranites exhibits three types of spatial regions: poorly damaged zircon, for which the structural alteration consists mainly in short-range disorder of SiO_4; moderately damaged zircon, characterized by faults in the long range order and presence of polymerised SiO_4 tetrahedra; heavily damaged zircon, exhibiting a high degree of long- and medium-range disorder and formation of zirconia polymorphs. The studied zircon samples separated from porphyritic metagranites exhibit incipient recrystallization with presence of nuclei that enlarge upon laser-induced heating. The spectroscopic data show that the width of the peaks at 357 and 439 cm^{-1}, originating from SiO_4 rotation and bending mode, respectively, can be used for estimating the degree of metamictization of zircon.

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OPTICAL AND SPECTROSCOPIC PROPERTIES OF SELF-ASSEMBLED NANOPARTICLES

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In recent years, there has been an increasing interest in the synthesis of nanostructures (LIU et al., 2003) due to their various potential applications such as optoelectronic (SHIPWAY et al., 2000), microelectronic (LYNCH et al., 1997), and bio-moleculars (GRABAR et al., 1995). Fabrication of nanostructures by self-assembled methods has attracted much attention due to their simplicity and flexibility (WANG et al., 1998). A method for control of surface morphology (KEATING et al., 1998; FREEMAN et al., 1995; XIA et al., 2000) is through assembly of small, spherical, uniformly sized particles at an interface, imparting a repeating feature size that is dependent upon the particles used. In the present work gold colloids were prepared and self-assembled onto glass substrates by using an organic coupling agent as 3-aminopropyltrimethoxysilane (APTMS). Moreover, polystyrene beads were also assembled in a regular hexagonal lattice on hydrophilic glass slides surfaces. The substrates were characterized by transmission electron microscopy (TEM) and optical absorption spectroscopy (Fig. 1). The optical absorption spectra show a well defined surface plasmon resonance peak at 520 nm for the self-assembled gold monolayers and at 632 nm for the gold coated polystyrene nanospheres. The as prepared substrates are under current investigation for applications in the field of surface plasmon resonance (SPR), optical biosensing as well as in surface-enhanced Raman spectroscopy (SERS) studies.

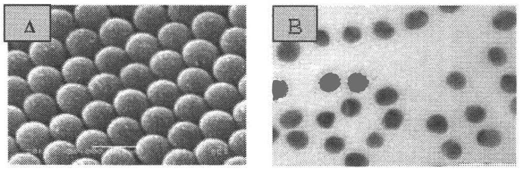

Fig. 1. TEM images of self-assembled nanoparticles:
(A) polystyrene nanospheres
(B) gold colloids

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GRADUAL RECRYSTALLISATION OF METAMICT FERGUSONITE: X-RAY DIFFRACTION AND RAMAN SPECTROSCOPY STUDY

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Fergusonite mineral samples, mainly represented as $YNbO_4$, are frequently metamict. Heating experiments induce crystal structure recovery, but also cause phase transition processes, since fergusonite is a polymorphic substance (WOLTEN & CHASE, 1967).

X-ray powder diffraction and Raman spectroscopy were employed to monitor the sequences of fergusonite recrystallisation. The corresponding Raman spectra were also used to reveal possible presence of original structure remnants in the metamict mineral. Two metamict mineral samples previously identified as fergusonite were heated in air at 400, 500, 650, 800, 1000 and 1300°C for 24 hours in each case.

The mineral sample from Bakkane-Steane, Norway, was completely amorphous to X-rays and started to recrystallise at 400 °C with scheelite type structure (space group $I4_1/a$) being stable up to 1000 °C. At 1000 °C monoclinic (space group $I2$) β-fergusonite dominated, with the tetragonal phase still present. At 1300 °C the transformation from tetragonal to monoclinic fergusonite was completed. Raman spectra confirmed the gradual fergusonite recrystallisation by sharpening and intensifying of vibrational bands. The number of bands increased with the lowering of the symmetry. For the metamict mineral the vibrational bands at 779, 685, 697, 310, 208 and 108 cm^{-1} were present indicating the residue of the original crystal structure. At lower heating temperatures the bands were broad, but at higher temperatures reappeared more sharpened, resolved and intensified. The second mineral sample, originating from Ytterby, Sweden, was almost completely metamict, with only a few low-intensity diffraction lines superimposed on the characteristic amorphous diffraction peak. At 400 °C pyrochlore phase started to recrystallise, being continuously present through the whole temperature range. At 1000 °C the monoclinic β-fergusonite appeared with recrystallisation completed at 1300 °C. Raman bands were similar to those of fergusonite from Bakkane-Steanne, although some of them had different intensities and were slightly shifted. Vibration bands were not present in the spectrum of the unheated metamict mineral.

The vibrational spectra of the complex oxide structures are difficult to calculate, but a relation to the analogous synthetic compounds (YASHIMA et al., 1997) could be established. McCONNELL et al. (1976) indicate that LO and TO Nb-O stretching modes of niobium oxides appear in the range 1010-620 cm^{-1} Therefore, the observed lattice vibrations reveal partial preservation of Nb-O polyhedra stacking in metamict fergusonite from Bakkane-Steane.

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A MUON SPIN ROTATION INVESTIGATION OF THE MAGNETIC STRUCTURE OF $CeRh_2Si_2$

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The muon spin rotation (μSR) technique makes use of a short-lived subatomic particle called muon, a spin-1/2 particle. Spin polarized muon beams can be prepared and subsequently implanted in various types of matter. The muons precess around the local magnetic field and then disintegrate preferentially in the direction pointed by their spins. Therefore muons can be used to investigate a variety of static and dynamic magnetic effects and hence to deduce properties concerning magnetism, superconductivity and molecular dynamics. The use of muons in condensed matter physics has shed new light on subjects as diverse as passivation in semiconductors, frustrated spin systems, vortex lattice melting, phase separation and phase coexistence in magnetic materials.

In general, μSR gives information that is complementary to that provided by other well-recognized techniques such as neutron scattering, ESR and NMR. The μSR technique has a unique time window for the study of magnetic fluctuations in materials that is complementary to other experimental techniques like those mentioned above.

We have used the muon spin rotation (μSR) method to investigate the magnetic properties of $CeRh_2Si_2$. $CeRh_2Si_2$ crystallizes in a body-centred tetragonal structure of $ThCr_2Si_2$ type (space group *I4/mmm*). It is an antiferromagnet with two magnetic transitions, at 36 K (T_{N1}) and 25 K (T_{N2}). The magnetic structure of $CeRh_2Si_2$ below T_{N2} is still ambiguous. From neutron diffraction experiments done by GRIER et al. (1984) and KAWARAZAKI et al. (1995), the magnetic structure is a modulated structure described by two ***k*** vectors, ***k1*** and ***k2***, which reflect either a multidomain structure or a multi-q structure. KAWARAZAKI et al. (2000), from another neutron diffraction experiment reported a 4-***k*** structure. We have performed μSR experiments to confirm/deny the proposed magnetic structures. Below T_{N2} we observed a slowly depolarized oscillating component superposed over two Kubo Lorentz depolarisation functions. This indicates that there are several magnetically inequivalent muon-stopping sites. The 4-***k*** structure predicts two magnetic inequivalent sites, one with zero field and one with finite magnetic field which should be detected in a μSR experiment as a flat component and an oscillating one respectively. By performing computer simulations we have tried to associate the depolarisation functions with imperfections of the magnetic (4-***k***) structure: tilted magnetic moments, missing magnetic ions, but this explains only partially the depolarisation rates observed in the μSR experiments.

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TEMPERATURE DEPENDENCE OF THE Fe^{2+} MÖSSBAUER PARAMETERS IN TRIPHYLITE ($LiFePO_4$)

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Triphylite ($LiFePO_4$) has an olivine type structure (Pnma) and has received much attention because of its application as possible electrode active material for lithium rechargeable batteries.

In this work, the temperature dependence of the Mössbauer parameters of Fe^{2+} in synthetic triphylite (ARNOLD et al., 2003) is determined between 4 K and room temperature. From the Mössbauer measurements a sharp magnetic ordening transition is observed at 53 K, which is in line with the Néel temperature as is determined by neutron diffraction (ROUSSE, 2003). The Mössbauer spectra in the paramagnetic region are well fitted by one Fe^{2+} quadrupole doublet with small linewidth. The spectra in the magnetic region are typical for Fe^{2+}, showing the maximum of eight absorption lines. They are analysed using the diagonalization of the full nuclear-interaction Hamiltonian and could be successfully fitted with a model independent distribution of hyperfine fields.

The hyperfine field is always collinear to the local principal axis of the electric field gradient tensor. The asymmetry parameter is about 0.79 and the quadrupole coupling constant is 2.79 mm/s, which is perfect in line with the quadrupole splitting $\Delta E_Q = 3.06$ mm/s at 80 K in the paramagnetic region.

The temperature dependence of the quadrupole splitting is interpreted within the ^5D orbital energy level scheme of Fe^{2+} by a crystal field calculation (VAN ALBOOM et al., 1993) based on the point symmetry of the Fe^{2+} site in triphylite (ANDERSON et al., 2000).

When triphylite is used as electrode material in lithium rechargeable batteries, there is a conversion of triphylite in its delithiated form $FePO_4$ (heterosite) and vice versa during the charge/discharge process. The characteristic Mössbauer temperature is an important parameter in order to determine accurate ratios of both compounds during the process (ANDERSON et al., 2000). From the temperature dependence of the isomer shift its value is determined to 390 K for Fe^{2+} in triphylite. The intrinsic isomershift is 1.45 mm/s.

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LUCIA, A MICROFOCUS SOFT XAS BEAMLINE

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The microfocus X-ray beamline LUCIA (Line for Ultimate Characterization by Imagery and Absorption) is devoted to microspectroscopy in the 1-8 keV energy range. The energy domain covers the K edges of low Z elements (from sodium to iron), the L edges from nickel to gadolinium, and the M edges of lanthanides and actinides. Thus, at the same time, it gives an unique access to the major elements constituting minerals (low Z elements) and it is also of importance in geosciences as well as in environmental sciences for which the energy range covers metals and other heavy pollutants. The goal of the beamline is to achieve a spot size on the sample of the order of 1x1 μm^2, while allowing energy scans on the entire range. Structural investigations of spatially complex systems will be therefore considered with various applications, including archeometry, Earth and extraterrestrial sciences or environmental science. This latest topic contains typical examples for which such *in situ* spatial investigations are particularly powerful. Indeed, it is now well known that toxicity and bioavailability of many compounds depends not only on their nature and bulk concentration but much more on their spatial distribution and chemical speciation.

Born from a collaboration between LURE, SOLEIL and PSI, this beamline installed on the Swiss Light Source is now in its commissioning phase. An Apple II insertion device has been installed (SCHMIDT et al., 2003) during the summer 2003. This undulator (54mm period length) provides X-rays in an energy range which corresponds to the best performances in term of brilliance of both machines, SLS and SOLEIL. This device emits linear light with variable polarization direction as well as circular polarized light. The period length was set such that no 'energy gap' appears between the harmonics in the 1-8 keV energy range. The horizontal photon source size is demagnified by a fixed spherical mirror. Two plane mirrors reject the higher harmonics contributions. The final focusing is accomplished through a Kirkpatrick-Baez (KB) mirror system aligned automatically (IDIR et al., 2003). A fixed exit double-crystal monochromator is equipped with five different types of crystals to cover the full energy domain. A motorized (xyz) stage allows the precise positioning and mapping of the sample. XAS measurements can be done by measuring the transmitted beam, the total electron yield or the fluorescence yield. For micro-XRF cartography, a single-element silicon drift detector is used.

Proposals can be submitted to the SLS Users Office. The next program committee is in September for beamtime allocation starting in December.

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WHITE MICA FROM THE BRNJICA GRANITOIDS (EASTERN SERBIA)

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Granitoids of East Serbia, associated with the Carpathian-Balkan arc, form a NNW-SSE elongated zone of about 200 km in length. It starts from the river Danube to the north and extends up to the southern slopes of Mt. Stara Planina, at the Yugoslavian-Bulgarian border. These granitoids were studied by numerous researchers from the end of 19th century till 1970, but many features related to mineralogy (i.e. mineral chemistry) are still unsolved. The magmatic activity in the above mentioned area was very intensive during Carboniferous and Permian time (259 to 342 Ma). In this paper we present new mineralogical data and chemistry of white mica and an attempt is made to investigate its origin in the Brnjica Granitoids (BG), located in the Danube Gorge. The BG (272-259 Ma - Rb/Sr) occurs in the Kucaj terrane (KARAMATA & KRSTIĆ, 1996), the oldest rocks of which are the Proterozoic metamorphic rocks, followed by the late Proterozoic to early Cambrian "Green Complex" During the Variscan magmatism the BG intruded the above rock formations as a late- to post-kinematic intrusion, causing extensive thermal metamorphic phenomena. The BG is a composite pluton consisting of (±Hb)-Bi tonalite (TON), (±Ms)-Bi granodiorite (GRD), two-mica granite (TMG), and leucogranite (LG). Fe-biotite is the main ferromagnesian constituent in all rock-types except LG. Mg-hornblende is present, in small quantities, only in TON. Plagioclase is of oligoclase-andesine composition. Late and/or subsolidus muscovite is present in small quantities in GRD, although some grains have features of primary muscovite, and also as the main phase in TMG and LG. White mica (1-10 vol%) occurs as primary idiomorphic or secondary flakes commonly 0.15 to 0.6 mm long, rarely up to 1.25 mm, emplaced between feldspar or intergrown with biotite in TMG, GRD and LG. The interlayering of muscovite and biotite is used as textural evidence for its primary origin. Sometimes it makes fine-grained elongated segregations. According to their chemical composition some grains in GDR are TiO_2-rich (1.96-3.27 wt%). Ti concentrations are relatively high for this mineral (~ 0.06-0.12 apfu), while Mn does not exceed 0.02 of an atom in octahedral site. The interlayer site is mainly filled with K (1.7 apfu on average) with lower amounts of Na (0.1 atoms), resulting in relatively low paragonite component (~6 % on average). The examined white micas have phengitic composition in GDR slightly approaching the muscovite end-member from TMG to LG. The phengitic component expressed as the percentage of the $(Fe^{2+}+Mg+Ti+Mn)/(Fe^{2+}+Mg+Ti+Mn+Al)$ ratio, ranges from 4 to 18 %. The chemistry of muscovite is characterized by variable levels of substitution of octahedral Al by Mg, Fe and Ti. X_{Mg} ranges from 0.32 to 0.62. The mean composition of muscovite suggests that biotites with high Al content coexist with muscovite close to the ideal composition (VASKOVIC et al., 2004).

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SPECTROSCOPIC INVESTIGATIONS ON SOME VANADIUM-CALCIUM-PHOSPHATE GLASSES

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IR and EPR investigations on $xV_2O_5 \cdot (1-x)[P_2O_5 \cdot CaF_2]$ glasses with $0.005 \leq x \leq 0.4$ are reported. Both methods give information about the structural effect of the V_2O_5 oxide component on the glass matrix.

IR spectra contain the absorption bands characteristic for both P_2O_5 and V_2O_5 oxides. The IR spectra for $0.005 \leq x \leq 0.1$ show the characteristic bands of phosphate glasses because of the small content of V_2O_5 oxide. These bands are: O-P-O and O=P-O bending vibrations at 518 cm^{-1} and P-O-P stretching vibrations at 760 cm^{-1} Between 920-1280 cm^{-1} a very large band with three distinct peaks dominates the spectra. These peaks are due to the P-O-P stretching vibration, ionic groups $P\text{-}O^{(-1)}$ stretching vibration and P=O stretching vibration respectively (DAYANAND et al., 1996). At high concentration of V_2O_5 ($x \geq 0.1$) the bands specific for P_2O_5 become weaker and at $x = 0.4$ the spectrum shows clearly all the typical bands belonging to V_2O_5 oxide. Thus at 595 cm^{-1} is present the V-O-V bending vibration, at 980 cm^{-1} the V-O stretching vibration and at 1080 cm^{-1} the V=O stretching vibration appears (BRATU et al., 1999). It can be concluded that with the increase of V_2O_5 content in the studied glasses the peaks attributed to P_2O_5 are partially covered by those attributed to V_2O_5 oxide; in consequence, the V_2O_5 oxide plays the role of a network modifier at low concentrations and network former at high concentrations.

The shape of the EPR spectra is also changed with the increase of the vanadium content, this consisting in a progressive disappearance of the hyperfine structure characteristic to the V^{4+} ions. This fact may be explained by the superposition of two EPR signals, one with a well-resolved hyperfine structure typical for isolated V^{4+} ions in a C_{4v} symmetry and the other one consisting in a broad line without hyperfine structure characteristic for clustered V^{4+} ions (RAMESH KUMAR et al., 2003). These EPR data are in agreement with those obtained from IR spectra and show that at low concentration V^{4+} ions destroy the phosphate matrix structure imposing their own coordination polyhedra in an isolated scattered manner. At high concentration ($x > 0.1$) the broad line typical for clustered ions shows that the magnetic interactions prevail between paramagnetic centers.

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SPECTROSCOPY APPLICATION FOR MODELLING OF TRANSFORMATIONAL MECHANISMS OF LATTICE DEFECTS IN DIAMONDS DURING ANNEALING AND IRRADIATION

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There is still some concern about mechanisms of defect transformations and structure of some lattice defects in diamonds. This work is performed for better understanding of processes which take place in diamond lattice during irradiation and annealing.

Samples of natural and synthetic diamonds were investigated by means of VIS-IR-range absorption spectroscopy (at room temperature), spectral (at liquid nitrogen temperature) and colour cathodoluminescence and laser induced photoluminescence. Among the studied samples there are several octahedral natural diamond crystals, synthetic diamond crystals, flat plates cut from natural and synthetic diamonds, and also treated black diamonds and natural black diamonds. Several samples (natural octahedral diamond crystals) have undergone annealing at temperatures of 1700-1800 °C under high pressure (6 GPa) and some samples (octahedral natural diamond crystals, natural and synthetic diamond flat plates) were irradiated by different types of radiation such as protons, gamma, and electron. Irradiated samples then were annealed at different temperatures in the range of 800-900 °C. At every stage spectroscopic data were acquired.

The colour of the irradiated samples has changed to green for natural diamonds and to greenish-yellow for synthetic diamonds. In the absorption spectra of the irradiated samples the line at 503 nm appeared (H3-center). Images of the colour cathodoluminescence of the irradiated natural diamond samples revealed no changing of colour and distribution of luminescence (remain blue), but the intensity seems to be weaker. Images of the colour cathodoluminescence of the irradiated synthetic diamond samples revealed changing of the intensity of luminescence, i.e. a weakening of red cathodoluminescence.

Interpretation of acquired data allows to model the structure of some lattice defects in diamond and also provides a useful information on mechanisms of the transformation and stability of lattice defects in diamonds and causes of diamond colour.

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ESR AND LUMINESCENT STUDY, *AB INITIO* MODELLING OF ATOMIC AND ELECTRONIC STRUCTURE OF NATURAL CARBONATE MINERALS (Ca,Mg)CO_3:Mn^{2+}

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The scheme of calcite and dolomite classification based on the data of ESR, thermo- and X-ray luminescense (in the temperature range 77-400 K) of the typical impurity Mn^{2+}-ions replacing Ca^{2+} (Mg^{2+})-ions in carbonates is under consideration. The scheme is based on the statistical analysis of more than 1000 carbonate samples of different Mn^{2+} content, genesis and age (from Riphean up to the modern sediments). Numerical ESR and luminescense databases have been created. It has been shown that under the temperature changes analytical spectroscopic Mn^{2+} line widths, their intensities and their dynamics varied essentially in the samples and depended on the minerals content, their structure defectness and genesis. Suggested scheme of carbonates classification has been used for the analysis of stromatolite-containing limestones, dolomites and interstromatolithic layers from all main South Urals Riphean formations series and some Riphean carbonates from other Russian and world regions. The experimental spectroscopic data have been analyzed using the results of theoretical modelling for calcite and dolomite. The atomic and electronic structures of the minerals were simulated by *ab initio* quantum-chemical cluster methods in terms of GAMESS and X_α-DVM codes on the base of the multiprocessing computer system MVS-1000 of the Institute of Mathematics and Mechanics UrB of RAS (Ekaterinburg). For investigation of pure calcite we used 53-atomic $[Ca_{cent}Ca_6C_6O_{42}]^{46-}$ and 64-atomic $[C_{cent}C_{12}Ca_6O_{45}]^{26-}$ clusters containing the central octahedron $Ca_{cent}O_6$ and the central CO_3-group, respectively. For investigation of dolomite we used 71-atomic $[Ca_{cent}Ca_4Mg_6C_6O_{54}]^{62-}$, $[Mg_{cent}Mg_4Ca_6C_6O_{54}]^{62-}$ and 49-atomic $[C_{cent}C_6Mg_3Ca_6O_{36}]^{32-}$ clusters corresponding to its structure. The isomorphic substitutions of Ca (Mg) by Mn, Sr, Fe, Mg, Ca-ions have been analyzed as well. The relaxed structure of the clusters with the impurities was determined by the total-energy minimization using the GAMESS software. Using the spatial integrating of the electron density in the clusters the effective charges of atoms have been calculated. Taking into account the peculiarities of spatial distribution of the total and deformation electronic density in the clusters the high covalency within the CO_3-groups has been revealed. The variations of the spectroscopic properties of the Mn impurity ion in calcites and dolomites of the different geneses have been explained due to the variations of settlement values of Mn effective charge, the ionicity degree and Mn-O length in MnO_6 octahedrons.

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SPECTROSCOPIC CHARACTERISATION OF $YAl_3(BO_3)_4$: Gd^{3+} CRYSTALS

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Yttrium aluminium borate is a non-linear optical material with excellent chemical and physical properties. It is a possible self-frequency-doubling UV-VIS laser material when doped with rare earth ions. The aim of this work is to characterise the Gd^{3+} in $YAl_3(BO_3)_4$ single crystals with EPR and optical spectroscopy. $YAl_3(BO_3)_4$ belongs to the double borates having a trigonal structure with space group R32. There are two different boron sites (with C_3 and C_2 point symmetry, respectively), three differently oriented but energetically equivalent Al sites (C_2 symmetry) and only one Y site with D_{3h} symmetry.

0.01 Gd/ $YAl_3(BO_3)_4$ molecule was added to the starting material and the crystal samples were grown from $K_2Mo_3O_{10}$-B_2O_3 flux by High Temperature Top Seeded Solution Method.

The angular variation of EPR spectra of Gd^{3+} was measured in two different planes: around the *c* axes the spectra are isotropic, however, rotating from *c* to *a* crystallographic axis, strong anisotropy is observed. The D_{3h} symmetry of the EPR spectra for Gd^{3+} ions unequivocally means that the dopant ion substitutes for Y. The angular variation data are fit and the spin Hamiltonian parameters are determined.

The optical absorption of Gd^{3+} has three groups of bands in the UV range attributable to $^8S_{7/2} \rightarrow {}^6D$, ^6I and ^6P transitions, respectively. Relatively strong luminescence is observed at 314.4 nm due to $^6P \rightarrow {}^8S_{7/2}$ transition, when excited at the above absorption bands.

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SPECTROSCOPIC STUDY OF CANADA BALSAM USED AS FILLER SUBSTANCE IN EMERALD

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It is a common practice to fill fractures or voids in cut emerald gemstones to enhance their clarity (KIEFERT et al., 1999; NASDALA et al., 2001). A variety of filler substances is used, ranging from volatile and, therefore, easily removable oils (e.g., oil of cedar wood) to glass and durable hydrocarbons (e.g., epoxy resins). After being applied to the stone, fillers undergo an aging process in the course of which they may even decompose. Because solidified fillers or decomposition products may lower a stone's value appreciably, these substances need to be identified prior to the sale. We have studied a suite of cut emerald stones treated with Canada balsam, and commercial Canada balsams. Even though all Raman spectra show somehow similar patterns of bands in the spectral regions of C-C (below 1700 cm^{-1}) and C-H vibrational modes (at around 2900 cm^{-1}), we found notable differences among them (Fig. 1). It is obvious to assume that Canada balsam is not well defined in terms of its composition. Unambiguous identification of Canada balsam in cut stones is even more difficult because of (1) strong Cr^{3+}-related luminescence of emerald, (2) often a strong broad-band luminescence of the balsam, and (3) changed Raman spectra of balsams that have been applied several years ago already.

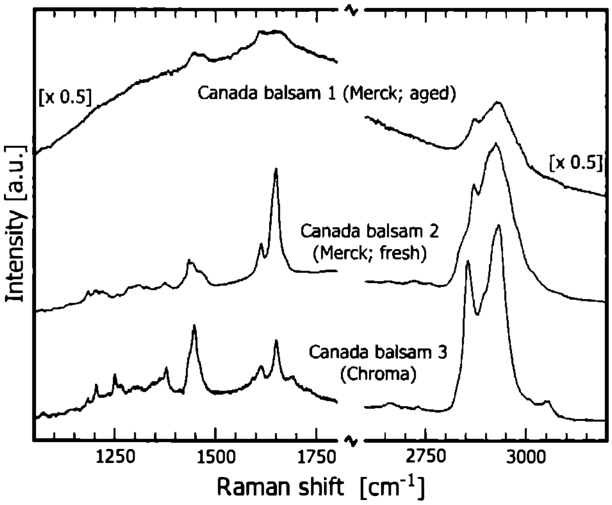

Fig. 1 Three Raman spectra of Canada balsam (stacked). There are already significant differences among spectra of the commercial chemicals (compare 2 and 3). Variations among Raman spectra become even more significant as a result of aging (see the broadening and intensity loss of Raman bands especially in the region below 1700 cm^{-1}). Aging of Canada balsam is often accompanied by a dramatic increase of the background luminescence (compare 1 and 2)

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APPLICATIONS OF MÖSSBAUER SPECTROSCOPY IN MANTLE PETROLOGY

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Since the Earth's mantle is composed predominantly of minerals that are Fe-bearing solid solutions, Mössbauer spectroscopy (MS) is an essential tool for helping to understand many geochemical and petrological processes that occur at depth. The oxygen fugacity (fO_2) plays an important role in many processes since it influences mineral stability, the volatile species, as well as the rheological and transport properties of minerals. The fO_2 can be estimated through chemical equilibria involving the Fe^{3+} and Fe^{2+}-bearing components in mantle minerals, such as spinel and garnet (WOOD et al., 1990). Thus, a primary task for MS is the accurate determination of the Fe^{3+}-contents in such minerals. Extended Voigt-based fitting (LAGAREC & RANCOURT, 1997) yields a better overall fit for spinel compared to a pure Lorenzian line shape model. For garnet, unequal recoil free fractions for Fe^{3+} and Fe^{2+} need to be accounted for (e.g. WOODLAND & ROSS, 1994). Regional variations and depth profiles in mantle fO_2 can be derived from such data (e.g. WOOD et al., 1990; WOODLAND & KOCH, 2003).

Spectroscopic measurement of $Fe^{3+}/\sum Fe$ in coexisting pyroxenes allows a test of redox equilibrium within the mantle assemblage by comparing cpx-based (LUTH & CANIL, 1993) and spinel-based oxybarometers. Fe^{3+}-partitioning between phases can also be assessed, along with the estimation of whole rock Fe_2O_3 contents in mantle samples. This yields a better understanding of the behaviour of Fe^{3+} at high pressures and temperatures.

Many crystal chemical aspects of mantle phases can also be investigated by MS. For example, ordering of Mg and Fe^{2+} on the M1 and M2 sites in pyroxene can be determined (WOODLAND et al., 1997). In mixed valence phases such as garnet, spinel and the spinelloid polymorphs, MS allows investigation of magnetic properties and site occupancies of Fe^{2+} and Fe^{3+}, and provides information complementary to magnetic susceptibility and XRD measurements.

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SPECTROSCOPIC INVESTIGATION OF SOME MINERALS FROM CAVE NO.4 – RUNCULUI HILL (METALIFERI MTS, ROMANIA)

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Trestia-Băita is a metallogenetic region located in the central part of the Metaliferi Mountains (South Eastern Apuseni Mts), characterised by a complex geological setting: Tithonic reefal limestone blocks disposed over an Early Jurassic ophiolitic basement (volcanoclastic basalts). Both limestone and ophiolites are part of the Căpâlnaş – Techereu Nappe (BALINTONI, 1997), affected by the Neogene volcanic activity. The hydrothermal activity associated to the Neogene volcanism resulted in the formation of several sulphide veins, emplaced both within limestone and basalt.

Cave no. 4 from Runcului Hill (D = 127.4 m, H = 10 m) is the largest cave in the respective karst area and consists of several rooms linked by small pits and narrow passages. One of the cave passages connects with a 13 m long and 2 m high mine gallery, with collapsed entrance, which ends in a hydrothermal vein.

The geological complexity of the area complicates the range of cave mineralogy. Fourteen minerals were identified by means of X-ray diffraction. Along with common minerals in limestone caves (calcite, aragonite and gypsum), an interesting range of other minerals were reported, few of them being exotic for cave environment.

IR and Raman spectroscopy have been used to analyse the most interesting minerals: sulphates such as serpierite $Ca(Cu,Zn)_4(OH)_6(SO_4)_2 \cdot 3H_2O$ and barite $BaSO_4$, and carbonates such as smithsonite $ZnCO_3$ and cerussite $PbCO_3$ (the last one occurring together with galena PbS).

One Raman spectrum was recorded from serpierite in the range up to 3700 cm^{-1} The other three minerals were analysed by means of IR spectroscopy, the spectra being obtained in the range of 400-4000 cm^{-1} For each spectrum the wavenumbers, characters and intensities of the bands are reported. The bands were assigned to vibrational modes of different structural groups.

Due to the fact that spectroscopic methods provide information about local structure (as site, symmetry, coordination number, local chemical and crystallographic environment) (PUTNIS, 1992), the aim of this paper is to present an interpretation of IR and Raman spectra recorded for the above-mentioned minerals, in order to give a better crystal chemical characterisation in each case.

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X-RAY DIFFRACTION AND IR-SPECTROSCOPY OF BOTTOM SEDIMENTS IN LAKE HOVSGOL FOR PALEOCLIMATIC RECONSTRUCTIONS

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Lake Hovsgol, on the territory of Mongolia, lies in a region critical for understanding global climate change in central Asia during the late Cenozoic. Biogenic silica is known to serve as a useful climate proxy. Biogenic silica tends to increase in the sediments as a result of elevated diatom productivity in the lake, which is responding to warmer water temperatures, but it does not provide any information about paleoclimatic changes in catchment basin. Clay minerals, in particular, would therefore be more likely to preserve the conditions of hydrolysis that generated them in the weathering profile. We focus on determining whether patterns in the mineralogical composition of the sediments can also be used as a supporting tool for paleoclimatic interpretation.

The series of short cores (up to 1.15 m depth) have been obtained from different parts of this lake during 2001-2002 as a part of the Russian Academy of Sciences' expeditions. The cores show two distinct sedimentary divisions. The upper part of core is dominated by fine-grained silts and the lower part is generally sandier with numerous intervals of graded bedding. The mineral composition of the original samples and their fine granulometric fractions were analysed by X-ray powder diffraction and IR spectroscopy. For X-ray the oriented mounts were prepared by transferring the suspension of bulk sample in distilled water onto a glass slide and drying at room temperature. Then they were solvating for about 24 hours with ethylene-glycol vapor in an evacuated exicator. The measurements were conducted on a DRON-4 automated powder diffractometer system with CuKα radiation, graphite monochromator. Scans were performed from 2° to 35° 2θ with speed of 0.05° 2θ/s. A new method was proposed for modeling X-ray diffraction profiles in order to identify correctly clay minerals and evaluate the amount of each clay mineral. The method is based on the calculation of the interference function of the one-dimensional disordered crystals with finite thickness and using a specially developed optimization procedure. Quantitative estimations of the composition of minerals such as quartz, plagioclase, carbonate and biogenic silica were made by IR. Samples were prepared using the KBr pellet method. The measurements were conducted on a Specord-75 IR spectrometer.

A consistent clay mineral assemblage containing illite, illite-smectite, chlorite, chlorite-smectite, muscovite and kaolinite, characterizes much of the studied sediments. Dominating illite and smectite layers in illite-smectite indicate chemical weathering condition under a warm and humid climate in an interglacial period. Prevalence of muscovite and illite layers in illite-smectite shows the influence of physical weathering in the glacial period. The clay-mineral-based fluctuations are correlated well with the abundance of biogenic silica and provide an independent tool for gaining insight into the paleoclimate of interior continental site.

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INTERPRETATION OF IR SPECTRA OF MIXED-LAYER ILLITE-SMECTITES AND ILLITE-TOBELITE-SMECTITES IN THE REGION OF OH-STRETCHING VIBRATIONS

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Illite-smectite (I-S) and illite-tobelite-smectite (I-T-S) samples of various compositions were studied by infrared (IR) spectroscopy. A special sample preparation technique was used to eliminate the contribution of molecular water. The OH-stretching regions of the spectra were decomposed and curve-fitted, and the individual OH stretching bands were assigned to all the possible types of OH-bonded cation pairs that involve Al, Mg and Fe. The integrated optical densities of the OH bands were assumed to be proportional to the contents of the specific types of OH-linked cation pairs with the absorption coefficients being the same for all individual OH bands. Good agreement between the samples' octahedral cation compositions calculated from the IR data and those given by chemical analysis was obtained for a representative collection of samples in terms of a unique set of individual OH band positions that vary within narrow wavenumber intervals. This has allowed minimizing the ambiguity in spectra decomposition imposed by the poor resolution of smectite spectra and confirmed the validity of the resulting band identification.

For I-S and I-T-S with relatively low proportions of expandable layers (up to 25%) and high total amount of fixed interlayer K and NH_4, the OH stretching bands attributions found by BESSON & DRITS (1997) for dioctahedral micas was found relevant. For samples having higher proportions of expandable layers, the bands associated with specific OH bonded cation pairs may tend to be shifted to greater wavenumbers with respect to the corresponding bands in micas. In addition to OH bands that refer to the smectite structure, AlOHAl and AlOHFe bands of the pyrophyllite structural fragments were identified.

Unambiguous interpretation of the OH stretching vibrations was found to be possible only for I-S and I-T-S samples with known chemical compositions, so that IR data cannot be used for quantitative determination of octahedral cation composition of mixtures of dioctahedral 2:1 phyllosilicates. In the case of monomineral samples with known chemical compositions, IR data can provide information on the short-range order/disorder in the distribution of octahedral cations along cation-OH-cation directions. This information can be employed, in combination with the data of other spectroscopic and diffraction techniques, in the analysis of two dimensional octahedral cation distribution.

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