

EUG XI



Symposium PCM8

Transformation Processes in Minerals

Convenors

Michael Carpenter

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PCM8 Transformation Processes in Minerals

Tuesday PM Session

PCM8 : TUpm25 : G6 Domain Walls in Ferroelastic Minerals

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Plamier-type crystals are ideal candidates for detailed studies on defect-induced renormalization phenomena and patterns of ferroelastic walls. In chemically diluted samples the long-ranging ferroelastic field interacts with the strain-induced defect-field. Because of symmetry conditions the resulting order parameter coupling is biquadratic. The structure of twin domain walls is described in the bulk and at the crystal surface. Diffraction techniques using synchrotron radiation have been applied to study mesoscopic structures, such as densely packed parallel twin domains for the description of their inner structure. AFM techniques allow to identify complex wall structures and spectroscopic methods like Raman and IR techniques yield signals stemming from the order parameter profile of the inner wall structure. Hard mode techniques are applied to study the influence of ferroic patterns on the scattered light.

Financial support is acknowledged by the DFG and the BMBF (05 SM8 GUA9).

Bismayer U, Mathes D, Bosbach D, Putnis A, Van Tendeloo G, Novak J & Salje EKH, *Mineralogical Magazine*, **64**, 233-239, (2000).

Bismayer U, *Reviews in Mineralogy and Geochemistry, MSA*, **39**, 265-283, (2000).

PCM8 : TUpm26 : G6 Role of Internal Pressure at Ferroelastic Phase Transition

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We present a model of the proper ferroelastic phase transition (FPTs), in which the internal pressure is introduced as driving force. As an example, which illustrates this model, we have used the proper monoclinic-triclinic phase transition in Sr-anorthite ($(\text{Sr,Ca})\text{Al}_2\text{Si}_2\text{O}_8$) induced by Ca and Sr cation exchange. A correct physical description of the FPT requires a consideration both of the atom shifts and the forces which cause them. The introduced internal pressure explains the common mechanism of the effect of cation composition of Ca-Sr, Al-Si ordering, and temperature variations on the phase transition. As indicated, the replacement of Sr cations in the lattice cavities by Ca cations of smaller ionic radius causes compression of the lattice around these small Ca cations. This local compression is equivalent to the effect of the internal pressure, increasing as Ca concentration increases. The influence of Al-Si order on the phase transition can be similarly considered. Since atoms of Al and Si also differ in size and occupy improper positions at disordering, an additional internal pressure of the disordered structure occurs. As a result, the phase transition point is linearly dependent on the concentration of disordered Al-Si cations. A temperature rise causes the lattice widening, which is equivalent to the influence of the negative internal pressure, linearly changing with temperature. To conclude, it should be said that the analytical expressions, describing the proper FPT with the internal pressure as the driving force of the transition, have been obtained. Essentially new as compared to the existing theory is the use of the symmetric along with the asymmetric strain components as order parameters in the Gibbs potential. It has been also found that the mechanism causing the occurrence of the soft acoustic mode is the linear quadratic interaction of the symmetric and the asymmetric components of the strain tensor which was earlier neglected. In addition, the introduction of the internal pressure has allowed us to visualize the common micromechanism of the effect of cation composition Ca-Sr, Al-Si ordering, and temperature on the phase transition.

Carpenter MA, Salje EKH, *Eur. J. Mineral.*, **10**, 693-812, (1998).

PCM8 : TUpm27 : G6 Critical Elasticity and Internal Friction of BaTiO₃ Perovskite

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The elastic shear modulus of barium titanate perovskite has been measured by dynamical mechanical analysis through the cubic - tetragonal phase transition. This zone-centre improper ferroelastic phase transition is marked by a sharp drop in the elastic modulus at 388 K. Elastic softening above T_c on cooling towards the transition is related to fluctuations which lead to softening of a set of phonon branches. The temperature-dependence of the elastic modulus in this regime is an indicator of the dispersion and anisotropy of this softening. The critical exponent for this behaviour that we measure most closely corresponds to that expected for isotropic strong dispersion of three branches which all soften by coupling to the driving soft mode. The mechanical loss below T_c , due to frictional losses associated with domain wall motion, is revealed in the temperature-dependent behaviour of $\tan \delta$. Above T_c , this value is zero, confirming the absence of domain walls. At T_c it rises sharply, with the domain wall density being a maximum. On continued cooling the domain wall density decreases, as does $\tan \delta$. The frequency and load-dependent nature of the frictional losses has been examined in a matrix of temperature-sweep measurements using these parameters as variables. Dynamical mechanical analysis is shown to be an extremely useful tool for the study of domain wall movement below elastic phase transitions, as well as identifying the critical behaviour in the fluctuation-dominated regime above T_c .

PCM8 : TUpm28 : G6 Strain Analysis of Phase Transitions in Ca₂Sr-Titanate Perovskites

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A single Landau free energy expansion has been developed to describe phase transitions from cubic perovskites to tetragonal and orthorhombic superstructures. This expansion permits relationships between symmetry-adapted forms of the spontaneous strain and individual order parameter components to be predicted. Data from the literature for Ca₂Sr-titanate perovskites have been analysed in the light of these predictions. Shear strains for I4/mcm, Pnma and Cmcn structures tend to conform to the predicted pattern. The cubic to I4/mcm transition has nearly tricritical character as a function of temperature in calcium titanate and more nearly second order character as a function of composition at the Sr-rich end of the solid solution. Coupling with the volume strain appears to be both temperature and composition dependent, however, which may be a general feature of phase transitions in perovskites. Renormalisation of fourth order terms by changing the volume coupling coefficients could be responsible for the unusual order parameter evolution shown by calcium titanate and for changes in thermodynamic character of the phase transitions as a function of composition. The pattern of strain variations also correlates closely with patterns of variations in heat capacity from the literature, allowing a revised form of subsolidus phase diagram to be suggested for the Ca₂Sr-titanate solid solution above room temperature.

PCM8 : TUpm29 : G6 Hard Mode Infrared Spectroscopy of Perovskites along the Join CaTiO₃-SrTiO₃

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The analysis of $(\text{Ca}_{1-x}\text{Sr}_x)\text{TiO}_3$ perovskite solid solutions has attracted considerable interest over the last decades. The results of these studies (see for example: Kennedy et al., 1999, Qin et al., 2000) showed that several phases existed across the solid solution. The Sr end member is cubic with space group Pm3m, and the Ca end member has an orthorhombic structure at room temperature. It is known that a composition with $x_{\text{Sr}} > 0.92$ is tetragonal with space group symmetry I4/mcm. In a recent study by Ball et al. (1998) it was proposed that an intermediate, orthorhombic phase with Bmmb symmetry should exist between the Ca-end member and the tetragonal I4/mcm phase. An analysis of the spontaneous strains associated with the observed transitions (Carpenter et al., 2001) showed that this intermediate phase has a pseudo-cubic, distorted structure.

Powder Infrared experiments were performed to reveal the response of different parts of the structure on a local scale to changes in composition. The spectroscopic data were analysed using the autocorrelation method.

It is shown that, in spite of the spectra showing the typical broad features of perovskites, changes in line width and peak position can be distinguished which indeed represent features that correlate with the results of the strain analysis.

Ball CJ, Begg BD, Cookson DJ, Thorogood GJ, Vance ER, *J. Solid State Chem.*, **139**, 238-247, (1998).

Kennedy BJ, Howard CJ, Chakoumakos BC, *J. Phys. Cond. Matter*, **11**, 1479-1488, (1999).

Qin S, Becerro AI, Seifert F, Gottsmann J, Jiang J, *J. Mat. Chem.*, **10**, 1-8, (2000).

Carpenter MA, Becerro AI, Seifert F, *Am. Min.*, (2001).

PCM8 : TUpm32 : G6 Oxygen-Deficient Perovskite Phase in the System CaSiO₃-CaFeO_{2.5} at Transition Zone Conditions

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Experiments indicate that the lower mantle consists predominantly of Mg-rich silicate perovskite, Ca-rich silicate perovskite and (Mg,Fe)O ferropericlaase. The physical and chemical properties of silicate perovskite can be influenced by the substitution of trivalent cations in the crystal structure through a defect mechanism (replacement of 2Si^{4+} by 2R^{3+} and one oxygen vacancy). Previous studies have already shown significant changes in the elastic and transport properties of Mg-rich silicate perovskite upon substitution of minor amounts of Fe^{3+} and Al^{3+} , which have significant implications for the interpretation of geophysical data. Studies of the analogue system $\text{Ca}(\text{Ti}, \text{Fe}^{3+})\text{O}_{3-x}$ suggest the possibility that a similar defect mechanism may occur in lower mantle Ca-rich silicate perovskite. In this study we focus our attention on the substitution of Fe^{3+} in CaSiO_3 perovskite.

Initial experiments were conducted along the join CaSiO_3 - $\text{CaFeO}_{2.5}$. Powdered mixed oxides were loaded into a Re capsule and run at 16 GPa and 1600°C using a multi-anvil press. Run products were examined using optical microscopy, X-ray diffraction, Mössbauer spectroscopy, the electron microprobe, transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) at the Ca L_{2,3}, O K, Si L_{2,3}, Si K and Fe L_{2,3} edges. In several experiments we obtained a perovskite phase with composition approximately $\text{CaFe}_{0.8}\text{Si}_{1.0}\text{O}_{2.8}$, where all iron appears to be trivalent. Iron occurs predominantly in octahedral co-ordination, and there are indications from EELS that Si occurs in a mixture of co-ordinations. High resolution TEM images show a strong periodicity of 2.17 nm, possibly related to ordering of oxygen defects, and bright field images show twinning on a scale of approximately 500 nm.

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This new phase is related to the rhombohedral perovskite phase $\text{Ca}_2\text{AlSiO}_5$, reported by Fitz Gerald and Ringwood (1991), but differs in detail by its Si/R³⁺ ratio and a doubled c-repeat (2.17 versus 1.07 nm).

These results confirm that large amounts of Fe^{3+} can be incorporated into CaSiO_3 perovskite through a defect mechanism resulting in oxygen vacancies. Our results suggest that lower mantle Ca-rich silicate perovskite incorporates iron almost exclusively in the trivalent form, and could provide a sink for Fe^{3+} , depending on the local chemistry. While the endmember CaSiO_3 perovskite becomes amorphous during decompression, the addition of Fe^{3+} stabilises the phase such that the crystal structure is preserved during quenching and the phase is relatively stable in the electron beam. The stability of the structure allows a detailed study of the oxygen-deficient perovskite, including the degree to which physical and chemical properties are influenced by the oxygen vacancies, with implications for the lower mantle.

Fitz Gerald JD & Ringwood AE, *Phys.Chem.Minerals*, **18**, 40-46, (1991).

PCM8 : TUpm33 : G6 Order Parameters Associated with the Displacive Phase Transition in Cummingtonite

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Mg/Fe cummingtonites are naturally occurring minerals belonging to the amphibole group. The structure of cummingtonite consists of double chains of SiO_4 tetrahedra parallel to the c-axis and linked laterally by Mg and Fe cations which occupy four crystallographically distinct sites M1, M2, M3 and M4. In Mg-rich cummingtonites a displacive phase transition from $P2_1/m$ to $C2/m$ occurs with increasing temperature. The difference between low and high-symmetry phases can be described in terms of the degree of distortion of the tetrahedral chains and a consequent change in the coordination of the cations at the M4 sites. In order to characterise the phase transition at both macroscopic and microscopic scales, two different techniques have been used.

Neutron powder diffraction data were collected for a sample with 36 mol% Fe in the temperature range of 4-580K. This interval includes the phase transition itself and order parameter saturation effects at low temperatures. Spontaneous strains and evolution of the long-range order parameter associated with the phase transition were obtained from the refined lattice parameters.

Mössbauer spectra of a cummingtonite with 37 mol% Fe were collected in the temperature range between 100 and 550 K. The hyperfine parameters, which can be determined experimentally from the line positions in a Mössbauer spectrum, provide information on the local atomic environment around the nuclei. The quadrupole splitting (QS) of the M4 doublet shows a change in slope at the critical temperature of the $P2_1/m$ to $C2/m$ phase transition. Assuming that the valence contribution to the QS is similar for both $P2_1/m$ and $C2/m$ phases, the most likely effect to cause the observed variation is a change in the lattice contribution related to the distortion of the M4 sites. The difference between the QS data of the low-symmetry phase and the values obtained at the same temperatures by extrapolating the QS data of the $C2/m$ phase has been used as a measure proportional to the short-range order parameter associated with the phase transition.

PCM8 : TUpm34 : G6 The MgSiO_3 Orthoenstatite-Clinoenstatite Transitions at High Pressures and Temperatures Determined by Raman-Spectroscopy on Quenched Samples

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Mg-Fe pyroxenes form 3 different polymorphs at the pressure - temperature conditions prevailing in the earth upper mantle: the orthoenstatite phase (Oen), the low-clinoenstatite phase (LCen) and the high-clinoenstatite phase (HCen). The HCen phase, stable at pressures in excess of 6 GPa, is non-quakeable and inverts to the LCen phase during pressure release from high-P-T conditions. To date the phase boundaries limiting the stability fields of different MgSiO_3 phases have been derived from X-ray diffraction studies on quenched samples from high-P-T experiments or determined by in-situ X-ray diffraction experiments at ambient temperature.

Raman-spectroscopy performed on enstatite $\text{Mg}(\text{Fe})\text{SiO}_3$ pyroxenes from high-pressure experiments on 'peridotite-like' hydrous mantle compositions reveals that there are subtle but significant differences between the spectra of Oen and samples quenched from within the stability field of HCen. The most prominent differences are: Additional peaks at 369 and 431 cm^{-1} in the Cen-spectrum never observed in the Oen spectrum and a systematic shift of the peak at 236 cm^{-1} in the Oen to 243 cm^{-1} in the Cen. However, no distinction can be made between samples quenched from the HCen and LCen stability fields, consistent with the fact that the HCen-phase is non-quakeable and the pyroxene phase observed in the run products is LCen as verified by powder X-ray diffraction.

A large number of experiments performed in our laboratory in the pressure - temperature range 1.2-14 GPa and 750-1900K have been used to constrain the $\text{Mg}(\text{Fe})\text{SiO}_3$ phase diagram. Pyroxene compositions cover the range from pure MgSiO_3 to $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$ with minor amounts of Al, Ca, Na, Cr. The results are generally consistent with previous determinations from X-ray studies and tightly constrain the HCen - Oen phase boundary that can be expressed by the equation P (GPa) = $0.00454 T$ (K) + 1.673. The slope differs slightly from the equation proposed by Pacalo and Gasparik (1990) for MgSiO_3 , but is perfectly parallel to the FeSiO_3 system determined by Woodland and Angel (1997). The LCen - Oen boundary is not as well constrained, but the data are sufficient to locate the invariant point where all three MgSiO_3 phases coexist at 6.6 GPa and 1100 K.

Pacalo REG & Gasparik T, *J. Geophys. Res.*, **95**, 15853-15858, (1990).

Woodland AB & Angel RJ, *Eur. J. Mineral.*, **9**, 245-254, (1997).

PCM8 : TUpm35 : G6 HT-Study of Displacive Phase Transition in Pigeonites

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The pigeonite structure is monoclinic $P2_1/c$ at room temperature and contains two symmetry independent chains which are S- and O-rotated. Cations in octahedral coordination are distributed between two different sites (M1 and M2) and non-convergent ordering takes place, depending on the closure T for Fe^{2+} -Mg intracrystalline exchange. Non-convergent ordering in pigeonites at equilibrium has been recently studied by Pasqual *et al.* (2000), and an intracrystalline geothermometer has been calibrated.

Several previous HT and HP studies (HT: Brown *et al.*, 1972; Smyth, 1974; HP: Arlt *et al.*, 2000) have shown that pigeonite undergoes a structural change $P2_1/c - C2/c$. This

symmetry change is ascribed to a displacive co-elastic phase transition, which involves rotation of tetrahedra in the tetrahedral chains until both become O-rotated and equivalent. This displacive phase transition in clinopyroxenes has been described as being first-order (Smyth, 1974; Arlt *et al.*, 2000) both for high-T and high-P transitions. However, evidence for a non first-order transition has been recently given for Mg-Ca synthetic samples (Tribaudino, 2000). Prewitt *et al.* (1971) suggested a dependence of the transition temperature (T_c) on composition; increase of both Fs and Wo components leads to a lowering of T_c .

We carried out an in situ high temperature single crystal diffraction study on a natural, exsolution-free pigeonite sample with significant Wo content ($\text{Wo}_{10}\text{En}_{70}\text{Fs}_{10}$) previously studied by ex-situ Pasqual *et al.* (2000), in order to re-examine the HT displacive phase transition. We followed the continuous transition by performing data collection at 650°, 750°, 850° and 950°C in the 2θ range 4.5-55° and refinement of the structure. Our results show that, for this sample, the displacive phase transition may be better described in terms of a 246 Landau expansion. Several important geometric parameters of tetrahedra and octahedra show a continuous variation with increasing temperature. The geometry of the structure at 950°C nearly corresponds to a $C2/c$ structure.

We annealed the crystal in situ for long enough to reach equilibrium for the intracrystalline ordering at the various temperatures. Measured KD values at each T agree with the equation of Pasqual *et al.* (2000) for the same sample. Our results show a direct linear correlation between the non-convergent intracrystalline order parameter (Q_{00}) and the displacive order parameter (Q, measured as the intensity ratio between several $h + k = 2n + 1$ reflections and $h + k = 2n$ reflections), giving evidence of coupling between the two order parameters.

Arlt T, Kunz M, Stolz J, Ambruster T. & Angel R, *Contrib. Mineral. Petrol.*, **138**, 35-45, (2000).

Brown GE, Prewitt CT, Papike JJ & Sueno S, *J. Geophys. Research.*, **77**, 5778-5789, (1972).

Prewitt CT, Brown GE & Papike JJ, *Geochim Cosmochim. Acta Suppl.*, **2**, 59-68, (1971).

Pasqual D, Molin G & Tribaudino M, *Am. Mineral.*, **85**, 953-962, (2000).

Smyth JR, *Am. Mineral.*, **59**, 1069-1082, (1974).

Tribaudino M, *Am. Mineral.*, **85**, 707-715, (2000).

PCM8 : TUpm36 : G6 Nanoquartz vs. Macroquartz: A Study of the α - β Phase Transition

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Nanocrystals, consisting of small crystallites with diameters 1-100 nm, often have novel physical and chemical properties, differing from those of the corresponding bulk materials. Some of these materials undergo phase transformations in the bulk. The question arises now whether these phase transformations also exist in the nanocrystal and if so, to what extent the characteristics of the transition are themselves size dependent. It appears that modifications relate to two physical effects. Firstly, an increase of the surface to volume ratio leads to an increase in surface related relaxation phenomena, which may significantly modify the order parameter profiles of the nanocrystal. The second effect is the implementation of boundary conditions through intergrain contacts.

Besides a large body of theoretical work, little is known about the performance of ceramics built from nanocrystals. In contrast to thin films, it is experimentally more difficult to produce powders with uniform and narrow grain size distribution. In nature, such materials do exist. A typical example is the mineral agate which, in the case of this study, is a compact intergrowth of nanoparticles (between 50-90 nm) of α -quartz. Under elastic 3D-clamping conditions, it is predicted (Pertsev *et al.*, 2000) that the fourth-order term in the free-energy expansion is renormalised in nano-size quartz by the mechanical interaction between each grain and the surrounding nanocrystallites. The first-order character of the transition is thus destroyed and the transition becomes continuous. Three different experimental techniques (differential scanning calorimetry, x-ray diffraction and second-harmonic generation) have been applied to a series of agates in order to evaluate the variation of the character of the transition. The first-order

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character of the α - β transition in micron-size quartz is thus shown to be strongly reduced in nano-size quartz with no significant variation of the transition temperature. The excess entropy of nanoquartz is described in the framework of Landau theory where the renormalisation of the fourth-order term arises from the elastic 3D-clamping. The anomalous increase in the peak width of diffraction maxima at the transition temperature is related to surface relaxation phenomena.

Pertsev NA & Salje EKH, *Phys. Rev. B*, **61**, 902-908, (2000).

PCM8 : TUpm37 : G6 Pressure Induced Phase Transitions in Malayaite $\text{CaSnO}_3\text{SiO}_4$

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Minerals of the ABO_3 type are of potential interest for the optical industry. KTiOPO_4 (KTP) is widely used in optical industry due to its capabilities of frequency doubling. The non-linear optical properties in this material are linked to the out-of-center distortion of the octahedrally coordinated Ti atoms. Titanite, CaTiOSiO_4 , is structurally related to KTP. Its Ti-atoms also show out-of-center distortions but unlike in KTP, the distortion vectors are correlated in an antiparallel way. The mineral malayaite, $\text{CaSnO}_3\text{SiO}_4$, is isostructural to the aristotype of titanite. Both structures are characterized by corner-sharing MO_6 -octahedra (M= Sn,Ti) that form chains along the a-axis. The chains are mutually linked via isolated SiO_4 -tetrahedra. CaO polyhedra form chains parallel [101] within the MO_6 - SiO_4 framework.

Having the d^0 -transition metal Ti of titanite replaced by the main-group element Sn, malayaite does not exhibit any out-of-center distortions. It is thus of interest to compare its P- and T-behaviour with the one of titanite [Kunz et al., 2000] in order to differentiate topological effects from electronic effects. This is essential in order to understand the mechanisms controlling the correlation between out-of-center distortions of octahedrally coordinated d^0 transition metals.

We performed a single crystal high-pressure diffraction study between room pressure and 7.3 GPa in a diamond anvil cell (DAC). This study revealed an interesting pressure behavior for malayaite: At 5 GPa the α and γ angles start to deviate from 90° to 89.1° and 91.1° (7.3 GPa), respectively. Surprisingly, calculations of the principal components for the spontaneous strain indicate a phase transition already at 3 GPa. This indicates the existence of an intermediate phase between 3 and 5 GPa, where we did not observe any violations of the $A2/a$ symmetry. This suggests an isosymmetric phase transition around 3 GPa. Structure refinements of malayaite at 7.3 GPa reveal structural details of the triclinic (P) phase: The Ca polyhedra show the most striking difference between RT and 7.3 GPa. They form chains parallel [101] in the $A2/a$ RT-phase, but polymerize to sheets parallel (11) in the triclinic phase. This involves a shift relative to the octahedral chains, which separates the SnO_6 octahedral chains into two symmetrically distinct chains.

The structural evolution of malayaite under pressure will be shown in detail as well as the equation of state, strain calculations and compressibility of the mineral.

Kunz M, Arlt T & Stolz J, *American Mineralogist*, **85**, 1465-1473., (2000).

PCM8 : TUpm38 : G6 Correlation between Raman Spectra and Structural Units Changes in Zeolites at High Pressure

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To find correlation between changes of structure of aluminosilicates and changes of frequencies of vibrational spectra, Raman spectra of zeolites were recorded and the frequencies and forms of modes were calculated, using the lattice dynamics (LADY program) as well as the cluster modelling.

The high-pressure behavior of natural analcime (Nidym, Siberia), its K- and Rb- forms, as well as natural leucite (Orvieto, Italy), was studied by Raman spectroscopy in the diamond anvil cell up to 5 GPa. Natural analcime exhibited 3 phase transitions at 0.7, 2 and 3.7 GPa, the latter being characterized by strong anomalies in the region of the framework vibrations. Waterless K- and Rb-analcimes show similar high-pressure behavior with single transition in the region of 2.2-2.6 GPa. Leucite exhibits the sharp transition at 2.3 GPa. These transitions are related with the distortions of secondary building units of the framework.

The correlation has been found between the most pressure-dependent O-T-O bending mode near 500 cm^{-1} , located on some four-membered ring, and mean T-O-T angle in the analcime and leucite frameworks. This allows to introduce the model of distorted four-membered ring composed of $(\text{Si,Al})\text{O}_4$ -tetrahedra to interpret the mechanism of observed transitions. The distorted four-membered ring was used as a geometrical model to investigate the pressure-induced changes in the framework vibration modes. Calculations of cluster vibration forms allows to examine the effect of the ring distortions on the O-T-O bending mode. Thus the preliminary results were obtained considering the numerical correlation between structural and spectroscopic parameters changed with pressure.

The empirical correlation between the O-T-O Raman mode split and the tetragonality parameter enables to estimate structural parameters of high-pressure phases of ANA-topology using Raman measurements. This correlation is proved by theoretical modelling with calculation of the modes localized in the structural units.

Tuesday PO Session

PCM8 : TUpo01 : PO Active Acid Sites in Natural Zeolites

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The acid sites in zeolites are being studied intensively in the context of the catalytic properties of these materials. Much attention is given to the protonated synthetic zeolites while the role of the proton centers in determining the properties of natural zeolites still remains unclear. Moreover, until recent years there were not direct evidences on the existence of these sites in natural zeolites. Recently, we developed a NMR approach to in situ precise determination of the proton exchange rate in water molecules sorbed on zeolites which can be applied when the average time between events of H-exchange lies in the range of 0.1-0.0001 seconds (Afanassyev et al., 1999, 2000). It has been shown that the observed proton exchange is due to the interaction of water molecules with the acid sites and hence can be used to detect these sites in the zeolite channels. Using this approach, we studied various natural zeolites as well as their cation-substituted forms. The typical concentration of proton sites is found to be about 0.001 per one Al atom or below. In spite of low concentration, the centers considered may have a pronounced effect on physical and chemical properties of zeolites. For example, they exert primary control over proton transfer through the zeolite structure. Relying on the experiments performed, it was deduced that the active centers are presented by Bronsted acid sites Al-O(H)-Si (hydroxyl groups) and the protonating intrazeolitic water molecules leading to the formation of hydroxonium ions does not take place. For the substances studied, the barrier for proton transfer from acid site to water molecule is found to vary in the range 30-60 kJ/mol. The treatment of the natural sample in weak acid solutions or holding it at elevated temperature leads to the significant increase in the concentration of acid centers. These results allow us to suggest that the data on the active acid sites may tell something about the formation and evolution of zeolites in natural conditions. This work is supported by the Russian Fund for Basic Researches (grant No. 01-05-65414).

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PCM8 : TUpo02 : PO The Al-Si Configuration in Strontium Feldspar Quenched from 1640°C

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A metastable disordered Al-Si configuration was observed by Benna et al. (1995) in strontium feldspar ($\text{SrAl}_2\text{Si}_2\text{O}_8$) crystallized from the melt in very short times (space group: $C2/m$; macroscopic order parameter $Q_{\text{sd}} = 0$). Isothermal annealing of the disordered feldspar caused evolution towards higher Al-Si ordering. The change in space group from $C2/m$ to $I2/c$ with progressive Al-Si ordering can be followed during thermal treatments. This change in space group corresponds to a zone boundary phase transition inducing the appearance of b -type ($h+k = \text{odd}$, $l = \text{odd}$) superstructure reflections, that evolve with the degree of order. The size of b antiphase domains (APD) increases with increasing annealing time. This evolution under non-equilibrium conditions is not so different from that observed in anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) by Carpenter (1991) and allows to investigate the Al-Si configurations that cannot be experimentally achieved at equilibrium. As concerns the highest degree of disorder that can be attained at equilibrium at temperatures near the melting point, it has been shown (Bruno et al., 1976; Angel et al., 1990) that at equilibrium anorthite has a $Q_{\text{sd}} = 0.78$.

In the present work single-crystal X-ray diffraction of ordered $I2/c$ strontium feldspar (SrF) was performed. Subsequent structural refinement of the same crystal, treated at temperatures ($T = 1640^\circ\text{C}$ for 5h) near the

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melting point ($T_{\text{melt}} \sim 1660^\circ\text{C}$) and quenched at room temperature in air (SrFQ), was done. The average T-O bond lengths (\AA), Q_{Si} values and average APD sizes (\AA) are:

SrF: $T_1(0)=1.622$, $T_1(z)=1.734$, $T_2(0)=1.731$,
 $T_2(z)=1.621$. SrFQ: $T_1(0)=1.634$, $T_1(z)=1.728$,
 $T_2(0)=1.720$, $T_2(z)=1.627$.

SrF: $Q_{\text{Si}}=0.82$, $\Sigma \text{Fo}^2(b) / \Sigma \text{Fo}^2(a) = 0.028$, $\delta \sim 2000$. SrFQ:
 $Q_{\text{Si}}=0.69$, $\Sigma \text{Fo}^2(b) / \Sigma \text{Fo}^2(a) = 0.022$, $\delta > 5000$.

In SrFQ the significant decrease of Q_{Si} and the increase in the APD sizes, caused by thermal treatment near the melting point, suggest that the modifications observed in the Al-Si configuration are due to intradomain disorder. The hypothesis that the premelting effects observed in anorthite are related to disorder almost complete near the melting point (Courtial et al., 2000) does not agree with the dimensions of the b APDs (about 3300 \AA) observed by Carpenter (1992) and with the coarsening of the APDs observed in SrFQ in this work.

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PCMS : TUp03 : PO A TEM Study of Annealed Synthetic Mg-Cordierite

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Magnesian cordierite is stable below 1465°C at atmospheric pressure (Schreyer and Schairer, 1961). The high symmetry form ($P6/mcc$) is believed to be stable between ~1465 and ~1450°C, and the low symmetry form ($C2cm$) is believed to be stable below ~1450°C (Schreyer and Schairer, 1961; Smart and Glasser, 1977). Because of the closeness of the hexagonal/orthorhombic transition temperature to the melting point, one might speculate that melting and Al/Si order/disorder effects could be related. The purpose of our study was to search for premelting textures and related order disorder textures in anhydrous magnesian cordierite annealed in the temperature interval ~1440-1470°C. In natural samples with compositions close to the Mg-cordierite end-member which had been annealed at high temperatures, we observed a pervasive texture of submicroscopic glassy needles parallel to [001]. These features were detected in samples annealed at temperatures as low as 1310°C without any sign of transformation towards high-cordierite. Significant amounts of Na contained in these samples could explain both the lowering of the melting point and the strong crystallographic control of these defects, as Na is mobile in the direction of structural channels parallel to [001]. No glassy needles parallel to [001] have been found in synthetic samples after annealing at temperatures up to 1460°C. Nor was evidence for disordering, such as a tweed microstructure, detected either. The synthetic crystals all displayed lamellar or cross-hatched twinning typical of synthetic orthorhombic cordierite. Significant amounts of partial melting were present in all the synthetic samples starting from annealing temperatures as low as 1400°C, however. The melting products are cordierite, mullite and liquid (glass after quenching). The composition of the liquid, when compared with experimental work in the MgO-SiO₂-Al₂O₃ system of Schreyer & Schairer (1961), deviates from the equilibrium composition, and depends on annealing temperature and the size of the melt pools. At lower temperatures it is much richer in SiO₂, at higher temperatures it becomes comparatively richer in MgO. Only in the larger melt pools of a sample annealed at 1460°C did the glass composition

match with the expected composition. Embedded within these larger pools, euhedral grains of cordierite have been observed optically and are probably the source of diffraction maxima consistent with hexagonal symmetry in X-ray powder diffraction patterns. It is tentatively concluded that premelting occurs in Mg-cordierite at temperatures well below its accepted melting point. The change in stoichiometry of the residual cordierite could then be responsible for changes in X-ray indicators of small amounts of Al/Si disorder as the melting point is approached. We have not been able to find any evidence for a stability field of stoichiometric Mg-cordierite with hexagonal symmetry.

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PCMS : TUp04 : PO X-Ray Single-Crystal Study of Spinel: In Situ Heating

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A microfurnace allowing operation with a crystal directly glued to a small rounded thermocouple mounted on a modified goniometer head was installed on a Siemens AEDII 4-circle single-crystal diffractometer (Molin et al., 2000). Researches on synthetic and natural spinels of various compositions, both stoichiometric and defect, were initiated, with the aim of studying thermal expansion and order-disorder transformations by X-ray diffraction. Our major interest is essentially devoted to natural crystals because their thermal history differs significantly from that of synthetic ones. During in situ experiments, single sets of 87 non-equivalent reflections were collected, cleared from the effect of the microfurnace shield, and used for structure refinements without chemical constraints. Initial results are as follows: 1) A flux-grown spinel (MgAl₂O₄), synthesized at 1200°C and slowly cooled down to 800°C (Andreozzi, 1999) underwent several back-and-forth runs at temperatures from room temperature to 400°C, in 100°C steps. It was observed that the oxygen coordinate remained constant, while the cell edge changed proportionally with temperature, both on heating and cooling but following the same path. This indicates that, in this temperature range, thermal expansion is reversible, since intracrystalline exchanges did not occur. This allowed us to determine the thermal expansion coefficient for this crystal. 2) A natural highly ordered sample from a regional metamorphic rock with major cations Al(1.95) Mg(0.99) Cr(0.05) for four oxygens, initially disordered at 1000°C, was reordered in runs of increasing duration with decreasing temperature, in 100°C steps, down to room temperature. It was observed that the oxygen coordinate steadily increased with decreasing temperature at high temperatures (600-1000°C) but became stable from 600°C down to room temperature, assuming a value (about 0.2625) much lower than the original one (0.26336(8)). Instead, the cell edge decreased continuously with decreasing temperature, also reaching a value smaller than the original one. In general, it was observed that the evolution of the spinel structural state on cooling and heating between the same temperatures does not follow the same path. Thus, in the 600-1000°C range, only partially reversible order-disorder processes occur.

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PCMS : TUp05 : PO Experimental Deformation of Omphacite outside its Stability Field

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In order to better constrain the rheological behaviour of eclogites we performed creep experiments on polycrystals of omphacite outside its stability field. Deformation experiments were realized in a dead load apparatus for a duration

of months at creep rates ranging from 10⁻⁸ to 10⁻⁹ s⁻¹ under controlled oxygen partial pressure at temperatures between 850°C and 950°C and with an axial compressive deviatoric stresses (σ) between 150 and 300 MPa. Synthetic iron-free omphacite glass (Jd50-Di50) was sintered from elementary oxides mixed in adequate proportions and melted in a High Frequency furnace. The glass was subsequently crushed and then cold pressed at 300 MPa to form 4-mm diameter cylinders. The cylinders were enclosed into a soft iron jacket and annealed in a piston-cylinder at 1000°C and 2 GPa for about 140 hours. After opening the iron jacket, samples were recovered free of crack, and rectangular blocks of 2x2x5 mm³ were cut with a diamond saw. X-ray and electron microprobe analyses prove these specimens to be homogeneous omphacite. The grain size of the recrystallized glass is ~5 μm as observed under optical microscope (prior and after deformation runs). Characterization of microstructures and initial and final grain sizes by electron microscopy is under way. Despite the fact that omphacite is a high pressure phase, our deformation experiments performed at room pressure show that destabilization of our samples was absent in many of our runs (1 run = 1 set of imposed parameters T, σ , pO₂), or weak for T~950°C (slow kinetics). In the narrow T domain investigated (850°C-950°C), we obtain the preliminary result: $\epsilon = A \cdot \sigma^n \exp(-E/RT)$ with $E = 450$ kJ/mol. The stress exponent is around 2 but with large uncertainty due to a narrow stress range.

PCMS : TUp06 : PO Study of the Possible Pentacoordination of Si in the High-Pressure Phase CaAl₂Si₂O₁₁

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A new phase of composition CaAl₂Si₂O₁₁ (named CAS phase) was observed amongst the transformation products of CaAl₂Si₂O₈ (anorthite composition) at 14 GPa and 1,500°C (Gautron et al., 1996) and in a continental crust composition equilibrated at (P,T) conditions of the Transition Zone (Irifune et al., 1994). The structure of this phase was refined by single crystal X-ray diffraction: the unit cell is hexagonal and the structure-type is that of the hexagonal barium ferrites with the space group P6₃/mmc (Gautron et al., 1999). This structure presents an original five-coordinated trigonal bipyramidal site which consists in two face-sharing tetrahedra. The latter study of quenched crystals showed that Al and/or Si could occupy this site, which could only be considered as a four-fold coordinated site at room conditions. It is very interesting to know if the high-pressure CAS phase presents some five-fold coordinated silicon, since we know that in general silicates are built up with four-fold or six-fold coordinated Si at low and high pressures respectively. Such pentacoordinate silicon is believed to play a central role in many dynamic processes. Two questions remain as to the possibility of a transition from five to four-fold coordination occurring on quenching from room conditions, and as to the distribution of Al and Si in these trigonal bipyramids. This latter question should be answered with a forthcoming Nuclear Magnetic Resonance study performed on crystals of CAS synthesized with Si²⁹. In order to investigate a possible transition between five and four-fold coordination with pressure, we performed X-ray diffraction measurements on a single crystal of the CAS phase loaded into a diamond anvil cell. Up to the maximum pressure achieved (8.175 GPa), there are no discontinuities or detectable changes in slope of the unit-cell parameters with pressure. After a previous study (Gautron et al., 1996) which showed that the stability field for CAS is probably restricted to depths corresponding to the Transition Zone, we expect to observe a change in the slope of the unit-cell parameters at pressures above about 12 GPa. The volume-pressure data can be fitted with a third order Birch-Murnaghan equation of state with parameters: $V_0 = 323.49(2) \text{ \AA}^3$, $K_{0T} = 189.8(1.5) \text{ GPa}$, $K'_{0T} = 6.4(4)$ with $\chi_w^2 = 0.91$ A third order Birch-Murnaghan equation of state was fitted to the a-axis data while a second order Birch-Murnaghan equation of state was fitted to the c-axis data. The refined parameters are: $a_0 = 5.4239(2) \text{ \AA}$, $K_{0T} = 264.4(5) \text{ GPa}$, $K'_{0T} = 8.8(1.5)$, with $\chi_w^2 = 1.2$ $c_0 = 12.6969(3) \text{ \AA}$, $K_{0T} = 121.6(7) \text{ GPa}$, $K'_{0T} = 4$ (fixed), with $\chi_w^2 = 0.5$ The structure is therefore significantly anisotropic: the a-axis is not only more than twice as stiff as the c-axis, but stiffens more rapidly. The bulk modulus of 189.8 GPa is significantly softer than that of Al₂O₃ (~ 255 GPa).

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PCM8 : TUpo07 : PO Supergene Alteration of Primary Ore Assemblages from Low Sulfidation Au-Ag Epithermal Deposits (Pongkor, Indonesia; Nazareno, Peru)

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The textures and mineralogical assemblages of high grade ore samples from the Au-Ag low-sulfidation epithermal deposits of Pongkor (2 Ma; West Java, Indonesia) and Nazareno (10 Ma; Cordillera Shila, South Peru) were studied to investigate processes related to post depositional alteration. Both deposits are characterized by a late primary high-grade base and precious metal stage composed of chalcocopyrite-sphalerite-galena-pyrite-polybasite/pearceite-grey copper-electrum. Primary Ag-bearing phases and base metal sulfides are found to be corroded by acanthite, locally associated with native silver. Acanthite also occurs filling veinlets, in rhythmic alternance with iron oxo-hydroxides replacing pyrite grains as well as combined with barite and covellite. Primary electrum grains with a composition of around $Au_{0.6}Ag_{0.4}$ are partially replaced by Au-Ag sulfide (locally identified as uytendogaardite) and/or by acanthite commonly associated with higher fineness (up to $Au_{0.8}Ag_{0.2}$) secondary electrum wires. None of the observations made conceivably suggest that hydrothermal remobilization gave rise to these destabilization features. On the other hand, the presence of these replacing assemblages in the more surficial levels of the mineralized systems, and the mineralogical evidence of typically associated supergene phases, plead for a supergene origin. Therefore, the existence of these secondary phases must be taken into account in the different models dealing with vertical distribution of mineral species as well as chemical variation in a mineralized body.

PCM8 : TUpo08 : PO Transformation of Calcium Carbonate Minerals in Model Biofilms

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The thin films present on natural aquatic systems are a complex mixture of organic substances like lipids, proteins and polysaccharides and their diagenetic products present in solution, as dissolved and particular organic matter. These biofilms are responsible for important natural processes such as carbonate precipitation in the ocean. Research in this area is based upon the premise of surface activity of anionic functional groups of the macromolecules. One strategy for creating functionalized interfaces for controlled $CaCO_3$ -crystallization are Langmuir films of lipids at the air/water interface (Heywood & Mann, 1994). They provide well defined interfaces of known charge density and head group spacing. In biology there are many examples for the transformation of amorphous calcium carbonate to calcite or aragonite as well as vaterite to aragonite. Amorphous phases in biology can thus be stabilized and then transformed rapidly into crystalline phases (Lowenstam & Weiner, 1989; Aizenberg et al., 1996). However, the mechanisms controlling the transformation are still unknown. The focus of our interest is the site where nucleation starts as well as the time dependence of the transformation and crystallization processes. Crystal nucleation and growth under Langmuir monolayers has been characterized using Brewster angle microscopy (BAM). We prepared monolayers from lipids which are also present in natural biofilms. These films are formed on $CaCO_3$ subphases to test the influence of the lipid headgroups on the different crystallization processes.

In a first step to achieve a better understanding of these processes we have investigated the crystallization of $CaCO_3$ underneath pure and mixed monolayers of stearic acid (C18) and methyl stearate (SME) by varying the ratio of neutral (SME) to charged (C18) headgroups in the

monolayers. The results of the BAM studies demonstrate a spontaneous crystallization of calcite on the pure C18 monofilm on the $CaCO_3$ -subphase. In contrast to the pure monofilm, the crystallization underneath the mixed films is delayed and the crystallization products are formed in well defined crystal phases, as calcite or aragonite, depending on the ratio of the components. This may be attributed to a better lattice geometry in the mixed films, which optimizes the crystal nucleation conditions. In contrast, preliminary results of the same monofilms prepared on a subphase comprised of $CaCO_3$ and a polysaccharide (x-carrageenan) demonstrated a delayed crystallization; however in this case, crystallization was always preceded by the presence of an amorphous phase.

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PCM8 : TUpo09 : PO Ixiolite Exsolution in Nb-Rutile from the Deposit Greenbushes (Australia)

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Presently, there is a growing demand for niobium and tantalum in the industrial world. These elements form minerals which occur in nature either as individual grains or as inclusions in host minerals such as rutile or cassiterite. The object of study was a heavy-mineral concentrate from the pegmatite deposit Greenbushes (Australia). It consists mostly of cassiterite, among which a 1 mm grain of rutile was found. The grain was studied by reflection microscopy, electron microprobe (EDS), single-crystal X-ray diffraction (the precession method) and transmission electron microscopy (TEM). In reflected light, dark grey lamellae (~ 5 x 50 µm in size) in light grey rutile are observed. The chemical composition of host rutile and the lamellae was determined on an electron microprobe: host - rutile (wt.%): $FeO_{0.10}$, $MnO_{0.04}$, $TiO_2_{51.13}$, $CaO_{0.01}$, $SnO_2_{0.37}$, $Ta_2O_5_{17.43}$, $WO_3_{2.03}$, $Nb_2O_5_{18.87}$, $Na_2O_{0.09}$ lamellae - ixiolite (wt.%): $FeO_{0.16}$, $MnO_{0.16}$, $MnO_{0.16}$, $TiO_2_{4.30}$, $CaO_{0.02}$, $SnO_2_{0.35}$, $Ta_2O_5_{16.88}$, $WO_3_{5.73}$, $Nb_2O_5_{54.41}$, $Na_2O_{0.00}$ These analyses are representative compositions based on about a dozen analyses. Points representing the chemical composition of rutile and ixiolite in the triangular diagram Ti - (Fe+Mn) - (Nb+Ta) plot on a line that passes through the Ti-apex of the triangle. The possibility that the lamellae represent ixiolite exsolved from an original rutile-like phase is further supported by single-crystal X-ray diffraction which permits the determination of ixiolite's structural orientation within the host phase. The ixiolite lamellae are exsolved along all planes of $\{101\}$ of rutile so that the reciprocal axis c_{ix}^* of each individual of ixiolite is parallel to the rutile directions $[101]^*$, $[011]^*$, $[-101]^*$, $[0-11]^*$, respectively. The ixiolite a_{ix}^* axis is parallel to the a_r^* axis of rutile. The direction of axis b_{ix}^* is not parallel to any rational reciprocal direction of rutile. This may be the first documented case when mutual crystallographic orientation between host rutile and ixiolite exsolutions has been determined. The grain apparently represents a low-temperature exsolution assemblage that resulted by a drop of temperature (and/or pressure) from a phase primarily formed in the deposit. According to the volume ratio of rutile to ixiolite (3:1) the probable bulk composition of the primary phase is (at.%): $Ti_{0.52}(Nb+Ta)_{0.30}(Fe+Mn)_{0.18}$.

PCM8 : TUpo10 : PO X-Ray Investigation of the Structural Transformation in Viscous and Solid Hydrocarbons

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No text submitted.

PCM8 : TUpo11 : PO Thermal Stability of NH_4 -Natrolite

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Natrolite, a narrow-pore zeolite, may be regarded as a model object to study the thermal behavior of ammonium in natural framework aluminosilicates. Natrolite has one of the most aluminum-rich frameworks among natural zeolites and appears to be unstable in H-form. To elucidate the mechanism of thermal decomposition of NH_4 -natrolite and to estimate the influence of NH_4^+ -ions on its thermal stability the ammonium-exchanged natural natrolite was studied by TG, X-ray diffraction, IR spectroscopy, microprobe analysis and gas chromatography at 25-750°C.

The DTG curve of NH_4 -natrolite contains a strong peak at 470°C of 11.6% weight loss, which is related with a sharp amorphization observed at calcination in air at 400-500°C and the decomposition of NH_4^+ -ions fixed by IR spectroscopy at calcination in vacuum at 300-400°C. At 400°C no bands occur in the region of stretching vibrations of hydroxyl groups in the IR spectrum. Thus the decomposition of NH_4 -natrolite proceeds in a one step including dissociation of ammonium ions, the formation and simultaneous removal of water - dehydroxylation, which is confirmed by gas chromatography.

Microprobe analysis shows the presence of about 3 wt.% of nitrogen (about one third of the initial amount) in the samples calcined up to 750°C in non-vacuum conditions. At calcination in vacuum at 400-550°C several bands of ammonia bonded to Lewis sites 1336, 1622, 3330 cm^{-1} (Yin et al., 1997) are observed in IR spectrum. This is probably due to the high aluminum content and intensive dehydroxylation of the framework, resulting in formation of large number of Lewis sites. These sites are known to form stable complexes with ammonia (Corma, 1995). Narrow channels of the natrolite framework apparently prevent fast diffusion of ammonia formed at dissociation of NH_4^+ -ions. The interaction between ammonia and Lewis sites seems to be the intermediate step in fixing of a part of nitrogen in destroyed sample. As IR analysis shows no any nitrogen-containing complexes at 750°C (in vacuum), we may assume that ambient conditions play an important role in diffusion of ammonia throughout the natrolite framework.

Thus the thermal stability of NH_4 -natrolite is fully determined by stability of NH_4^+ -ions, as their decomposition leads to the full amorphization of the structure. The one-step decomposition includes the dissociation of ammonium ions and dehydroxylation. Structural and chemical peculiarities of natrolite cause an active interaction between the product of dissociation of NH_4^+ -ions, ammonia, with Lewis sites. This may be regarded as the main reason for the fixing of a considerable part of nitrogen in destroyed sample after calcination under non-vacuum conditions. Further investigation will be made to clarify the chemical form of nitrogen present in destroyed sample after calcination of NH_4 -natrolite.

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PCM8 : TUpo12 : PO Leverage Analysis of XRD Data from Pigeonite and Orthopyroxene

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Studies of the kinetic and thermodynamic aspects of the Fe-Mg intracrystalline ordering processes in orthopyroxene [*Pbc*; (Mg,Fe) $_2$ Si $_2$ O $_6$] and pigeonite [*P2₁/c-C2/c*; (Mg,Fe,Ca $_{0.2}$)Si $_2$ O $_6$] require an accurate determination of the site occupancies. Leverage analysis proved to be very useful in suggesting the most convenient strategy for data-collection and structure refinement in garnet, amphibole

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and olivine (Merli *et al.*, 1999, 2000). This statistical approach, which allows to know the influence of each reflection on the estimate of each refined variable, was applied to the structure refinement of orthopyroxene and pigeonite in order to achieve the best results in terms of atomic positions and site scattering. Even if symmetry is different, leverage patterns are very similar for both pyroxenes. The role of certain groups of reflections in constraining the value of some crucial variables was pointed out. The incorrect intensity measurement of even a single low-medium θ reflection appeared to be responsible for the wrong assignment of the degree of order. Another significant result is that the leverage of reflections on atomic positions is not correlated with that on site scattering at the M1 and M2 sites. This implies that site-occupancy assignments involving refined site-scattering and mean bond-lengths are not biased by internal correlations. Pigeonite shows a displacive phase transition at high temperature: the two tetrahedral chains become equivalent and the space group changes from $P2_1/c$ to $C2/c$. Application of leverage analysis to in situ XRD high temperature data (from 650° C to 950° C) of a pigeonite crystal with composition $Wo_{10}En_{77}Fs_{13}$ showed that $h+k = (2n+1)$ reflections have very low influence on the site scattering determination at M1 and M2. Nevertheless, this group of reflections has a great influence on determining the atomic positions of M1, M2, O3A and O3B. This influence increases with temperature even if the intensity of these reflections becomes very low. Therefore an accurate measurement of weak $h+k = (2n+1)$ reflections, often excluded from the set of "observed data" by I σ I cut-off or by weighting schemes, is crucial to follow the geometrical changes involved in the phase transition.

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PCM8 : Tupo13 : PO Reexamination of the Thermal Expansion of Natural and Synthetic Cordierite between 25 and 800°C

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A reinvestigation of the thermal expansion of cordierite on natural and synthetic material by X-ray powder diffractometry as been conducted between 25-800°C at 1 atm.

In a general way the lattice constants confirm results of previous workers exhibiting small positive thermal expansion for the basis parameters and a negative expansivity for the c-parameter. Detailed analysis of the data reveals, however, a discontinuous behavior of the lattice constants in the temperature region at 250-300°C and 550-600°C.

While the first discontinuity displays a small but distinct volume change, the second one is only indicated by a change in thermal expansion coefficient. The three regions separated by the two discontinuities are characterized by distinctly different trends of the thermal expansion coefficient. The discontinuous behavior is not manifested by a change in crystal symmetry (space group). However, the first discontinuity is accompanied by a distinct, isothermal increase of the strongest powder reflection (200,110) intensities, while the second is characterized by a sharp trend change in the intensities only.

These findings confirm previous work (Mirwald, 1981; Schneider and Mirwald, 1999). They are supported by results obtained from electrical conductivity measurements (Schmidbauer and Mirwald, 1998a,b) as well as by the H₂O incorporation behavior as reflected by changing slopes of the isohydrans (Mirwald *et al.*, 1979).

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PCM8 : Tupo14 : PO Thermal Strain and Structural Response in Mica

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The structural response on heating has been studied for $2M_1$ phengite using *in situ* high-temperature neutron diffraction. A natural sample of composition $(K_{0.95}Na_{0.05})(Al_{0.76}Fe_{0.14}Mg_{0.1})_2(Si_{3.25}Al_{0.75})O_{10}(OH)_2$ was investigated using the D2B diffractometer at ILL. The macroscopic thermal expansion has been measured and linked to the microscopic atomic displacements using the method of Catti *et al.* (1989). In the tetrahedral sheet, these are characterised by rotations of the TO_4 tetrahedra, with large displacements of the basal oxygens parallel to (001). The rotations result in a decrease in the ditrigonal distortion of the silicate rings on increasing temperature, and a decrease in the distortion of the 12-fold K^+ site. The neutron diffraction data also allow refinement of the hydrogen position, and its variation with temperature. We find that the apparent O-H bond length decrease with temperature. We can ascribe this to either thermal libration of the (OH) group, or to changes in the incipient hydrogen bonding to other oxygens in the silicate ring, with concomitant changes in the O-H bond length. Having elucidated the thermal response of phengite $2M_1$ structure we are now extending our studies to micas intercalated with deuterated $(NH_4)^+$, replacing K^+ . Preliminary results show a possible order-disorder transition of the $(NH_4)^+$ on cooling below 150K. The thermal strain associated with this phenomenon results in co-elastic spontaneous strains, which we have followed using X-ray powder diffraction.

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PCM8 : Tupo15 : PO Phase Transition of a Mineral during Acid Dissolution: Possible Application in Battery Research

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A mineral phase with d-spacing corresponding to PDF card # 35-782 has been observed as a residual phase during acid ($HF+HNO_3+HClO_4$) dissolution of serpentinized spinel-harzburgite from the ophiolite complex of the Himalaya. This mineral occurs as coarse grained crystals in highly serpentinized ultramafic rocks of the ophiolite sequence in Ladakh region of the Himalaya, India. It is black macroscopically and also in powder form. It is brittle and has metallic lustre. In reflected light the mineral is light grey, isotropic and has no internal reflections. The d-spacings of this mineral phase after acid dissolution are: 4.7663, 2.4846, 2.3875, 2.0690, 1.5913, 1.4626, 1.3865, 1.2621 and 1.1947; and the d-spacings of the same mineral before acid treatment are: 5.2545, 6.3190, and 3.6278. However, the mineral corresponds to PDF card # 35-782 which is a synthetic phase with chemical composition $LiMn_2O_4$ - spinel for which the natural occurrence has not been reported so far. The mineral phase of this kind is of considerable interest as a result of its importance both as a material for rechargeable lithium battery and an academic curiosity of not occurring as a natural mineral. Therefore, the results of this study may have important implications in the field of lithium battery research as well as in understanding the geological, mineralogical and geochemical environment conducive for its formation and thus insights into its natural occurrence.

Key words: mineral, phase transition, acid dissolution, lithium battery, natural occurrence.

PCM8 : Tupo16 : PO Crystal Structure Defects of Minerals from Archean Complex Rocks in the Section of Kola Superdeep Borehole as the Reflection of Physical State of Crystal Substance in the Condition of Middle Earth Crust

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In accordance purposes of subproject "Crystal structure defects of minerals from Archean complex rocks in the section of Kola superdeep borehole (KSDB) as the reflection of physical properties of crystal substance in the condition of Middle Earth crust" amphiboles (cumingtonites, actinolites and actinolite homblendes) and micas (phlogopites and low-alumina biotites) from amphibolites in the section of Archean complex of KSDB from the depth 7926.0, 7964.7, 9670.0, 9675.2, 10100.3, 10171.8 and 11334.2 m were studied by X-Ray, Mossbauer and Infrared spectroscopy. It was established that amphiboles from the section of Archean complex and ones from surface metamorphic and igneous rocks on the degree of isomorphous cation distribution between nonequivalent sites (long-range order) and the iron oxidation are similar. However, as in cumingtonites, as in actinolites from the borehole the short range cation order is absent, while in surface actinolites the cation clustering is distinctly showed. The degree of iron oxidation and octahedral cation order-disorder of micas from Archean complex amphibolites of KSDB and of micas from the surface metamorphic and magmatic rocks do not differ. But the micas from KSDB are characterized by abundant vacancies in the octahedral layer, which amount increases with depth, presence of crystalline water in the interlayer, low degree of layer ordering and higher values of c and unit cell volume in comparison with micas of the same fm values from the surface rocks and synthetic phlogopite-anneal end member series. So micas from Archean complex have a large amount of crystal structure defects. The obtained data show the uncommon crystal structure of micas from the Archean complex in the depth range of 7900 to 11350 m.

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PCM8 : Tupo17 : PO New Synthetic Mn²⁺-Bearing Hydrated Silicates, Potentially fO_2 Sensors

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Two sodic amphiboles, ungarrettiite $NaNa_2(Mn_2^{2+}Mn^{2+})Si_4O_{22}O_2$ (Hawthorne *et al.*, 1995) and kornite $NaNa_2(LiMg_2Mn_2^{2+})Si_4O_{22}(OH)_2$ (Armbuster *et al.*, 1993) and a mica, norrishite $K(Mn_3^{2+}Li)Si_4O_{10}O_2$ (Eggleton and Ashley, 1989) have been described in different geological environments. Ungarrettiite and norrishite occur in greenschist facies and kornite occurs in meta-volcanogenic sediments.

All three end-members have been synthesized under hydrothermal conditions, starting from gels of appropriate composition, in an Internally Heated Pressure Vessel (IHPV), using the Shaw membrane (Ag_2Pd_7) technique for controlling the fO_2 conditions, with Ar-H₂ gas mixtures used to set the pressure. Ungarrettiite, could be synthesized at 450°C, 2.5 kbar, under NNO fO_2 conditions. Kornite has been synthesized at 600°C, 3 kbar, and the mica, norrishite, has been obtained at 600°C, 3.5 kbar, both under NNO conditions.

The fO_2 equilibrium at 450°C is probably not reached because the hydrogen diffusion in the gold capsule is slower than through the AgPd membrane at this temperature. Then, fO_2 constraints on ungarrettiite stability are uncertain.

At 600°C, kornite and norrishite are stable under reducing conditions, NNO-2. In order to determine the stability field of these phases as a function of fO_2 , syntheses have been

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performed under drastic reducing conditions, NNO-3.5. No amphibole and no mica have been obtained. Mica gel products manganoo roederite and a lithium silicate. The presence of kornite and norrishite in a natural paragenesis indicates that fO_2 conditions lie between NNO-2 and NNO-3.5.

From XRD, the two amphiboles are single phase but norrishite coexists with minor cryptomelane (KMn_8O_{16}). Cell dimensions closely coincide with previously published data from naturally occurring samples.

For ungarrettite and norrishite, FTIR spectrometry in the OH-stretching region, indicate the absence of hydroxyl groups according to the nominal structural formula.

The band intensity for kornite in the OH-stretching region is particularly weak compared to usual amphibole spectra. The spectrum presents two bands at 3727 and 3660 cm^{-1} . The main band at 3727 cm^{-1} can be assigned to OH-group pointing towards [A]Na. The band at 3660 cm^{-1} is allotted to OH-group pointing towards a vacant A site. The decomposition in elementary Gaussians indicates 8% of vacant A sites. This suggests two kinds of deviations from the ideal structural formula, with less OH-groups than expected and partially vacant A-sites.

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Armbruster T, Oberhänsli R, Bermanec V & Dixon R, *Schweiz. Mineral. Petrogr. Mitt.*, **73**, 349-355, (1993).
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PCM8 : TUpo18 : PO Mixed Layering Stability Studied by Microcalorimetry and Lattice-Energy Calculations

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Mixed-layer illite-smectite minerals typically appear during the transformation of smectite into illite in diagenetic or hydrothermal environments. The stability of these minerals is here studied by new approaches: experimental microcalorimetric measurements and theoretical lattice-energy calculations. The purpose of the microcalorimetric experiments is to estimate the stability of mixed-layer minerals compared with the stability of the two end-member phases. In this way, microcalorimetric measurements are made on a smectite-to-illite conversion series from hydrothermally altered rocks. These samples are characterised by X-ray diffraction and high-resolution transmission electron microscopy as mixed-layer illite-smectite minerals, showing all the compositions from 0% to 100% of smectite layers. The enthalpy of dissolution of each sample is measured by microcalorimetry, as the heat liberated during dissolution in a reference $HF+HNO_3$ solution, at constant pressure of 1 atm, and at 298 K (initial and final temperatures). We show that the enthalpy of formation of a mixed-layer illite-smectite is approximately represented by a linear combination of the enthalpies of formation of the two end-member phases (as this occurs for the enthalpies of dissolution), *i.e.*, that the enthalpy of mixing of illite and smectite layers is nearly equal to zero. From this energetic point of view, mixed-layer illite-smectite may then be as stable as an assemblage of discrete illite and smectite. A first approximation to the lattice energy is given by the electrostatic energy, which is calculated with our overlap method, of very rapid convergence [1]. These lattice-energy calculations are first used to determine the structure of the illite-smectite interstratification, which corresponds to the minimum energy. The obtained structure may be described as the superposition of $O_8T_1T_1O_{15}$ unit layers of illite or smectite (O, T, and I', respectively, denote the octahedral and tetrahedral sheets, and the interlayer). Such arrangements produce a polar model for TOT layers, which display a $T_1O_8T_1$ structure in the case of IS adjacent layers (I=illite layer, S=smectite layer; the subscripts I, S, and M respectively refer to compositions of illite, smectite, and midway between at 0.5) [2]. Furthermore, the difference *E (energy of mixing) between the energy of the ordered mixed-layer mineral (...ISIS...) and the sum of the energies of the two phases, illite and smectite, is found to be nearly equal to 0. In addition, this value *E may be lowered

(*i.e.*, favouring mixed-layering stability) by considering identical octahedral composition for illite and smectite, or by ordering cations in the interlayers. It is also shown that mixed layering in finite crystals is more stable than in infinite ones. These theoretical results are in agreement with the above microcalorimetric results and confirm that mixed-layer illite-smectite is - at least - as stable as the assemblage of the two phases, illite and smectite.

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PCM8 : TUpo19 : PO Phase Transitions and Ionic Mobility in Proustite (Ag_3AsS_3) at High Temperature

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Proustite (Ag_3AsS_3) is known as a photosensitive semiconductor and has attracted attention in non-linear optics, acousto-electronics [1] and electro-optics, as well as in the field of dielectric relaxations [3,4]. It has been reported to have several phase transition connected to Ag^+ ion mobility space [5]. The temperature- and frequency-dependent dielectric properties of natural and synthetic proustite have been studied between 70 K and 600 K. Special emphasis was put on the trigonal phases in the temperature range of 288K to 600K. The presence of two phase transitions, one at around 305K and a transition to a fast-ion conducting phase at around 470K has been detected by dielectric spectroscopy. The data show a significant peak in the dielectric loss $\tan\delta$ between 305K and 470K, which is not seen below room temperature according to [3]. A Debye model for dielectric relaxation processes can be applied to the dielectric loss function. The relaxation is related to hopping processes of Ag^+ within possible sites in the structure with a calculated activation energy of approximately 0.42 eV. Anomalies in the thermal expansion of the unit-cell volume and edges are seen at approximately the same temperature, as revealed by X-ray powder diffraction data. The spontaneous strains has been calculated and reveals a second order phase transition at 470K. Neutron experiments are planned to get a more detailed picture of the high temperature structure and changes in behaviour of proustite.

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PCM8 : TUpo20 : PO Formation of Ca-Sr-Ba Complex Carbonates in Carbonates of the Sebyavir Massif (Kola Peninsula, Russia)

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In carbonates of Sebyavir alkaline ultramafic massif among of Ca-Sr-Ba complex carbonates (CCSB) with the general formula $AB(CO_3)_2$ three polymorphic modifications are known: barytocalcite, alstonite, paralstonite and stromantian analogue paralstonite - olekminksite. Calcite, dolomite, barite, ancylite-(Ce), stromantianite, pyrochlore, zircon, belkovite, pyrite, sphalerite, galena, chlorites are established in association with these minerals and monazite-(Ce) is rare. Barytocalcite crystallizes first among CCSB. It occurs as dense granular masses and bladed-prismatic crystals. These mineral crystals are usually not preserved in late associations, they are dissolved. Destruction and the transformation barytocalcite results in formation alstonite and stromantianite. Aggregates of alstonite crystals frequently contain inside prismatic crystals of barytocalcite. Alstonite is formed later than barytocalcite, it is the most widespread mineral in late hydrothermal associations of carbonates and steady mineral form among

CCSB polymorphic modifications. It forms two generations - alstonite-I and alstonite-II. Alstonite-I accrues on barytocalcite or stromantianite, partially at the expense of their dissolution and replacement. Frequently the end of stromantianite crystallization coincides with the beginning of alstonite formation and during some time crystallization of these minerals occurs simultaneously. Then alstonite crystals without obvious transformation acquire stromantianite inclusions and a new generation of alstonite-alstonite II is forming on them. Thus the cyclicity of CCSB formation is established according to the circuit: alstonite-I - stromantianite - alstonite-II. Paralstonite and olekminksite are rare among CCSB. These minerals are rare because of their instability in hydrothermal solutions, which were formed by late associations in carbonates of Sebyavir massif. These minerals are mostly latest during the association formation. The chemical composition of barytocalcite and alstonite from carbonates of Sebyavir massif is steady enough and even for zone crystals the content variations of basic cations are insignificant. The research of chemical composition of CCSB from another alkaline ultramafic massif - Vuoriyarvi in the Kola peninsula has shown, that it can be more complex. For alstonite and paralstonite wide variations in relation to Ca, Ba and especially to Sr are marked. Besides actually occurred alstonite and paralstonite, olekminksite is met here rather frequently. The process of formation of CCSB in late carbonates of Vuoriyarvi massif is represented as barytocalcite - alstonite-I - stromantianite - alstonite-II - paralstonite - olekminksite - stromantianite. Late hydrothermal carbonate associations have the barium specificity in Sebyavir massif. It is revealed in formation of complex barium oxides and silicates of rare metals in uniform association with CCSB, that emphasizes the general tendency of barium mineral formation in late carbonates of Sebyavir massif.

PCM8 : TUpo21 : PO Mg-Fe Substitution in Silicates: Microscopic vs Macroscopic Behaviour

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Mg-Fe substitution is the most common solid solution mechanism in the crust and mantle. In terms of their standard thermodynamic mixing properties, the solid solutions tend to be close to ideal. Nevertheless when a small Mg^{2+} cation is substituted for a larger Fe^{2+} cation, local structural distortions occur. In addition, the occurrence of non-convergent ordering implies that the difference in ionic radius between Mg and Fe^{2+} , although small, is a significant factor. These local strains need not correlate over a sufficiently large length scale to produce a phase transition but they are expected to contribute to the macroscopic elastic energy of the material.

Two suites of natural and synthetic orthopyroxene and olivine samples, close to the binary join En-Fs and Fo-Fa respectively, have been characterised by means of X-ray single crystal diffraction and IR spectroscopy. Crystals of the same sample have been annealed in order to obtain different degrees of non-convergent order. The objectives of this study were to characterise the microscopic mixing and ordering mechanism at a phonon length scale, for comparison with the average structure from X-ray data. Local strains arising from cation substitution and ordering have been quantified by means of an autocorrelation function. Comparison of line broadening data from IR spectra with calorimetric determinations of enthalpy for selected mineral systems confirm a close relationship between local structural heterogeneity and enthalpy variations. The relationship between microscopic and macroscopic structure was also constrained and will be discussed in the light of structural differences between ortho and chain silicates.

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Wednesday AM Session

PCM8 : TUpo22 : PO Metals in Solid Bitumens from the Pechora-Barents Sea Basin, Russia

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Such metals as vanadium, nickel, molybdenum, uranium, and thorium are found in resins and asphaltenes, porphyrin complexes and sulphur-organic compounds in petroleum. That is why metal concentrations increase when metal-enriched heavy oils are transformed to solid bitumens, thus giving rise to metalliferous bitumen accumulations comparable to metal ore deposits. This allows solid bitumens to be viewed as a promising source of some rare metals like vanadium, nickel, molybdenum, and uranium. We have studied metal content in solid bitumens: asphaltites, kerites and anthraxolites from hypergenic oil pools in the Pechora-Barents Sea basin. Solid bitumens associated with the oil pools and localised in eroded arched uplifts occur as either near-surface eruptions and sheets (Malya Kozhva deposit) or buried deposits under erosional surfaces (Yarega, Izhma, Nizhnay Omra, Nibel, Talot, Nyade-yu, South Lyzha, Voya deposits) or natural outcrops of small accumulations and occurrences (Akimyel, Kezvel, Zelents, Kozhva-Kamen, Dia-Kos', Tarkoy Shora occurrences and those in Franz Josef Land). The latter were formed due to liquid-viscous bitumen migration from deep oil pools up the pre-existing fractures in anticlinal structures. While metalliferous oil deposits of hypergenic-sedimentary type normally have low metal concentrations, solid bitumens in the above-mentioned deposits have metal concentrations of commercial significance, a result of biochemical and chemical oxidation of originally metalliferous oils, leading to an increase in metal concentrations in the solid bitumens to form. We have examined the mineral and chemical composition of micro-inclusions in asphaltites, kerites, anthraxolites from hypergenic-sedimentary deposits in the Pechora-Barents Sea basin. It has been shown that solid bitumens contain metals not only as impure elements, like vanadium, but as metal inclusions as well. An electron microprobe study with a JSM-6400 scanning electron microscope with an energy dispersion Link ILS-300 facility has disclosed several types of metal inclusions: native metals, metal oxides, melts and films (gold, iron, titanium, nickel, tin, lead).

PCM8 : WEam01 : G6

The Origin of Stable Remanent Magnetization in Exsolved Titanohematite: Insights Through the Application of Neutron Diffraction, Transmission Electron Microscopy, Electron Energy Loss Spectroscopy, and Monte Carlo Simulations

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The ilmenite-hematite solid solution is one of the most important magnetic phases in nature. Unusual magnetic behaviour is often observed in intermediate compositions due to the interaction between cation ordering, magnetic ordering, and exsolution. This presentation provides significant new insight into the effect of phase transformations on the magnetic properties of this system through a combination of experimental and computational techniques.

Metamorphic titanohematites from the Swedish Granulite Region carry an unusually strong and stable remanent magnetization. We argue on the basis of detailed rock-magnetic and petrographic analysis that the stable remanence is caused by the presence of exsolution microstructures at the nanometer scale. Transmission electron microscopy (TEM) reveals a microstructure consisting of unit cell-scale disk-shaped precipitates with diameters around 10-20 nm and thicknesses of 1-2 nm or less. Quantitative chemical analyses are obtained using electron energy loss spectroscopy (EELS) and electron spectroscopic imaging (ESI). The precipitates are shown to be almost pure ilmenite (> 90% FeTiO₃) within an almost pure hematite (> 90% Fe₂O₃) host.

To provide insight into the effect of these precipitates on the bulk magnetic properties, we have performed a detailed series of Monte Carlo simulations, which successfully model the interaction between cation ordering, magnetic ordering, and exsolution in the ilmenite-hematite system. Cation exchange interaction parameters were constrained by the temperature- and composition-dependence of the long-range cation order parameter, determined by Rietveld refinement of in-situ powder neutron diffraction data. Magnetic exchange interaction parameters were taken from the literature (Burton and Kikuchi 1984). All previously known features of the equilibrium phase diagram are reproduced.

The simulations allow the magnetic transition in chemically heterogeneous systems to be studied. At low temperatures (< 525°C) they predict an intergrowth of antiferromagnetic hematite and paramagnetic ilmenite. Despite the antiferromagnetic nature of the hematite component, the simulation cells as a whole are ferrimagnetic, with small but significant net magnetization associated with the interface between exsolved phases. Competition between chemical and magnetic interactions leads to a characteristic cation distribution at the interface, which ensures a local imbalance between the numbers of up and down magnetic spins. The interface moment acts as a defect moment of the antiferromagnetic hematite, and has both the magnitude, coercivity, and thermal stability required to explain the remanence properties of the metamorphic samples, thus establishing exsolved titanohematite as a potential carrier of stable remanence.

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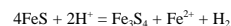
PCM8 : WEam02 : G6

A Sulphide Mineral Switch

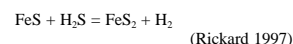
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We report that iron sulfide mineral products of different compositions and oxidation states are produced by the catalytic activity of simple aliphatic and aromatic aldehydic carbonyls. We show that the product of the oxidation of iron (II) monosulfide (FeS) by aqueous H₂S at temperatures between 25-100°C under strictly anoxic conditions is

dependent on the presence of catalytic quantities of aldehydes. The products switch between the ferrimagnetic thiospinel, greigite (Fe₃S₄) and the iron disulfide, pyrite (FeS₂). Compared with other mineral switches, the effect of this first observed switch in the iron sulfide system is quite dramatic. In the presence of aldehydic carbonyls, two thirds of the Fe(II) in iron (II) monosulfide is oxidised to Fe (III), but the S(-II) is unaffected:



In the absence of aldehydic carbonyls, the S(-II) in the iron (II) monosulfide is oxidised but the Fe (II) remains unchanged:



Voltammetric evidence suggests that dissolution of FeS_(s) to form an FeS_(aq) cluster complex (Rickard and Luther 1997) is limited by aldehydes. This interpretation is consistent with HRTEM observations of the comparative particle size of the greigite and pyrite products. The effectiveness of the aldehyde switch is such that it suggests that the presence of trace organics can determine the stoichiometry and oxidation state of the iron sulfide product. The results provide a potential new pathway for the development of biogenic greigite, especially in magnetotactic bacteria (Postfai *et al.*, 1998), have implications for the development of remanent magnetism in sediments and suggest possible constraints on the use of greigite as a biomarker in Earth and planetary sciences (McKay *et al.*, 1996). The switch has further implications for "iron-sulphur world" models for a chemolithotrophic origin of life based upon catalysis of organic molecule synthesis by FeS and (Fe,Ni)S (Russell and Hall 1997, Wachterhauser 2000).

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McKay DS, Gibson EK Jr, Thomas-Keptra KL, Vali H, Romanek CSS, Clemett SJ, Chiller XDF, Maechling CR & Zare RN, *Science*, **273**, 924-930, (1996).

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Wachterhauser G, *Science*, **289**, 1307-1308, (2000).

PCM8 : WEam03 : G6

Reductive Dissolution of Synthetic Goethite with Ascorbic Acid Observed by Scanning Force Microscopy

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The reductive dissolution of synthetic sub- μ goethite particles by 10 mM ascorbic acid was observed in situ by tapping and contact mode scanning force microscopy.

The mean solid/solution ratio was 0.7 g L⁻¹ of goethite. After a large initial dissolution rate, the rate approached a steady state after approximately 1 hour. The ascorbic acid solution was replenished after approximately 2 hours and no changes in dissolution rate was observed.

The (100) and (110) faces of goethite exhibited similar dissolution rates with 5.6 $\mu\text{mol Fe min}^{-1} \text{m}^{-2}$ and 5.1 $\mu\text{mol Fe min}^{-1} \text{m}^{-2}$, respectively. Perpendicular to these directions, along the crystallographic c-axis [001], a 7 times higher dissolution rate was determined.

These results were in agreement with crystallographic considerations based on morphology, namely a higher growth rate in [001] should be reflected by a higher dissolution rate in [001] when compared to the [100] and [110] directions.

Dissolution rates for the (100) and (110) faces was determined by contact mode were twice as high as found by tapping mode.

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PCM8 : WEam04 : G6 Transformation of the (010) Olivine Surface by HF-Etching. Study by RBS in Channeling Geometry

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Precise experimental studies of the evolution of olivine surfaces subjected to various processes relevant to geological or planetological conditions first require good quality and good description of the initial state of these surfaces. We have studied and evaluated quantitatively the quality of surfaces prepared by two classical procedures: mechanical polishing and chemical etching by hydrofluoric acid after mechanical polishing. Millimeter-sized (010) surfaces of olivine and forsterite were prepared from oriented single crystals of gem quality. They were studied by Rutherford backscattering spectrometry (RBS) using the Van de Graaff accelerator of the Groupe de Physique des Solides (Paris) with a 2 MeV ⁴He⁺ beam. Spectra were collected either in channeling geometry with an incident beam parallel to the [010] zone axis, or in random orientation with respect to the beam. Composition profiles were probed by RBS in random mode over several hundreds of nanometers below the surface and successfully simulated. The compositions, averaged over 20 nm thick layers (instrumental resolution), are all equal to the bulk composition of the crystal. Then, characteristics of the few top atomic layers were probed by RBS in channeling mode. This method allows to get a quantitative assessment of surface quality. The crystalline quality of the surface of chemically etched samples is, as expected, better than that of simply mechanically polished samples. High quality mechanical polishing with no further chemical processing disturbs the olivine and forsterite lattices in a 40 nm thick layer below the surfaces without modifying significantly the initial chemical composition. Quality of such samples is too poor to carry on precise surface studies. Chemical etching by hydrofluoric acid combined with mechanical polishing induces a very weak structural disorder (if any) that is confined to a region thinner than 10 Å (one unit cell). On average, less than one atom per [010] atomic row is displaced from its mean crystallographic position. The surface composition of forsterite and iron-bearing olivine crystals is identical to the bulk composition except in the case of iron-bearing olivine for which our results can be interpreted in terms of a slight Fe enrichment at the surface. Combined mechanical and chemical polishing thus allow to prepare olivine surfaces having a "quasi-ideal" crystalline quality. It provides a useful reference frame for further studies and brings new data to constrain theoretical calculations on olivine surfaces (Watson et al. 1997).

Watson GW, Oliver PM & Parker SC, *Physics and Chemistry of Minerals*, 25, 70-78, (1997).

PCM8 : WEam05 : G6 Microstructural and Compositional Changes in Olivine during Electron Irradiation

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Finely divided matter that condensates within circumstellar environments, among which olivine (Fe,Mg)₂SiO₄ is believed to predominate, is subjected to irradiation by energetic particles (ions, electrons, photons). Circumstellar solids have small grain sizes (10 nm - 1 µm), large surface/volume ratio and are consequently particularly sensitive to irradiation processes. Better understanding of irradiation-induced chemical fractionation by the early sun is necessary for modelling the protosolar nebula, and the bulk composition of asteroids and planets.

We have performed a series of electron irradiation experiments on thin (Mg_{1-x}Fe_xSiO₄) olivine samples in situ in a transmission electron microscope (TEM) operating at 300 kV. The thin samples (thickness < 100 nm) in the TEM have surface/volume ratio comparable to those of astro-

physical dusts. Such a geometry is likely to emphasise the role played by the surfaces during volatilization of atoms which is believed to contribute significantly to the chemical evolution of interstellar dusts. The chemical changes were studied using the EDS (energy dispersive spectrometer) attachment on the microscope as a function of irradiation time in various experimental conditions (fluence and sample thickness). The structural changes were studied by electron diffraction. The irradiation-induced modifications occur in two distinct stages. (1) The first stage is a non-equilibrium phase transformation of olivine into tiny crystallites of MgO and an amorphous SiO₂-rich phase. This phase separation is a bulk dissociation process, due to the creation of abundant Mg and O Frenkel pairs in the material, leading to the olivine breakdown. A moderate stoichiometric loss of Mg and O also occurs during this first stage. (2) In a second stage, we observe an important oxygen loss leading to reduction of the amorphous SiO₂-rich phase by the disruption of Si-O bonds. Bulk diffusion of chemical species is evidenced from the inside to the outside of the irradiated area and atoms, mostly oxygen, are desorbed from the surface and are gradually lost in the vacuum of the microscope, leading to a strong evolution of the composition. Rates of elemental loss follow first order kinetic exponential laws, with exponential factor directly proportional to electron fluence and inversely proportional to sample thickness. These electron irradiation experiments show that the structure and the composition of solids having a high surface/volume ratio can be strongly modified by ionizing radiation. Such effects might also affect the finely divided matter present in the interstellar medium.

PCM8 : WEam08 : G6 He⁺ Irradiation-Induced Structural and Chemical Modifications in Olivine

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The Infrared Space Observatory (ISO) has recently shown the presence of crystalline silicate dust grains the circumstellar shells around young and evolved stars. To the contrary, silicates in the diffuse interstellar medium and in the molecular clouds around protostars are thought to be completely amorphous. Such observations show that silicates undergo major modifications during their lifetime. The amorphisation of the silicates might be due to irradiation with H⁺ and He⁺ ions that are accelerated in supernovae shocks and thus abundantly present in the interstellar medium. In addition to these structural modifications, the chemical composition seems to vary also, from an olivine-like to a pyroxene-like composition.

We present the results of irradiation experiments on olivine (close to the forsterite composition) with He⁺ ions accelerated to 4 and 10 keV to simulate the effect of ion bombardment in shocks in the interstellar medium on the silicate dust grains. The samples are thin crystalline films having a high surface/volume (S/V) ratio, comparable to the expected S/V ratio of the silicate dust in the interstellar medium (typically 100 nm in diameter). The samples were analysed by transmission electron microscopy (TEM) with an energy dispersive spectrometer (EDS) attachment. Within the regions of thickness comparable to the penetration depth of the ions, samples irradiated at fluences from 5 x 10¹⁶ ions/cm² to 10¹⁸ ions/cm² are amorphous, as shown by the diffuse rings in the electron diffraction patterns. The amorphisation is accompanied by the appearance of porosity due to the implantation of helium which forms tiny bubbles (typically 50 nm in diameter). The composition of the starting olivine is also modified. In this amorphised layer we observe a depletion of Mg and O, leading to a lower O/Si ratio. This ratio continuously decreases with the increasing fluence. This chemical evolution can be due to selective sputtering of atoms near the surface, but the ionising effects (that cause radiolysis) can also be efficient. In any case some atoms diffuse from the bulk and are preferentially desorbed from the surfaces. These experiments show that irradiation induced by fast ionic species in the interstellar medium can efficiently modify the silicate dust structure and composition. Some new experiments are in progress in order to better quantify the amorphisation and chemical modification of ion irradi-

ated laboratory silicates, as well as for the implication and the understanding of physical processes relevant to interstellar medium evolution.

PCM8 : WEam09 : G6 The Degree and Nature of Radiation Damage in Zircon Observed by ²⁹Si Nuclear Magnetic Resonance

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A quantitative analysis of ²⁹Si NMR spectra of radiation damaged, natural zircons showed that the local structure in crystalline and amorphous regions depends explicitly on radiation dose. A continuous evolution of the local structure of the crystalline phase, as determined by ²⁹Si NMR chemical shift, is evidenced up to an α -dose of 3.5 x 10¹⁸ α -events/g which coincides with the first percolation point determined by x-ray scattering. The local structure of the amorphous phase evolves up to a higher dose consistent with the second percolation point. The silicon NMR chemical shifts are consistent with an increase in the average polymerisation of the amorphous phase from approximately Q² to approximately Q³. The quantitative nature of the NMR experiment allows the total number of permanently displaced atoms per α -recoil event to be determined. This is ~3800 atoms for low radiation doses and decreases to ~2000 atoms for 10 x 10¹⁸ α -events/g. No indication of partitioning of paramagnetic impurities between crystalline and amorphous regions was found for these natural zircons. The amorphous fractions of the metamict zircons were determined as a function of their accumulated radiation dose. These values coincide closely with those recently determined by x-ray diffraction studies. They are much greater than previously assumed based on density measurements. The dose dependence is consistent with the concept of direct impact amorphisation in the atomic cascade following an α -recoil event.

PCM8 : WEam10 : G6 Hydrous Olivine Mg_{2-x}SiO₄H_{2x} - The HMS Phase with Ordered Mg-Vacancies and Ordered Planar Defects

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Nominally anhydrous minerals such as olivine (α -phase) and its polymorphs (β -phase) and (γ -phase) are considered to be OH-bearing phases under mantle conditions. Hydrous wadsleyite β -Mg_{2-x}SiO₄H_{2x} and hydrous ringwoodite γ -Mg_{2-x}SiO₄H_{2x} were synthesized at high pressure - high temperature conditions (Kudoh et al. 1996, 1999, 2000). Hydrous α -olivine (H-Ol) has not been synthesized till now. Hydrous olivine (H-Ol) Mg_{2-x}SiO₄H_{2x} can exist as nanometer-sized inclusions in mantle olivine Fo92. The sample was investigated using TEM including AEM, EELS, SAED and HRTEM techniques. Arrays of lamellar precipitates about 20-50 nm in thickness, which are oriented parallel to either (001), or (102), or (10) of the olivine matrix were observed. A composition Mg_{2-x/3}SiO₄H_{2x} was estimated from AEM and EELS measurements. Energy filtered HRTEM lattice fringe images show a coherent olivine/lamellar precipitates interface. The olivine lattice fringes were observed in HRTEM images of lamellar precipitates. From this observation a disordered olivine structure with disordered vMg and OH-point defects is deduced. HRTEM images of lamellar precipitates show a periodic band-like contrast, which represents a modulation in the periodicity of the olivine lattice along certain directions. The corresponding SAED patterns of lamellar precipitates exhibit a superperiodicity of the olivine structure, which is consistent with the HRTEM observations. The superperiodicity is explained by vMg associated with OH-point defects, which are ordered in the olivine structure. Five different types of superperiodicity are observed in the SAED patterns as well as in HRTEM lattice fringe images. These data are interpreted in terms of unit cells of H-Ol polytypes. The vacancy concentration per unit cell of Mg_{2-x/3}SiO₄H_{2x} was calculated for different kind of supercells and x was determined to be x = 0.25; 0.33; 0.166 and 0.125. We assume that hydrous olivine is exsolved from the olivine matrix initially saturated with

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vMg and OH-point defects. From the data obtained, the following sequence of the defect arrangement in the olivine structure is suggested: Mg-vacancies associated with OH-point defects in the olivine structure (disordered olivine structure); Mg-vacancies and Mg-ions ordered in M1 sublattice of olivine; M1-vacancies and OH-point defects segregated along (100), (001), (101) or (102) planes of olivine forming planar defects; periodic planar defects ordered in the olivine crystal lattice. The ordered planar defects result in the formation of hydrous olivine.

Kudoh Y & Inoue T, *Physics Chemistry Minerals*, **26**, 382-388, (1999).

Kudoh Y, Inoue T, Arashi H, *Physics Chemistry Minerals*, **23**, 461-469, (1996).

Kudoh Y, Kuribayashi T, Mizobata H & Ohtani E, *Physics Chemistry Minerals*, **27**, 474-479, (2000).

PCM8 : WEam11 : G6 The Dehydration Products of Normal Tobermorite and Clinotobermorite

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The minerals of the tobermorite group are hydrated calcium silicates characterized by wollastonite-like chains connected to sheets of seven-fold coordinated calcium cations. Additional calcium cations, as well as water molecules, may occupy the structural cavities between adjacent layers. The known members of the tobermorite group are: tobermorite 14Å (or plombierite), tobermorite 11Å, tobermorite 9Å (or riversideite), and clinotobermorite. The (002) spacings of 14, 11 and 9 Å, quoted in the names of the different phases, are related to the amount of H₂O molecules between the layers. The partial dehydration of tobermorite 14Å at 90°C results in the formation of tobermorite 11Å. Moreover, it is known that some samples of tobermorite 11Å transform into tobermorite 9Å upon dehydration at 300°C. They were called 'normal' tobermorites (Mitsuda & Taylor, 1978), to distinguish them from the 'anomalous' tobermorites, which do not shrink upon heating. Recently, a similar 'normal' behavior was observed also in clinotobermorite from Wessels mine, South Africa (Merlino *et al.* 1999, 2000), which decreases its *c* parameter from 22 to about 18 Å upon heating to 300°C. The reaction was topotactic, and it was possible to obtain a single crystal of the dehydration product and to refine its crystal structure. Here, single wollastonite-like chains connect two adjacent sheets of calcium polyhedra, and no H₂O molecules are present. The chemical formula of the dehydration product is Ca₅Si₄O₁₆(OH)₂. This new phase was provisionally named 'tobermorite 9Å', even if some details in its diffraction pattern pointed to minor structural differences with tobermorite 9Å *s.s.* (riversideite). Actually, both the phases may be described as formed by the stacking along *c* of the same kind of layer, with *C12/m1* layer symmetry. The OD theory indicates two possible OD groupoid families corresponding to this layer symmetry. For both the OD families, infinite polytypic modifications exist; the OD theory indicates that there are two MDO polytypes for each family.

The phase we obtained from clinotobermorite belongs to one of the two OD families, whereas the product of dehydration of tobermorite 11Å belongs to the other. The structural refinement of the MDO₂ polytype for the phase obtained upon heating of clinotobermorite confirm the goodness of this model. The observed powder pattern of tobermorite 9Å *s.s.* (riversideite) closely corresponds to the calculated one for the second OD groupoid. The structural differences between the two dehydrated phases, as well as the mechanisms of transformation during the dehydration process, will be discussed.

Merlino S, Bonaccorsi E & Armbruster T, *Am. Mineral.*, **84**, 1613-1621, (1999).

Merlino S, Bonaccorsi E & Armbruster T, *Eur. J. Mineral.*, **12**, 411-429, (2000).

Mitsuda T & Taylor HFW, *Mineral. Mag.*, **42**, 229-235, (1978).

PCM8 : WEam12 : G6 The Fate of Structure-Bound Mn(II) in a CaO-MgO-H₂O-CO₂ System during Phase Transformation

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Cation substitution in mineral phases (e.g. carbonates, ferric oxides) has been studied extensively. Rather little is known about the fate of structure-bound cations during phase transformation. Mn(II) was analysed in a CaO-MgO-H₂O-CO₂ system with dolomite CaMg(CO₃)₂ as starting mineral.

Structure-bound Mn(II) in the untreated dolomite sample was detected by elec-tron paramagnetic resonance (EPR) spectroscopy. The signal showed characteristic six-line patterns and an overlap of two series of five doublets corresponding to forbidden transitions. X-ray diffractometry (XRD) of the sample heated at 800°C showed the generation of lime (CaO) and periclase (MgO). EPR spectroscopy of the heated sample revealed the generation of a new Mn(II) signal with a low intensity. The newly formed signal with *g* = 2.0015 ± 0.0006 and *A* = 8.64 ± 0.05 mT had only weak forbidden transitions, and could be assigned to Mn(II) in CaO and MgO, two mineral phases with cubic symmetry. The comparison of the signal intensity at 800°C with the one of the untreated sample revealed a decrease by a factor of approximately 20, which indicates that the major part of Mn(II) was expelled from the structure during transformation.

XRD revealed partial conversion of CaO into portlandite (Ca(OH)₂) during storage at ambient conditions. No hydration was observed for MgO. The formation of portlandite was also indicated by a change of the EPR spectrum. The comparison of the spectrum of the fresh and the aged samples exhibited the generation of a six-line pattern signal with *g* = 2.0054 ± 0.0006 and *A* = 9.08 ± 0.06 mT which could be attributed to Mn(II) in portlandite. The occurrence of this new signal indicates that Mn(II) in CaO survived the conversion into Ca(OH)₂.

Dispersing the thermally treated sample in bidistilled water led to a change in mineralogical composition. MgO completely hydroxylated to brucite (Mg(OH)₂) and CaO converted into Ca(OH)₂. In addition, calcite was formed. The EPR spectrum recorded of the hydrated sample showed a very weak signal with *g* = 2.0019 ± 0.0006 and *A* = 9.05 ± 0.03 mT which was similar to the one for Mn(II) in Ca(OH)₂. No evidence was found for structure-bound Mn(II) in calcite which was formed during hydration. This suggests that during carbonatation all structure-bound Mn(II) is expelled from the host mineral.

PCM8 : WEam13 : G6 Transformations and Overgrowths in Serpentine Microstructures: An HRTEM Survey

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From an HRTEM/AEM survey of numerous vein and matrix serpentinites close to the end-member Mg₃Si₂O₅(OH)₄ composition, we attempt a description of serpentine microstructures in relation with their geological conditions of formation. We observed the following microstructures, corresponding to an increasing degree of crystallographic organization of serpentine material: truly amorphous matter as a gel (*am-g*); poorly crystallized nanosheets forming protoserpentine (*pr-s*); discoidal serpentine, flat along *x*, made of curved or polygonal

lamella running along their circumference (*dsc-s*); normal chrysotile as long rolls and scrolls (*chr*); shorter and thicker fibers of polygonal serpentines with either 15 or 30 sectors (*PS*); columnar lizardite elongated along *c** (*c-liz*); lizardite twinned on prismatic planes (*t-liz*); lizardite single crystals (*sgc-liz*); defectuous antigorite (*df-atg*) and a new variety modulated along *y* ("para-antigorite"), sometimes occurring as navel-shaped microstructures associated with *chr*, and antigorite as large single crystals, usually well ordered (*sgc-atg*). The *am-g* and *pr-s* varieties are usual precursors that recrystallize as *chr*. The *am-g*, *pr-s*, *dsc-s*, *chr*, *PS*, and *df-atg* microstructures form in open microsystems (high fluid-rock ratios) while *liz* and *sgc-atg* tend to crystallize inside narrow, reacting interfaces. Isothermal maturation of synthetic serpentine at low pressure (1 kbar) indicates that *pr-s* evolves successively to *chr* then to *PS* and eventually to *sg-liz*. This corresponds to the elimination of interlayer defects and then to the progressive elimination of the sheet curvature. Tubular forms turn out to be metastable products favored by crystallization kinetics, and only lizardite and antigorite seem to own a stability field. The lamellar forms of *dsc-s* are promoted when small quantities of Al (or possibly Fe³⁺) are added to the MSH system. Centrifugal overgrowths of different microstructures on tubular varieties (*PS* on *chr*, *atg* on *PS*, etc.) and tubular (*chr*, *PS*) overgrowths on translational lattices (*liz*, *atg*) mostly illustrate prograde or retrograde serpentinisation events, respectively. Polygonal serpentines are virtually absent from oceanic serpentinites, but are frequently observed in orogenic (e.g., alpine) serpentinites.

PCM8 : WEam14 : G6 Postmagmatic Alterations of Accessory Minerals in the Ultrapotassic Rocks of the Trebic Pluton (Bohemian Massif)

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Ultrapotassic rocks belong to the oldest members within the Variscan plutonic sequences. This type of magmatism was documented along the whole Variscan chain, but locally names are often used in the individual parts of the Variscan Europe. The ultrapotassic rocks are termed Vaugnerites in the Massif Central and Vosges, Redwitzites in the southwestern part of the Bohemian Massif and finally durbachites in the Czech and Austrian part of the Bohemian Massif. Common feature for the whole group is high content of LIL elements (K, Rb, Ba), radioactive (U, Th) and light REE, which is accompanied by elevated Mg, Cr, Ni at the same time. The origin of this geochemically unusual suite is still a matter of discussion. Anyhow origin by mixing of the mantle derived, ultrapotassic mafic magma with leucogranitic crustal melt prevails in the recent literature. The studied samples come from the biggest durbachites body in the Bohemian massif, called Trebic pluton, situated close to the eastern border of the Bohemian Massif. In spite of their relatively high basicity, durbachites are very rich in radioactive elements. On the average, the durbachites of the Trebic pluton contain around 10 ppm U and 45 ppm Th. The major part of these contents occurs in accessory minerals - both as major components in proper uranous and thorious minerals (huttonite, brabantite, thorianite, uraninite), and as minor components of common accessory minerals - allanite, zircon, monazite, xenotime, apatite. The minerals containing Th and/or U occur usually as very small (X - X0 mm) grains. The rocks underwent postmagmatic changes, which had significant impact on the U- and Th-bearing minerals. Many of the primary accessory minerals were dissolved, and new phases precipitated. The composition of secondary phases indicates the solutions contained fluorine and carbon dioxide, which lead to origination of REE carbonates and fluorocarbonates (mostly bastnaesite and parisite) as well as of fluorite. In places, the rock transformation had the character of ferruginization. In such instances, the thorium minerals are surrounded by haematite or iron oxyhydroxides. Ferruginization is probably responsible for another effect connected with accessory mineral transformation - LREE fractionation. The original LREE minerals of the durbachites - monazite and allanite - were Ce-dominant; while the secondary phases (e.a. parisite, bastnaesite) are often La-dominant. The post-magmatic, hydrothermal processes lead not only to dissolution of primary accessory minerals, but also to redistribution of radionuclides included in them. As a result, radionuclides concentrated in places in deposit-grade accumulations. These accumulations (in the past times also mined) are often confined to tectonic zones.

