

EUG XI



Symposium OS05

Recent Advances in the Physics and Chemistry of Minerals

Convenors

David Vaughan
Matthias Gottschalk
Mark D. Welch
Thomas Armbruster
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Monday PM Session

OS05 : MOp21 : G6
Chemical and Magnetic Properties of Hematite Produced by Phase Separation from Hematite-Ilmenite Solid Solution during Slow Cooling

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Members of the ilmenite-hematite solid solution series are either paramagnetic, ferrimagnetic or antiferromagnetic, depending on cation ordering and spin structure. The well known self-reversing composition (~ilmenite70) is produced by rapid quenching across the R3c to R3 Ti-ordering transition to produce a fine intergrowth of antiferromagnetic disordered hematite with weak normal magnetism and strongly ferrimagnetic ordered ilmenite with lower temperature reversed magnetism. This magnetism is known to be destroyed by annealing. By contrast, members of this series that occur in very slowly cooled rocks contain abundant exsolved lamellae within host ilmenite or hematite grains, and the rocks have strong remanent magnetization, high coercivity, and high Q values. Here we discuss examples from intermediate, hematite-rich, ilmenite-rich compositions where rock-magnetic analyses, and compositional data from the microprobe, Mossbauer and EELS help constrain possible remanence carriers. A strongly annealed pyroxene granulite in Southern Sweden contains 2-3% of highly exsolved titanohematite (~ilmenite40) and < 0.05% coexisting multidomain (MD) magnetite. The rock has unusually high NRM, average of 9.2 A/m, coupled with very high stability and high unblocking temperature. Optical, electron probe, and TEM observations of titanohematite show exsolution lamellae from 4 micrometers to 1-2 nanometers thick (One hematite-ilmenite unit cell has 6 oxygen layers and thickness 1.375 to 1.409 nanometers!). Probe analyses of hematite and ilmenite indicate ~ilm22-25 and ~ilm92-93; EELS analyses of hematite and enclosed ultrafine ilmenite indicate ~ilm16 and ~ilm88 respectively. Microcline-sillimanite gneisses from Adirondack Mtns., USA, have ~3% of hematite rich-titanohematite containing ilmenite, pyrophanite and rutile exsolution. Rogaland, Norway, provides examples of the ilmenite side of the solid solution with very-fine hematite exsolution lamellae usually less than 1 µm wide. Adirondack and Rogaland samples also show very high stability, NRM and Q-values. Possible explanations for the observed magnetic properties are (1) SD magnetite residing in the silicate grains, (2) fine-scale exsolution of a ferrimagnetic ilmenite phase with composition in the range ilm60-80, or (3) ultra fine-scale exsolution microstructures that either stabilize the NRM due to domain-wall pinning or produce a 'new' material with magnetic properties unrelated to those of the bulk oxides. Earlier researchers, using synthetic specimens (Uyeda, 1958; and Meiklejohn and Carter, 1960), found that specimens of the same compositions, made by different methods, did not always have the same magnetic properties. This points out the importance of thermal history in determining microstructures, and that the microstructural features we have found in some slowly cooled rocks may not be reproducible at all in the laboratory. On the basis of our present experience, we think the high coercivity and strong remanence in these rocks lies in the properties of very fine-grained hematite-rich lamellae produced during slow cooling, but the exact atomistic mechanism has still to be determined.

Uyeda, S, *Japan Journal of Geophysics*, **2**, 1-123, (1958).
 Meiklejohn W. H. and Carter, R.E., *J. App. Physics*, **30**, (1959).

OS05 : MOp22 : G6
A Neutron-Diffraction Study of the Amblygonite-Montebasite Solid Solution

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The anion solid solution exhibited by the amblygonite (LiAlPO₄F)-montebasite (LiAlPO₄(OH)) solid solution is common to a wide range of oxides. The crystal structure is triclinic and consists of a corner-linked mixed tetrahedral-octahedral framework. Corner-sharing aluminate octahedral chains extend along *c*, and these are cross-linked by phosphate tetrahedra. This polyhedral framework topology is common to many compounds, including the kieserite and titanite mineral groups. The bridging anion in the octahedral chains is OH or F. Simonov and Belov (1958) reported a large and extremely anisotropic displacement parameter for the Li atom and suggested that the site is split into two fractionally-occupied positions. Groat et al. (1990) studied the entire solid solution using single-crystal X-ray diffraction and showed that the splitting varies nonlinearly with the F/(F+OH) content. The crystal structures of a number of members of the series with different F/(F+OH) contents were refined for temperatures between 15 and 295 K using neutron single-crystal data collected at the High Flux Isotope Reactor at Oak Ridge National Laboratory. Thermal contraction increases with F/(F+OH), primarily due to a reduction in the *a* and *c* cell dimensions (because the OH vector is close to the *a-c* plane), and the Al-anion distance decreases. With respect to the Li site(s) the results corroborate the earlier findings and further suggest that the positional disorder is largely static. The disorder is caused by the substitution of F for OH, and the driving force is the loss of the hydrogen bond to O(4). The results show that the split Li sites are unequally populated. In the previous X-ray diffraction studies the H atom position was inferred from bond-valence analysis. The neutron diffraction results show that the H atom position is imbedded within the distorted octahedral oxygen coordination of the Li atom. We are presently using Li nuclear magnetic resonance at varying temperatures to further study this solid solution.

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OS05 : MOp23 : G6
X-Ray Topography of Spinel Twinned Crystals by Synchrotron and Conventional Sources

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Extended growth defects [1] of some natural spinel crystals coming from Pegu (Burma) have been studied by means of X-ray diffraction topography (XRDT). Some of them are twinned crystals, according to the spinel twin law with {111} composition planes, and XRDT both with conventional (MoKα radiation) and synchrotron (white beam) sources has been taken on them. By conventional XRDT all of them originally resulted complex twinned crystals containing a number of twin boundaries, mutually either parallel or intersecting. Due to the complex relations existing among the numerous twin sets, the samples have been consequently studied using white beam synchrotron X-radiation at LURE (Orsay). In particular, white beam synchrotron XRDT showed a common feature in two samples, labelled SP84RL and SP198B, of dimensions (3.4 mm x 1.6 mm x 0.7 mm) and (3 mm x 2.7 mm x 0.8 mm) respectively. In fact there are twin lamellae similarly oriented in both samples, that are too narrow to be detected by means of conventional XRDT. This observation finds support in a previous description by Ming and Sunagawa [2] of twin lamellae in f.c.c. crystals, introduced by a series of parallel stacking faults between a pair of (111) planes, interpreted as possible self-perpetuating step sources. The morphologies of the two samples are quite different, even if both of them are bounded by {111} octahedral faces. In fact, SP84RL is elongated parallel to the twin lamella, whilst SP198B has a flattened morphology. Selective adsorption of impurities (both optically and topographically detected) along the twin boundary in SP84RL, accounting for the accelerated growth of the faces meeting

at the twin junction due to the heterogeneous 2D nucleation around the impurities [3], gives reason for such a morphological difference.

Fregola RA, Scandale E & De Lorenzo G, *Materials Chem. Phys.*, **66**, 149-154, (2000).

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 Sunagawa I & Lu T, *Mineral. Journ.*, **13**, 328, (1987).

OS05 : MOp24 : G6
Crystal Chemical Characterization of Natural Ti-Bearing Garnets: Solved Problems and Open Questions

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Different analytical methods (Electron Microprobe, Single Crystal X-ray diffraction, X-ray Photoelectron Spectroscopy, Mössbauer Spectroscopy) were combined to study the crystal chemistry of natural Ti-bearing garnets with compositions representative of the different content of TiO₂ in natural specimen (up to about 20 wt%). The studied samples have different origin and provenance. Ti-bearing garnets are characterized by a complex crystal chemistry, mainly due to the large number of cation substitution affecting the three independent X(8-fold), Y(6-fold) and Z(4-fold) crystallographic sites which constitute their structure. The coexistence of transition elements (Fe and Ti) which may occur in more than one valence state is a further source of complication. Previous studies have shown that different cation distributions can occur in natural samples, even when the Ti content is almost the same.^{1,2,3} The X-ray Photoelectron Spectroscopy turned out to be a suitable technique for the study of Ti in garnets, since the chemical shifts of this element are related to its valence state and quantitative peak area evaluation directly provides Ti-site populations.⁴ On the other hand Mössbauer spectroscopy has always been the preferred method for the study of Fe valence and it is used here to determine both iron site population and (indirectly) Ti distribution. In the present work XPS analyses was carried out both on the Ti2p and Fe2p photopeaks. In most samples, Ti2p binding energies are intermediate between the Ti³⁺(458 eV) and Ti⁴⁺(459 eV) positions, whereas Fe2p position (711 eV) indicates that Fe is predominantly trivalent. For the fitting of Ti2p photopeaks a procedure developed in another work⁴ was used whereas the Fe2p_{3/2} photopeaks were fit to a model developed for oxides⁵. Up to five doublets were fit to Mössbauer spectra and assigned to Fe²⁺(X), Fe³⁺(Y), Fe³⁺(Z), Fe²⁺(Z), Fe²⁺(Y). Generally speaking, ambiguities cannot always be avoided in fitting procedures. However the multi-method approach adopted here allows the cross-checking of results and a better handling of the most difficult cases.

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OS05 : MOp25 : G6
Time-Temperature Dependent Variation of the Elastic Modulus of MgAl₂O₄ Spinel and its Relationship to Order-Disorder

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The time-temperature dependence of cation disordering of Mg and Al between the octahedral and tetrahedral cation sites in spinel has considerable petrological importance. A number of recent studies have focused on the temperature dependence of the order-disorder behaviour (e.g. Redfern et

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al., 1999; Suzuki et al., 2000). Dynamic Mechanical Analysis (DMA) is a technique widely used in the field of material science but, until recently, has rarely been used in the study of minerals. In this study the time dependence of cation ordering in synthetic spinel ($MgAl_2O_4$) at high-temperatures has been studied through DMA in three-point bend geometry with a frequency of 1 Hz. The elastic shear modulus (E) of stoichiometric $MgAl_2O_4$ quenched from 1200°C was measured at 8 temperature steps between 300 and 500°C with the sample held isothermally for 20 hours. We find that the elastic modulus varies with time in an isothermal experiment, increasing from its initial value. It seems that the variation of the elastic modulus reflects the variation in cation order, as the quenched (disordered) sample orders during the annealing experiment. As expected E shows the greatest variation at higher temperatures yielding an initial value $(dE/dt)_{300} = 1.65 \text{ MPa s}^{-1}$ compared with $(dE/dt)_{400} = 1.40 \text{ MPa s}^{-1}$ and $(dE/dt)_{525} = 1.10 \text{ MPa s}^{-1}$. However, due to the nature of the equilibrium curve it was expected that the overall variation ΔE would be greater at lower temperatures as shown by $\Delta E_{300} = 8.8 \text{ GPa}$ and $\Delta E_{400} = 9.2 \text{ GPa}$. The variation in the modulus, as the sample moved back to the equilibrium cation distribution, has been analysed with reference to the non-equilibrium order-disorder behaviour in order to determine the activation energy for ordering, ΔH^* , using the Ginzburg-Landau rate law (Carpenter and Salje, 1989; Salje, 1988).

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OS05 : MOPm28 : G6 Morphology of Forsterite Dendrites

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Textures of rapid growth are usually used to estimate the cooling rate or the degree of undercooling in magmatic rocks (pillow-lavas, dykes, komatites...). However, the relationships between morphology and thermal parameters are not well established. To better constrain this relationships we performed a series of dynamic crystallisation experiments in the CMAS system at 1 atm. The starting materials (48.67 SiO₂, 13.92 Al₂O₃, 19.30 CaO and 18.11 MgO) is a glass is prepared from a mixture of reagent oxides, first melted for 24h at 1400°C (about 50°C above the liquidus) and then quenched by dropping in water. The resulting glass was then grounded in an agate mortar, and the resulting powder was formed as pellets placed onto a platinum wire loop. The charges were first re-melted one hour above the liquidus (30°C) and then they were cooled down at a constant rate varying from 2°C/h to 1890°C/h. At the end of the experiments, at temperature T_q the samples are quenched by dropping them into water. More than 90 experiments have been carried out. For the same cooling rate, samples were quenched at various temperatures (T_q). Forsterite morphology has been studied by combining three complementary microscopes: optical, SEM and TEM. For the present starting glass composition, forsterite morphology evolves essentially as a function of T_q, although a minimum cooling rate of 180°C/h is necessary in order to obtain skeletal or dendritic crystals. The forsterite dendrites are limited by the usual forms of olivine: (010), (021), (110), (120), (101) and also by less common form: (001), (130) and (140). In sections parallel to the (010), forsterite morphology evolves as a function of T_q from tablets to hopper (skeletal) crystals, and then to swallowtail shapes (dendritic morphology). The dendrites are formed by a succession of hopper-shaped units. The other shapes described in the literature (chain, branching and lattice olivine) can be interpreted as particular sections of those three basic shapes. As an example, chain olivine corresponds to (h0l) sections of swallowtail morphology (with h or l possibly equal to zero).

OS05 : MOPm29 : G6 EPR, ESEEM and SQUID Magnetometry of Sulfides: Magnetic Properties of the Synthetic Analogue of Tetrahedrite Cu₁₂Sb₂S₁₃

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Electron Spin Resonance and SQUID techniques are well established tools for investigations of valence states and to correlate magnetic properties and the electronic structure of solid inorganic compounds as well as biologic materials. The explanation of the nature of magnetism in minerals with peculiar structural features is of significant help in the fields of crystal chemistry and of materials science. Continuous wave electron paramagnetic resonance (EPR) has been applied to the study the magnetic features in sulfides (e.g. Bernardini et al., 2000) and other classes of minerals (e.g. Calas, 1988). Beside SQUID and continuous wave EPR, Electron Spin Echo experiments on the synthetic analogue of tetrahedrite have been run, since the nuclear modulation of the echo signal (ESEEM) is suitable for detailed information on the structural arrangement around the paramagnetic center. Tetrahedrite group minerals, (Cu, Ag)₁₀(Fe, Zn, Cu, ...)₂(Sb, As)₂S₁₃, are characterised by a complex structure (I-43 m), with 3 different cation sites, M1 tetrahedral, M2 triangular and M3 pyramidal; in particular M1 presents a mixed occupancy of monovalent Cu, Ag and divalent Cu, Fe, Zn cations in the ratio 2:1. The valence states and site occupancies of the different cation substitutions in synthetic and natural samples have been proposed respectively on the basis of theoretical considerations (Makovicky & Karup-Møller, 1994) and spectroscopic investigations (Patrick et al., 1993). Pure synthetic Cu₁₂Sb₂S₁₃ appeared to be an important standard to clear up crystal chemistry aspects and the effect of substituents on the overall structure. On the other side the occupation of M1 site with both mono- and divalent Cu leads to magnetic properties that couldn't be observed in natural Fe, Zn substituted samples. SQUID magnetometric measurements show a dependence of susceptibility versus temperature well described by the Bleaney-Bowers relation, accounting for the presence both of monomeric and dimeric Cu(II). Cluster population analysis contributes to the evaluation of higher dimension cluster effects on magnetisation. EPR signals evidence two different absorptions: a broad and structured line imputable to Cu(II) atoms paired in dimeric form, and a narrow and strong line at the free-electron g-value, probably due to the presence of F-centres in the material. While the broad line changes its feature by lowering the temperature, the narrow line stays unchanged down to 4K. Electron spin echo experiments have been run on the maxima of both the principal absorptions detected in cw-EPR spectra. The analysis of the ESEEM on the broad absorption seems indicative of the interaction of Cu(II) unpaired electrons with the surrounding nuclei (Sb and/or Cu), being S nuclei (I=0) silent in ESEEM. The ESEEM on the narrow absorption band is very weak and could be attributed to a weaker electron-nucleus interaction, thus confirming the hypothesis of free electrons in the material, such as F-centres.

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OS05 : MOPm30 : G6 MIE Scattering and Charge Transfer Phenomena as Causes of UV Absorption in Natural and Synthetic Almandine Garnets

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The UV absorption edge in electronic spectra of minerals, which often strongly influence their colour, is usually interpreted as caused by excitation of electronic charge transfer (CT), predominantly in ligand - metal, but also in metal-metal systems. *dd*-transitions may contribute in some cases (e.g. Burns, 1993). On the other hand, Mie scattering theory shows that the presence of randomly distributed small submicroscopic particles (inclusions) that differ from host mineral matrix in their refractive index, can lead to λ -specific UV scattering (e.g. Kortum, 1969), which is so far not considered to contribute to the UV-absorption. Single crystal electronic absorption spectra of eight natural almandine rich garnets (Alm₉₇-Alm₉₈), two synthetic almandine samples (Alm₁₀₀), all of different colour, and synthetic spessartine were studied by means of Zeiss microscope-spectrometer between 40000-20000 cm⁻¹. Special techniques of spectra measurements with crossed analyzer and polarizer that makes possible to register scattering effect directly, were used as well. Five of the above garnets were investigated using transmission electronic microscopy.

Different types of inclusions, from 10 to several hundreds nm in size, were observed in the garnet matrix. They are abundant and randomly distributed in synthetic garnet, whereas very rare in the natural almandines studied. Electronic absorption spectra of the natural almandine garnets show largely varying UV edge intensity that correlate with the intensities of broad Fe²⁺-Ti⁴⁺ CT band at 20000 cm⁻¹ and spin-forbidden *dd* bands of Fe³⁺ ions, imposed on it. There are also positive correlations between Ti and Fe³⁺ content, the latter recalculated on the basis of garnet stoichiometry, and UV edge intensity. Thus, presence of Ti and Fe³⁺ ions, even in very low concentration (0.0n at pfu), leads to CT phenomena, that involve Fe²⁺ ions in edge shared dodecahedron position and intensifies drastically ligand to metal CT. Different colours of natural almandine garnets with similar Fe²⁺ contents studied here are caused by this effect. Consistent with the absence of inclusions in natural garnets studied, λ -dependent scattering plays no role in their UV absorption. Contrary, in synthetic almandine and spessartine crystals different intensity of UV absorption was observed in inclusions-free rims and inclusion-enriched core parts. As a consequence, the latter demonstrated typical scattering 'transparence' patterns of spectra measured with crossed polarizers.

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OS05 : MOPm31 : G6 X-Ray Spectrometry of Light Elements and Transition Metals using the Electron Probe Microanalyser

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The latest electron probe microanalysis instruments are equipped with wavelength dispersive spectrometers of sufficient sensitivity and resolution to enable investigation of previously intractable problems in X-ray emission spectroscopy and in microanalysis. The Cameca SX100 at the University of Manchester is a state-of-the-art instrument which is being used to investigate the spectra of elements of low atomic number (Be to F), and spectral variations as a function of oxidation state in the transition metals. Two examples of such studies currently underway are work on the K-alpha spectra of boron, and the L spectra of iron.

In the case of boron, sinhalite (MgAlBO₃) has been studied in crystallographically oriented single crystals, which show variation in peak shape as a function of orientation. Spectra from a suite of borate and borosilicate minerals have been collected and are being used to develop methods for routine boron microanalysis and to investigate the stoichiometry of these minerals.

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Tuesday AM Session

Measurements of the iron L spectra (and where appropriate oxygen K spectra) have been made on a series of oxide and silicate samples of known compositions and containing Fe²⁺, Fe³⁺ or both in a range of coordination environments with oxygen. The oxidation states and site occupancies of the iron in these samples has been independently investigated using Mossbauer spectroscopy. Careful analysis and deconvolution of the spectra are being used to develop microanalytical methods for the measurement of iron concentrations in the different oxidation states and for micron-scale mapping of ferrous:ferric iron ratios.

OS05 : MOPm32 : G6 Valence Determination of Iron in Clays by Electron Energy Loss Spectroscopy

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Electron Energy Loss Spectroscopy at Fe L_{2,3} edges is used in order to investigate and quantify the ionisation state of iron in clays. Iron oxides have been used as reference to establish a calibration curve from L₂ and L₃ chemical shift of iron. We used pure FeO, Fe₂O₃ and Fe₃O₄ to provide iron at various ionisation state, 2, 2.67 and 3 respectively. A solution of MnBr₂ is added to the preparation to provide Mn²⁺ as internal reference considering its L₃ maximum at 641.8 eV. After spectral calibration in energy and baseline treatments, Fe white lines are measured both in position and intensity. The presence of Mn²⁺ on the sample does not affect the Fe L_{2,3} edges. L_{2,3} white lines of Fe^{II} are located at lower energy than L_{2,3} white lines of Fe^{III}. Calibration has been applied to untreated and modified natural clay minerals. Comparison of our results with Mössbauer spectroscopic analysis shows a good accordance. Therefore, EELS that is an individual, no-time consuming, technique, can be routinely applied to nanometric particles such as clay minerals. However, it is important to take into account the relative stability of iron species inside mineral during sample preparation and analysis. This analytical development should allow us to use clay minerals as redox markers for applications in metallogeny, sedimentology, diagenesis and environment sciences.

OS05 : MOPm33 : G6 Mechanical Fibration in Crystals and Bitumens

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Spalling of fibers on splits during brittle crystal failure was discovered in natural quartz by V.I. Vasilyev in 1969 and confirmed by our data on halite. It appears that this phenomenon is of structural nature, and fibers are a sort of mechanical whiskers, i.e. outspits of dislocation-free crystal blocks ("crystal chips" according to V.G. Balakirev).

Our further studies showed that mechanical fiber outspitting, or mechanical fibration, is characteristic not only of crystalline substances but of some natural solid hydrocarbons (bitumens), in particular, of asphaltite from Glasberget pegmatite (Sweden), gilsonite from limestone (Cape Sin'kin Nos, Pechora Sea, Russia), shungite (Karelia, Russia).

Hydrocarbon fibres in bitumens are split from splitting plane faces or from crests of conchoidal fracture. The fibres are 1-3 µm in diameter, most commonly about 1 µm, which corresponds to the thickness of textural plates observed as steps of the fracture where splitting occurs.

Fibration normally takes the following course. A shallow crack, one step deep, appears parallel to the fracture step face, 1-2 µm away from it. The crack then gives rise to an even band rolling away in the form of a cylinder or a spiral from the new fracture face. The band surface has a fine fibrous relief, its features frequently winding around the fibre axis, reflecting the distribution of stresses during rolling. The fibres are often segmented, cross-grooves separating them into 2-3 µm long blocks reminiscent of cyanobacterial cells, for which reason mechanical fibres are often mistaken for microfossils.

Thin rods, isometric in the cross-section, about 1 µm thick, rather than bands, are occasionally separated from the split steps. Peculiar branching presumably formed by rolled films can be sometimes observed.

Hydrocarbon fibres are plastic, bending to form rings and semi-rings, while the body of the material is extremely brittle. These fibers can hold pieces of disintegrated bitumen together.

Mechanical fibration in bitumens occurs due to their structural features and interaction of rupture and shear stresses brought about by combination of waves of different frequencies on the crack front. The structural factor plays the major role, because fibre formation is restricted to the substances with layered or layered-fibrous supermolecular ordering. A typical example is wurtzilite, which fracture is all made up of split fibres.

To draw a line, in bitumens, fracture can bear information on some features of their supermolecular structure.

OS05 : MOPm34 : G6 Elastic Moduli of Low-Symmetry Structures from First Principles

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Elastic moduli have been calculated from first principles for a number of minerals including diaspore and the Al₂SiO₅ polymorphs andalusite, sillimanite and kyanite, using the CASTEP density-functional theory code, with the GGA. Elastic moduli have already been calculated from first principles for many high-symmetry systems, by the imposition of several amplitudes of one or two carefully-chosen strains. In many electronic structure codes the stress may be calculated directly: the elastic moduli c_{ij} can then be calculated from a stress-strain fit. However, the computational cost of a fully-converged calculation for a large unit cell has until now precluded the calculation of elastic constants for low-symmetry minerals. Empirical calculations can usually produce good results for the diagonal elements of the elastic constant tensor, but are often much less reliable for other moduli.

With the use of ultrasoft pseudopotentials and increases in computational efficiency, first principles simulations of low-symmetry minerals are becoming routine. Careful choices of imposed strains and use of any remaining symmetry help to minimise both the computational effort required and the uncertainty in the final values. Bulk moduli calculated from the individual c_{ij} are typically within 1% of those obtained from the predicted equations of state, demonstrating the internal consistency of the calculations. We have determined the full set of elastic moduli of diaspore (Winkler *et al.*, 2001a) and hexagonal BeO (Milman & Warren, 2001). The elastic properties of the Al₂SiO₅ polymorphs andalusite, sillimanite (both orthorhombic) and kyanite (triclinic) were also predicted (Winkler *et al.*, 2001b). Only c_{13} for andalusite and c_{23} of sillimanite were more than 11% from the experimental values. The predictions for kyanite are believed to be of similar accuracy although no experiments had been performed when the calculations were made.

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OS05 : TUam01 : G6 Crystal Structure Paths to a Phengite Geobarometer?

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Massonne and Schreyer (1986, 1989) showed, in synthetic phengites, a contraction of the c parameter (and layer thickness t_c) with the increase of the Si content and proposed two phengite barometers based on the increase of Si with the metamorphic pressure (P): the influence of the temperature is small). The present work confirms, on natural samples, the contraction of t_c and tests the possibility of a direct correlation between crystal-structure parameters and P . The trigonal rotation α vs. Si shows the same behaviour of t_c .

The decrease of α with the increase of the Si content is well explained by the improvement of the fit between the tetrahedral (T) and octahedral (O) sheets promoted by the aluminoceladonic substitution (Mg for ^{VI}Al and Si for ^{IV}Al). Also the contraction of c (t_c) vs. Si can be related to a better T/O fit; in fact, a smaller α means a wider pseudo-hexagonal ring formed by the basal O_c oxygen atoms within which the interlayer cation I is allowed to sink, thus reducing t_c . Also in terms of bond-length (L)/bond-strength (s) correlation it can be shown that a decreasing (increasing) of α requires a contraction (expansion) of c . Let us call, in the order, L_{in} and L_{ou} , the shorter (inner) and longer (outer) $I-O_c$ bonds and label α_{Δ} and Δ variations related to α and c , respectively. To estimate the bond-strength s_i of a bond with length L_i , the equation $s_i = s_0(L_i/L_0)^N$ (Brown and Shannon, 1973) is used; the second Pauling's rule requires $\Sigma s_i = \text{charge of the interlayer cation } I$. For α decreasing it can be shown that $|\alpha \Delta s_{in}| > |\alpha \Delta s_{ou}|$; consequently $|\alpha \Delta s_{in}| > |\alpha \Delta s_{ou}|$, and an overall decrease of Σs_i would be observed. For c decreasing $|\alpha \Delta s_{in}| > |\alpha \Delta s_{ou}|$ holds; consequently an overall increase of Σs_i would be observed. It turns out that, in order to satisfy the Pauling's second rule, a decreasing (increasing) of α must be coupled with a decreasing (increasing) of c .

Plots of $\ln P$ vs. t_c and α for a number of natural phengites, for which the structure and some estimate (not based on a phengite barometer) of the genetic P (kbar) are known, show the following correlations.

$$\ln P = -29.03t_c + 291.0 \quad (R^2 = 0.78; 32 \text{ cases}).$$

$$\ln P = -0.348\alpha + 5.01 \quad (R^2 = 0.89; 21 \text{ cases}).$$

Availability of more samples with well defined genetic conditions (e.g., Smyth *et al.*, 2000) should allow improvements of the given equations and the possibility of taking into account the octahedral contents. Anyway, when c or, even better, the trigonal rotation α is known, an estimate of P can be obtained from crystal structure data.

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OS05 : TUam02 : G6
Fulleren, Carbon Nanotubes and Diamond-Like Phase Formation at the Metamorphic Parameters

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At low temperatures and pressures (750 C and 5 kbar) from the methane and hydrocarbon gases graphite, a-carbin, fullerite structures, carbon nanotubes and diamond-like cubic modification of carbon, which is more closed to C8 were synthesised. Fullerite formations have overall forms and multilayers structure. Nanotubes has length up to 1 µm, diameter nearly 600 Å and diameter of the channel nearly 40 Å. Cubic and oktaedral forms phase reached in size 2000 Å were determined. Microdiffraction shown it cubic structure, the calculations of the D-values data show that it's mainly closed to the rare cubic modification of carbon - C8 with cell parameter $a = 4.3 \text{ \AA}$. (This modification was determined yealy in the diamond-like films formed at very high temperatures from the carbon plasm.) As a result we can conclude that rare phases of the carbon - fullerene-like structures, nanotubes and cubic carbon which are known for very high temperatures processes could be formed at the metamorphic P-T parameters.

OS05 : TUam03 : G6
Powder Refinement of Maya Blue: A Palygorskite-Indigo Complex

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Maya Blue is a synthetic pigment, produced by the Mayas around the VIII century AD. Its colour ranges from bright turquoise to dark greenish blue. In modern times it was 'discovered' in the middle of the last century, together with the remains of the Maya civilisation, and until recently (Kleber et al. 1967) its nature was unknown. Maya Blue is extremely stable: it can resist boiling, concentrated nitric acid, alkali and organic solvents. It is composed of the colourless clay palygorskite and the organic blue dye indigo, extracted from the leaves of *Indigofera Suffruticosa*. This hypothesis was proved to be correct by photoluminescence spectroscopy (Ajò et al., 2000). The present study elucidates the pigment structure and gives information to understand its preparation.

Palygorskite has two different polytypes, monoclinic and orthorhombic, presenting zeolitic-like channels along the z-axis occupied by zeolitic water. The relative abundance of the different polytypes may be a key to understand if MB was produced in one site only or not. Indigo molecules can enter the channels and form stable bonds inside the clay. Theoretical calculations showed that zeolitic water has to be removed in order to accommodate indigo in three unit cells along z. A molecular mechanics optimization was carried out, using the Discover program. Fixed-framework simulations proved that indigo can fit in the palygorskite channels with minor structure distortions, by displacing the structural water molecules. Indigo is calculated to be in the center of the channel, its major axis coinciding with the channel direction and its symmetry center superposed to the one located at (0, 1/2, 1/2) of the superstructure. No symmetry was imposed during this calculations.

To confirm this structural hypothesis, Rietveld refinements (GSAS) were carried out on a palygorskite from Mexico and on Maya Blue prepared from the same clay, according to the techniques probably used by the Mayas (C. Reyes-Valerio, 1993). Data were collected using synchrotron radiation at ESRF, Grenoble (Gilda beamline, G.Artilioli). The initial co-ordinates for both monoclinic and orthorhombic palygorskite were taken from Artilioli et al. (1994). The clay

refined co-ordinates were used to construct the 3-cells superstructures for both polytypes. In the complex there is a high-grade disorder: a) indigo can enter the channel in 2 different ways, but once inside it cannot rotate on its axis; b) provided that the indigo inversion centre coincides with one of the clay, indigo can occupy 3 different positions along the superstructure z axis, evidencing a sixfold disorder; c) not all the zeolitic water molecules are eliminated from the channels. For these reasons, the indigo position was not refined. In spite of all these difficulties, the refinement converged satisfactorily, giving evidence of the correctness of the calculated model.

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OS05 : TUam04 : G6
Evidence of Migrating Fluids in the Upper Mantle: An EPMA Investigation of Trace Elements and Oxidation Ratios of Clinopyroxenes and Glasses in Mantle Xenoliths from Massif Central (France)

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Silicic glasses are common in mantle xenoliths from many alkaline volcanic series. Their origin has been considerably debated: glasses were formerly interpreted as products of host magma infiltration or decompression melting of hydrous minerals during ascent. In the last decade, the emergence of new microanalytical techniques has allowed to test hypotheses considering glasses as trapped samples of melts formed during partial melting or migrating by porous flow through the mantle. Trace elements are key tools to characterize contrasted styles of metasomatism, in particular to evidence the passage of carbonate or silicate melts in the mantle. Moreover, migrating fluids may induce large variations of the redox state of the mantle, although recent studies have revealed a complex picture with contradictory results: correlation or not between oxygen fugacity and metasomatic enrichment and different imprints left by different metasomatic fluids.

It is thus of great interest to be able to analyze at a scale of a few µm both major and trace elements and to measure directly the ferric-ferrous concentrations. The recent developments of the electron microprobe analytical procedures carried out in our laboratory allow such investigations. For low-level trace element analysis (a few tenths of ppm), the improved procedure includes fractional counting time, background modelling and data statistical filtering (Wagner & Fialin, 1999; Fialin et al., 1999). The determination of the oxidation state of iron is based on the measure of the self-absorption induced shift of the emitted Fe L α peak (Fialin & Wagner, 1999; Fialin et al., 2000; Fialin et al., in press).

These techniques have been applied to the study of glasses and clinopyroxenes from amphibole-bearing spinel lherzolites from Massif Central. Glass occurs as veinlets along grain boundaries and in pockets around amphiboles or between spinels and anhydrous phases. The pockets contain secondary clinopyroxene, olivine, spinel and abundant bubble-like voids, testifying for a former high content of volatiles. The glasses are silica- (50-58 oxide wt%) and alkali- (up to 12 wt% total alkalis) rich, and aluminous (18-23 wt%) with a large range in composition as observed in glasses from world-wide xenoliths. Despite the frequent association of glassy pockets with amphibole, which is in favor of *in situ* melting of the hydrated phase, the breakdown of amphibole cannot explain all the chemical characteristics of glasses. Mass balance calculations carried out with major elements show that additional components are required, in particular alkalis for which external sources have to be considered. Preliminary results show an enrichment in Sr (756 ppm) and Nd (40 ppm) in secondary clinopyroxenes compared to primary lherzolite clinopyroxenes (200 ppm and 34 ppm respectively) and higher Fe³⁺ / ΣFe (up to 0.9 / <0.1).

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OS05 : TUam05 : G6
Complete Solid-Solution between Amphiboles with Li and Na at the B-Group Sites

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The importance of low-Z elements in the crystal chemistry of many rock-forming and accessory minerals has greatly increased recently also due to the availability of analytical techniques that allow their detection and quantification. Structure refinement and comparative crystal chemistry allow to accurately model their site preference and partitioning especially in complex mineral families such as the amphiboles.

The presence of Li in amphiboles had been previously constrained to the B-group sites in the A-vacant Mg-Fe-Mn-Li amphiboles, the root-name of reference being holmquistite and clinoholmquistite (Li₂Mg₃Al₂Si₄O₂₂OH). In the last ten years, a number of sodic amphiboles with significant Li contents ordered at the octahedral M3 site were found in peralkaline granites and in manganeseiferous metasediments, the root-name of reference being leakeite (Na Na₂ Mg₂Fe³⁺LiSi₆O₂₂OH); Li at M3 had been locally associated with Na at A and Si at the T sites. We can now provide more than one hundred analyses of amphiboles from the Pedriza Massif (Spain), that show complete - and totally unexpected - solid-solution between the two main amphibole groups. SIMS analyses and structure refinement of selected compositions allowed to obtain accurate crystal-chemical formulae and reliable constraints to identify and quantify the presence of Li in apparently deficient analyses. All these amphiboles were found in hydrothermal episyenites outcropping is a small region (1.5 x 1 km wide); they all formed by interaction of former granitoids with hydrothermal fluids of meteoric origin at estimated P, T conditions around 150-170 MPa and 520°C.

Thus the amount of Li incorporated in amphiboles (up to 3.0 apfu) seems to be controlled solely by the chemistry of the system. Li might be far more frequent in amphiboles than previously supposed. Its presence strongly affects the evaluation of the f_{O2} conditions of formation, since octahedral Li is locally balanced by further octahedral Fe³⁺. Moreover, the evidence that Li may completely substitute Na at the B-group sites throws a bridge across the two groups, and may even suggest revision of the present nomenclature.

OS05 : TUam08 : G6
New Forms of Cluster Self-Organisation at the Nano-Level and their Role in Crystalline and Non-Crystalline Materials Formation

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The most important recent advances in mineral physics and chemistry are connected with nano-level investigations of the mineral structure, properties and formation (Yushkin, Askhabov, 1999). Moreover, whether this or that type of solids (crystalline or non-crystalline) will be formed is determined by peculiar nanoforms of structural organisation of substance: 'hidden phase' clusters - quatarons (Askhabov, 1999a,b). In physical terms, quatarons are pre-crystallisation transient-phase clusters. Geometrically, quatarons are interpreted as finite fragments of (R, r) systems. Quatarons are characterised by a quasi-spherical shape and loose bonds between the constituting atoms. Their non-crystalline character is retained till quatarons achieve a critical radius ca. 1.2 nm. Quatarons to ~0.3 nm in size give rise to tetra- or octahedral atom arrangements (polyhedra) close to structural modules of crystals. Their

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are the basic building units in crystal growth (Askhabov, 1999b). Once rigid atom bonds have been established in large hollow quaternions, they transform to fullerene-like clusters (Askhabov, 2000), in which atoms form a network of regular penta- and hexahedra on a spherical surface. Dense critical-size (~1.2 nm) quaternions evolve into crystal nuclei (nanocrystals) or icosahedral non-crystalline clusters. If for some reason, like fractal structure of the cluster's surface or the cluster's non-crystallographic (icosahedral) shape, crystallisation of quaternions or their aggregates becomes impossible, they give rise to a peculiar class of ultra-disperse solids of different degrees of ordering, termed quaternites. The closest analogue of such materials is opal, a substance made up of monodisperse spherical silica particles. The highly-ordered material formed by carbon fullerenes is known as fullerite. The new cluster theory of self-organisation accounts for formation of tetra-coordinated amorphous substances, glasses, quasi-crystals as well as for crystallochemical patterns in phase transformations in minerals with modular structures. The research was partially supported by RFBR (grant # 99-05-64883) and INTAS (grant # 99-0247).

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OS05 : TUam09 : G6 Kinetics of Fe-Mg Disordering Process in Ca-Rich Orthopyroxene

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Anomalous kinetics for the Fe-Mg disordering process in the Ca-rich orthopyroxene from the Johnstown meteorite has been recently reported by different authors (Zema et al., 1999; Heinemann et al., 2000). This orthopyroxene has composition $Wo_3En_{74}Fs_{23}$ (Zema et al., 1999) and contains exsolved (100) augite lamellae and Guinier-Preston (GP) zones. Annealing experiments at different temperatures showed that the kinetics of the disordering process in this orthopyroxene is extremely slow. The Arrhenius relation $\ln K_{dis} = \ln K_0 - Q/RT$ yielded an activation energy of ~ 100 kcal/mol which is in strong contrast with the value of ~ 63 kcal/mol calculated by Ganguly & Tazzoli (1994) averaging selected experimental measurements available in literature. The surprisingly high value of the activation energy was ascribed to the presence of microstructures within the Johnstown orthopyroxene. On the basis of a very accurate microstructural study by TEM (Cámara et al., 2000), the high density of GP zones, rather than the presence of exsolved augite lamellae, has been proposed to be responsible for this anomalous kinetic behaviour. The confirmation of this result may have strong implications in geothermometry and geospeedometry since the Fe-Mg exchange reaction in orthopyroxene is a very useful tool for modeling the thermal histories of the host rocks.

In this work, the kinetics of the disordering process at T = 750°C in the Ca-rich orthopyroxene from the volcanic rock L3 (Aeolian Islands, Italy) was studied. This orthopyroxene has composition $Wo_3En_{66}Fs_{36}$ (Molin, pers. comm.) and it does contain exsolved augite lamellae but does not contain GP zones (Cámara et al., 2000). A series of isothermal annealing runs followed by quenching was performed on one single-crystal having dimension 0.28 x 0.32 x 0.42 mm. Oxygen fugacity was controlled by WI buffer. After each annealing run X-ray single-crystal diffraction data were collected and the structure refinement procedure for a *Pbca* phase coexisting with a *C2/c* exsolved phase (Domeneghetti et al., 1996) was applied. Analysis of the kinetic data was performed according to the theoretical model proposed by Mueller (1967). A disordering rate constant of $3.98 \cdot 10^{-3} \text{ min}^{-1}$ at T = 750°C was obtained. Such value is very close to what expected for a "normal" kinetic behaviour.

Therefore the presence of Ca in the orthopyroxene lattice and the presence of exsolved augite lamellae should not be responsible for the anomalous kinetics showed by the Johnstown orthopyroxene. The hypothesis that it is the pervasive presence of GP zones in this sample to slow down the disordering process is then enforced by this result.

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OS05 : TUam10 : G6 Real-Time Observation of High-Pressure Phase Transformations with Complex Impedance Spectroscopy

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The recent success in our efforts to determine the electrical properties of minerals at high pressures has motivated us to use this technique as an in-situ probe in order to follow high-pressure phase transformations in real time. By using complex impedance spectroscopy in a multianvil apparatus, we can precisely monitor the progression of any transformation in which there is a measurable difference in the electrical conductivities of the two phases. We have applied the technique to the transformation of San Carlos olivine to wadsleyite, for which the electrical conductivity is expected to increase by about two orders of magnitude. The bulk electrical conductivity of a partially transformed sample does not necessarily vary proportionally with the volume fractions of the two phases as their spatial distribution also can play an important role. To address this, we have also carried out quench experiments in order to analyze the microstructural development at various stages of the transformation. In particular, we aim to recognize the electrical signature in the in-situ measurement that corresponds to the formation of an interconnected network of the more conductive wadsleyite phase along grain boundaries. At this point, not only should the bulk electrical properties of the two-phase sample change, but other properties as well, such as the overall strength of the aggregate material. Experiments have been conducted up to 15 GPa at temperatures ranging from 850 to 1000°C on both single crystal and polycrystalline samples. A unique feature in the measurement of the polycrystalline samples can be observed at an early stage of the transformation as the rate of increase in conductivity abruptly changes. We attribute this feature as the point in the transformation when an interconnected network of wadsleyite has been formed along grain boundaries, as no such feature can be observed in the trace of the single crystal experiment in which only homogeneous intracrystalline nucleation and growth mechanisms are expected. Powder diffraction, SEM and micro-Raman analyses of partially transformed samples from our parallel quench study help us to understand how the amounts and distribution of the two phases relates to the electrical response of the bulk sample. Results from these analyses indeed show that interconnectivity occurs at early stages of transformation corresponding to low volume fractions of wadsleyite, and support our conclusion that it is possible to extract some details of microstructural development of phase transformations using this in-situ technique. Continued efforts to extract more quantitative information, particularly related to transformation kinetics, will prove useful towards our understanding of subduction processes.

OS05 : TUam11 : G6 Computational Study of Al-Si and Al-Mg Ordering Schemes in Muscovite and Phengite

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The nature of Al-Si ordering across the tetrahedral sites in muscovite $K_2Al_3(Si_4Al_2O_{20})(OH)_4$ was investigated using various computational techniques. Values of the atomic

exchange interaction parameters J_i were obtained. From these parameters, a two-dimensional Al-Si ordering scheme was deduced. The transition temperature T_i for this two-dimensional ordering is 1900 K. There are several possible ordering schemes in three dimensions, based on different stacking sequences of ordered layers of tetrahedral sites. Monte Carlo simulations of both two-dimensional and three-dimensional ordering were performed, but in the three-dimensional simulation only the two-dimensional ordering is seen, implying that three-dimensional ordering is too slow to be attained during the timescale of the simulation. The effect of the three-dimensional interactions is to raise the two-dimensional ordering temperature to 2140 K. From the three-dimensional Monte Carlo simulation, the frequency of occurrence of $4Si_4Al$, $3Si_4Al$, $2Si_4Al$ and $1Si_4Al$ clusters was determined, which match those inferred by ²⁹Si MAS-NMR measurements reasonably well. In fact, the match suggests that the cation ordering seen in experiments corresponds to an equilibration temperature just above the two-dimensional ordering temperature.

Similar investigation is now in progress on phengite, $K_2(Al_3Mg)(Si_7AlO_{20})(OH)_4$, to investigate the effects of octahedral Al-Mg ordering in addition to those of tetrahedral Al-Si ordering, such that three sets of atomic exchange interaction parameters ($J_{T,T}$, $J_{T,O}$, $J_{O,O}$ where T denotes tetrahedral layers and O denotes octahedral layers) are necessary.

OS05 : TUam12 : G6 Short and Long-Range M-Site Ordering in Amphiboles

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The long and short-range partitioning of Mn²⁺, Fe²⁺ and Mg over M (1), (2), (3) and M(4) in two natural manganogrunites (Fe, Mn-rich amphiboles) has been studied by neutron powder diffraction. ⁵⁷Fe Mössbauer and infrared spectroscopy at room temperature. The partitioning of Fe determined by Rietveld refinement of neutron data and agrees well with the number obtained by fitting the hyperfine parameters of the Mössbauer spectra. Direct interpretation of FTIR peak areas in the fundamental hydroxyl-stretching region reveals differences in the cation occupancies of the M(1)-M(3)-M(1) triplet compared to occupancies derived by Rietveld refinement that cannot be explained by processes of short-range ordering (clustering/ segregation) alone. This suggests that one must be cautious when using the FTIR OH-absorption spectra to infer patterns of long-range order in these compounds.

Our high-temperature studies of cation disordering using in situ neutron diffraction show Mn to be preferentially ordered on to M(4) with an exchange energy of around -18 kJ.mol⁻¹. Substitution of Fe by Mn into the smaller M(1) and M(2) octahedral sites commences on heating at 350 and 450°C in the Mn-rich and -poor samples, respectively. Cooling experiments show high-temperature cation distributions are quenched in below these temperatures.

Infrared absorption spectra from a series of synthetic amphiboles along the Mn-Mg cummingtonite binary provide further insights into the distribution of Mn within the amphibole structure, especially in compositions where X_{Mn} exceeds 2.0 p.f.u.

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OS05 : TUam13 : G6

Local Structural Heterogeneity in Spessartine-Grossular Solid Solutions and their Saturation Behaviour

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HMIR-spectra of the spessartine-grossular (Mn-Ca) solid solution have been analysed in terms of effective line width and peak shifts and compared with the results from the HMIR investigation on (Mg, Fe, Ca-) garnet solid solutions by Boffa Ballaran et al. (1999). Their findings were confirmed, where the main points are: (a) All investigated Ca-bearing solid solutions show softening of the lowest frequency mode. (b) The main contributions to the excess enthalpies of mixing in solid solutions probably derive from elastic energies created by local structural heterogeneities. The calibrated effective line width has been used to predict the enthalpy of mixing in grossular-spessartine to be $\Delta H^{\text{mix}} = W_{\text{H}} X_{\text{G}} X_{\text{Sp}}$, with $W_{\text{H}} = 14.3(7) \text{ KJmol}^{-1}$. A symmetric mixing model and the calibration of calorimetric grossular-pyrope data used in Boffa Ballaran et al. (1999) have been applied. (c) The value of W_{H} fits very well to a model derived from computer simulations by Bosenick et al. (in press), where the symmetric Margules parameter, and therefore ΔH^{mix} , is supposed to scale quadratically with the volume difference of the end-members.

Due to the third law of thermodynamics, entropy must tend to zero as T goes towards 0K. A plateau can occur already at higher temperatures. This saturation is observed for thermal expansion data and for a number IR frequencies of grossular-pyrope solid solutions (Boffa Ballaran et al., 1999; Bosenick et al., 1997) and has now been determined in spessartine-grossular solid solutions. The molar volumes of Gr40Sp60, Gr50Sp50 and Gr90Sp10 become independent of T at high temperatures ($T_{\text{H}} = 400, 500$ and 200K respectively) compared to their end-members ($T_{\text{H}} = 170\text{K}$). This could be explained in terms of relaxation of the atoms during cooling which might be hindered in the case of mixed garnet crystals by local strain caused by the substitution of smaller or larger atoms in the dodecahedral X-site. The shrinking process can continue in pure crystals down to lower temperatures because the relaxation is not restricted by local heterogeneities (Boffa Ballaran et al., 1999). This effect, if real, could have a significant influence on the thermodynamic mixing properties.

Boffa Ballaran, T, Carpenter MA, Geiger, CA & Kozziol, AM, *Phys. Chem. Minerals*, **26**, 554-569, (1999).

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OS05 : TUam14 : G6

Cd Distribution Coefficients in Calcite as a Function of the Precipitating Fluid Supersaturation

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Otavite-calcite (Cd,Ca)CO₃ solid solutions have been synthesised from aqueous solutions in order to investigate the influence of supersaturation on the distribution of substituting ions between the aqueous and the solid phase. Crystallisation experiments were carried out under controlled conditions of supersaturation rate by counter diffusion of reactants in a gel medium and the so called 'hanging drop' method. The solids were analysed for Ca and Cd by electron microprobe. The extremely low solubility of otavite compared to that of calcite involves a strong preferential partitioning of the less soluble Cd endmember towards the solid phase (Königsberger et al., 1991). This means that Cd-poor aqueous solutions are at equilibrium with Cd-rich solids. As a consequence, the geochemical conditions to precipitate intermediate solid solutions are very restrictive: only a narrow compositional range of aqueous solutions can coexist in equilibrium with intermediate solid solutions, i.e., the solid tend to either Ca-rich or Cd-rich over a very small range of fluid

compositions (Prieto et al., 1997). Under non-equilibrium conditions, this 'bimodal' crystallisation tendency decreases, although a strong preferential partitioning of Cd towards the solid phase remains. Depending on the supersaturation level at nucleation, we have obtained effective distribution coefficients for cadmium in calcite ranging between 4169 (the equilibrium one) and 66.09 for crystals grown in gels at high supersaturation rates.

Königsberger et al., *Geochim. et Cosmochim. Acta*, **55**, 3505-3514, (1991).

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Tuesday PO Session

OS05 : TUpo01 : PO

Minerals Transformation in an Hydrothermally Altered Basalt from Morocco

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In Morocco, triassic basalts overlay large areas. They consist of accumulations of basaltic lavas of fissural origin associated with extensive dikes (Bertrand et al., 1982). For the most part, they have suffered an extensive hydrothermal alteration and show all stages of mineral decomposition leading to clay minerals as secondary products. The formed clay minerals - mainly phyllosilicates - are important to understand the alteration processes as related to chemical exchanges between basalts and fluids. Detailed textural, structural, and chemical characterization of phyllosilicates can provide valuable information about the nature of the continental hydrothermal system, the evolution of hydrothermal fluid and the global transformation story.

In this study, petrographical and mineralogical approaches were used to investigate phyllosilicates in basalts from two selected areas (El Khab and Bhalil) of the middle Atlas (Morocco) in which they occur as complete or partial replacement of olivine, pyroxenes, plagioclase, interstitial materials and as filling of vesicles, fractures and cleavages. Clay minerals were characterized by various complementary methods such as optical microscopy, X-ray diffraction, scanning and transmission electron microscopies coupled with microanalyses (Dekayir et al., 2000).

Results show that these phyllosilicates are identified as saponite, corrensite, talc and chlorite, and mainly correspond to trioctahedral and Mg-rich phases. The two main phases (saponite and corrensite), from a variety of alteration environments in selected areas, present homogeneous chemical compositions. This illustrates that the chemistry of secondary phyllosilicates is not significantly influenced by the association and the composition of the host primary phases but is rather probably controlled by the composition of the hydrothermal pore fluid. Such an observed mineral association, with mainly saponite, little amounts of other phyllosilicates, and no evidence of albite and zeolite, suggests that these basalts have suffered minimal alteration at relatively low temperatures (Tomasson & Krismannsdottir, 1972). Some samples (from Bhalil) contain chlorite and might have suffered a higher temperature (< 350°C, Alt et al., 1986).

Lastly, only discrete phyllosilicates were observed here. No random mixed-layer minerals were detected. Such assemblages of relatively stable discrete phases probably indicate that equilibrium was nearly achieved and that dissolution-crystallization process was probably the main operating transformation mechanism. These observations suggest that corrensite is more stable than random mixed-layer chlorite-smectite and that the assemblages smectite + corrensite and corrensite + chlorite are more stable than mixed-layer smectite-corrensite and corrensite-chlorite, respectively.

Bertrand H, Dostal J & Dupuy C, *E.P.S.L.*, **58**, 225-239, (1982).

Dekayir A et al., *Clay Miner. (submitted)*, (2000).

Tomasson J & Krismannsdottir H, *Contr. Miner. Petrol.*, **37**, 235-247, (1972).

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OS05 : TUpo02 : PO

A ⁵⁷Fe Moessbauer and Powder IR Spectroscopic Study of Sapphirine

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Sapphirine is a rock-forming silicate found in Mg- and Al-rich high-grade metamorphic rocks. It has the general formula (Mg_{4-x}Al_{4-x})(Al_{4+x}Si_{2-x})O₂₀ and Fe²⁺ can substitute for Mg and Fe³⁺ for Al³⁺. Little is known, however, about the extent of these substitutions over the different structural sites. In addition, the ferrous-ferric iron ratios of natural

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sapphirines and the site distribution of the Fe cations have not been investigated in detail. In order to address these issues, ^{57}Fe Mössbauer spectroscopic measurements at 77 K and 298 K were made on five natural sapphirines. The IR powder spectra were measured to better characterize the state of order and the role of composition on structural properties. X-ray powder measurements were made to differentiate between the two polytypic varieties 2 M and 1 Tc, using the criteria given in Christy et al. (1989).

The sapphirine samples studied have been described in the literature and their mineral assemblages and petrologic environments are well known. They have Fe/(Fe + Mg) mole fractions ranging between 0.02 and 0.25. The Mössbauer spectra of the different samples are roughly similar. They can be fitted by at least two distinct Fe^{2+} doublets (I.S. of about 1.18 and 1.20 mm/sec at RT) and at least one Fe^{3+} doublet (I.S. = 0.2 to 0.4 mm/sec). The Fe^{2+} can be assigned to octahedral sites and the Fe^{3+} to tetrahedral sites. Some samples may also contain octahedral Fe^{3+} . The atomic ferric/ferrous ratios lie between 5 and 20%. The blue-green color of sapphirine is probably related to charge transfer between Fe^{2+} and Fe^{3+} , although it is not clear if it occurs between edge-shared octahedra-octahedra or tetrahedra-octahedra.

The vibrational spectra in the MIR region between 1300 and 400 cm^{-1} are similar to those presented by Christy et al. (1989). The number of bands and their energies are difficult to quantify due to the large number of modes and their strong overlapping. In the FIR region, which has been measured for the first time, the bands are fewer and they tend to be broad and weak. A moderately strong envelope with three major absorption features is present between 350 and 220 cm^{-1} . Weak modes can be observed down to at least 170 cm^{-1} . Due to the complexity of the sapphirine structure and the interlinking of crystallographically independent polyhedra, many of the bands likely represent mixed or coupled vibrations. Their assignment needs to be done in combination with state-of-the-art lattice dynamic calculations.

Christy AG, Phillips, BL, Güttler, BK & Kirkpatrick RJ, *Am. Min.*, **77**, 8-18, (1992).

OS05 : TUp03 : PO Characterisation of a Ca-Rich Oneillite-Like Member of the Eudialyte Group- Evidence for the Presence of $(\text{CO}_3)^{2-}$

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The eudialyte minerals belong to a fastly increasing group of complex cyclosilicates which occur in peralkaline rocks. The Si-tetrahedra form three- and nine-membered rings which are connected by (Zr,Ti)-octahedra to form (001) modules; these modules are common to all the known members of the group. Within this layered-framework, several sites can host a wide range of cations; thus specific mineral species are obtained. The following general formula, which however does not yet put in evidence all the crystal-chemically differentiated sites, can be written as (Johnsen & Grice, 1999): $\text{Na}_{15}(\text{M}1)_6(\text{M}2)_3(\text{M}3)(\text{Zr,Ti})_3(\text{Si}_2\text{O}_7)_2\text{Y}_2\text{X}_2$. The known eudialyte minerals are rhombohedral; they show different space group types ($R\bar{3}m$, Rm and $R3$); the presence of the centre depends from the M3 content and that of the mirror plane m from the splitting of the M1 site) and c parameters (~ 30 and ~ 60 Å; depending on cation ordering).

A sample of eudialyte, from peralkaline pegmatites of the Dara-i-Pioz alkaline massif (Tajikistan), has been fully characterised, including X-ray single-crystal diffractometry which allowed to obtain a satisfactory crystal-chemical formula by matching the analysed chemical elements (WDS microprobe) with the electron density contents of the independent crystallographic sites. After recognising twinning by merohedry, which is due to the inversion centre present in other eudialytes, the structural refinement in the space group $R3$ converged to $R = 0.026$ for 3454 observed reflections collected (MoK α radiation) on a crystal with $a = 14.239(3)$ and $c = 30.039(8)$ Å; and c/a ratio. In the space group $R3$, the M1 site splits into two sites, M1a and M1b; the Dara-i-Pioz eudialyte group mineral corresponds to a Ca-rich oneillite (Johnsen et al., 1999) with Ca dominating both in M1a and M1b sites while in oneillite the

M1b is dominated by Mn. Further, an 'Na site' is mainly occupied by REE and the M2 site is dominated by Mn in our sample and by Fe in oneillite.

As already reported for oneillite, the infrared spectrum clearly shows the presence of $(\text{CO}_3)^{2-}$ in the Dara-i-Pioz sample. For the first time in a eudialyte group mineral, in our sample the structural position for $(\text{CO}_3)^{2-}$ has been identified on the three-fold axis as an X site which, in minor part, is alternative to a small quantity of Cl which is coordinated by Na. In conclusion, the following simplified crystal chemical formula for the studied oneillite-like mineral can be written: $\text{Na}_{12}(\text{REE}, \text{Ca}, \text{Sr})_3\text{Ca}_6(\text{Mn}, \text{Fe})_3\text{NbZr}_3(\text{Si}_{25}\text{O}_{73})(\text{O},\text{OH})_4(\text{CO}_3)_1\text{Cl}$.

Johnsen O & Grice JD, *Canad. Mineral.*, **37**, 865-891, (1999).

Johnsen O, Grice JD & Gault RA, *Canad. Mineral*, **37**, 1295-1301, (1999).

OS05 : TUp04 : PO Correlation between the Temperature of Homogenization of Liquid Inclusions in Fluorite Crystals and Crystal Shape

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Mineral fluorite of various colours and shapes can be found in several outcrops in the broader region of the Mt. Blegos in Slovenia. We tried to prove the correlation between the shape of the crystals and the temperature of homogenization of the fluid inclusions as well as to analyse the largest possible number of the solid inclusions. The results of our work are presented in this article. Fluorite can be violet or green coloured as well as colourless. The following minerals were discovered as solid inclusions in fluorite: valentinite, dolomite, quartz, stibnite, rosenite and chalcotibite. Cube, dodecahedron, tetrahedron, tetragon-trioctahedron and hexoctahedron planes were discovered on the crystals of fluorite. Crystals with the cube and dodecahedron planes are most commonly found in the Blego deposit. The rest of the combinations are rare. Besides the solid inclusions fluorite contains fluid inclusions too. In the majority of the cases, fluid inclusions which appear along the colour zones show the negative cube shapes. The homogenization temperature of the primary inclusions in the violet-coloured crystals is between the 172 and 200 degrees centigrade, whereas in the green-coloured zone the homogenization temperature drops to the 95 - 100 degrees centigrade. According to the measured homogenization temperatures we confirmed the Glikin's (Glikin, 1981) and Kiryanova's (Kiryanova & Glikin, 1999) results that the crystal shape correlates with the temperature of the crystallization.

Glikin AE, *Journal of Crystal Growth*, **52**, 98-103, (1981).
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OS05 : TUp05 : PO FeMg-Exchange Experiments on Chlorite in the System MgO-FeO-Al₂O₃-SiO₂-H₂O

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Fe-Mg-chlorite is widespread in metamorphic and hydrothermal rocks. Stable assemblages in a wide range of temperatures and pressures indicate that iron-rich chlorites are more aluminous than Mg-rich ones. Data from (ultra)mafic and pelitic rocks constrain the Fe/Mg partitioning (K_p) with several coexisting silicates and oxides. Experimental studies on chlorite so far have been performed mainly in the iron-free system. For intermediate and pure Fe-chlorite systems experimental data are more sparse and partially discrepant, probably owing to sluggish reaction kinetics of chlorite and the growth of metastable assemblages. To date, few experimental studies have analyzed the Tschermak-contents of chlorite.

In the present study FeMg-exchange experiments between natural chlorite and synthetic olivine and spinel are conducted at 3-6 kb, 450-650°C with oxygen fugacity defined by Fe-Fe₂O₃ buffer. Various electrolyte solutions were tested as flux because reaction rates were found to be insignificant in pure water. However, even with the aid of 1 M-electrolyte solutions the amount of FeMg-exchange between the reacting minerals is limited to < 10 mol% in runs of four weeks duration at 550°C/5 kbar. Reaction extents observed at T>600°C, P=5 kbar are more encouraging. Product textures indicate that chlorite reacts by a dissolution-precipitation mechanism under these conditions and the experimental results do confirm the trend observed in nature that more iron-rich chlorites are more aluminous. For these reasons exchange experiments are now performed near 600°C, using starting materials lying close to tie-lines known from natural K_p -values.

In parallel with the experiments, this study also aims to formulate and calibrate a comprehensive thermodynamic model for chlorite taking into account both Al,R²⁺,Si⁴⁺- and FeMg₁ exchanges. Most published formulations do not expanded to a non-ideal solution model that covers the desired composition range. So far, the new model has been tested on natural phase relationships from ultramafic rocks.

OS05 : TUp06 : PO Re-Examination of the Crystal Chemistry of the Kimzeyite from Stromboli, Aeolian Islands, Italy

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Kimzeyite is a rare Zr-rich mineral of the garnet family ($\text{X}_3\text{Y}_2\text{Z}_2\text{O}_{12}$), mainly characterized by the occurrence of Ca at X (8-fold) site, of Zr at Y (6-fold) and extensive substitution (usually Al and Fe for Si) at Z (4-fold) site. In fact its crystal chemistry is quite complex since a great number of atoms (e.g. Fe, Al, Mg, Mn, Ba, REE, Ti) may be distributed over the three crystallographic sites. In addition, due to remarkable TiO₂ amounts, kimzeyite shares some of the Ti-bearing garnets problems, i.e. coexistence of transition elements with different coordination environments and/or valence states¹. The Stromboli kimzeyite was studied for the first time by other Authors² by means of chemical (electron microprobe, EMP) and crystallographic methods (structure refinement, SREF). However poor agreement between EMP and SREF-estimated mean atomic numbers³ was obtained and some ambiguities in the cation partition could not be solved. In the present work, EMP analyses and crystallographic investigation with synchrotron radiation have been performed on the same single crystal (about 40 μm size) studied by those Authors². The chemical composition was measured via a CAMECA SX50 (WDS mode), whereas the diffraction data were collected by means of an Imaging Plate MAR 345 at the ELETTRA X-ray Diffraction beamline. From 4643 measured reflections 198 (out of 252) unique reflections, with $I > 3\sigma(I)$, were used in the anisotropic refinement. The latter (performed with CRYSTALS⁴) converged at $R=2.39$, $R_w=2.13$. The crystal cell parameter was $a=12.350$ Å. The very good agreement between EMP and SREF mean atomic numbers allowed to determine the correct crystal chemical formula and to work out qualitatively and quantitatively the substitution mechanisms affecting the Stromboli kimzeyite structure: 1) schorlomite substitutions, 29%; 2) kimzeyite substitutions, 55%; 3) morimotoite-like⁵ substitutions, 16%. The results are compared to those from another natural specimen, recently investigated⁶.

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