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HIGH-PRESSURE STUDY OF CHONDRODITE, $Mg_5(SiO_4)_2(OH/OD,F)_2$: STRUCTURE, O-D...F/O GEOMETRY AND COMPRESSIBILITY

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Chondrodite is a dense hydrous magnesium silicate that could transport water into the Earth's interior. As F-incorporation extends the thermal stability of chondrodite (Stalder and Ulmer, 2001), we examined the influence of the OH \leftrightarrow F substitution on the high-pressure crystal-chemical behaviour.

The compressional and high-pressure structural behaviour of chondrodite ($X_{OH} = 0.42$) and its deuterated analogue were investigated using single-crystal X-ray (diamond-anvil cell, quartz internal pressure standard, $P_{max} = 9.6$ GPa) and powder neutron (Paris-Edinburgh cell, SME gasket, $P_{max} = 7.04$ GPa) diffraction methods.

The compressibility data ($K_{0,T} = 117.0(4)$ GPa; $K_T = 5.59(11)$) suggest a slight softening of the chondrodite structure with OH incorporation, which is consistent with the unit-cell volume increase associated with the substitution of the larger OH ion for F. The largest differences with pressure occur in the M2 octahedron. Cation-cation repulsion moves the M2 cation off-center. Hence, M2-O2 and M2-O3 are the longest bonds and most easily compressed, which is consistent with the large compressibility parallel to the *b* axis. This is also reflected by a kinking between corner-sharing Si tetrahedra and M2 octahedra. Small changes in the O-D...F/O geometry reveal several trends with pressure. The donor-acceptor distances decrease and the covalent O-D distance decreases slightly at the highest pressure obtained. The strong hydrogen bond strengthens, as indicated by an increase of the O-D...F angle and a slight decrease of the D...F hydrogen bond. The positive shifts of Raman O-H stretching frequencies with pressure (Lin et al., 1999) may be related to the shortening of the O-D bond length. The weak hydrogen bond, however, weakens with pressure, as expressed by the increase of the O-D...O1 angle and a minimal increase of the D...O1 hydrogen bond. These changes can be interpreted in terms of a rotation of the O-D vector into the cavity surrounding the D atom.

Stalder R & Ulmer P, *Contr. Min. Petr.*, **140**, 670-679, (2001).

Lin C-C, Liu L-G & Irifune T, *Phys. Chem. Minerals*, **26**, 226-233, (1999).

MEASUREMENT OF FERROUS AND FERRIC IRON CONTENT IN BIOTITE Mg-Fe SOLID SOLUTION

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In order to obtain the oxygen fugacity controlled by anthracene ($C_{14}H_{10}$), Fe^{2+} and Fe^{3+} composition in biotite Mg-Fe solid solution was measured. Standard cold-seal autoclaves and internal-heated pressure vessel were used. Experiments were performed at 100 MPa, 600°C. Oxygen fugacity were controlled by QFI, WI, NNO, HM and anthracene. The content of Fe^{2+} was examined by colorimetry measurement with o-Phenanthroline. The ratio of Fe^{2+} and total Fe in biotite were 0.9 in QFI and 0.7 in NNO buffer. These result agrees with ferrous and ferric ratio in annite (Rebbert et al., 1995). In the case of the oxygen fugacity controlled by anthracene revealed that ferrous and ferric Iron ratio was nearly 0.7. The value of Fe^{2+}/Fe^{3+} was constant up to $X_{Mg} = Mg/(Mg+Fe)$ in biotite ≤ 0.8 , but $X_{Mg} > 0.8$, Fe^{2+}/Fe^{3+} ratio was decrease with increasing of Mg content. This tendency can be seen in natural biotite.

Rebbert CR, Partin E & Hewitt DA, *American Mineralogist*, **80**, 345-354, (1995).

CRYSTALLIZATION OF Fe-LAYER ALUMINOSILICATES FROM HETEROGENEOUS NUCLEATION ON 'SILICA GARDEN' SUBSTRATES

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The "silica garden", are well known tubular microstructures formed by dissolution of crystals from metal salts in aqueous solution of sodium metasilicate. Although the process is known for long time, only recently has been the subject of a precise structural characterization. (Collins et al, 1998, 1999). These studies shown that the silica garden are framework aluminosilicates with 6-coordinate-Al and a variable degree of Si substitution by 4-coordinate-Al. In addition a great variety, from domain to hierarchical, microstructures have been reported.

In this work the initial stages of the Fe-layer silicates formation by heterogeneous nucleation at the internal surfaces of this tubular microstructures were firstly investigated. Secondly, both, the structural and compositional aspects of the obtained crystals, were characterized and compared with those of natural Fe-Layer silicate minerals.

Low-temperature syntheses experiments were performed by the precipitation Fe-Al-Mg salts during the silica garden formation under reducing conditions and basic pH-s. Soluble salts containing Fe^{2+} , Mg^{2+} , K^+ , Al^{+3} , were employed. In order

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to limit the extents of the Fe²⁺ oxidation, solutions of Na-dithionite in water were prepared at first (Harder, 1978). In addition small amounts of ferrous crystals were seeded into the solution, so that silica microtubular structures were obtained. These structures are formed via continuous polymerization of the amorphous silica as result of abrupt pH reduction induced by the Fe-salt dissolution.

The growth of crystal phases takes place in a second step by the selective nucleation at the sites provided by the porous silica matrix in the internal walls of the "silica garden" microtubules. No direct precipitation from the solution by three-dimensional nucleation was observed. This fact clearly indicates that the crystallization products are connected with a heterogeneous nucleation process, related to the inner surface of the silica garden.

From the morphological point of view, the SEM micrographs of the resulting crystals, Figure 1(a) closely resemble the natural occurrence of glauconitic minerals from siliceous substrates. In addition, elemental analysis performed at the level of a single crystal, by EDX, approach the stoichiometry of glauconitic minerals with low potassium content.

Further structural characterization carried-out by HREM has revealed the existence of a gradient variation in the structural characteristics of the microtubules across the radius fig1(b). Lattice fringes analysis shown the existence of single-crystal domains with average sizes in the order of 15 nm and d-spacing corresponding to (001) and (003) reflections of 2:1 layer silicates, in sharp contact with the amorphous silica host in the internal surfaces. Single domains, with kaolinite and smectite-like layers, were also observed fig 1(c).

The XRD spectra of the whole sample shown the presence of a crystalline fraction over-imposed to the background from the amorphous silica. Rietveld analysis of the crystalline part was performed by using the Celadonite (s.g. C2/m) as starting structural model. XPS analysis was employed to determine the Al-coordination and the relative Si/Al ratios .

The previous study suggests that a complex structural transformation take place just at the internal wall of the microtubules, leading the formation of layered Al-Fe-Mg-silicates. The obtained crystals have several ordering degrees as result of non-stoichiometric interface reactions, in a similar way to the "smectite" to "illite" transformation in natural systems.

Furthermore, the polymerization process heavily determines thermodynamical conditions inside the tubes. In particular a nearly neutral pH and the availability of silica monomers are expected to occur at the interface. These factors and the presence of reducing conditions seem to be determining conditions for layer silicate formation.

Collings C, Zhou W, Mackay A & Klinowski J, *Chemical Physics Letters*, **286**, 88-92, (1998).

Collings C, Zhou W & Klinowski J, *Chemical Physics Letters*, **306**, 145-148, (1999).

Harder H, *Clays and Clay Minerals*, **26**, 65-72, (1978).

CHEMICAL MIGRATION ASSOCIATED WITH IRON OXIDATION-REDUCTION IN SILICATE MELTS

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Since pioneering works of Bowen and later Osborn, the impact of iron redox state on structure, viscosity and phase equilibria in silicate melts has received great attention. In contrast, kinetics and mechanisms of iron oxidation-reduction in geologically relevant silicate melts remain poorly understood. We have developed several experimental approaches to determine the rate-laws and mechanisms of iron oxidation-reduction in aluminosilicate melts/glasses. The general strategy consists of monitoring the chemical changes that occur after a given duration of exposure of a ferric iron-bearing glass to a reduced environment. The reducing media used are pure H₂, Ar/H₂, H₂/CO₂ and CO₂/CO mixtures in one-atmosphere furnaces or cold seal pressure vessels. Run products are analyzed through (1) the color changes in the glass due to ferric-ferrous transformations, (2) Mössbauer spectroscopy and (3) EMPA or FTIR for chemical analyses of run products. In nominally anhydrous glasses (Alb+iron and Andesites) under reducing conditions the growth rate of the reduced layer is reaction-limited. The rate of the limiting reaction is controlled by the amount of iron in the melt and the CO content of the gas. Opposed migrations of K and Na are also observed with the reduced layer being Na-richer. No increase of the OH-content in the quenched glasses is observed and the mechanisms are identical in H₂/CO₂ and CO/CO₂ gases. In the Ar-H₂ mixture, no alkali migration is observed. In an H₂-bearing atmosphere, ferric iron in natural rhyolitic obsidians is reduced by the incorporation of H-bearing species without migration of other major elements. In a CO/CO₂ mixture, no reaction is observed after an exposure of 4 days. The growth rate of the reduced layer is a diffusion-limited process. In addition, the reduction-rate is positively correlated with fH₂. Inward migration of either H₂ or proton-electron pairs could explain the macroscopic observations.

THE BREAKDOWN OF SYNTHETIC POTASSIC CORDIERITE AT LOW P-T CONDITIONS - AN EXPERIMENTAL STUDY

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An experimental study on the breakdown of K-cordierite into phlogopite and Mg-cordierite has been studied at 1 Kbar and 700-900°C, under hydrothermal condition. Potassic cordierite was obtained by sintering the co-precipitated gel of composition K_{0.2}Mg₂Al_{4.2}Si_{4.8}O₁₈ at 1200°C. The synthetic K-cordierite was taken in Pt-capsule with 3 wt% of distilled water and sealed by arc-welding. Isobaric runs between 700 and 900°C

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were carried out using Tuttle reactors (LECO Corp., USA). Water was the pressurising medium and the measured P-T have an accuracy of ± 50 bars and $\pm 5^\circ\text{C}$. respectively.

The formation of phlogopite along with Mg-cordierite started at 700°C . This phlogopite with Mg-cordierite were persisted upto 800°C . Above this temperature, the formation of phlogopite reduced and Mg-cordierite increased, but at 850°C , little formation of phlogopite was noticed. At 900°C , only single phase of Mg-cordierite without phlogopite formation was observed. The presence or absence of phlogopite and Mg-cordierite formation in every experiment was confirmed by XRD. The chemical analysis of the phases was done using EPMA and the water in the channels of Mg-cordierite was confirmed by IR studies. It is confirmed that K-cordierite (containing 1.6 wt% of K_2O) would breakdowns to ideal phlogopite + Mg-cordierite at low temperature and as the temperature increases only ideal Mg-cordierite was the stable phase without the formation of phlogopite. Also, it would be possible that the formation of melt occurs only above 900°C along with Mg-cordierite

INDUCED PHASE TRANSFORMATION BY ELECTROCHEMICAL TREATMENT IN ARCHAEOLOGICAL MARINE OBJECT. XRD-RIETVELD ANALYSIS OF THE PRODUCTS

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The conservation of marine archaeological iron objects must start with a stabilisation treatment to remove the chlorides from the iron corrosion products and the residual metal in order to prevent the development of cyclic corrosion. In this work we have studied the electrolytic method applying low current densities, inserting a resistor in the electric circuit between the artefact and the power supply. To study the changes that this treatment produces, we made an electrolysis on a cast iron cannon ball fraction recovered from a marine water environment. To control the induced variation in the mineral phase by the chlorides extraction, we have analysed the XRD spectra by the Rietveld method, the mineralogical variation of the surface and the interior of the artefact before and after the treatment. Before the treatment, the main compound found on the corroded surface was Akaganeite, that has been structurally transformed by the electrolysis to goethite and magnetite. The inner composition of the object remains unaltered before and after the treatment and the main compounds are α -iron and cementite.

PREDICTION OF NON-ARRHENIAN VISCOSITY OF MULTICOMPONENT SILICATE MELTS

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Magma dynamics can control volcanic eruptions. Thus a description of the rheology of magma is an essential input variable for forward simulations of magmatic eruptions and for the interpretation of volcano monitoring data related to magma movements. Accurate quantification of magma rheology must be based on a robust model for the viscosity of the liquid. The first parameterizations of the viscosity of multicomponent silicate melts for geological purposes employed an Arrhenian dependence of the viscosity on temperature. Although a useful approximation over restricted ranges of temperature, the Arrhenian approximation leads to serious errors over larger temperature ranges. When such models are compared with the more complete viscosity data sets for multicomponent silicate liquids which have been coming on line in the past decade the discrepancy is apparent. As a response to this growing inadequacy of Arrhenian models, Hess and Dingwell (1996) developed the first empirical non-Arrhenian viscosity model for the binary system calcalkaline rhyolite – H_2O . Here, on the basis of ca. 350 viscosity data obtained on anhydrous melts, we present the first multicomponent non-Arrhenian model. Based on 350 new determinations of Newtonian viscosities of multicomponent liquids, ranging from basanite through phonolite and trachyte, to dacite in the range of (100 to 1012 Pa·s) and regressions using the 3-parameter Tammann-Vogel-Fulcher equation, a relationship between the chemical composition of the multicomponent defined in terms of the mole fraction of network modifiers, yields a good predictive tool for the calculation of the viscosity of multicomponent silicate melts. This parameterisation is proposed as the first reliable non-Arrhenian description of the Newtonian viscosity of multicomponent silicate melts.

Hess, K-U & Dingwell, DB, *Am. Mineral*, **81**, 1297-1300, (1996).

SOLUBILITY OF SULFUR IN WATER-SATURATED AN-DI MELTS UNDER VARIOUS CONDITIONS

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The effect of red/ox conditions on the solubility of sulfur under the pressure of gases of the H-O-S system in melts of the An-Di composition close to eutectics ($\text{An}_{35}\text{Ab}_{10}\text{Di}_{55}$ mol%) was experimentally studied on a high-gas-pressure equipment at a temperature of 1200°C and different pressure, from 2250 to 4760 bar. The powdered sample (150 mg) was molded in a platinum ampoule with a diameter of 5 mm and a height of 25 mm. Then sulfur (15-30 mg) and water (50 ml) were added. The fugacity of S was monitored by the Pt-PtS buffer reaction and amounted $\log f_{\text{S}_2} = -0.394$. The fugacity of hydrogen was specified outside by argon-hydrogen mixtures in which the molar fraction of hydrogen varied from 0.05 to 0.3. The capsule was sealed and placed in another capsule (diameter 8 mm) that also contained water. This second ampoule is needed to restrict diffusion of hydrogen from the reaction ampoule, which is observed at high temperatures. The pressure and composition of the fluid were selected in such a way that the fugacity of

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water in the H-O system at 1200°C, 2Kbar and specified molar fraction of hydrogen. The duration of the experiments was 3 days. The products of experiments were studied by optical methods and on the microprobe. The solubility of S varies in range 0.018-0.126 wt%, increase with increasing of the fugacity of oxydation components of fluid (O₂, SO₂, H₂O) and decrease with increasing of the fugacity of the reduction species (H₂, H₂S).

Table 1: Physicochemical conditions in experiments on studying the solubility of sulfur (T=1200°C).

Entry no	P, bar	X _{H2}	f _{H2}	f _{H2O}	f _{H2S}	f _{SO2}	lgf _{O2}	C _s %
1	2250	0.05	142.50	1943	394.79	0.2200	-9.483	0.126
2	2530	0.10	331.12	1836	915.98	0.0330	-10.275	0.064
3	3370	0.20	971.90	1631	2699.2	0.0030	-11.310	0.034
4	4760	0.30	2376.8	1427	6573.0	0.0005	-12.302	0.018

THERMAL EXPANSIVITIES OF SUPERCOOLED HAPLOBASALTIC LIQUIDS

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Knowledge of the expansivity of silicate melts is a vital component in the construction of accurate pressure-volume-temperature (PVT) equations of state. The present study is a contribution in directly determining supercooled liquid expansivities by container-based dilatometry. The thermal expansion of supercooled liquids in the haplobasaltic (anorthite-diopside) system have been determined. The expansivity data obtained in this study agree well with estimates provided by previous dilatometric determinations in the system that have relied on alternative experimental strategies. The data have been combined with high temperature, superliquidus determinations of melt density to obtain expressions for the volume-temperature relationships of liquids in the anorthite-diopside system. The volume-temperature data clearly indicate a non-linear temperature dependence of volume for all melts investigated. The variation is most striking for diopside where the coefficient of volume thermal expansion decreases about 56% from temperatures near the glass transition to superliquidus temperatures. With increasing anorthite content the degree of variation appears to decrease. An₄₂Di₅₈ exhibits a decrease of 39% of its coefficient of thermal expansion and An₉₈Di₀₂ of 33%, respectively. The expansivities obtained in this study cannot be reproduced using published models based on linear volume-temperature relationships. They require instead a reanalysis of existing P-V-T-equations of state for silicate melts.

EXPERIMENTAL DATA ON GEOCHEMISTRY OF REE AND Y IN THE FLUORINE-BEARING GRANITE AND NEPHELINE-SYENITE MAGMAS

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Distribution of REE (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Lu) and Y between coexisting alumina-silicate and aluminium-fluoride melts has been investigated in the model system Si-Al-(Na, K, Li)-O-F with H₂O excess at 8000°C and 1 kbar. As it was shown in previous publications (1993, 2001) compositions of the silicate melts correspond granites, syenites and nepheline syenites widely widespread in the nature. Atomic ratios of (K, Na, Li)/Al/F in fluoride melt are close to that in cryolite: 3/1/6. Partition coefficients K_p (silicate melt / fluoride one) are not depended on element concentration (Henry's law). For all parts of the system without lithium K_p value typically lies between 2 and 50. Their spectra are similar: the value of K_p increases from La up to Sm, has a maximum between Eu and Ho, and further decreases towards Lu. In common coefficients for light REE are higher then for heavy ones. Yttrium has the highest coefficients. Distinctions between Na-, Na-K- and K- quartz normative parts of the system are not significant for elements of the cerium group. In the range between Tb and Lu K_p decrease from 40-12 in the Na- to 5-2 in the K- part of the system. Partition coefficients in nepheline normative parts of the system, especially in myaskitic one are lower then quartz normative one. In the case of Na and K are partly replaced by Li, partition coefficients decrease dramatically down to values of the order of 10⁻³. They increase little by little from La towards Lu. They are the most negligible for Y. Coefficient distinctions between the potassium and sodium lithium compositions are not significant. Experimental results make more understandable some geochemical regularities. The work is supported by Russian Fund of Fundamental Researches, grant 01-05-64512.

Gramenitskiy EN & Shchekina TI, *Geochemistry International*, **31(1)**, 52-71, (1993).

Gramenitskiy EN & Shchekina TI, *Geokhimiya*, 621-635, (2001).

EFFECTS OF H₂O ON THE RHEOLOGY OF ECLOGITE AND ITS CONSTITUENT MINERALS

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We previously studied the rheology of "dry" eclogite reconstituted from a sample from the Dabie-Sulu, UHPM belt, China (Jin et al., 2001); garnet was very much stronger and omphacite significantly weaker than a ~50:50 mixture. Deformation conditions were T = 1300-1600K, P = 3 GPa, and strain rate = 10⁻⁴/s-10⁻⁶/s. Infrared spectroscopy showed <10 ppm H₂O in garnet and 150-200 ppm in omphacite. We are now investigating a "wet" eclogite of similar composition from this terrane with 300-400 ppm H₂O in garnet and 1000-1200 ppm in omphacite. Preliminary results show that garnet of the "wet" sample is much weaker, omphacite strength is similar, and the rock strength is ~30% reduced. Thus, increase in H₂O content of garnet by a factor of >30 produced a profound weakening

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whereas 7-8 fold increase for omphacite had little effect. In both cases, the microstructure after laboratory deformation was closely similar to that of the natural sample - little evidence of deformation in garnet and extensive deformation of omphacite in the "dry" sample and significant flattening of garnet in the "wet" sample. Whether or not garnet flowed by dislocation creep is not yet known.

Deformation of "wet" eclogite at temperature just above the wet solidus resulted reproducibly in exsolution of H₂O, fluxing of ~0.1 vol.% melt, and triggering of a shearing instability. The fault gouge appears indistinguishable from gouge produced in normal brittle failure except for small amounts of glass. In contrast, the gouge is distinctly different from that of transformation-induced faulting associated with the olivine-spinel transformation or during dehydration of antigorite under conditions of negative net volume change. In the former cases, the "gouge" consists of sharply angular particles with a fractal size distribution whereas in the latter cases an extremely fine-grained matrix of the stable phase(s) occurs, in many cases containing irregularly-shaped clasts of the original material.

Jin Z-M, Zhang, J, Green HW & Jin, S, *Geology*, **29**, 667-670, (2001).

EXPERIMENTALLY-DETERMINED TRACE ELEMENT CHARACTERISTICS OF AQUEOUS FLUID FROM DEHYDRATED MAFIC OCEANIC CRUST AT 3.0 GPa, 650-700°C

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Altered oceanic crust undergoes dehydration as it is subducted. The released aqueous vapour has the potential to remove important amounts of trace elements and to modify trace element ratios in the overlying mantle wedge and in the residual eclogitic crust. To experimentally assess this process an oceanic tholeiite (MORB) has been enriched (10-100 ppm) in 25 trace elements and crystallized at 3.0 GPa, 650 and 700°C for 2 weeks, with 30-50wt.% added water. At 650°C the fluid coexists with omphacite, lawsonite, staurolite, coesite and accessory phengite, rutile, Ti-magnetite and talc. Changes at 700°C are that garnet is conspicuous, but lawsonite and staurolite are rare and talc is absent. LAM ICP-MS analyses establish patterns of trace element partitioning between minerals (data for omphacite, lawsonite, phengite, staurolite and garnet) and fluid, but not absolute values. Similarly ratios of trace element partitioning can be well constrained. The fluid shows strong enrichment of LIL relative to HFSE, but also shows decrease in Rb/Sr, Cs/Sr and Ba/Sr from 650 to 700°C, apparently controlled by residual lawsonite, and increase in La/Lu, clearly controlled by garnet. In addition, omphacite fractionates both Zr/Nb and La/Lu, contributing to a decrease in Zr/Nb and an increase in La/Lu in the fluid. Rutile (analyzed with an electron microprobe) with Nb/Ta ≈ bulk starting composition strongly takes up Nb and Ta, but cannot cause the almost 4-fold increase in the Nb/Ta ratio observed in the fluid relative to the bulk. If these results are applied to the trace element characteristics of convergent zone magmatism, relative to MORB, then involvement of a fluid derived by dehydration processes may increase

LIL/HFSE and decrease Zr/Nb. Absence of major change to La/Lu restricts the role of garnet. Residual rutile may explain Nb and Ta depletion without affecting Nb/Ta ratios.

THE ENTHALPY OF FORMATION AND INTERNALLY CONSISTENT THERMODYNAMIC DATA OF Mg-STAUROLITE

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The enthalpies of drop-solution in lead borate (2 PbO B₂O₃) of four Mg-staurolite samples, synthesized at 720°C and pressures between 2 and 5 GPa, were measured by high-temperature oxide-melt calorimetry at 702°C. Staurolite compositions, determined by electron microprobe analysis, Karl-Fischer titration, and thermogravimetry, are: Mg_{3.71}Al_{18.17}Si_{7.60}O_{44.31}(OH)_{3.69}, Mg_{3.87}Al_{17.65}Si_{7.75}O_{43.68}(OH)_{4.32}, Mg_{3.66}Al_{17.76}Si_{7.68}O_{43.31}(OH)_{4.69}, and Mg_{3.58}Al_{18.05}Si_{7.43}O_{43.01}(OH)_{4.99}. The enthalpy of drop solution of the bulk samples (as well as the calculated values for the enthalpy of formation from the elements of Mg-staurolite) are strongly correlated to the hydrogen content of the samples. The enthalpy of formation from the elements is best described by the linear relation $\Delta_f H_{298}^0$ (Mg-staurolite) = (-25357.58 + 87.35 N) kJ mol⁻¹, where N = number of hydrogen atoms per formula unit in Mg-staurolite. The enthalpy of drop solution of two partly dehydrated Mg-staurolite samples is in a good agreement with the linear relation. Phase-equilibrium data for Mg-staurolite (Fockenberg 1998) were recalculated using the stoichiometric formula Mg_{3.5}Al₁₈Si_{7.75}O₄₄(OH)₄. Based on these mineral equilibria and the internally consistent data set of Berman (1988), a mathematical programming analysis of the thermodynamic data of Mg-staurolite gave $\Delta_f H_{298}^0$ (Mg_{3.5}Al₁₈Si_{7.75}O₄₄(OH)₄) = -25005.14 kJ mol⁻¹, and S_{298}^0 (Mg_{3.5}Al₁₈Si_{7.75}O₄₄(OH)₄) = 937.94 J K⁻¹mol⁻¹. Thus, for the first time, reliable thermodynamic data for Mg-staurolite, based on experimental constraints, are provided.

Fockenberg T, *Contrib.Mineral.Petrol*, **130**, 187-198, (1998).

Berman RG, *J. Petrol*, **29**, 445-522, (1988).

THE ROLE OF H₂O IN MELTING AND DIFFERENTIATION OF THE EARTH'S MANTLE

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Water has a profound effect on the melting and differentiation of the earth's mantle. I will discuss the recent advances in experimental petrology, mineralogy and geochemistry that have provided a quantitative understanding of the role of water in petrogenetic processes. New experimental evidence and petrologic observation on the 3.5 Ga Archean komatiites and basaltic - komatiites from the Barberton Mountainland have

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established an important role for water in early Earth history. The most important role for water in modern melt generation environments has been in subduction zones. Experimental studies have illuminated the influence of water on the composition of silicate melts in equilibrium with the rock forming minerals (Olivine - Plagioclase - Clinopyroxene). The surprising result is that subduction zone magmas often contain large amounts of magmatic water (from 6 to 10 wt. percent). Studies of the influence of water on mantle melting have shown that water dramatically decreases the melt production rate by spreading the melting interval over a broad temperature range. This fact must be reconciled with the observation that mantle-derived subduction - zone melts represent some of the highest extents of melting found in the mantle. The resolution of this problem lies in the inverted thermal gradient present in subduction zones. Melting is initiated at the base of the mantle wedge under water-saturated conditions, and the melt ascends into shallower, progressively hotter mantle, where it reacts. As the melt ascends and flux melts the shallower mantle its water content continually decreases. The temperature - depth structure of the mantle wedge controls the melting process. Water also has an important influence on melt physical properties, and melt ascent occurs rapidly by porous flow. Trace element partitioning must be considered in terms of fluid transport from the slab as well as element partitioning in the mantle wedge.

EFFECTS OF ALUMINIUM AND MINOR ELEMENTS ON THE LOWER MANTLE MINERALOGY

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Even if we only consider the presence of major elements (O, Si, Mg, Fe, Al, Ca), the lower mantle models are complicated by partitioning of these elements between the different phases, and the complex substitution mechanisms in the perovskite lattice. The lower mantle perovskite composition is close to (Al,Fe)-MgSiO₃, with Al and Fe contents closely correlated with each other (see Wood and Rubie, 1996). The mechanisms of Al substitution and the amount of Fe (and of the FeIII/ΣFe) in the perovskite depend on pressure, temperature, Al-content and oxygen fugacity: an unique and definitive vision of the perovskite crystal chemistry is difficult for the whole mantle. Furthermore, the perovskite modulus K₀ is affected by the composition, particularly by the Al-content, and the amplitude of these effects remains controversial (Andraut et al., 2001 ; Daniel et al., 2001).

If we now integrate minor and trace elements to our model, things become more complex : perovskite can possibly accommodate a little amount of these elements, but in the case of Na that is the most abundant minor element in the lower mantle, previous experiments evidenced the formation of two phases : NaAlSiO₄ with the Ca-ferrite structure (Liu, 1977) and (Na,K,Ca)₁(Mg,Fe)₂(Al,Si)_{5.5-6.0}O₁₂ NAL-phase (Miyajima, 1999). We present here the equations of state of both phases, and discuss their role in Na hosting in the lower mantle.

We emphasize that these phases are not only Na host phases, but also Al-rich phases. The presence of aluminous phases in the lower mantle was thought to be unlikely because Al-amounts well above the mantle content can be integrated into

the perovskite structure (Irifune, 1994). But in this study, we clearly evidence that the presence of minor elements, particularly alkaline elements, imposes the existence of at least one aluminous phase in the lower mantle.

- Wood BJ & Rubie DC, *Science*, **273**, 1522-1524, (1996).
Andraut D, Bolfan-Casanova N & Guignot N, *Earth. Planet. Sci. Lett.*, **193**, 501-508, (2001).
Daniel I, Cardon H, Fiquet G, Guyot F & Mezouar M, *Geophys. Res. Lett.*, **28**, 3789-3792, (2001).
Liu L, *Geophys. Res. Lett.*, **4**, 183-186, (1977).
Miyajima N, Fujino K, Funamori N, Kondo T & Yagi T, *Phys. Earth Planet. Inter.*, **116**, 117-131, (1999).
Irifune T, *Nature*, **370**, 131-133, (1994).

H₂O ACTIVITY IN H₂O-N₂ FLUIDS AT HIGH PRESSURE AND TEMPERATURE MEASURED BY THE DISPLACEMENT OF THE BRUCITE-PERICLASE EQUILIBRIUM

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The activity of water in binary H₂O-N₂ fluids has been determined experimentally at pressures of 5-13 kbar and temperatures of 680°-840°C. Temperature displacement of the simple brucite dehydration reaction was used to monitor H₂O activity. The experiments were performed in a conventional 22 mm piston-cylinder apparatus with NaCl pressure medium and silver azide, AgN₃, as a source of nitrogen. Reversals of the dehydration reaction were used to bracket the equilibrium fluid compositions. Final fluid compositions were obtained by a weight loss method. Reaction progress was additionally confirmed by optical and X-ray inspection of the solid run products.

Water activities were computed relative to the equilibrium brucite dehydration conditions in pure H₂O as determined by Aranovich and Newton (1996) using thermodynamic data of Holland and Powell (1998). The mixing properties of the binary H₂O-N₂ fluid were modelled with a van Laar-type equation:

$$RT \ln \gamma_1 = (X_2)^2 W \{ V_1^o (V_2^o)^2 / [(V_1^o + V_2^o)(X_1 V_1^o + X_2 V_2^o)^2] \}$$

where γ_1 is the activity coefficient of H₂O, X_i is the mole fraction of endmember i ($1=H_2O$ and $2=N_2$), V_i^o is the molar volume of the pure endmember i at the pressure (P) and temperature (T) of interest, and W is a regular solution parameter. The parameter W was fit as a function of pressure and temperature with the expression $W = (A - BT)[1 - \exp(-20P)] + CP^{0.3}T$, with $A = 40005$ J, $B = 51.735$ J/K, $C = 14.848$ J/(K-kbar^{0.3}), P in kbar and T in K. With these expressions, the activity-composition relations in H₂O-N₂ fluids can be reconstructed over a broad P-T-X range using any equation of state (EOS) for pure H₂O and N₂. The activity-composition relations are similar to those predicted by the semi-empirical EOS of Duan et al. (2000) and the theoretical EOS of Churakov and Gottschalk (2001), although the former somewhat underestimates activities within the experimental pressure range while the latter overestimates activities of the components at pressures above 20 kbar.