

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

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:

$$RT \ln \gamma_1 = (X_2)^2 W \{ V_1^0 (V_2^0)^2 / [(V_1^0 + V_2^0)(X_1 V_1^0 + X_2 V_2^0)^2] \}$$

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^0 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.

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

- Aranovich LY & Newton RC, *Contrib. Mineral. Petrol.*, **125**, 200-212, (1996).
Churakov SV & Gottschalk M, *Geochim. Cosmochim. Acta*, in press, (2001).
Duan Z, Moeller N & Weare JH, *Geochim. Cosmochim. Acta*, **64**, 1069-1075, (2000).
Holland TJB & Powell R, *J. Met. Geol.*, **16**, 309-343, (1998).

CARBONATE STABILITY AT HIGH PRESSURE IN SUBDUCTION ZONES

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In order to constrain the fate of subducted carbonates carried by altered oceanic floor, high pressure experiments have been conducted in a multi-anvil apparatus in the pressure range 5 - 10 GPa. Starting material consisted in a mixture of glass having the composition of an altered basalt, plus 10 wt% calcium carbonate (calcite). After recovery, polished samples were analysed by electron microprobe. At 5 GPa, the solidus was located between 1100 and 1150°C. A silicate melt was found to coexist with a vapour phase (presumably CO₂) and an eclogitic residue (garnet + omphacite + coesite). At 7 GPa calcium-rich carbonatitic melts are produced and the upper limit for the solidus is at 1000°C. At 10 GPa a carbonatitic melt was also found, and the solidus appears to be located between 1000 and 1100°C. The presently available results show that the topology for the eclogite + carbonate system in the P - T space is qualitatively similar to that of peridotite + CO₂. With increasing pressure, the solidus displays a temperature drop (cusp) corresponding to the transition from silicate to carbonatitic melts. However, in the eclogitic system the P - T location of this transition is shifted toward lower temperatures (by approximately 300°C) and higher pressures (by approximately 3 GPa) compared to the peridotitic system. This difference is attributed to the presence of iron whose effect is to depress the solidus (as in any silicate system) while increasing the pressure stability of calcite at the expense of dolomite/ankerite. One consequence of the presently determined phase relationships in the eclogite + carbonate system is that carbonates are likely to be removed from a subducting slab, either by decarbonation or by melting reactions.

EXPERIMENTALLY INDUCED NUCLEATION OF MONAZITE FROM FLUORAPATITE: THE IMPORTANCE OF FLUID COMPOSITION

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The (Y+REE) chemistry of either a metamorphic or an igneous rock is partly a function of the phosphate minerals it contains, e.g. fluorapatite (Ca₅(PO₄)₃F), monazite ((Ce,LREE)PO₄), and/or xenotime ((Y,HREE)PO₄). Studies of natural fluorapatite (Harlov and Förster, 2002) as well as experimental studies of chlorapatite (Harlov et al., 2002) indicate that these inclusions have originated in the apatite itself from the (Y + REE) budget available (> 0.5 oxide wt%) as the product of coupled

substitution and mass transfer during fluid-triggered metasomatic alteration. There is no evidence to suggest that they are the result of exsolution in the apatite during cooling or that they could represent independent grains later overgrown by the apatite. A natural inclusion free fluorapatite (Durango) has been experimentally metasomatised using a series of fluids (pure H₂O; concentrated KCl, NaCl and CaCl₂ brines; CO₂-H₂O). This consisted of placing 20 mg fluorapatite + 5 mg fluid in a 3 mm/1 cm Pt capsule using either the piston cylinder apparatus (600-900°C; 1000 MPa; 1-4 weeks) or the hydrothermal apparatus (300-600°C; 500 MPa; 2-24 weeks). Nucleation of monazite from the fluorapatite occurred when the fluid was H₂O; 50/50 KCl/H₂O or 50/50 CO₂/H₂O. At 900°C, monazite nucleated in the interior of the fluorapatite grains and, at lower temperatures, only on the fluorapatite grain surface. These fluids (specifically H₂O) allow for the leaching of Si⁴⁺ and/or Na⁺ from the apatite. The resulting charge imbalance, due to the coupled substitution reactions Si⁴⁺ + (Y + REE)³⁺ = P⁵⁺ + Ca²⁺ and Na⁺ + (Y + REE)³⁺ = 2 Ca²⁺, induces the nucleation and growth of monazite in or on the fluorapatite via dissolution-precipitation. In contrast, Ca²⁺ and Na⁺ in NaCl or CaCl₂ brines can enter the fluorapatite structure and replace Si⁴⁺, Na⁺ and/or (Y+REE)³⁺ thus maintaining charge balance and discouraging formation of monazite.

Harlov DE & Förster H-J, *J. Petrol.*, in press, (2002).

Harlov DE, Förster H-J & Nijland TG, *Am. Mineral.*, in press, (2002).

FLUID INDUCED DEHYDRATION OF THE MAFIC LOWER CRUST FROM AMPHIBOLITE TO GRANULITE FACIES: NATURE AND EXPERIMENT

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Natural evidence for the role of low H₂O activity fluids (CO₂ or concentrated brines) in the dehydration of H₂O-rich, mafic amphibolite facies rocks to H₂O-poor, orthopyroxene-bearing granulite facies rocks (700-900°C and 500-1000 MPa) for both highly localised dehydration zones (CO₂; cm's) as well as regional terranes (brines; km's) (Harlov et al. 1998; Perchuck et al., 2000; Harlov and Förster, 2002) include the presence of K-feldspar micro-veins along quartz-plagioclase grain boundaries; plagioclase grains metasomatised in a K-rich fluid; monazite and/or xenotime inclusions in the apatite grains; biotite enriched in Ti, F, and Cl; and apatite enriched in Cl and F. These features are not seen in the "source" amphibolite facies terrane along the same traverse. When f_{HF}/f_{H_2O} for either biotite or apatite is plotted as a function of the distance from the fluid/heat source, a uniform decrease in f_{HF}/f_{H_2O} is observed across the granulite to amphibolite facies traverse suggesting the presence of a uniform low H₂O activity uniform fluid front. Dehydration experiments (900°C; 1000 MPa; 3 weeks; Au cylinder) involving a cylinder of natural tonalitic biotite gneiss (plagioclase, quartz, biotite) (220 mg) and a concentrated KCl brine (20-30% H₂O; 80-70% KCl) (8 mg) placed at the base of the cylinder have been conducted in the piston cylinder apparatus (CaF₂ setup). Micro-veins, primarily of K-feldspar, volunteered along quartz/plagioclase grain boundaries though only where biotite and quartz were in contact and caused the biotite to breakdown along its grain boundaries to numerous small orthopyroxene and clinopy-

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

roxene grains + minor ilmenite. The same experiment involving a concentrated NaCl brine (20-30% H₂O; 80-70% NaCl) resulted in veins approximating a granitic composition along quartz/plagioclase grain boundaries with numerous small orthopyroxene grains + minor ilmenite volunteering along biotite grain boundaries, again only when the biotite and quartz were in contact.

Harlov DE & Förster H-J, *J. Petrol.*, **in press**, (2002).

Perchuk L, Safonov OG, Gerya TV, Fu B & Harlov DE, *Contrib. Mineral. Petrol.*, **140**, 212-232, (2000).

Harlov DE, Hansen EC & Bigler C, *Chem. Geol.*, **151**, 373-386, (1998).

HYDROTHERMAL SYNTHESIS OF ALLUAUDITE IN THE Na-Mn-Fe²⁺-Fe³⁺-P-O SYSTEM

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Alluaudite, a Na-Mn-Fe-bearing phosphate mineral, is known to occur in Li-rich granitic pegmatites. During the past decade, several compounds with the alluaudite structure were synthesized, but their stability was scarcely envisaged. This is the reason why we decided to investigate the Na-Mn-Fe²⁺-Fe³⁺-P-O system.

Starting from compositions ranging from Na₂Mn₂Fe³⁺(PO₄)₃ to Na₂Fe²⁺Fe³⁺(PO₄)₃, the hydrothermal syntheses were carried out between 300 to 800°C and 0.1 to 0.5 GPa, using horizontally arranged Tuttle-type cold-seal bombs. Pure alluaudite is obtained between 300 and 400°C, whereas alluaudite is associated with maricite, Na(Fe²⁺,Mn)PO₄, between 600 and 800°C. Maricite exhibits a crystal structure different from that of natrophilite, NaMnPO₄, which is isotypic with olivine (Le Page & Donnay, 1977; Moore, 1972). Surprisingly, as far as we know, maricite has never been observed in granitic pegmatites.

Between 700 and 800°C, alluaudite and maricite are associated with fillowite and/or with an undetermined phase. This phase could correspond to an orthorhombic polymorph of the arrojadite structure (Moore et al., 1981), with $a = 25.892(4)$, $b = 14.792(5)$, and $c = 10.364(2)$ Å, space group *Pnma*. A single crystal with a chemical composition close to NaMn₄(PO₄)₃, recently investigated by Keller et al. (2001), has shown a crystal structure corresponding to that of fillowite (Araki & Moore, 1981).

From the electron microprobe analytical results on the alluaudite crystals, the presence of both Fe²⁺ and Fe³⁺ in the structure can be deduced, in agreement with the chemical data on natural samples. Compared with the starting compositions, the alluaudite solid solutions are also enriched in bivalent cations and depleted in Na and Fe³⁺, according to the substitution mechanism Na⁺ + Fe³⁺ = (Fe²⁺,Mn²⁺) + Fe²⁺. Additionally, the morphology of the alluaudite crystals shows significant variations with the experimental conditions.

Araki T & Moore PB, *Am. Miner.*, **66**, 827-842, (1981).

Keller P, Lissner F, Hatert F & Schleid T, *Z. Kristall. Suppl. Issue*, **18**, 150, (2001).

Le Page Y & Donnay G, *Can. Miner.*, **15**, 518-521, (1977).

Moore PB, *Am. Miner.*, **57**, 1333-1344, (1972).

Moore PB, Araki T, Merlino S, Mellini M & Zanazzi PF, *Am. Miner.*, **66**, 1034-1049, (1981).

INTERACTION OF HYDROUS GRANITIC MELTS WITH CARBONATES: IMPLICATIONS FOR DEVOLATILISATION IN SUBDUCTION ZONES

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Interlayered pelites and carbonates are common in subducted oceanic sediments. The interaction of hydrous granitic melts produced in deeply subducted metapelites with carbonates has been investigated by piston cylinder sandwich experiments. At 1000°C, 4.5 GPa the paragenesis in a synthetic simplified pelite composition (KCMASH) containing 2.5 wt.% H₂O consists of phengite + garnet + clinopyroxene + kyanite + coesite + hydrous granitic melt. Dolomite embedded in the pelite reacts with the hydrous granitic melt and produces the paragenesis garnet + clinopyroxene + dolomite + liquid. Qualitative mass-balance constrains this liquid composition to 60 wt.% CO₂, about 10 wt.% of each of H₂O, K₂O and CaO and very small amounts of SiO₂, MgO and Al₂O₃. This liquid therefore reflects rather a carbonatite melt than a water-rich CO₂-H₂O fluid. In the pelite adjacent to the dolomite layer, an increasing abundance of garnet, kyanite and melt and a decreasing amount of clinopyroxene, phengite and coesite has been observed. This suggests that the presence of carbonate enhances melt production in the pelite. No clear separation between the hydrous granitic melt and the "carbonatite-like" liquid has been observed indicating complete miscibility. Carbonate solubility in hydrous granitic melts has been further investigated in the range 3.5-4.5 GPa and 900-1000°C by mixing a pelite with different amounts of dolomite and calcite. The runs contain hydrous granitic melts coexisting with garnet, coesite, omphacite, carbonate and occasionally phengite and kyanite. Mass balance reveals that about 1.5-2 times more CO₂ than H₂O is dissolved in the melt. We therefore propose that hydrous granitic melts are capable of transferring not only H₂O but also significant amounts of CO₂ from subducted sediments to the mantle wedge. The physical properties, the ability to transport trace elements and the interaction with the mantle wedge of such melts are yet to be determined.

STATIC COMPRESSION OF IRON SILICIDES TO MEGABAR PRESSURE

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Seismic data indicates those both inner and outer cores are less dense than pure iron at core pressures and temperatures. This suggests that light elements as iron compounds are contained in the inner and outer core. The preferred candidates for the light element are sulfur, oxygen, carbon, silicon, and hydrogen. Because silicon is one of the most abundant elements in the Earth, silicon could contribute to the density deficit. However, there are little experimental data at the core pressures on the properties of iron-silicon alloys. We have investigated the in-situ high-pressure behavior of iron silicides, Fe with 17 wt.% Si

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

and Fe with 9 wt.%Si, at room temperature using diamond-anvil cell. X-ray diffraction patterns of iron silicides were collected from ambient pressure up to 125 GPa using monochromatic synchrotron x-ray radiation and the imaging plate at the BL-13A beamline at the Photon Factory, National Laboratory for High Energy Physics (KEK). Pressure was determined by the ruby fluorescence method. In the pressure range, no pressure induced phase transitions are observed Fe-17 wt.%Si alloy, while Fe-9 wt.%Si alloy transforms from bcc phase into hcp phase between 16 and 35 GPa and the hcp phase is stable at least to 100 GPa. A third-order Birch-Murnaghan equation of state fitted to the pressure-volume data yields the bulk modulus of two iron silicides. The iron silicides are less compressible than the other iron compounds, such as FeS, FeC and FeH, and pure iron. This could provide constraints on the physical and chemical properties of the iron compounds under core conditions.

ORDER-DISORDER IN FELDSPARS AND ITS INFLUENCE ON HEAT TRANSPORT PROPERTIES

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Thermal transport properties are important parameters to constrain dynamical processes within the Earth's crust. Alkali feldspars are among the most abundant rock-forming minerals and are responsible for ca. 12 vol.% of the crust. Albite $\text{Na}[\text{AlSi}_3\text{O}_8]$ and orthoclase $\text{K}[\text{AlSi}_3\text{O}_8]$ show a temperature depending miscibility and ordering behavior. We have chosen a variety of 5 single-crystal alkali-feldspars from different origin to study thermal diffusivity as a function of chemical composition and ordering of the crystals. Thermal diffusivity a is related to the mean velocity of phonons v and their mean free path length l according to $a = 1/3 v l$. The ordering of the distribution of Si and Al in tetrahedrons is refined by the Rietveld method from XRD-data. A transient technique was used to determine the anisotropic thermal diffusivity behaviour of feldspar between 22°C - 800°C. At temperatures lower than 350°C the thermal diffusivity behavior is dominated by a phonon-mechanism. At higher temperatures some samples show a pronounced temperature variation, which is described by a radiative heat transport mechanism characterized by a T^3 dependency. For the phononic heat transfer the optical quality of the sample has a minor effect. The chemical variation of the crystals leads to different average phonon-velocities depending on chemical composition. However, these variations can only explain some small oscillations in the observed diffusivity behavior. The thermal diffusivity behavior of alkali-feldspars seems to be dominated by the ordering of the crystals. From a structural point of view, the distribution of Si-Al in the tetrahedrons is important for the scattering probability for phonons and therefore determines the mean free path length of phonons. With increasing disorder the scattering probability increases and the disordered structural units can be viewed as point defects for phononic heat-transfer.

EXPERIMENTAL STUDY OF Fe-Mg INTERDIFFUSION IN LOWER MANTLE PHASES

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The lower mantle of the Earth, between 670 km and 2900 km depth, forms the largest part by volume of our planet. The two dominating phases of the lower mantle are $(\text{Mg,Fe})\text{SiO}_3$ perovskite and $(\text{Mg,Fe})\text{O}$, magnesiowustite. Knowledge of diffusional properties of these phases is essential in understanding different fundamental processes such as rheology, chemical exchange during plume ascent and residence times of subducting slabs. In this study diffusion couple experiments of single crystals of magnesiowustite in Ni capsules and polycrystalline samples of $(\text{Mg,Fe})\text{SiO}_3$ perovskite in MgO single crystal capsules have been performed or are currently in progress. To achieve pressures up to 26 GPa the multianvil apparatus has been used. Run durations of the experiments ranged from 40 minutes to 1 day at temperatures up to 2373 K. Diffusional behavior of the two investigated phases are very different and requires different analytical procedures for profile analysis. For $(\text{Mg,Fe})\text{SiO}_3$ perovskite a transmission electron microscope, equipped with an energy dispersive spectrometer, has been used, whereas for magnesiowustite, profiles are long enough to be measured by conventional electron microprobe analysis. TEM investigations of microstructures also shows that subgrain boundaries can have pronounced effects on very short diffusion profiles in perovskite.

Preliminary results show that Fe-Mg interdiffusion coefficients for $(\text{Mg,Fe})\text{SiO}_3$ perovskite are $3.66 \cdot 10^{-20} \text{ m}^2/\text{sec}$ at 2023 K and relatively reducing conditions, and for magnesiowustite $1.9 \cdot 10^{-13} \text{ m}^2/\text{sec}$ at 2023 K, $f\text{O}_2$ close to the Ni-NiO buffer and containing 21 mole% FeO. Therefore, any process dominated by Fe-Mg interdiffusion in $(\text{Mg,Fe})\text{SiO}_3$ perovskite takes place at considerably longer timescales than estimated by diffusional properties of magnesiowustite or upper mantle phases as long as no unusually strong oxygen fugacity effect exists.

EFFECT OF QUARTZ-COESITE TRANSITION ON P-WAVE VELOCITY IN SiO_2 AND QUARTZ-BEARING ROCKS AT 4.1 GPa AND 4.5 GPa

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Compressional wave velocities (V_p) in quartz and quartz-plagioclase pyroxenite have been measured in multi-anvil apparatus at 4.1 GPa and 4.5 GPa, and up to 1570 K, using the reflecting-transition combined method (Liu et al. 1999). Pressure is raised at a rate of $4 \cdot 10^5 \text{ Pa/s}$ and temperature at a rate of 20 K/s. After keeping the temperature steady for 35 minutes, V_p is measured. At 4.1 GPa and temperature less than 900 K, V_p in quartz decrease with increasing temperature at slow rate. The temperature coefficient is $0.00005 \text{ km}\cdot\text{s}\cdot\text{K}$. At temperature higher than 900 K, V_p increase with temperature quickly.

EMPG IX

Ninth International Symposium on Experimental Mineralogy, Petrology and Geochemistry

Observing the recovered samples indicate that at 4.1 GPa and 920 K, about 5 vol.% quartz has been transitioned to coesite, which suggests that the new-formed coesite is the main cause for the increase of V_p . The content of coesite increases with temperature. At 1050 K, the content of coesite is about 75 vol.%. The variation of V_p with temperature in quartz-plagioclase pyroxenite at 4.5 GPa is similar to that in quartz. At temperature higher than 1173 K, V_p in quartz-plagioclase-pyroxenite increase with increasing temperature. At 1243 K, about 3vol.% coesite have been in the sample and the other minerals (plagioclase and clinopyroxene) show no significant variation. This phenomenon again indicates that the quartz-coesite transformation may increase V_p in quartz-bearing rock. V_p in quartz-coesite system have been calculated using the Voigt-Reuse-Hill model. The results are in consistent well with our experimental results.

Liu Yonggnag, Xie Hongsen, Guo Jie, Zhou Wenge, Xu Ji-an & Zhao Zhidan, *Chin Phys Lett*, **17**, 924-926, (1999).

AN IN-SITU X-RAY DIFFRACTION STUDY ON KINETICS OF HIGH-PRESSURE TRANSFORMATION OF ENSTATITE

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Enstatite is one of the most abundant minerals in the Earth's upper mantle. It transforms to (modified) spinel plus stishovite, and to ilmenite at the depth of 500-600 km. Under subduction zone conditions, there is a possibility that these transformations are kinetically inhibited due to low temperatures (Hogrefe et al., 1994). In order to clarify kinetics of high-pressure transformation of enstatite, we performed *in-situ* X-ray diffraction experiments using "SPEED-1500" multi-anvil high-pressure apparatus installed at SPring-8, Japan.

Starting material is a powder of natural enstatite, ($\text{Mg}_{0.99}\text{Fe}_{0.01}\text{SiO}_3$). It was annealed at 12-16 GPa and 1200°C for 100 minutes in the stability field of high-pressure clinoenstatite or spinel plus stishovite, and then compressed to the desired pressure at 500°C. Finally we heated the sample to the desired temperature at constant oil pressure with taking X-ray diffraction patterns every 10 seconds. In this way, we observed transformation kinetics from high-pressure clinoenstatite to ilmenite, and from spinel plus stishovite to ilmenite at 19.8-20.7 GPa and 950-1500°C. At 20.1 GPa and 1090°C, the enstatite-ilmenite transformation completed immediately in 10 seconds. At 20.0 GPa and 1000°C, the transformation started in 40 seconds and completed in 180 seconds. At 19.8 GPa and 950°C, the transformation started in 110 seconds and did not complete even in 40 minutes. On the other hand, the reaction rate from spinel plus stishovite to ilmenite was much slower even at higher temperature. The transformation started in 120 seconds and did not complete in 145 minutes at 20.7 GPa and 1500°C. These results imply that once enstatite decomposes into spinel plus stishovite, it becomes difficult to transform to ilmenite under subduction zone conditions.

Hogrefe A., Rubie D. C., Sharp T. G. & Seifert F., *Nature*, **372**, 351-353, (1994).

ENTHALPIES OF MIXING FOR SYNTHETIC GERMANIUM-BEARING ALKALI FELDSPARS AND DIRECT HF SOLUTION CALORIMETRIC MEASUREMENT OF ENTHALPIES OF ELASTIC STRAIN ASSOCIATED WITH EXSOLUTION

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Hydrofluoric acid solution calorimetric measurements have been made at 50°C on a nine-member series of synthetic germanium-bearing alkali feldspars. Because of the rapid dissolution of these samples, the measured heats of solution are of particularly high precision, with an average standard deviation per sample of just ± 0.37 kJ/mol. A plot of enthalpy of solution against composition for the Ge-bearing samples parallels that for normal disordered Ge-free (sanidine-analbite) alkali feldspars (Hovis, 1988). Enthalpies of K-Na mixing for the Ge-bearing series are maximized at sodic compositions, consistent with asymmetry of the Ge-feldspar solvus (Kusatz et al., 1987), at a value of 5.4 kJ/mol, similar in magnitude to that of normal disordered alkali feldspars (Hovis, 1988).

Several exsolved Ge-bearing alkali feldspar samples were synthesized via subsolvus annealing of homogeneous specimens at temperatures ranging from 500 to 640°C and periods from 48 to 480 days. All such samples were examined by TEM and confirmed to have coherent and regularly spaced exsolution lamellae, with wavelengths in the various specimens ranging from 300 to 800 Å.

Enthalpies of elastic strain were determined for four of the exsolved Ge-bearing feldspars by comparing their heats of solution to those of unstrained versions of the same coexisting phases. The resulting enthalpies of elastic strain were found to be small, and in fact near the detection limits of the calorimetric system despite the high precision of the data. Collectively the results indicate elastic strain enthalpies that are less than 2.0 kJ/mol. These are consistent with values estimated independently by Tullis & Yund (1979) and Brown & Parsons (1993). The enthalpy of elastic strain determined for an exsolved Ge-free sanidine-analbite feldspar was less than the standard deviation of the calorimetric data.

Brown WL & Parsons I, *Defects and Processes in the Solid State: Geoscience Applications (Boland & Fitz Gerald, editors)*, Elsevier Science Publishers, 267-290, (1993).

Hovis GL, *Journal of Petrology*, **29**, 731-763, (1988).

Kusatz B, Kroll H, Kaiping A, & Pentinghaus H, *Fortschritte der Mineralogie*, **65**, 203-248, (1987).

Tullis J & Yund RA, *American Mineralogist*, **64**, 1063-1074, (1979).

THE NUCLEATION AND GROWTH OF POLYCRYSTALLINE QUARTZ: PRESSURE EFFECT FROM 0.05 TO 3 GPa

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Polycrystalline quartz was formed from amorphous silica with sea- and distilled-water at temperatures and pressures ranging from 50 to 450°C and 50 MPa to 3 GPa. The data, which show a sigmoidal curve on a ζ -t plot, can be reasonably modeled using Avrami's nucleation and growth equation. The results reveal a dramatic pressure effect on the transformation rate, which increases by five orders of magnitude as pressure increases from 50 MPa to 3 GPa at 400 deg.C. For instance, it takes only 1 day at 3 GPa, instead of 300 years at 50 MPa, to transform 50% of silica to quartz at 100 deg. C. The pressure effect is more prominent at low-pressure than at high-pressure regimes; the transition pressure between the high- and low-pressure regimes depends on temperature; it is around 300 MPa at 400 deg.C. The nucleation rates were calculated using the measured growth rates and the extent of the transformation by fitting to the Cahn's kinetic model. The results show that pressure can significantly enhance both the nucleation and growth rates although the effect is stronger on nucleation than growth. This has been confirmed by the SEM observations, which show that grain sizes significantly decrease with increasing pressures, and has led to a new method to synthesize nano-size (< 100 nm) polycrystalline quartz in neutral solutions. The results also reveal that metastable quartz was nucleated and grown in the coesite stability field at low temperatures (< 400 deg.C). Polycrystalline quartz has been formed at temperatures as low as 50 deg.C at 3 GPa in a few days. This allows us to predict that polycrystalline quartz or coesite may be synthesized at ambient temperature within laboratory time if the pressure is high enough (e.g. > 4 GPa).

CRYSTAL CHEMISTRY AND THERMODYNAMIC MIXING PROPERTIES OF HEDENBERGITE-PETEDUNNITE-JOHANNSENITE-DIOPSIDE SOLID SOLUTIONS

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Clinopyroxenes are common minerals in skarns and occur in phase assemblages with iron-, zinc- and manganese-ores. We directed our attention to the properties of diopside(di)-hedenbergite(hd)-johannsenite(jo)-petedunnite(pd)-solid solutions: $\text{Ca}(\text{Mg,Fe,Mn,Zn})\text{Si}_2\text{O}_6$. The zinc-content in pyroxenes is an indicator for the metallogenesis of a skarn (Nakano et al., 1994).

The binary solid solutions di-hd, di-jo and hd-jo show complete miscibility (Capitani & Mellini, 2000 and Nakano, 1998). For the solid solution hedenbergite-petedunnite a complete miscibility can be confirmed at pressures > 1.0 GPa. While hedenbergite is stable at low pressures, petedunnite is stable at pressures > 1.0 GPa. At lower pressures, petedunnite reacts with quartz to zinc feldspar, corresponding to the reaction jadeite + quartz = albite (Fehr & Huber, 2001).

The thermodynamic behaviour of multi-component solid solutions is controlled by the binary solid solutions of their end-members. The solid solution hedenbergite-diopside shows asymmetric mixing properties and two Margules parameters are necessary to describe the thermodynamic mixing behaviour (Meyre et al., 1997). The alteration of the molar volumina implies a non-ideality of the solid solution hedenbergite-petedunnite (Huber et al., 2000). At higher f_{O_2} hedenbergite decomposes to andradite, magnetite and quartz: $9 \text{CaFeSi}_2\text{O}_6 + 2 \text{O}_2 = 3 \text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12} + \text{Fe}_3\text{O}_4 + 9 \text{SiO}_2$. The equilibrium constant of this reaction is determined by oxygen fugacity, which can be measured by means of emf methods. If hedenbergite-petedunnite solid solutions, take part in this reaction, the equilibrium constants reflect chemical potentials of hedenbergite in hedenbergite-petedunnite solid solutions. The activities of this solid solution were determined by emf-methods, directly. The measured activities lead to two Margules parameters to describe the hd-pd solid solution, showing asymmetric mixing properties. Thermodynamic parameters describing these ternary resp. quaternary solid solutions are still unknown.

- Capitani GG & Mellini M, *Eur. J. Mineral*, **12**, 1215-1227, (2000).
Fehr KT & Huber AL, *Am. Miner.*, **86**, 21-28, (2001).
Huber AL, Heuer M, Redhammer G & Hochleitner R, *Beih. Eur. J. Mineral*, **12**, 85, (2000).
Meyre C, De Capitani C & Partzsch JH, *J. Metam. Geol.*, **15**, 687-700, (1997).
Nakano T, Yoshino T, Shimazaki H & Shimizu M, *Econ. Geol.*, **89**, 1567-1580, (1994).
Nakano T, *Mineralized intrusion-related skarn systems. Min. Ass. Can. Short Course Series*, **26**, 147-166, (1998).

STRUCTURAL AND CHEMICAL RESPONSE TO VARYING ¹⁴B CONTENT IN OLENITE FROM KORALPE, AUSTRIA

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Long thought to be stoichiometric and contain only trigonal B, tourmaline has recently been shown to incorporate B on tetrahedral sites: a colorless olenite from the Koralpe, Austria contains approximately one ¹⁴B for every six tetrahedral (T) sites (Ertl et al. 1997; Hughes et al. 2000). Even greater amounts of ¹⁴B can substitute for Si in synthetic olenitic tourmaline (Wodara and Schreyer 1998, 2001). These discoveries have important implications for the crystal chemistry of the more widespread elbaite-schorl-rossmanite tourmalines typical of rare-element pegmatites.

To characterize the response of the tourmaline atomic arrangement to differing amounts of substitution of B for Si, five samples were separated from a rim-to-core section of the Koralpe tourmaline (nearly colorless rim to dark green core), over a distance of approximately 0.5 cm. After grinding to spheres, the crystal structures of the samples were undertaken using three-dimensional X-ray methods and yielded R values < 0.018.

From rim to core, the amount of tetrahedral boron decreases monotonically from 0.65 to 0.35 *apfu* ^{14}B as refined from X-ray structure data. Over that range of ^{14}B content, the mean T-O distance increases from 1.6103 to 1.6215 Å. Preliminary EMPA analyses undertaken before the structure crystals were separated show that the extensive substitution of ^{14}B for Si that decreases from rim to core yields an increase in Si and a decrease in B from rim to core. In addition, FeO content increases from <1.0 wt.% at the rim to >7.5 wt.% in the core, reinforcing the assertion that ^{14}B increases with increasing Al in tourmalines.

Ertl, A., Pertlik, F., & Bernhardt, H.-J., *Österreichische Akademie der Wissenschaften, Mathematisch-Naturwissenschaftliche Klasse*, **134**, 3-10, (1997).

Hughes, J.M., Ertl, A., Dyar, M.D., Grew, E., Shearer, C.K., Yates, M.G., & Guidotti, C.V., *Canadian Mineralogist*, **38**, 861-868, (2000).

Wodara, U., & Schreyer, W., *Terra Nova*, **10**, 68-69, (1998).

Wodara, U., & Schreyer, W., *Eur. J. Mineral.*, **13**, 521-532, (2001).

Fe-Mg EXCHANGE EXPERIMENTS ON CHLORITE IN THE SYSTEM $\text{MgO-FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$

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Fe-Mg chlorite is widespread in metamorphic and hydrothermally altered rocks. Stable assemblages in a wide range of temperatures and pressures indicate a positive correlation between Al^{3+} - and Fe^{2+} -contents in Fe-Mg chlorite. Data from (ultra)mafic and pelitic rocks constrain the Fe/Mg partitioning (K_D) with several coexisting silicates and oxides.

Experimental studies on chlorite so far have been performed mainly in the Fe-free system. For intermediate and pure Fe-chlorite experimental data are more sparse and partially discrepant. To date, few experimental studies on chlorite have analyzed the chemical composition of reaction products.

In the present study Fe-Mg exchange experiments between natural chlorite and synthetic olivine and spinel have been performed to calibrate the relationship between $\text{R}^{2+}\text{SiAl}_{-2}$ - and FeMg_{-1} exchange in chlorite as a function of temperature and bulk XFe^{2+} . Experiments are conducted at 25 kbar using piston-cylinder equipment technique because low pressure experiments turned out to yield overly sluggish reaction progress.

Phase equilibrium data so obtained are combined with data from the literature to derive a consistent set of thermodynamic data including mixing properties of Fe-Mg chlorite. Available site-mixing activity models for chlorite do not expand to a Gibbs Free Energy function required to compute chemical equilibria by G-minimization. The present study uses a concise speciation formulation to model the non-ideal Fe-Mg chlorite solution. The Gibbs Free Energy function is based on the four configurations amesite, Fe-amesite, penninite and Fe-penninite. These cover the whole compositional range accessible to chlorite in the system $\text{MgO-FeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (FMASH).

The derived solution model adequately reproduces available data on phase relations in the system MASH, including the composition of pure Mg-chlorite at its upper thermal stability. In the system FMASH, the positive correlation between Al^{3+} - and Fe^{2+} -contents in Fe-Mg chlorite as documented from natural assemblages is adequately predicted by the model.

ARGON DIFFUSION CHARACTERISTICS OF SINGLE GRAIN PYROXENES USING LASER STEP HEATING

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Pyroxenes are seldom used in K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating. This is due to its low potassium content as an impurity, little knowledge of their diffusion characteristics and difficulty in mineral separation. Pyroxenes neither dehydrate during heating, nor make a structural transition and/or breakdown up to the melting point. These characteristics make them ideal candidates for argon diffusion studies in vacuum in spite of their low potassium content. Single grain analysis also requires little separation work.

We have developed a temperature controlled laser step heating system, and applied it to pyroxene dating. Sample temperature during laser heating is monitored by an infrared thermometer, which has a probe area of 330 micrometers diameter. Temperature of a grain is sent to a personal computer, and is converted to a voltage increment of the laser power supply to achieve a preset temperature within 30-60 seconds. In contrast to a heater-current temperature control, the system does not allow overshoot of the preset temperature, adopting a relatively long relaxation time for thermal diffusion.

The diffusion characteristics of pyroxenes vary among analyses. This may be a reflection of compositional dependence, but the estimated closure temperatures of the pyroxenes are relatively uniform. They are above muscovites and below hornblendes.