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3. The prevalent mechanism producing growth zoning is fractionation in the closed system (the Rayleigh fractionation). Nonmonotonic zoning can appear at fluid flow through metamorphic rock.

4. The fractionation can produce both normal and reversed zoning. The normal zoning arises at the growth from the neutral aqueous fluid whereas the crystallization from alkaline fluid should result in reversed zoning.

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PHASE TRANSFORMATIONS IN CaCO_3 AND SiO_2 UP TO 2.5 GPa FROM ELECTRICAL IMPEDANCE MEASUREMENTS

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The phase transformation in calcite I-IV-V, calcite \Leftrightarrow aragonite and in SiO_2 have been characterised by electrical impedance measurements at temperatures 500-1200°C and pressures 0.5 - 2.5 GPa in a piston cylinder apparatus. The bulk conductivity σ has been measured from Argand plots in the frequency range $10^5 - 10^2$ Hz. The cell represents a coaxial cylindrical capacitor with a geometric factor c . 6 cm [1]. As a starting material the synthetic polycrystalline powder of CaCO_3 , natural crystals of calcite (Spain) and of quartz Mont Rose (France) were used. The transformation temperature was identified from a bulk resistivity-temperature curves as a kink point of the activation energy. In a low temperature phase (calcite I), the activation energy E_a of $\sigma \cdot T$ is $c. 1.05 \pm 0.05$ eV, and in high temperature phase (calcite V) E_a is $c. 0.75 \pm 0.05$ eV. The pressure dependence of T_c for the transformation in calcite V is positive for pressures up to 1 GPa $dT_c/dP \sim +20^\circ/\text{GPa}$ and becomes negative for the pressures 1-2 GPa: $-20^\circ/\text{GPa}$. The transformation calcite I-IV is less evident from the present observations. The activation energy of electrical conductivity between I and V phases increases gradually to from 0.95 to 1.05-1.15 eV and then decreases to $c. 0.75$ eV. The gradual increase of E_a may correspond to a kinetic phenomena of retaining R-3c symmetry at temperatures above $c. 850^\circ\text{C}$. However, the pressure dependence of the kink of the activation energy is also $+20^\circ/\text{GPa}$. The kinetics transformation of calcite in aragonite has been monitored by measuring a variation of the electrical resistance of calcite at 10^3 Hz with time in the stability field of aragonite. Products of the phase transformation have been analysed with a powder diffractometer. Variations of the electrical resistance with time correlate with the degree of phase transformation $\xi(t)$. The degree of transformation calcite to aragonite has been fitted to the expression: $\xi(t) \sim [1 - \exp(-t/\tau)]$, where τ is a characteristic time of the phase transformation at a temperature T. For example, τ of the transformation of calcite to aragonite at 2.5 GPa and 760°C is 7.5 h, at 1.5 GPa and 680°C is 8.8 h. The temperature of a-b-phase transition in quartz has been characterise at 0.5, 1, 1.5 and 2 GPa from the electrical impedance measurements of

polycrystalline samples. The difference in activation energies of $\sigma \cdot T$ in α - and β - quartz is rather small and increases with the pressure. For example at 0.5 GPa the activation energies E_a of $\sigma \cdot T$ for a and b-phase are 1.04 and 1.26 eV, at 1 GPa 1.1 and 1.3 eV, at 1.5 GPa 1.18 and 1.41 eV, at 2 GPa 1.23 and 1.53 eV, respectively. The calculated activation volume ΔV for α - and β -phases is about the same 0.18 and 0.25 cm^3/mol . The estimated phase transition temperature T_c from heating and cooling cycles are slightly different. dT_c/dP obtained in this study from heating and cooling cycles is smaller than has been reported from laser interferometry $256^\circ/\text{GPa}$ [2] and close to the T_c and dT_c/dP data reported in [3].

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GROWTH OF TOPAZ SINGLE CRYSTALS FROM SUPERCRITICAL AQUEOUS FLUIDS AND ITS CHARACTERIZATION

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Topaz often occurs in some kinds of pegmatites, greisens and hydrothermal veins. Until the last time large crystals of topaz haven't been received, but a spontaneously crystallization was realized many times [1, 2]. However, topaz synthesis becomes an important problem because solving can help to comprehend the genesis of topaz in nature, and help to solve problem of synthesis of gem-quality crystals. Our team accomplished synthesis of topaz single-crystals, based on recently got experimental data on studying of processes of joint transfer of SiO_2 and Al_2O_3 in supercritical fluids in terms of straight temperature gradient [3]. Crystals were grown in autoclaves (volume 50 cm^3) with temperatures from 600 up to 800°C, pressures from 20 up to 200 MPa and temperature difference between top and bottom parts of autoclave from 20 up to 100°C. Acid (pH 1-2 after experiments) aqueous-fluorine fluid was chose as a crystallizing medium. Nutrient was presented by quartz and topaz single-crystal bars with ZX-orientation, sizes 4x4x50 mm, and was placed in the top part (colder part) of autoclave, and sections of topaz with different orientations were hanged up in the bottom part (the hotter part) of autoclave. Intense dissolution of nutrient bars and growth of topaz crystals were observed with fluid density from 0,1 to 0,45 g/cm^3 (pressure about 40-200 MPa). However with density less than 0,33 g/cm^3 quartz began intense transferring to the bottom part of autoclave and crystallizing there jointly with topaz as a small spontaneous crystals. In general, as a result of made experiments, a method of reproducible synthesis of topaz single crystals on seed (cuts {001} and {112}) with growth rates 0,15-0,22 mm/day is found.

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EXPERIMENTAL STUDY AND COMPUTER SIMULATION OF DEPENDENCE OF MORPHOLOGY OF QUARTZ CRYSTALS ON GROWTH CONDITIONS

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The experimental study and computer simulation were carried out to investigate morphological variations of polyhedral quartz crystals depending on their growth conditions. The quartz crystals were grown under temperature range (T) from 210 up to 900°C and pressure (P) from 2 up to 500 MPa in both isothermal (T>400°C) and temperature gradient conditions (T.210°C). As medium of crystallization, pure water (alone or with addition of some surface-active substances) and aqueous solutions of different electrolytes (NaCl, LiCl, LiF, NH₄F, AlF₃, H₃BO₃, NaOH, KOH, etc) were used. In isothermal conditions, amorphous silica or cristobalite were used as nutrient [1,2], and quartz crystals smaller than 1 mm were formed. In temperature gradient experiments, synthetic quartz was used as nutrient, and plates and bars with different forms, sizes and crystallographic orientations prepared from synthetic quartz were used as seeds. The runs were performed in heat resisting autoclaves (T up to 800°C, P up to 200 MPa) as well as in installations of high gaseous (T up to 900°C, P up to 500 MPa) and hydrothermal (T up to 700°C, P up to 300 MPa) pressures. The computer simulation of time-depending morphological evolution of quartz crystals was performed using on earlier designed program, and morphodroms were drawn [3]. The experimental results have shown that the habit of crystals are controlled by many parameters: initially by given form, sizes and crystallographic orientation of seeds, as well as by T-P parameters, composition of solutions, and growth time. The computer simulation has allowed to visualize morphological evolution of habit of quartz crystals in time in dependence on relative growth rates of main faces. As whole the experimental results have confirmed that growth temperature influences on habit of quartz crystals similarly as observed earlier for natural quartz crystals. In addition to this, it was experimentally proved that other factors such as composition, pH, density, supersaturation of solutions, sizes and shapes of primary quartz grains or blocks, position of growing crystals in space as well as duration of their growth have considerable influence upon growth rates of major faces and thus habit. The work of Russian author has been supported by Russian Basis Research Foundation (Grant No 00-05-64525).

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HIGH-PRESSURE DEFORMATION MECHANISM IN THE ZEOLITE SCOLECITE: A COMBINED EXPERIMENTAL AND COMPUTATIONAL STUDY

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Scolecite (Na_{0.32}Ca_{7.71}Al_{15.60}Si_{24.36}O₈₀·26.51H₂O; s.g. F1d1) is a calcium fibrous zeolite with an ordered distribution of the Si and Al cations. Its crystal structure displays tetrahedral chains parallel to the *c* direction, forming channels which host one calcium atom and three water molecules. The pressure-induced structural modifications in scolecite were studied by means of *in-situ* synchrotron XRPD and by density functional computations. The unit cell parameters were refined up to 8.5 GPa and reductions of 5.0, 7.0, 2.0, 2.0 and 13% were found in *a*, *b*, *c*, β and *V*, respectively. A slight increase in the slope of the linear pressure-volume dependence was observed at about 6 GPa, suggesting an enhanced compressibility at higher pressures. The weakening and broadening of the diffraction peaks revealed the increasing of structural disorder with pressure, preventing the refinement of the lattice parameters above 8.5 GPa. Diffraction patterns collected in decompression showed that the disordering is irreversible. Since it was impossible to perform crystal-structure refinements, atomic coordinates were determined by means of Car-Parrinello simulations, within unit cells of dimensions suggested by the XRPD experiments. The discontinuous rise in compressibility at about 6 GPa was reproduced by the computation, that allowed us to attribute it to the re-organization of the hydrogen bonding network, with the formation of water dimers. Moreover, we found that, with increasing pressure, the tetrahedral chains, parallel to *c*, rotate along their elongation axis - with the progressive squashing of the channels - and display an increasing twisting along an axis perpendicular to *c*. We also observed modifications of the Ca polyhedra under pressure and the increase (from 4 to 5) of the coordination number of one of the two Al atoms, resulting from the approach of a water molecule. This last transformation should trigger the irreversible disordering of the system.

VAPOUR-LIQUID EQUILIBRIUM STUDY OF SILICON TETRACHLORIDE-CO₂ SYSTEM

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Supercritical CO₂ (critical P and T are 73.8 bar and 31.1 °C respectively) occurs as fluid inclusions over a wide range of conditions in the Earth's crust from greenschist facies to granulite facies. Whether it can transport inorganic components at elevated P-T conditions has not been considered in the geological literature. Numerous studies have been conducted on

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vapour-liquid equilibrium of various organic compounds and carbon dioxide; however, there is very little published work on the phase equilibria of binary systems involving inorganic compounds and CO₂, particularly metal and non-metal chlorides like silicon tetrachloride (SiCl₄). Initial studies on solubility of TiCl₄ in supercritical CO₂ by Tolley and Tester (1989) were followed by studies on TiCl₄-CO₂ and SnCl₄-CO₂ systems (Giles et al., 1992; Tolley et al., 1993; Wiegand and Seward, 1997). In this study we present experimental results for the binary system SiCl₄-CO₂ at temperatures up to 150 °C and pressures up to 140 bar. Experimental approach involved separate sampling and analysis of both liquid and vapour phases (with minimal disturbance to the equilibrium) using thermal conductivity detector (TCD), as well as sealed-ampule experiments in order to determine homogenization temperature at the optically observed point of disappearance of the liquid-vapour phase boundary. The results demonstrate that the binary system exhibits a two-phase equilibrium region extending up to approximately 160 bar. Theoretical calculations using ab initio Monte Carlo approaches are underway for the modeling of the experimental data as well as reconstruction of the phase envelope at elevated P-T conditions.

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LOCALIZATION OF DEFORMATION IN A TWO-PHASE ROCK: TORSION EXPERIMENTS ON CALCITE-ANHYDRITE AGGREGATES

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We deformed calcite-anhydrite aggregates in torsion to large amounts of shear strain in order to study the influence of the two phases on the deformation behaviour, and to test whether localization may occur in two-phase aggregates. We chose deformation conditions where calcite and anhydrite have approximately a similar strength. Torsion experiments were performed on fine-grained (5 - 8 µm) calcite/anhydrite samples with volume proportions of 0/100, 30/70, 50/50, 70/30 and 100/0. The experiments were performed at 600°C, 300 MPa confining pressure and a constant shear strain rate of 1.10⁻³ s⁻¹, up to a maximum shear strain of 12.5. Rheological data show that the pure anhydrite (peak stress = 125 MPa) is the strongest material and calcite the weakest (peak stress = 70 MPa). The calcite-anhydrite mixtures have strengths in between the end-members. However after a shear strain of 1, the anhydrite end-member weakens dramatically (50%), whereas the calcite end-member shows no or hardly any weakening. The 50/50 sample shows a significant weakening (40%), whereas weakening in the sample containing 70% calcite is much less pronounced, suggesting that at this composition, calcite still controls the deformation behaviour. At a shear strain of 3,

approximately similar steady-state stress values are observed for all the different compositions, indicating that composition does not have a large influence anymore on the strength once steady-state conditions are achieved. It is concluded that the evolution of the deformation behaviour with strain is strongly dependent on the distribution and the volume ratio of the two-phases. In addition, several experiments (calcite/anhydrite 50/50) were stopped at various amounts of shear strain. On the bulk sample scale, we observe a progressive localization of the deformation in the two-phase aggregates, while deformation of monophase rocks is always very homogeneous. This suggests that in nature localization may be triggered by the presence of a second phase.

HIGH PRESSURE-TEMPERATURE AQUEOUS SYSTEMS IN THE HYDROTHERMAL DIAMOND ANVIL CELL (HDAC)

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The hydrothermal diamond anvil cell (HDAC) has been used to place aqueous samples under conditions up to 2.5 GPa and 1000°C (Bassett, et al., 1993). Optical microscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF), X-ray absorption fine structure (XAFS), infrared absorption, luminescence, and Raman spectroscopy have been used to analyze these samples (Bassett et al., 1996). Critical behavior, melting, phase transitions, reactions, ionic structure and speciation, and compositional changes have been observed and measured. Shen et al. (1992) accurately determined equation-of-state (EOS) relationships of aqueous fluids by maintaining a constant sample volume in the HDAC. Visual observations are all that are needed to establish EOS relationships, which have been both an objective and a means for determining density and pressure in aqueous samples and in fluid inclusions. Darling and Bassett (2002) determined the P-T conditions of metamorphism in natural fluid inclusions from the Adirondack Mountains using the HDAC to prevent decrepitation resulting from high homogenization pressures due to the presence of carbon dioxide. Visual observation and X-ray diffraction are used for studying phase transitions. Wu et al. (1997) showed that dehydration-rehydration in montmorillonite is a reversible phase transition. XRF has been used for in-situ measurements of chemical changes in phases. Bassett et al. (2000) have used XAFS to determine species and their structures in aqueous solutions of Zn, Cu, and La using two modifications to the HDAC for XAFS analyses of elements with low-energy absorption edges, e.g., first-row transition elements (K-edge) and rare-earth elements (L(3)-edge). In the HDAC for XAFS by transmission, the amount of diamond in the beam has been reduced to 0.3 mm. In the HDAC for XRF and fluorescence XAFS, the amount of diamond traversed has been reduced to 0.16 mm.

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SOLUBILITY OF H₂O AND CO₂ IN SILICIC MELTS - IMPLICATIONS FOR MAGMA DEGASSING

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The solubilities of H₂O and CO₂ in rhyolitic to dacitic melts coexisting with a H₂O-CO₂ fluid were investigated at pressures 100-500 MPa and at temperatures 800-1250°C using internally heated argon pressure vessels at relatively oxidizing conditions (ca NNO + 2). The water content of the quenched glasses was determined by IR spectroscopy and/or by KFT. At 1250°C the water solubility is higher in dacitic and rhyodacitic melts than in rhyolitic melts at 200 MPa. At 500 MPa, the same trend is observed at low melt water content (<7 wt.% water), but at higher water contents (higher water fugacities) the trend inverts. In rhyolitic glasses carbon is only incorporated as molecular CO₂ which can be accurately measured using the IR absorption band at 2340 cm⁻¹ (Tamic et al. 2001). In contrast, in dacitic and rhyodacitic glasses, carbon is incorporated as both CO₂ and CO₃²⁻. The quantitative determination of the total dissolved C-species by IR-spectroscopy is complicated because the weak carbonate band is difficult to separate from the background in the spectra, especially in water-bearing glasses. Moreover, the CO₂/CO₃²⁻ ratio systematically decrease with water content. Thus, SIMS was used to quantify total CO₂ contents. At same pressure and fluid composition, the CO₂ solubility is systematically higher in dacitic than in rhyolitic melts, e.g., by 0.05 wt% at 200 MPa and equilibrium with pure CO₂ fluid (dacite: 0.15 wt% at 1250°C; rhyolite: 0.095 wt% at 800-1100°C, when using the newly determined molar absorption coefficient of 1266 l/mol cm). In both melts at constant pressure the CO₂ solubility increases non-linearly with CO₂ fugacity indicating an enhancement of CO₂ solubility by dissolved water. Using the volatile solubility data, the evolution of a dacitic magma fluid-saturated at 200 MPa and 850°C (equilibrated with pure H₂O or H₂O/CO₂=1:1) during isothermal decompression was modeled.

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DISTRIBUTION AND SPECTROSCOPIC PROPERTIES OF Cu(II) IN SYNTHETIC Cu(I)₁₀Cu(II)₂Sb₄S₁₃ TETRAHEDRITE: EPR AND SQUID INVESTIGATION

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Tetrahedrite, (Cu, Ag)₁₀(Fe, Zn, Hg, [])₂(Sb, As)₄S₁₃, a very important mineral for its wide chemical variability, presents a peculiar structure and electronic features. Crystalline powders of pure Cu-bearing tetrahedrite, Cu(I)₁₀Cu(II)₂Sb₄S₁₃, have been synthesized in order to fully characterize the nature of the Me-substitution and the relative stabilization of natural Me-bearing tetrahedrites. The spectroscopic and magnetic techniques confirmed the presence of two Cu(II) atoms per formula unit. Cu(II) appeared randomly distributed together with Cu(I) over the tetrahedral site, with a ratio Cu(I)/Cu(II) 2:1. EPR spectra, collected at different temperatures ranging from 130K to 298K, point to the presence of S-bridged Cu(II) dimers, constituted by two adjacent corner-sharing tetrahedral sites. The temperature dependence of the spectra was attributed to changes of the interaction between paramagnetic centers, which could be related to small structural variations of the unit cell. Pulsed EPR experiments, performed at liquid helium temperature, revealed a small fraction of superficial paramagnetic Cu(II) atoms, which show an electrostatic interaction with protons belonging to the wax used for incorporating the sample for the magnetic investigations. As concerns the bulk magnetic properties of the pure synthetic compound studied, SQUID measurements have revealed a strong variation in the χT versus T data, which appear completely reversible. No evidence of magnetic hysteresis was detected. A model, consistent with all magnetic and spectroscopic features, is proposed, taking into account not only of the Cu(I)-Cu(II) interaction, as a function of their distribution, but also of the rotation of tetrahedra due to the changes of cell dimensions with temperature.

PHASE RELATIONS IN MORB'S AT 200 MPa: THE EFFECT OF WATER AND OXYGEN FUGACITY

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Phase relations in a MOR-basaltic composition have been investigated experimentally in an internally heated pressure vessel at 200 MPa, 950 to 1150°C, as a function of the bulk water content present in the system and as function of fO₂. The vessel was equipped with a rapid quench system and a H₂-membrane to determine the fO₂ prevailing in the samples. The combination of these two techniques allows to quench large

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volume samples (several cm³) in highly depolymerised systems (a MORB melt with 9 wt% H₂O can be quenched to a bubble- and crystal-free glass). The capsules were filled with a water-bearing glass (containing between 0.5 and 4.5 wt% H₂O). Experiments were made at two fO₂ corresponding to that of the buffers MnO-Mn₃O₄ (oxidizing) and QFM (reducing). At reducing conditions, capsules of AuPd were pre-saturated with iron and the glasses were also pre-equilibrated at the corresponding fO₂. Following phases were observed: glass, olivine, clino- and orthopyroxene, plagioclase, magnetite, ilmenite and amphibole. Amphibole is only observed at water-saturated conditions and below 1000°C. The increase of X_{fo} in olivine and of melt Mg# due to increasing aH₂O is confirmed. In addition, it is shown that increasing the bulk water content (at constant fO₂) has the same effect due to increasing melt fraction. The CaO content of olivine is dependent on the anhydrous melt composition, but also on aH₂O. Thus, CaO content of olivine is a potential hygrometer. The comparison of the experiments at different fO₂ allows to quantify the effects of the crystallization of oxides (ilmenite and/or magnetite) on liquid lines of descent. Water has no stabilizing effects on Fe-Ti oxides, in contrast to observations of Sisson and Grove (1993). The different liquid lines of descent (calc-alkaline vs. tholeiitic) at reducing and oxidizing conditions result mainly from the absence or presence of magnetite.

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SOLID STATE TRANSFORMATIONS OF CARBONACEOUS MATERIALS UNDER PRESSURE (UP TO 8 GPa) AND TEMPERATURE (UP TO 1473 K)

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High-pressure (up to 8 GPa), high-temperature (up to 1473 K) experiments have been carried out with two synthetic cokes, a lamellar graphitizing anthracene-based coke (AC) and a microporous non graphitizing saccharose-based coke (SC), and a coal. The structural and microtextural evolution of the products has been characterized by coupling high-resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. With all precursors, graphitization is strongly enhanced, or even initiated in the case of the non graphitizing SC, by hydrostatic pressure. Indeed, triperiodic graphite was detected by HRTEM in all samples synthesized at 1273 K and 2 GPa. Additionally, the increase of average degree of ordering is linearly correlated with the duration of the experiment. The evolution of the coal is intermediate between the two synthetic cokes. In these experiments, graphitization under pressure appears to be a progressive and continuous process which proceeds heterogeneously through the carbonaceous matrix. The products recovered from high-pressure experiments are therefore strongly structurally and microtexturally heterogeneous and this heterogeneity raises important problems for the characterization. We discuss the causes of this heterogeneity and the way to take it into account in the study of such materials. In order to complete these experiments, we have

performed kinetic experiments under pressure (2.5 GPa, 1273 K), with in situ energy dispersive X-ray diffraction using a multi-anvil apparatus at the HASYLAB-DESY synchrotron facility (Hamburg). A new diffraction band appears quasi immediately under temperature with a low d₀₀₂ and an increasing intensity with time. These preliminary results show that very fast transformations occur in comparison to the slow general process represented by the evolution of the products recovered from quenched experiments.

CHLORIDE DISTRIBUTION BETWEEN HYDROUS FLUID AND BASALT AT 0.1 - 0.2 GPa ; EFFECT OF CHLORIDE ON Pt SOLUBILITY

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Experiments were performed on a synthetic haplobasaltic melt (Ab25-An55-Di20) as starting material. Experiments were performed at 1200°C, 0.1 and 0.2 GPa on a synthetic haplobasaltic melt (Ab25-An55-Di20) to determine the partitioning of chloride between fluid and silicate melt. Starting materials were diluted HCl solutions (5.0 to 25.0 wt% Cl) and dry glass sealed in Pt capsules. All experiments (total: 20) were conducted in internally heated pressure vessels equipped with a rapid quench set-up. The experimental products were always bubble free glasses (except one experiment with vesicles). Chlorine in glasses and free fluid was analyzed by microprobe and chloridometer, respectively. Water in glasses was analyzed by Karl Fischer Titration and microprobe (by difference method). The chloride content in the glasses varies between 0.4 to 2.9 wt% Cl, depending upon the amount of fluid and also on fluid concentration. The calculated distribution coefficient [D_{cl}=(wt%Cl in fluid/wt% Cl in melt)] varies from 2.0 to 8.4, which is in agreement with previous results of Webster et al. (1999). No pressure effect on D_{cl} is observed. However, D_{cl} increases slightly with increasing chloride content of the charge. Experiments performed with pure H₂O fluids show that water solubility is higher when Cl is present in the melt (4.9 and 6.1 ±0.15 wt% H₂O in melts containing 0 and 2.9 wt% Cl, respectively). This suggests that the solubility of water in basaltic melts does not vary inversely with Cl content in melts containing up to 2 wt% Cl, in contrast to observations of Webster et al. (1999). Determination of Platinum concentration in glass is in progress and is made by isotope dilution. Preliminary results show that Pt solubility is higher in H₂O bearing basaltic melts when compared with anhydrous melts.

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HYDROGEN MOBILITY IN PYROPE

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The quantification of hydrogen mobility in nominally anhydrous major mantle minerals is an important parameter for modeling the hydrogen cycle in the Earth's interior (Ingrin and Skogby, 2000). Recently, Wang et al. (1996) performed dehydrogenation experiments in air, on natural pyrope megacrysts ($\text{Py}_{70}\text{Al}_{16}\text{Gr}_{14}$) leading to the diffusion law :

$$D_{\text{out}} \text{ (m}^2\text{/s)} = 1.77 \exp [-(254.3 \text{ kJ/mol}) / RT]$$

In order to identify the mechanism of hydrogen mobility and the different defects involved, this study compares the results obtained by FTIR spectrometry from two types of experiments : dehydrogenations and hydrogen-deuterium exchanges. The samples used are cut from a natural pyrope megacryst ($\text{Py}_{80}\text{Al}_{15.5}\text{Gr}_{3.5}$) from Dora Maira.

H-extraction annealings performed at five temperatures between 800 and 1000°C show two distinct H-defects (at 3602 and 3650 cm^{-1}) with two different kinetics. The absorption band at 3650 cm^{-1} becomes empty six times faster than the other. This suggests that hydrogarnet substitution ($\text{SiO}_4 = \text{H}_4\text{O}_4$) is not the only mechanism for hydrogen incorporation in pyrope (Lager et al., 1989; Rossman et al., 1989). The activation energies for the two defects are equal (230 kJ/mol) and are very close to the previous data which suggests the same mechanism for the H-extraction control. However, both kinetics are more than one order of magnitude lower than Wang's data. The defects may be different since the OH absorption bands they observed are not located at the same wavenumbers (3575 and 3680 cm^{-1}).

The H-D exchange experiments executed at four temperatures between 700 and 950°C, show that exchange kinetics are identical for both defects and that the H-D exchange is faster than its extraction. Moreover, the measured activation energy is almost half that of Wang (138 versus 254 kJ/mol), but agrees with those of pyroxenes and olivine. Consequently, the H mobility mechanism is expected to be the same as for these other mantle minerals.

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HYDROGEN DIFFUSION IN POLYCRYSTALLINE DIOPSIDE: FIRST RESULTS

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The quantification of the hydrogen mobility in upper mantle rocks requires the knowledge of diffusion laws of hydrogen inside minerals including that at the grain-boundaries. However, up to now no diffusion data for hydrogen at grain-boundaries have been published. The frequent contamination at grain-boundaries of natural mantle rocks by hydrous phases as well as the too large grain size of these rocks precludes their use for experiments. A polycrystalline diopside sample has been synthesised in a piston cylinder from powder of a natural gem quality diopside (grains size 60 to 100 micron). The sample has been sintered at 800°C, 20 kbar for 24 hours in presence of deuterated water. A slice of the sample (85 micron thick) has been cut and kept as a reference. The remaining part ($2.2 \times 3.4 \times 3.4 \text{ mm}^3$), has been annealed at 700°C during 1h in Ar/10% H_2 gas flowing through H_2O . A 54 micron thick section has been cut at the surface and another, 67 micron thick, in the centre, at 1.1 mm from edges. Analyses have been conducted by micro-FTIR at the synchrotron light source at LURE (MIRAGE beamline). The reference slice exhibits a homogeneous concentration of D defects equal to 300 ppm D_2O . In the surface slice, after annealing in hydrogen, analyses show that 75-80 percent of D were replaced by H. A loss of H and D (in the same proportions) is also visible, the average concentration of hydrous species decrease to 50 ppm H_2O . Analyses performed on the central slice show that the D-H exchange was also efficient at the sample core, with a mean H/D ratio of 60 percent, with ratios that can decrease up to 30 percent in the middle of some grains. Comparison of these results with the diffusion data on diopside single crystal (Hercule and Ingrin, 1999) shows that hydrogen diffusion in polycrystalline samples is at least one order of magnitude faster than in single crystal. *This study was financially supported by the EU through the Human Potential Program HPRN-CT-2000-00056.*

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SILICON - IRON EXCHANGE IN CALCIUM SILICATE PEROVSKITES AT TRANSITION ZONE CONDITIONS

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CaSiO₃ perovskite is likely an important constituent of the Earth's transition zone and lower mantle. From studies performed on MgSiO₃ perovskite it is known that the incorporation of trivalent cations introduces oxygen vacancies in the system, which in turn causes appreciable changes in physical properties such as elasticity and electrical conductivity. This has important implications for the interpretation of geophysical data. In this study we focus on the effects of iron incorporation into CaSiO₃ perovskite.

In multianvil experiments performed on the CaSiO₃ - CaFeO_{2.5} join we have observed that, at the P - T conditions of the Earth's transition zone, iron can be incorporated into CaSiO₃ perovskite, although solubility in the endmember CaSiO₃ perovskite is limited. We have, however, synthesised an intermediate perovskite phase in this system with the composition Ca(Fe_{0.4}Si_{0.6})O_{2.8}, which we observe to be stable above 11 GPa over a large P - T range. Unlike CaSiO₃ perovskite, which becomes amorphous upon decompression, the incorporation of iron stabilises the crystal structure such that it is preserved during quenching and can be examined in detail by optical microscopy, X-ray diffraction, Mössbauer spectroscopy, electron microprobe, transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). All observations indicate that the structure can be characterised by oxygen deficient tetrahedral double layers perpendicular to the pseudocubic [111]-direction, alternating with eight octahedral perovskite layers, which are one half each occupied by silicon and iron. This phase displays a new type of defect perovskite superstructure. The structure seems to be related to a distorted rhombohedral structure, which raises the possibility that a high temperature phase transition may occur. In more iron rich compositions no further phases with the perovskite structure were identified, and the endmember Ca₂Fe₂O₅ composition with the brownmillerite structure breaks down into CaFe₂O₄ and CaO at pressures below 7 GPa.

MELTING RELATIONS OF CARBONATE-SILICATE ROCKS FROM DIATREMES OF THE CHAGOTAI COMPLEX (WEST UZBEKISTAN): EVIDENCE FROM EXPERIMENTS AT 1200-1700°C AND 4-7 GPa

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The Chagotai Complex is located in the Southern Nuratau (West Uzbekistan). Carbonate-silicate rocks including essentially carbonate varieties (melanocratic carbonatite) prevail in this complex; they compose dykes and two diatremes. Carbonate-silicate rocks contain diamond crystals; their spatial distribution is extremely non-uniform and varies from single up to hundreds of grains per 15-20 kg of rock (Djuraev, Divaev, 1999). The grain size ranges from 0.05 to 0.2 mm and the forms are mainly octahedral with smooth, sharp edges.

Melting relations were experimentally studied for two natural samples of melanocratic carbonatite (Grt, Cpx, Cal, Bt, Chl, Ap, Mag). The study was aimed on (1) experimental reconstruction of high-pressure mineral associations in carbonate-silicate rocks and (2) investigation of carbonate-silicate magma crystallization under high PT-parameters. Experiments were carried out on an "anvil with hole" apparatus (Litvin, 1991).

Experiments at 1700°C provide skeletal Prp-Grs-Alm garnet (in the first sample) and Hd-Di clinopyroxene (in the second sample) crystals in the groundmass of close-grained carbonate-silicate intergrowths (Grt+L and Cpx+L parageneses). At 1600°C garnet appears in the second sample (Grt+Cpx+L). Carbonate is registered in both samples at 1500°C (Grt+Cpx+Cal+L). All other experiments conducted under 1400-1200°C demonstrate subsolidus association of garnet, clinopyroxene, and carbonate (Grt+Cpx+Cal). Cpx in experiments under 7.0 GPa contains potassium (>0.5 wt% K₂O); at 4.0 GPa clinopyroxene is K-free, but K-phases (biotite, K feldspar) are observed.

Based on the experiments, the schematic diagram of melting relations in carbonate-silicate system under 7.0 GPa and 1200-1700°C was plotted. The silicate mineralization obtained is typical for high-Ca eclogite from kimberlite pipes (Sobolev et al., 1969).

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HIGH-PRESSURE PHASE TRANSITIONS IN LAWSONITE

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The compression behavior of lawsonite $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ has been studied under hydrostatic conditions at room temperature up to 9.8 GPa. The P-V data of the orthorhombic phase have been analysed using a 3rd-order Birch-Murnaghan equation of state (EoS). The derived EoS parameters for the volume data are: $V_0=676.10(3) \text{ \AA}^3$, $K_0=122.1(4) \text{ GPa}$ and $K''=5.6(1)$. The isothermal bulk modulus is in good agreement with the value of $K_{0T}=123(2) \text{ GPa}$ calculated from the elastic moduli measured by Brillouin spectroscopy (Sinogeikin et al., 2000). The values of the room pressure linear moduli do not show the same agreement with the Brillouin data, however. A careful analysis of the plot of the "normalised stress", F_E , versus the finite strain, f_E , (Angel, 2000) for the lattice parameters a , b and c , reveals a change in slope at a pressure of $\sim 4 \text{ GPa}$ for all three lattice parameters. In addition, reflections with $h+k=\text{odd}$ forbidden by $Cmcm$ symmetry are present at pressures above 4.1 GPa. We conclude that the phase transition is from the low-pressure $Cmcm$ structure to a $Pm\bar{c}n$ phase, similar to that found on cooling below 273 K at 1 bar. Considering only the lattice parameters up to 4 GPa for the 3rd-order Birch-Murnaghan EoS fitting, we obtain linear moduli in very good agreement with the results of previous Brillouin measurements of the elastic tensor at room conditions. The evolution of the spontaneous strain associated with the phase transformation has been calculated in order to characterise the transition behaviour. A further phase transition from the orthorhombic $Pm\bar{c}n$ phase to a monoclinic phase has been observed on increasing pressure above 9.5 GPa.

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PHASE EQUILIBRIA AND P-T-f H_2O -f O_2 CRYSTALLIZATION CONDITIONS OF THE LYNGDAL GRANODIORITE (SOUTHERN NORWAY) AND THE ORIGIN OF A-TYPE GRANITES IN ANORTHOSITE COMPLEXES

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The Proterozoic Lyngdal granodiorite (300 km², 60-65 wt% SiO_2 , 930 Ma) belongs to a series of A-type granitoids (the HBG suite: Vander Auwera et al., submitted). This suite is coeval and spatially associated with the post-collisional Rogaland Anorthosite-Mangerite-Charnockite (AMC) suite (930 Ma, Schärer et al., 1996) and shows a trend from ca. 59 wt% SiO_2 to ca. 76 wt% SiO_2 . It shares many geochemical

characteristics with anorogenic rapakivi granitoids, yet granodiorites dominate over granites, the latter being derived by fractional crystallization from the granodiorites (Bogaerts et al., submitted). In order to constrain both crystallization (P, T, fO_2 , H_2O in melt) and source conditions, crystallization experiments on two samples of the Lyngdal granodiorite (60 and 65 wt% SiO_2) were conducted in a IHPV at 4-2 kb (Al-in-hornblende, Johnson & Rutherford, 1989), at an fO_2 of NNO/NNO+1 (presence of titanite-magnetite-quartz, Wones, 1989), and under fluid-saturated conditions with various $\text{H}_2\text{O}/\text{CO}_2$ ratios for each temperature. At 4 kbar and H_2O -saturation, the liquidus for both compositions is near 1000°C with magnetite, ilmenite, apatite and clinopyroxene as near-liquidus minerals. The stability field of low-Ca pyroxene is restricted to $\text{H}_2\text{O}/\text{melt} < 6 \text{ wt\%}$ for all temperatures. Plagioclase is the sole feldspar between 775-950°C and amphibole appears at ca. 880°C for high aH_2O at 4 kbar. It breaks down to pyroxene when $\text{H}_2\text{O}/\text{melt} < 5 \text{ wt\%}$, and is absent in the experiments at 2 kb for the sample at 65 wt% SiO_2 . The comparison between experimental and natural phase equilibria indicates that the Lyngdal granodiorite crystallized between 4 and 2 kbar, the magma having 6 wt% H_2O in melt at early stages and with an fO_2 of NNO/NNO+1. These oxidized and wet conditions sharply contrast with the dry and reduced characters inferred for the Rogaland anorthosite suite, on the basis on phase equilibria (Vander-Auwera and Longhi., 1994). This rules out the Lyngdal granodiorite being a fractionation product of the associated anorthosite complex. These results show that contrasted types of magmas can be generated during a single regional magmatic event within a restricted geographical area and that A-type granitic magmas need not necessarily to be dry and reduced.

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EFFECT OF ALUMINIUM ON THE COMPRESSIBILITY OF STISHOVITE

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The recycling of oceanic crust into the deep Earth offers a way of enriching the mantle in silica (Wyssession, 1996). In such a subduction context, the high-pressure phase of silica, stishovite, present in the basaltic and the sedimentary portion of the slab, has been shown to contain small amounts of aluminium (Ono, 1998). The incorporation of this element and its possible coupling with oxygen vacancies influences the density and the compressibility of mantle phases, as has been evidenced for silicate perovskite (Andraut et al., 2001). Such parameters are important in the assessment of the structure and the chemistry of the deep mantle. In this study, the effect of aluminium on the compressibility of aluminous stishovite was investigated using a laser-heated diamond anvil cell and in situ X-ray diffraction at the ID30 beamline of ESRF (European

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Synchrotron Research Facility). The starting material was an aluminous silica glass. Cryogenically loaded argon served as the pressure-transmitting medium. After each compression step the stresses were relaxed by annealing the sample with CO₂-laser radiation. The pressure was measured using the shift in the fluorescence doublet of a ruby chip located in the sample chamber. The X-ray diffraction patterns were treated using the Rietveld method. The spectra show the presence of argon, stishovite and corundum, the system being over-saturated in this last component. Comparing our data set with that of pure stishovite, also collected with ruby as a pressure standard, we observe a decrease of compressibility of aluminous stishovite respect to pure stishovite. This is consistent with a substitution mechanism of Al³⁺ into the structure charge compensated by the creation of oxygen vacancies, such as Si⁴⁺ = Al³⁺ + O⁻. It thus appears that the addition of aluminium into stishovite makes it softer, a result drastically different to that observed for silicate perovskite.

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THE ACTIVITY OF SILICA IN TiO₂-RICH MELTS, AN EXPERIMENTAL INVESTIGATION

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We have studied the effect of TiO₂ on the activity of silica in silicate melts using the Pd-equilibration method whereby silicate melts are equilibrated with pure Pd metal (Chamberlin et al., 1994). An anorthite-diopside eutectic composition (DA) was chosen as base for these experiments. TiO₂ was added to DA and mixtures with 5, 10, 17 and 32% wt. TiO₂ were produced. The composition with 32% TiO₂ is rutile saturated at temperature of 1300°C. By adding SiO₂ to DA composition up to silica saturation appropriate silica standard was produced. Experiments were conducted with a loop technique in a one atm vertical tube furnace with controlled oxygen fugacity. The Si and Ti contents in metal loops and oxide concentrations in glasses were determined using a JEOL Superprobe. We found, that TiO₂ contents at least up to 6-8 mol.% do not affect SiO₂ activity in silicate melts. It was found that Ti, like Si, a lithophile element, partitions readily into Pd-metal at reducing conditions. The activity coefficient of Ti in Pd-metal is estimated to 5.8·10⁻¹⁰ at 1300°C, two orders of magnitude below activity coefficient of Ti in Pd-metal (Fechner, 2000), for the same temperature. Additional experiments demonstrated that the Ti-Pt solid solution is even more non-ideal than the Ti-Pd alloy and that of γTi in Pt doesn't obey Henry's law. It was also found that at fO₂ below some critical value the liquidus phase rutile is replaced by a new so far unknown phase with a composition corresponding to MgTi₃O₇.

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ESTIMATION OF THE MANTLE SOURCE COMPOSITION FROM GABBROIC INTRUSION COMPOSITION

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The problem of estimation of the upper mantle composition might be decided by using the dynamic models of partial melting of the mantle source. The primary mantle magmas should be in equilibrium with the olivine composition Fo>89. The parental magma of gabbroic intrusions with Fe/Mg ratios capable of coexisting with mantle olivines, could be interpreted as primary mantle magmas. The calculation data of the mantle source compositions were used for examination of high-magnesia layered gabbroic intrusions - Centralnii (Western Mongolia) and Majalic (Tuva). Parental magma compositions of these intrusions were estimated by COMAGMAT program 3.0 (Ariskin et al., 1993). Our preliminary results show that the Centralnii intrusion parental magma was picritic magma with 100 Mg/(Mg+Fe)=83,6, and REE abundances 1-6 chondrites. The parental magma could have been in equilibrium with the olivine composition Fo-94,9. The Majalic intrusion parental magma is characterized by 100 Mg/(Mg+Fe)=86,9 and REE abundances 1-10 chondrites. The Majalic parental magma had Fe/Mg ratios capable of coexisting with olivine composition Fo-95,9. The behaviour of heavy rare earth elements of these intrusions parental magmas suggests that residual garnet remains in their mantle sources. The Al₂O₃ content in Centralnii intrusion parental magma is consistent with its generation at 25 kbar, while Al₂O₃ content in Majalic intrusion parental magma can be explained by melt segregation at upper mantle pressures that ranged from 35 to 40 kbar. Thermodynamic calculation of partial melting of peridotite using the MELTS algorithm (Ghiorso et al., 1994) indicates that parental magma of both Centralnii and Majalic gabbroic intrusions can be derived, in terms of major elements, from the same depleted lherzolite source (100 Mg/(Mg+Fe)=92,1). It appears to be similar to Vourinos ophiolitic complex (100 Mg/(Mg+Fe)=92,8) (Moore, 1970). The parental magma composition variations of these intrusions could be explained by different physical parameters of the melting process (pressure, temperature and degree of partial melting). The variations in composition of the gabbroic intrusions mantle sources situated in the same area seem to be controlled by local major element heterogeneity in the mantle.

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EXPERIMENTAL STUDY OF SULFUR AND CHLORINE SOLUBILITY IN RHYODACITE AND ANDESITE MELTS OF UNZEN VOLCANO, JAPAN

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Solubilities of sulfur and chlorine (H-O-S; H-O-Cl; and H-O-S-Cl fluids) have been studied for the rhyodacite (groundmass) and andesite compositions of Unzen magmas at T=850 and 1050°C, P=50-300 MPa, $f(\text{O}_2)=\text{NNO}$, t=120 hours. All experiments were fluid saturated (fl/melt ratio<0.05). Experiments at T=850°C were conducted in cold seal pressure vessels, pressurized by water. High-temperature runs were made in an internally heated pressure vessel equipped with a rapid quench device and a Shaw-membrane to control hydrogen fugacity inside the vessel (Berndt et al., in press). The formation of sulfides buffers the solubility of sulfur in rhyodacite melt in equilibrium with (H-O-S)-fluid at the level of 30-50 ppm at T=850°C. Pressure has a negligible influence on the sulfur solubility in the melt of rhyodacite composition at this temperature. Experiments at higher temperature (1050°C) and P=200 MPa show no buffering effect of sulfides but a continuous increase in the concentration of dissolved sulfur with the amount of added S (and fluid $f(\text{S}_2)$) both for rhyodacitic and andesitic compositions. Chlorine in (H-O-Cl)-fluid - melt system is preferentially partitioned into the fluid phase ($D_{\text{Cl}} = C_{\text{Cl}}(\text{fl}) / C_{\text{Cl}}(\text{m}) = 3.9-5.9$ for rhyodacite and $D_{\text{Cl}}=3.2-3.4$ for andesite at T=1050°C) and the distribution coefficient increases with increasing Cl content (up to 5 wt%) in the fluid. Increasing the Cl concentration in the melt at T=1050°C and P=200 MPa from 0 to ~1 wt% enhances the solubility of water from 5.5±0.2 to 6.0±0.1 wt% and from 5.7±0.2 to 6.0±0.1 wt% for andesitic and rhyodacitic melts, respectively. These results are in contrast with the conclusions of Webster et al. (1999) for andesitic and more silicic magmas. Increasing sulfur content in the (H-O-S-Cl)-fluid at T=850°C and P=200 MPa has no influence on Cl solubility in rhyodacite melt at low amount of added chlorine and decreases Cl solubility at high Cl concentrations.

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METAL-SILICATE INTERACTIONS AT HIGH PRESSURE AND TEMPERATURE IN A DIAMOND ANVIL CELL

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The main feature of the Earth is its differentiation into a iron-metal rich core and a silicate mantle. There is a little doubt that the density of the Earth's outer core, inferred from seismology, requires that it is constituted of an alloy of liquid iron and light elements (Birch, 1952). However, the nature of the light alloying elements is still uncertain as it depends in a large measure on the conditions of accretion of the Earth and formation of the core. In the present study we use the laser-heated diamond-anvil cell (LHDAC) to study the high-pressure and temperature interactions between metal and silicate. Our first aim is to compare our partitioning behaviour of Ni and Co between metal and silicate liquids at low pressures (5-12 GPa) with results from multi-anvil devices in the Si-Al-Fe-Mg-Ca-Ni-Co-O system (Thibault and Walter, 1995). For high-pressure and high-temperature experiments, we used diamond anvils with 500 microns culets, and stainless-steel gaskets preindented to a thickness of 40 µm and drilled to a diameter of 100-150 µm (depending on a maximum pressure reached). We used both compacted powders with several silicate glass compositions (ranging from SiO₂ to basaltic composition simulating that of model C1 chondrite) and a 25 µm thick Fe-Ni-Co alloy foil. Thermal insulation from the diamonds was achieved by solid argon pressure medium. Pressures were measured at room temperature before and after laser heating, with the ruby-fluorescence method. The samples were heated by a multimode YAG laser for an average of 10-15 minutes. Temperatures were determined spectro-radiometrically with a fit to a grey-body Planck function. Samples recovered after the runs were analysed by electron microprobe (the electron beam is less than 1 µm and the resolution is about 1 µm). In addition, we have analysed our samples using secondary ion mass spectrometry (SIMS) analysis. A successful overlap of results of these different analysis techniques will substantially increase confidence in the extension of experiments to lower-mantle conditions. Our preliminary results in the system Si-Al-Fe-Mg-Ca-Ni-Co-O, show a good agreement with those of multi-anvil experiments at low pressures (5-12 GPa) (Thibault and Walter, 1995), and with increasing pressure until 50 GPa we observe the expected decrease of the partition coefficients of Ni and Co for the same redox conditions. We will present and discuss our results in all the systems studied as well as the solubility of Ar in silicate melts and iron-rich metal phases.

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STABILITY OF SiO₂-POOR ALKALISILICATES IN AIR

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SiO₂-poor alkaalisilicate liquids are of great interest in Earth sciences and glass industry as part of model systems thanks to which the properties of more complex melts can be understood. In view of their high hygroscopicity and possible reaction with atmospheric CO₂, however, these materials have led to a number of difficulties which has long restricted their use. Preliminary experiments on a CO₂-bearing binary potassium silicate melt with 43 mol% K₂O have shown that water intake is reversible on slow heating below the glass transition range, so that viscosity or thermal expansion measurements could be made safely in the supercooled liquid field (Bourgue & Richet, 2001). To gain more detailed insight on this process, we have investigated in this study the reactions with air of sodium and potassium silicates at or near room temperature. To investigate the effects of water absorption, we have made density, thermal expansion and heat capacity measurements. Information regarding the kinetics of absorption and exsolution, and the mechanisms of these reactions has been obtained by Raman spectroscopy with a heating-wire cell as described by Mysen & Neuville (1995). The results will be presented and discussed. The thermodynamics of dissolution of some of these glasses into water will be evaluated and the difficulties met to extract all the CO₂ dissolved in these glasses will be mentioned. Finally, special attention will be paid to the bias that can affect measurements made on partially altered samples.

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FERROPERICLASE - A LOWER MANTLE PHASE IN THE UPPER MANTLE

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Ferropicrlase is common in diamonds from Guinea (Stachel et al., 2000) and coexistence with enstatite proves lower mantle origin. In one diamond, the inclusion paragenesis is olivine and ferropicrlase (touching and non-touching). Ferropicrlase and ringwoodite may coexist at the lower mantle boundary and the olivines could be retrograde products from ringwoodite. This is not feasible because (i) touching and non-touching olivines and ferropicrlases are chemically identical and retrograde adjustment of Fe and Mg of the touching pair could not be observed and (ii) an Fe/Mg distribution of 4 is consistent with Fe/Mg partitioning between ferropicrlase-olivine rather than ferropicrlase-ringwoodite (Fei, 1998). Thus, diamond, ferropicrlase and olivine grew in the upper mantle in a low silica-activity environment.

An argument used against this was the high sodium content of 0.36 wt.-% supposed to be indicative of very high pressures. Sodium may, however, be incorporated in ferropicrlase on crystal chemical grounds only together with Al and Cr. Our experiments from 3 to 5 GPa and 1300 to 1600°C along joins MgO-jadeite and MgO-ureyite yielded olivine + pericrlase + spinel + liquid. Sodium in pericrlase ranged from 0.6 to 2 wt.-% with aluminum in amounts necessary for charge balance. Up to 20 wt.-% Cr were found and Cr may also be incorporated as divalent or in a defect structure.

In conclusion, high sodium content in ferropicrlase is not indicative of lower mantle origin. In the present case, Na-bearing pericrlase together with olivine reflects a region of low silica-activity in the upper mantle which may originate by interaction of carbonatitic melts with dunite precipitating magnesite later to be reduced by methane on diamond formation. Alternatively, ferropicrlase, olivine and diamond may precipitate directly from carbonatite melt on interaction with a more reduced environment.

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PHASE RELATIONSHIPS AND TOPOLOGICAL CONSTRAINTS IN THE SYSTEM $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$ AT 1 ATM

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High temperature experiments were performed in the system $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Cr}_2\text{O}_3$ (MASCr) at temperatures ranging from 1250°C to 1560°C at 1 atm. Bulk compositions were prepared as oxide mixture pellets, with $\text{SiO}_2\text{:Al}_2\text{O}_3$ ranging from ~1:1 to 1:4.5 wt.%, and $\text{Cr}_2\text{O}_3\text{:Al}_2\text{O}_3$ ranging from 1:9 mol toward Al-free compositions. Run products were characterized by X-Ray Powder Diffractometry, BSE images and EDS-WDS microprobe analysis.

Chromium is strongly incorporated into crystals, coexisting with very chromium-poor glasses. The whole range of chromian solid solution in spinel and corundum is covered. Sapphirine is widespread in aluminosilicatic compositions. It presents a very high chromia content (up to 29 wt%), and appears to be the only quaternary compound in the system.

The presence of liquid at temperatures as low as 1250°C suggests that the thermal minimum in the system MASCr is shifted to lower temperatures compared to MAS. At 1400°C a chromian sapphirine is found in a subsolidus four phase assemblage, coexisting with Cr-mullite, magnesiochromite and cristobalite. Phase relationships at 1560°C and 1250°C, by comparison with available data, suggest a complex topology in the silica-rich region of the system, involving the existence of a cotectic quaternary line raising from the ternary invariant point at 1590°C in the SACr system, and the presence of one or more quaternary invariant points. Composition of liquids coexisting with sapphirine and enstatite in the quaternary system are much silica richer than they are in the MAS system. This suggests that the cotectic quaternary surface of cordierite is constrained to lower chromium contents. Applications of experimentally defined phase relationships include refinement of currently available thermodynamic datasets on Cr-bearing systems, processing of Cr-refractories, and industrial waste treatment to permanently incorporate dangerous heavy metals in stable crystalline assemblages.

AN EXPERIMENTAL INVESTIGATION OF HYDROGEN SOLUBILITY IN PYROXENES ALONG THE DIOPSIDE-JADEITE TIE-LINE

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Considerable focus has recently been placed on the study of structurally-bound hydrogen in nominally anhydrous minerals (NAMs) thought to be stable in the upper mantle. Previous studies of natural samples have demonstrated that the pyroxene omphacite contains the most water, and is possibly the most important mineral in terms of recycling water back into the

mantle during subduction. An experimental program is currently underway to investigate hydrogen solubility in pyroxenes along the diopside ($\text{CaMgSi}_2\text{O}_6$) – jadeite ($\text{NaAlSi}_2\text{O}_6$) solid-solution series. Hydrogen solubility in jadeite has been studied from 1.7 to 10 GPa using FTIR spectroscopy on synthetic samples. A technique has been developed to produce large mm-sized, relatively crack- and inclusion-free crystals. Starting materials with considerable excess water are used and experiments are run for up to 10 days. Run temperature is varied during each experiment to initially produce complete melting and then allow crystal growth from the quenched melt.

Unpolarised and polarised spectra for jadeite are characterized by sharp peaks at 3613 and 3372 cm^{-1} , and a broader hump centered around 3552 cm^{-1} . Spectra obtained from samples synthesised below 2.5 GPa also exhibit a large and very broad hump centered around 3430 cm^{-1} . A similar broad feature is noted in spectra from diopside-rich omphacite crystals synthesised at 1.0 GPa. This feature may be associated with M2 vacancies. The sharp peak at 3613 cm^{-1} noted in all the spectra is perhaps analogous to a similar sharp peak noted in natural and synthetic diopside samples which occurs at slightly lower wave numbers.

Hydrogen contents for the samples studied so far are high in comparison to other NAMs, up to 2000 ppm, which is in-line with data from natural samples. Full characterization of the effects of pressure on hydrogen content in jadeite and omphacite is in progress.

COMBINED EXPERIMENTAL PHASE-EQUILIBRIA AND LOW-TEMPERATURE ADIABATIC CALORIMETRY TO DERIVE ACCURATE ENTHALPY AND ENTROPY VALUES FOR ACCESSORY MINERALS

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The derivation of thermochemical data for minerals to predict their stability in natural systems is one of the major issues of the experimental mineralogy. The phase relations between main rock-forming silicates can now be accurately modelled using internally-consistent thermodynamic databases. Accessory minerals, like REE-bearing minerals or phosphate minerals, are absent from these thermodynamic databases although they can be of primary petrological and geochemical importance. The success of internally-consistent databases in tackling phase relations shows that the thermodynamic characterisation of new phases should combine both experimental brackets which put tight constraints on $\Delta_r G(T,P)$ (where “r” stands for reaction) and calorimetric measurements. We have already performed thermodynamic extractions out of experimental brackets for some phosphate minerals as bearthite, trolleite, lazulite or MgAlPO_4O . Every time, it appeared that additional low-T adiabatic calorimetry measurements could still better constrain the third-law entropy ($S^\circ_{i,298}$) derived for

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these phases. The range of formation enthalpy ($\Delta_f H_{i, 298}^\circ$) consistent with the brackets will also be significantly reduced when $S_{i, 298}^\circ$ is tighter constrained since both parameters are correlated. In this contribution, our low-T adiabatic calorimeter will be presented along with first Cp data obtained for lazulite, $MgAl_2(PO_4)_2(OH)_2$, from ambient down to 25 K. In addition, preliminary HP and HT phase relations in the La_2O_3 - SiO_2 - P_2O_5 - CaO - H_2O - MgO/Al_2O_3 systems will be shown, which aim at the derivation of thermochemical data for La-hydroxybritholite, $La_6Ca_4(SiO_4)_6(OH)_2$.

BACTERIAL BIOFILM DEVELOPMENT WITHIN A SIMULATED NEAR SURFACE FRACTURE : BIOFILM STRUCTURE AND ITS IMPLICATIONS FOR MINERAL-FLUID INTERACTIONS

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Bacterial biofilms (complex bacterial communities supported by a hydrated exopolymeric matrix) form a reactive biological interface between minerals and solutions in many geological systems, including saturated near surface fracture-dominated aquifers. The mineral-fluid interface, once modified to a mineral-biological-fluid interface, has a greater surface area, surface roughness and an altered number of active sorption sites presented to solutions. Hence such modified interfaces will display a modified reactivity with dissolved trace metals. However, the initial colonisation, development and resulting architecture of these biofilms is poorly understood in terms of mineral surface coverage, initial bacterial adhesion mechanisms and biofilm structural development within water saturated fracture systems. In this work, a single species biofilm (*P. Aeruginosa* PA01) was developed within a simulated fracture and imaged using confocal scanning laser microscopy (CLSM). Subsequent image segmentation and isosurface generation of biofilms allowed improved visualisation of biofilm structure and its relationship to colonised surfaces. We also present evidence of flow-induced biofilm features, including the first evidence of the mechanics of flow induced biofilm "sloughing". Subsequent experimentation using the same equipment under temperate groundwater conditions (bacterial growth on a quartz substratum at 10°C using low nutrient concentrations) should reflect typical bacterial colonisation behaviour in natural systems of this type.

EXPERIMENTAL DATA AT 6 GPa ON THE SYSTEM $CaCO_3$ - $MgCO_3$ AND A THERMODYNAMIC MODEL OF THE SOLID SOLUTION

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A series of multi-anvil experiments have been performed in the system $CaCO_3$ - $MgCO_3$ at 6 GPa between 800 and 1500°C. The starting materials consist of various mixtures of the trigonal carbonates pure ordered dolomite (natural), magnesite (natural), and calcite (synthetic) that cover the compositional range. At the experimental conditions $CaCO_3$ exists in its orthorhombic high-pressure form, aragonite. With increasing temperature Ca-Mg-disorder in dolomite increases and above 1200°C the Ca and Mg cations are randomly distributed.

The breakdown reaction of stoichiometric dolomite to aragonite and magnesite occurs at 6 GPa between 900 and 1000°C and is in agreement with Luth 2001. The solid solutions in the system are temperature dependent. Two miscibility gaps appear in the T-X $MgCO_3$ diagram: one between aragonite and dolomite, and one between dolomite and magnesite. The non-stoichiometry of the dolomite depends on its degree of disorder. On the Ca-rich side the difference in the crystal structures between aragonite and dolomite does not allow a complete solid solution. A small two-phase field for disordered dolomite plus aragonite remains until melting occurs. Dolomite melts incongruently to aragonite and liquid. On the Mg-rich side the miscibility gap is cut by the melting curve at around 1400°C where magnesite coexists with a dolomitic liquid.

Using Raman spectroscopy, X-ray powder diffraction, and electron microprobe analysis techniques phase and mineral compositions have been determined. Using the compositions of the coexisting phases two temperature dependent Margules parameters are derived for the dolomite - magnesite subsystem. Before melting occurs at 1350°C $Mg_{0.606}Ca_{0.394}CO_3$ -dolomite coexists with $Mg_{0.867}Ca_{0.133}CO_3$ - magnesite, the two calculated Margules parameters are $W_{12} = -30.6$ kJ and $W_{21} = -4.0$ kJ.

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RESIDUAL GASES IN LAVA FROM ACTIVE PU'U O'O, KILAUEA, HAWAII

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While the volatile content and composition of magmas characterizes the tectonic regime of their genesis, extensive degassing during ascent and emplacement of magmas leaves us with a residual gas content, only. Here, we consider the effect of emplacement on residual gases of basalt glass from Pu'u O'o, Hawaii, and specifically the effect of reheating and changes of their redox state. Residual gases, trapped during hammer-dipping and subsequent quenching of basalt melt from Pu'u O'o, Hawaii, were detected with mass spectrometry (DEGAS, [1]) during heating. Compared to the amount of gas liberated from other basalt glasses, e.g. MORB, this lava has a lower content by several orders of magnitude. Extensive degassing occurred probably during the approximately 12 km transport to the ocean. Gases escape, in principle, by two different mechanisms, sudden release resulting in one or more spikes, and gradual escape by diffusion. We observe no gas release at temperatures below the glass transition temperature T_g (680°C), and no direct relation with crystallization temperatures (850°C and > 920°C [2]). A sudden and intensive release of hydrogen at 820°C correlates with a reducing atmosphere (increasing EMF), and oxidation of the sample. The oxidation enthalpy derived for the entire EMF experiment that did not achieve equilibrium, is about -57.4 kJ/mol and agrees qualitatively with -67 and -105 kJ/mol, derived for powdered glass and chunks, respectively, that had been oxidized towards equilibrium conditions [2]. These results may indicate that the emplacement of lava that allows structural relaxation via cooling or reheating and concomitant crystallization effects the original oxidation state.

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HIGH TEMPERATURE, LARGE STRAIN DEFORMATION TESTS ON QUARTZ AGGREGATES

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Cylindrical samples of natural water-rich quartz aggregates (Dover flint, England) were deformed in torsion in a Paterson gas-medium apparatus at constant strain-rate of 10^{-4} s⁻¹, temperatures of 1250, 1300 and 1400 K, and 350 MPa confining pressure. Here we present the results of tests at 1400 K. Samples were heat treated at 350 MPa at 1400 K, for different period of time (0.5 to 6h) under drained and undrained conditions. According to the phase stability diagram of the system SiO₂-H₂O, melt can be expected to be present. FTIR analysis of as-

is samples showed bulk water content of about 10⁵H/10⁶Si. Samples pre-heated for 0.5h or longer contained less than 10⁴H/10⁶Si. Fluid loss was even higher in deformed samples.

Samples heat treated 0.5h and deformed to low shear strain ($\gamma < 0.2$) under undrained conditions yielded at half of the stress of those deformed under drained conditions, suggesting that the strength depends on the water content (or pore fluid pressure). Microstructures of undrained samples showed evidence of tensile fracturing, suggesting that the pore pressure was close to the confining pressure. On the other hand, drained samples showed no evidences of cracking.

Other samples heat-treated for 0.5h were deformed to high shear strains ($\gamma > 1.5$). These showed steady-state stress up to a shear strain of $\gamma = 2$, then they hardened. Strain hardening was primarily correlated with the development of cracks. Microstructural observations suggest that the strain accommodating mechanism was granular flow, probably enhanced by melting along grain boundaries, since no SPO and only a very weak LPO was observed.

The sample heat-treated for 6h and deformed to $\gamma = 2.4$ showed steeply inclined crystalite grains (metastable at this conditions). We interpret the crystalite as fibres growing parallel to the minimum shear stress.

MELTING RELATIONS ON THE OMPHACITE – GARNET JOIN AT PRESSURE OF 7.0 GPa: EXPERIMENTAL MODELING OF ORIGIN OF DIAMOND-BEARING ECLOGITES

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The eclogite system on the omphacite – garnet join was chosen for experimental study as a model for the mantle source region and diamond – bearing rocks. The boundary multicomponent compositions are represented (in mol.%) by omphacite of the diopside-46,24; hedenbergite-8,85; acmite-13,68; jadeite-31,23; composition and garnet of the pyrope-15,21; almandine-53,35; grossular-31,44 composition. The compositions were calculated as the most representative for the Maksutov complex (Southern Urals) and reflect some key peculiarities of eclogite minerals from the mantle nodules in kimberlite diatremes.

The omphacite – garnet join studied is the inner section of the ternary omphacite – (pyrope + grossular-30%) – (almandine + grossular-30%) system. The ternary system is expected to give more complete information as to evolution of the major mineral composition in the mantle source region. For the pressure of 7.0 GPa, the melting diagram of the omphacite – garnet join is constructed. Both clinopyroxene and garnet are presented as liquidus phases. For subsolidus conditions, the clinopyroxene solid solution and clinopyroxene + garnet assembly fields are identified. Melting relations are controlled by the pseudoinvariant equilibrium at 1500°C (the equilibrium seems to be eutectic in agreement with the reaction clinopyroxene + garnet = liquid).

Melting relations on the multicomponent omphacite – garnet join are more under influence of the eutectic jadeite – pyrope system than the peritectic diopside – pyrope one if the relation revealed at 4 GPa (Bell & Davis, 1969; Litvin, 1991) are of value for 7 GPa. Phase equilibria on the pyrope – almandine join at 7 GPa (Butvina et al., 2001) are characterized by the complete series of solid and liquid solutions without extreme points (Roseboom's type I). Constitution of the ternary omphacite – (pyrope + grossular) – (almandine + grossular) phase diagram may be rather influenced with jadeite – pyrope system than diopside – pyrope one, and it is expected to characterize by divariant eutectic line and not include invariant equilibria at 7 GPa. The ternary melting equilibria are of key importance for the origin and evolution of diamond – bearing eclogites in the mantle conditions. Support: grant 01-05-64508 Of RFBR, 215-05 Integracia.

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EXPERIMENTAL DEFORMATION OF CLINOPYROXENE AGGREGATES

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We have conducted an experimental deformation study on the rheological behavior of clinopyroxene aggregates under dry conditions at low strains in a uniaxial deformation apparatus and at high strains using a torsion set-up. Coarse-grained natural clinopyroxene samples from Sleaford Bay and fine-grained aggregates hot-pressed from Sleaford Bay powders were first dried in a 1-atm oven at 1000°C for 10 hours under controlled conditions. The samples were then deformed in a Paterson apparatus at confining pressures of 300 - 430 MPa and temperatures of 1150-1250°C with the oxygen fugacity buffered by either nickel-nickel oxide or iron-wüstite powders.

Our low-strain uniaxial study yielded a flow law for dislocation creep for natural clinopyroxenite with a stress exponent of $n = 4.7 \pm 0.2$ and an activation energy for creep of $Q = 760 \pm 40$ kJ/mol. In the hot-pressed samples, mixed-mode deformation behavior was observed, with diffusional creep ($n = 1$) at lower differential stresses and dislocation creep (with n and Q similar to those of the natural samples) at higher differential stresses. Within the dislocation creep field, the predried hot-pressed samples generally yielded creep rates that were about an order of magnitude faster than the natural samples. Optical and electron microscope investigations of the deformation microstructures of the natural and hot-pressed samples show evidence for mechanical twinning and activation of dislocation slip systems.

High-strain deformation experiments were performed in torsion on natural and hot-pressed aggregates under similar conditions. Simple-shear microstructures and textures were analyzed using optical microscopy and EBSD. Hot-pressed samples were significantly weaker than natural samples. Stepping tests were performed to determine the evolution of the stress exponent with strain. We present a comparison of our

rheological data at low and high strains, and discuss the difference in rheological behavior between natural and synthetic aggregates.

A HT-XRD STUDY OF SYNTHETIC MAGNESIAN-FERRISPODUMENE: TRANSITION TEMPERATURE VS. CATION COMPOSITION AND ORDERING

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We synthesised magnesian-ferrispodumene in the MgO-LiO₂-FeO-SiO₂-H₂O system. Single-crystal structure refinement at room T and EMP analyses show that this pyroxene is monoclinic $P2_1/c$ with composition $M^2(Li_{0.85}Mg_{0.09}Fe^{2+}_{0.06})M^1(Fe^{3+}_{0.85}Mg_{0.15})Si_2O_6$ ($a = 9.638(3)$ Å, $b = 8.709(2)$ Å, $c = 5.258(2)$ Å, $\beta = 109.83(3)^\circ$, $V = 415.2$ Å³). Li is ordered at M2, and Fe³⁺ at M1, Mg and Fe²⁺ distribute over both octahedral sites. Structure refinements done at different temperatures show that at 105°C magnesian-ferrispodumene undergoes a reversible displacive phase transition $P2_1/c \Rightarrow C2/c$. It is evidenced by the disappearance of the $h+k = 2n+1$ reflections and by abrupt changes in the unit cell parameters. It is known from previous HT-XRD work that in Li-clinopyroxenes the transition temperature is inversely related to the size of the M1 cation [70°C in LiCrSi₂O₆ (Behruzi et al., 1984); 10°C in LiGaSi₂O₆ (Sato et al., 1995); -44° in LiFe³⁺Si₂O₆, (Redhammer et al., 2001)]. The studied crystal has an aggregate ionic radius at M1 larger than LiFe³⁺Si₂O₆; therefore its transition temperature should be < -44°C. It is also known (Prewitt et al., 1971) that the transition temperature in ferromagnesian clinopyroxenes increases with decreasing aggregate cation radius at M1 and M2, and thus depends on the Fe²⁺ ordering between M1 and M2 (Cámara et al., 2002). The transition temperature experimentally measured for magnesian-ferrispodumene can be thus explained by the presence of significant Mg at M2 which shortens the aggregate radius at that site. This study suggests the possibility of a complex thermodynamic behaviour accompanying variable cation substitutions at both the M1 and M2 sites in clinopyroxenes.

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