

V42F-10 1605h

Coupled U-Pb isotopic studies and synchrotron x-ray microbeam analysis of geologic systems

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Analytical advances in thermal ionization mass spectrometry now allow for precise measurement of U and Pb abundance and Pb isotopic composition in minerals where U and Pb may only amount to a few picograms by weight. High precision analysis at such low levels means that a much wider variety of mineral species can be considered as potentially useful U-Pb chronometers. However, evaluating the potential use of these minerals for high-precision dating requires understanding the environmental and crystal chemistry of the U and Pb being analyzed in these minerals. Advances in the production of microfocused synchrotron x-ray beams allow more unambiguous evaluation of uranium partitioning and speciation in these geochemical systems. The microbeam capabilities of these instruments, such as the X26A beamline at the NSLS, allow for near simultaneous evaluation of major and trace elements using synchrotron XRF, elemental speciation and coordination using x-ray absorption spectroscopy (XANES and EXAFS), and mineralogy using micro-XRD at resolutions of 10 microns or less. Additionally, the synchrotron hard x-ray microprobe allows for non-destructive analysis of the same hand specimens or thin sections from which samples are separated for isotopic analysis with a detection sensitivity often of 1 ppm or better. Some examples illustrate how these combined studies can help characterize the U and Pb geochemistry of the host environments in which these minerals formed. Andradite garnets from the Grand Canyon Supergroup (1178±/-26 Ma) are shown to be compositionally homogeneous in U abundance (10-25 ppm), with U as a 4+ species. Fossilized Jurassic fish coprolites from the Shuttle Meadow Fm. (ca. 200 Ma) show that although they are dominated by apatite the highest U abundance is consistent with adsorption onto organic C at the time of sedimentation. Examples of U analyzed from a number of terrestrial carbonates shows that U can be incorporated as both 4+ and 6+ species and may also be strongly influenced by the amount of organic material present, fluid chemistry, and source materials.

V42F-11 1620h

Determining the age and Original Seawater ⁸⁷Sr/⁸⁶Sr From Altered Aragonite Marine Cements of the Laborcita Formation, New Mexico

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Water-rock interaction modeling suggests that altered aragonite marine cements with abundances of Sr greater than a thousand ppm should yield both accurate U-Pb ages and the original seawater ⁸⁷Sr/⁸⁶Sr ratio. The exact Sr concentration depends on the composition of the diagenetic fluids. Aragonitic botryoidal cements are common within the algal mounds of the Laborcita Formation of the Sacramento Mountains, New Mexico. While other aragonitic components underwent early dissolution, the botryoids have been converted to calcite but have preserved their original fibrous aragonite textures. Multiple aliquots of the altered aragonite cements with fibrous texture from several samples representing the stratigraphic range of the mounds yield a minimum ⁸⁷Sr/⁸⁶Sr of 0.708393±8 that is more radiogenic than is expected (0.70793) for the Early Wolfcampian age (earliest Permian) of the Laborcita Formation. There is no apparent trend with the position of the samples in the mounds. Samples lacking fibrous texture have much higher ⁸⁷Sr/⁸⁶Sr ratios. The

Sr isotopic compositions and the concentrations show a trend consistent with an end member value for the diagenetic fluids of 0.70993. The botryoidal cements also yield a concordant U-Pb age of 304±2. While the Laborcita Formation is considered to be Wolfcampian, the ⁸⁷Sr/⁸⁶Sr ratio and the age suggest that it may be equivalent to the Missourian (late Pennsylvanian) from the mid continent based on Denison and Keopnicks (1994) Sr isotope seawater curve. Marine cements are common in the Late Paleozoic and samples that can be precisely dated and retain their original Sr isotopic compositions offer great possibilities for sorting out biostratigraphic problems as well as for refining the Sr isotope seawater curve.

URL: <http://pbisotope.ess.sunysb.edu>

V42F-12 1635h

(U-Th)/He Geochronology of Zircon Using Nd-YAG Laser Heating

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Developments of (U-Th)/He dating have demonstrated its potential and applicability as a low-temperature thermochronometer (e.g., Zeitler et al., 1987; Farley et al., 1996; Farley, 2000, 2001; Stockli et al., 2000). Recent success of dating apatite and titanite using laser extraction (House et al., 2000) enabled faster He analysis as well as single crystal dating due to far lower, more reproducible He blanks compared to conventional furnace heating. Here we report results of a systematic attempt at (U-Th)/He dating of known-age zircons using Nd-YAG laser extraction.

We analyzed single zircon grains separated from four rapidly cooled rocks of known ages, i.e., Fish Canyon Tuff (FCT; 27.8 ± 0.7 Ma), Buluk Tuff (BT; 16.3 ± 0.2 Ma), Tardree Rhyolite (TR; 58.4 ± 0.7 Ma) and Utaosa Rhyolite (UR; 2.52 ± 0.02 Ma). Zircon-containing Pt micro-crucibles were outgassed at 1300 degree C for thirty minutes. The evolved helium was spiked with 3He, cryogenically concentrated and purified, and analyzed by quadrupole mass spectrometry. After He extraction, the same zircon was melted using Pt fluxing crucibles with about 7 mg of ultrapure Li metaborate at 1400 degree C for 2 hours. The sample was spiked with 235U and 230Th and dissolved with 250 micro l HNO₃ by heating for 10 hours at 90 degree C. The resulting solution was then analyzed on a double focusing inductively coupled plasma mass spectrometer.

Measured (U-Th)/He ages of FCT, BT and UR are overall in agreement with their reference ages, with their mean corrected ages of 28.6 ± 1.4 (1 standard error), 16.1 ± 2.2 and 2.48 ± 0.05 Ma, respectively. These data suggest that (U-Th)/He dating using Nd-YAG laser extraction is basically applicable for zircon single grains. However, the He ages of TR are consistently too old, with a mean age of 78.8 ± 7.0 Ma. We inspected spontaneous fission track densities of TR zircons previously analyzed for zeta calibration (Tagami, 1987) and found that about 80 percent of these zircons are strongly zoned, with high track density (i.e., high U content) at core and low density at rim. This causes an overestimation of the alpha ejection correction and explains the overestimation of He ages for TR zircons.

V51A MC: Hall D Friday 0830h

New Directions in Experimental Mineralogy and Petrology III (joint with T, MR, HG)

Presiding: S Webb,

Georg-August-Universitt; J Kung,
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V51A-0967 0830h POSTER

Fe-Mg interdiffusion in (Mg,Fe)SiO₃ perovskite

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(Mg,Fe)SiO₃ perovskite is the dominant mineral in the lower mantle. Understanding the chemical and physical properties of this phase is therefore essential for understanding processes such as metal-silicate separation during core formation and mantle convection. An important parameter in describing the kinetics of such processes is the diffusion coefficient as function of P, T and fO₂. Although there is a relatively large database for diffusion coefficients in metals, oxides and silicates at 1 bar, high pressure results are still scarce due to experimental difficulties. Developments in multianvil techniques during the last 20 years allow the synthesis of high pressure phases such as (Mg,Fe)SiO₃ perovskite. Only in the last few years have diffusion experiments become possible as the result of improved pressure-temperature control, the development of large volume presses and new analytical techniques. However, there has been only one study of diffusion in perovskite (Si self diffusion, Yamazaki et al., 2000, PEPI, 119, 299-309).

In this study of Fe-Mg interdiffusion, polycrystalline samples of (Mg,Fe)SiO₃ perovskite were synthesized and then used for diffusion experiments at conditions of 23-25 GPa, 1750 °C to 2100 °C with run durations of 4 to 24 hours. In a first set of experiments we used MgO single-crystal capsules together with added Fe foil which buffer the fO₂ at relatively reducing conditions. Fe-Mg diffusion profiles are extremely short even after 24 h and cannot be measured by the electron microprobe. We therefore used EDX-TEM with which concentration profiles down to approximately 10 nm in length can be measured with relatively good counting statistics. Diffusion profiles measured on our samples are 100-600 nm long. In one sample we clearly observe that diffusion can be influenced by subgrain boundaries. Such regions of the sample have to be carefully avoided when analyzing diffusion profiles. At 1750 °C and 24 GPa a Fe-Mg interdiffusion coefficient of 3.66 × 10⁻²⁰ m²/sec is derived from our measurements. Fe-Mg interdiffusion in perovskite is therefore several orders of magnitude slower than in other phases at comparable temperatures. Currently, experiments are being performed on samples contained in Re-capsules to produce a more oxidizing environment.

These type of experiments show that it is possible to investigate transport properties of lower mantle minerals. Future progress in experimental equipment will allow higher pressures to be achieved with large sample volumes and long run durations.

V51A-0968 0830h POSTER

Finite Element Modeling of Volume Changes Produced by Heating and Pressurization of Fluid Inclusions

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Fluid inclusions are used in a variety of geologic studies including studies of metamorphic terrains, hydrothermal systems, and ore formation. By studying phase changes within inclusions, information about the temperature and pressure of entrapment can be derived. One of the basic assumptions made in these studies is that the volume of the inclusion has not changed significantly since its formation or during measurement. In general this is a good assumption, but in the case of inclusions trapped at high pressure, deformation of the inclusion may become important. For this study we focus in particular, on the elastic volume changes of the inclusion-host system that occur as the inclusions are heated during homogenization experiments. We use two-dimensional, axially symmetric finite element models to study the development of stresses in the host mineral around fluid inclusions and the resulting changes in inclusion volume. Numerical modeling allows us to estimate volume changes for shapes that cannot be described analytically. We find that elastic volume changes are a function of inclusion shape, and the distance between the inclusion and the edge of the sample. The degree to which edge proximity effects volume change is also a function of inclusion shape. We present results for a variety of inclusion shapes, host minerals and external and internal loads. These models should be particularly useful for fluid inclusion studies conducted at high pressure in externally heated diamond anvil cells (e.g. Schmidt et al., 1998, Am. Min.).

V51A-0969 0830h POSTER

The effects of fluorine on the compressibility of chondrodite structure

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High-pressure single crystal X-ray diffraction study on OH-chondrodite (synthesis) and natural chondrodite were performed using a diamond anvil cell with graphite monochromatized MoK α radiation (50kV, 40 mA, $\lambda=0.71069\text{\AA}$) up to 4.1 GPa for OH-chondrodite and 7.2 GPa for Natural sample at room temperature. Chemical formula of these samples are Mg_{4.99}Si_{2.01}O₈(OH)_{1.97} and Mg_{4.76}Fe_{0.22}Ti_{0.02}Si_{1.99}O₈(OH)_{1.24}F_(0.76), respectively. OH-chondrodite was synthesized at 6 GPa, 900 condition and natural chondrodite was from Tilley Foster Mine, U.S.A.. In high-pressure experiments, 4:1 methanol-ethanol fluid was used as pressure medium and pressure was determined by ruby fluorescence method (Piermarini, 1974). Unit cell parameters at each pressure were determined using 20-25 centered reflections within 11.5° < 2 θ < 30.1° range. X-ray intensity data of natural chondrodite were collected up to 2 θ_{max} =60 at some pressure points (ambient, 3.6, 5.6 and 7.1 GPa). In high-pressure experiments, out of 1500 reflections in a reciprocal sphere through a diamond anvil cell, a total of 245-310 symmetrically independent reflections ($I_0 > 1.5\sigma(I_0)$) were obtained by averaging the equivalent intensities in Laue group 2/m. The isothermal bulk modulus of each sample, determined using Birch-Murnaghan equation of state, is 110(10) GPa (assuming K'=4) for OH-sample and 118(2) GPa (K'=4.3 (8)) for Tilley sample. These values are in good agreement with 115 GPa (K'=4.9(2)) for OH-chondrodite (Ross and Crichton, 2001) and 118 GPa for Fe-bearing chondrodite (Sinogekin and Basso, 1999). Also, the linear compressibility of each sample is $\beta_a=1.89(5)$, $\beta_b=3.18(4)$, $\beta_c=2.89(8) \times 10^{-3}$ /GPa for OH-sample and $\beta_a=1.72(5)$, $\beta_b=2.99(4)$, $\beta_c=2.77(2) \times 10^{-3}$ /GPa for Natural sample, respectively. Fe-bearing chondrodite is slightly less compressible than OH-chondrodite. The most compressible axis is b-axis (10 \AA length period) corresponded to b-axis of olivine (Pbmm). The anisotropy of compressibility of natural sample is the same trend as those ($\beta_b > \beta_c > \beta_a$) of Kuribayashi et al. (1998) and Ross and Crichton (2001).

V51A-0970 0830h POSTER

Structure and Bonding in Transition Metal Sulfides: Merging Experiment and Theory

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Experimental determinations of crystal structure at high pressure using synchrotron radiation provide valuable input into the development of crystal-chemical systematics that can guide our thinking about the evolution of structure and bonding in mineral systems. We are currently discovering that the relationships among structure types are quite different at high pressure than at ambient pressure. Transition metal sulfides are of considerable current interest in this regard, both for their unique crystal structures and for the contrast in structural properties that exists between sulfides and oxides of analogous composition. Understanding the differences in structure and chemical bonding between the simple oxides and sulfides provides a starting point for the development of crystal-chemical systematics that may be applied to more complex structure types, particularly those generated at high pressure. An analysis of the structural properties of the simple monosulfides of the first transition series metals shows that these compositions are increasingly unstable in the NiAs-type structure with increasing electron count at the metal. Ultimately, the result for the later transition metal monosulfides is a set of structures composed of the highly unusual troilite (FeS), Co₉S₈, millerite (NiS), and covellite (CuS) types. For more complex sulfides, the range of available structure types is also governed by the electron count at the metal. The structural properties of the monosulfides of the first transition series metals furnish a background for understanding structure and bonding in the metal-rich sulfides, and we also discuss these properties in light of our recent work on the high-pressure structure of the metal-rich sulfide Ni₃S₂.

V51A-0971 0830h POSTER

Temperature Distribution in Multi-Anvil Assemblies Derived From Spinel Layer Growth

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Experiments performed at pressures (P) and temperatures (T) relevant to planetary interiors often require uniform heating of the experimental charge. Quantitative knowledge of the thermal structure of high-pressure assemblies is needed to determine maximum sample volumes and optimize assembly design. We present measurements of the T distribution in a range of multi-anvil assemblies, at P between 6 - 14 GPa, and at T up to 2250 K, based on the growth rate of a MgAl₂O₄ spinel layer at the interface between MgO and Al₂O₃ assembly filler pieces.

Recently, Watson et al. (CMP, in press) presented an empirical equation linking the thickness of a spinel layer growing at the interface between MgO and Al₂O₃ to P, T, and time. Their equation is based on experiments performed in a piston cylinder apparatus, at P up to 4 GPa and T up to 2250 K. We extend the P range of this equation to 14 GPa, using standard 18/11, 10/5 and 8/3 pressure cells. In the 18/11 and 10/5 assemblies with straight graphite and Re furnaces respectively, the upper half contained an alumina rod (enclosing thermocouple wires) surrounded by an MgO cylinder, while the lower half consisted of alumina tubing sandwiched between MgO cylinders. The 8/3 assembly (with a Re foil heater) consisted of an outer alumina cylinder filled with MgO. Spinel layer thicknesses were obtained from high-resolution X-ray maps of sectioned and polished run products using an electron probe.

In the 18/11 assembly, at 6 GPa and 2123 K, axial T remains constant within 2 mm of the assembly center. From the edges of this 'hot spot' T decreases parabolically with distance. The radial gradient is small (on the order of 15 K over 0.5 mm distance from the center of the assembly). At 14 GPa in the 8/3 assembly the hot spot is close to 1 mm long. T gradients outside the hot spot are large: 2 mm from the assembly center T has decreased by around 175 K. At 14 GPa, spinel growth is significantly slower than expected from the Watson et al. equation, caused by a decrease in chemical potential gradient across the MgO-Al₂O₃ interface as the stability limit of spinel is approached.

V51A-0972 0830h POSTER

Phase Relations in the System Mg₂SiO₄-MgAl₂O₄ at 22 GPa

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High-pressure experiments indicated that the maximum solubility of Al₂O₃ in orthorhombic silicate perovskite significantly increases with increasing pressure. The effect of Al₂O₃ content on the postspinel transition boundary has not been studied and even the extent of the Al₂O₃ solubility in Mg₂SiO₄-spinel at high pressures is not known. In this study, we carried out multi-anvil experiments in the system Mg₂SiO₄-MgAl₂O₄ at 22 GPa and temperatures from 1550 to 1750 °C. Starting materials were prepared with different proportions of Mg₂SiO₄ and MgAl₂O₄. Oxide mixtures and pre-synthesized glass or mineral mixtures were used in the experiments. All experiments were run for 48 hours. The resulting charges were polished and examined using an electron microprobe. Raman spectroscopy and X-ray diffraction were used for phase identification and crystal structural analysis. At 22 GPa and 1750 °C where Mg₂SiO₄-spinel is stable, the Al₂O₃ solubility in Mg₂SiO₄-spinel is limited to 0.8 wt.%. The solubility decreases with decreasing temperature. With increasing MgAl₂O₄ component, the phase assemblages change from Mg₂SiO₄-spinel to spinel + majorite + MgO, and to majorite + MgO + Al₂O₃, and finally to MgO + Al₂O₃ oxide mixture in MgAl₂O₄ composition. Our experimental results indicated that Al₂O₃ content in a multi-component system may not significantly affect the postspinel transition boundary because of very limited Al₂O₃ solubility in Mg₂SiO₄-spinel.

V51A-0973 0830h POSTER

A Thermodynamic Solution Model for FeMg-chlorite: Experimental and Theoretical Constraints

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A thermodynamic solution model for FeMg-chlorite has been calibrated to predict the composition and the stability limits of FeMg-chlorite as a function of pressure, temperature and bulk rock composition. Available site-mixing activity models for chlorite do not expand to a Gibbs free energy function required to compute chemical equilibria by G-minimization.

In the present study a concise speciation formulation is used to model the non-ideal FeMg-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 FeO-MgO-Al₂O₃-SiO₂-H₂O (FMASH). Deviations from ideality are taken into account by a Margules-type excess function.

Experimental studies on chlorite so far have been performed mainly in the iron-free system. For intermediate and pure Fe-chlorite experimental data are more sparse and partially discrepant, probably owing to sluggish reaction kinetics of chlorite and the growth of metastable assemblages. To date, few experimental studies have analyzed the Tschermak-contents of chlorite.

In the present study FeMg-exchange experiments between natural chlorite and synthetic olivine and spinel have been performed to calibrate the relationship between Tschermak- and FeMg₋₁ exchange in chlorite as a function of pressure, temperature and bulk XFe²⁺. Experiments are conducted at 15 to 25 kbar using piston-cylinder equipment technique because low pressure experiments turned out to yield overly sluggish reaction progress even with the aid of 1M-electrolyte solutions.

Phase equilibrium data so obtained are combined with data from the literature to derive a consistent set of thermodynamic data including mixing properties of FeMg-chlorite. The derived solution model adequately reproduces available data on phase relations in the system MgO-Al₂O₃-SiO₂-H₂O (MASH), including the composition of pure Mg-chlorite at its upper thermal stability. In the system FMASH, the positive correlation between Al³⁺- and Fe²⁺-contents in FeMg-chlorite as documented from natural assemblages is adequately predicted by the model.

V51A-0974 0830h POSTER

Critical melt fraction for percolation of core-forming materials

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Previous measurement of dihedral angles well over 60° (e.g. 65 - 115°) for Fe metal alloy in olivine-rich matrix have been used as evidence against grain boundary percolation of metal alloys in Earth's upper mantle. However, a certain amount of liquid metal will connect along grain boundaries when the dihedral angle is above the critical value of 60°. An excess of melt over a critical melt fraction (CMF) can create permeability, allowing segregation from the silicate matrix and leaving residual melts trapped at grain boundaries and as inclusions in silicates. To determine the CMF for melt permeability in 3 dimensions, we performed experiments over a range of metal/alloy mass fraction up to 0.7 in San Carlos olivine + sulfide or iron mixtures. Experiments were made for 3 days in a piston cylinder apparatus at 1573-1673K and 1.5GPa. To access metal/sulfide connectivity, electrical resistivity through the retrieved sample was measured at room conditions using a digital voltmeter. From the above analysis, a lower bound for the CMF was determined. Run products of olivine-iron mixtures are composed of olivine, magnesio-wüstite (mw) and iron, whereas run products of olivine-sulfide mixture are composed of olivine and sulfide. In both systems, electrical conductivity was lost when percolation drainage had reduced the alloy volume to 20%, indicating a lack of interconnectivity. This threshold

value corresponds to an interconnection threshold for a nearly 150° dihedral angle. However, previously reported dihedral angles at the junction of metallosulfide melt with silicate are generally smaller, in the range of 65 – 115°. In addition, the percolation threshold does not change significantly with the sulfur content in the melt, although dihedral angles are very sensitive to the amount of S in the melt. These inconsistencies may indicate that the system did not establish textural equilibrium during the 3 day run duration or that our method for determining connectivity is limited to 20 vol.% due to a possible presence of microcrack generated by pressure release.

Preliminary results suggest that molten metal cannot segregate by porous flow when metallosulfide fraction is less than 20 vol.%. The core comprises approximately 15 vol.% of Earth, so core segregation by percolation from an olivine-rich mantle would be unlikely. Further work will include conductivity measurements at higher pressure, and X-ray imaging of run products to further access the CMF.

V51A-0975 0830h POSTER

Exploration of beta-Fe using sintered diamond anvils

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Based on the DAC experiments, it has been claimed that a new polymorph of Fe, called beta phase, exists at higher than 35 GPa and 1500 K. We have carried out a series of experiments using a multi anvil press equipped with sintered diamond (SD) to clarify if the beta phase is really existent. The SD anvil assembly was squeezed by the DIA-type press SPEED-1500 installed at SPring-8, Japan. A fine mixture of Fe + MgO (1:1 in wt.) was put into a sleeve of MgO, which was set at the center of a cylindrical Re heater. Diamond powder was packed into the remaining spaces of the heater. In situ X-ray observation was carried out by energy dispersive method using synchrotron radiation. The generated pressure was determined from the measured volume of MgO of the sleeve based on the pressure scale after Jamieson et al. (1982). In the first heating cycle at 662 tonf, Fe initially assumed epsilon at 37.7(4) GPa and 300 K. On heating, gamma appeared at 1400 K and 38.4(2) GPa. The peaks from gamma intensified in accord with weakening of those from epsilon to 1700 K. However, the peaks of epsilon still survived at 1700K presumably due to temperature gradient in the sample. On cooling, the diffraction peaks of gamma began to weaken accompanying with the increase of epsilon peaks at 1300 K and 36.9(1) GPa. In the second heating cycle at 803 tonf, no change in diffraction pattern was observed up to 1300 K. However, the growth of reflections from gamma was recognized at 1600K and 41.1(2) GPa, associated with the reduction of epsilon, and became prompt with increasing temperature. We obtained no evidence for the presence of beta-Fe with the dhcp (Saxena et al. 1995) or the orthorhombic Pbcm structure (Andraut et al. 1997) up to 42.2(3) GPa and ca. 1900 K. All the results obtained in the present study indicate that the epsilon-gamma phase boundary is approximated by an equation of T (K) = 670 + 18P (GPa) over pressures from 14 to 42 GPa.

V51A-0976 0830h POSTER

Trace Element Contents of Micas: Defining Signatures of Partial Melting Processes in the Crust

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Trace element contents of micas in the protoliths of crustal melts are thought to be low, but are poorly

understood. In view of their significant role in generating partial melts in the crust, a better understanding of their trace element chemistry, especially REE abundance patterns, is required. Important dehydration-melting reactions of muscovite and biotite consume mainly mica, quartz and feldspar. Therefore partial melt compositions should reflect the compositions of these phases. An additional complexity is the role of accessory phases because of their potential control on REE behavior.

As a complement to natural geochemical studies, we have investigated experimentally the partial melting behavior of two typical crustal rocks, under both static and dynamic (deformation) conditions. We are characterizing the trace element signatures of partial melt in experiments in which crack networks appear and contrasting the signatures with compositions in a dynamic experiments where melt-enhanced deformation occurs. Both static and deformation experiments were conducted on a two-mica pelite and a biotite gneiss at pressures of 0.7-1.0 GPa, and between 725°C and 950°C. Deformation was performed at 10-5/s strain rate. In both sets of experiments, we observe textures associated with the development of permeability, either by cracking associated with reaction or by melt-enhanced deformation. We use the development of these textures to establish melt segregation mechanisms. Trace element data for mica and the glass in cracks and in highly permeable glass-bearing zones have been determined in situ using SIMS and LA-ICPMS. Starting micas in both rock types and the have also been analyzed in situ for REE. Both muscovite and biotite have low abundance REE (<10xCI) with gently sloping pattern from >1xCI for the LREE to <0.1xCI for the HREE. There also is a slight positive Eu anomaly. Compared to published REE data for micas, these abundances are lower. However, previous data were obtained using mica separates and may be compromised by inclusions of REE-rich accessory phases. In situ analyses provides data that are unambiguously mica alone, without inclusions. Complementary LA-ICPMS and SIMS data from low volume, muscovite-derived glass in melt cracks show a flatter REE pattern compared to the muscovite, but have retained the slightly positive Eu anomaly. In longer duration experiments, flat patterns remain but the Eu anomaly becomes negative. The data suggest that mica alone does not produce the melt signature and accessory phases, in addition to minor feldspar, play a significant role in controlling the geochemical signatures of the melts under these experimental conditions.

V51A-0977 0830h POSTER

Water in Planets: Dissociation of H₂O at High Pressures and Temperatures to a New Form of Oxygen

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Water is thought to play an important role inside planets, from terrestrial to giant, so the state of the fluid at planetary-interior conditions is of broad interest. Experiments with the laser-heated diamond cell show that H₂O dissociates chemically to hydrogen and oxygen upon heating to 2000-5000 K at relatively modest pressures of 6-46 GPa. The presence of H₂ and O₂, after heating H₂O, is confirmed by Raman spectroscopy at pressure. The observed vibron frequencies are in quantitative agreement with published work, indicating the presence of H-H and O=O bonds. X-ray diffraction shows that the oxygen formed from H₂O is quenched not to one of the previously known (low-temperature) phases, but to a new phase that is similarly produced upon heating pure O₂ at pressures of 3-46 GPa. The new phase of oxygen is monoclinic in symmetry (P 2₁/m), and exhibits a bulk modulus (K=72 ±2) GPa, K'=4) that is high for molecular systems. Formation of the new state of oxygen appears to be thermodynamically important for the process by which H₂O breaks down.

V51A-0978 0830h POSTER

Carbon self-diffusion in diamond

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Experimental determination of diffusivity of carbon isotopic exchange in diamond can provide strong constraints to the formation age of diamond, because natural diamonds show isotopic heterogeneity down to tens of microns (Harte and Otter, 1992, Chem. Geol. 101, p177; and Hauri et al., 1998, 7th IGC, p317). Thus a diamond must be younger than the time required for diffusive homogenization of carbon isotopes under pressure-temperature conditions of cratonic lithosphere. We have conducted diffusion experiments at 10GPa and from 1533K to 2273K, conditions at which diamond is stable. The starting material is a small chip of an undeformed, faceted girdle portion natural IA diamond. A thin, approximately 60nm, isotopically enriched ¹³C is vapor deposited on top of the polished diamond surface. The surface topography of diamonds before and after experiments were characterized by a Dektak surface profilometer. Experimental conditions were obtained using a split sphere-type multi-anvil apparatus. Diffusion profiles were determined using a Cameca 5f ion probe. We have used the depth profiling technique on diamond. A focused oxygen beam was rastered over a 50µm square area, and an electronic gate was used to collect the signal from the central, approximately 35µm square, region. The largest uncertainty in the diffusion experiments is due to mixing of the diffusant layer caused by topography on the diamond surface. Over a distance of 100µm along the surface, a 40nm range of high frequency topography is common. This topography prevents the determination of a diffusion coefficient from a profile shorter than 40nm long. For experiments annealed at 2073K for less than 5 hours, the length scale of diffusion profiles are at the order 60nm, and the length of profiles do not differ significantly over annealing duration of 10 min to 4 hours. Thus the diffusion profiles determined from short duration, and/or low temperature experiments which result in short diffusion profiles do not provide significant information. A 24h annealing at 2073K produced a diffusion profile over 120nm in depth. This gives a carbon self-diffusion coefficient of approximately 3 × 10⁻²¹ m²/s. Considering small differences between depth profile range and surface topography, the present result needs to be confirmed with longer duration experiments, which should yield significantly longer diffusion profiles compared with the surface topography. The presented diffusion coefficient is a maximum possible value assuming insignificant surface mixing. The minimum possible value determined is 7 × 10⁻²³ m²/s which is calculated from a profile only due to surface mixing.

V51A-0979 0830h POSTER

Electronic Structuring of Diamond Anvils - New Advances and Possibilities for HP Research

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DACs are powerful tools in high-pressure research, combining the principal advantages of transparency with the very HP attainable with this device. Nevertheless, a serious drawback for many in situ applications is the lack of a sufficiently precise method for determining the actual P in the sample volume. Hydrothermal DAC designs relying on the EOS of the P medium are susceptible to a number of potential sources of inaccuracy. One solution to this problem is the use of electronic sensors obtained by the structured HT, high-energy implantation of boron ions into the anvil culets of the DAC [1]. Recently, the sensitivity of such sensors at P in the GPa range has been successively improved from 20 [2] to 0.2 MPa [3], far surpassing that of any spectroscopic method. In addition, such P-sensing structures can also be used as temperature sensors, with a precision of 0.01 K [3].

To clarify and understand the principles on which these sensors function, we have performed conductivity and hall-effect measurements down to 4 K. The sensors show three conductivity mechanisms, depending on the T range involved. The HT (> 300K) mechanism is

based on the activation of B acceptors in the diamond lattice. The two mechanisms at lower T are related to a defect conductivity. Because of these specific defect mechanisms the sensor structures are still operative at temperatures down to 4 K.

A problem affecting HT DACs arises from heating via external resistance coils [4]. In such DACs the anvil seats are the weakest link and limit the force that can be applied to the anvils. Even when made of WC, the seats may deform considerably at P as low as 0.3 GPa at 1100 K. To overcome this drawback, we have implanted internal resistance heaters directly into the anvils next to the sample volume. These heaters are also composed of B-doped diamond produced by the same technique used to fabricate the P-T sensors [1,2,3]. In addition, it is possible to implant heavy ions such as silicon at RT to form graphite heaters in the anvils. The T of the seats can then be kept below 700 K, providing much better mechanical stability of the cell. No evidence of deformation was observed even on softer steel seats under a P of 0.7 GPa with the anvils heated to 1150 K. The use of steel as seat material makes it possible to adapt the seat design efficiently to the experimental set-up required. Further advantages of DACs with internally heated anvils are: 1) rapid heating at rates exceeding 500 K/s, and 2) the possibility of imposing large T differences between the anvils.

Special holders have been designed to hold anvils in their seats and to provide the electrical contacts up to 1400 K. In addition, new anvil geometries are being tested to avoid the chipping at the edges of the culets observed when hard materials are used as gaskets. Although it can be shown that HT B-implantation has no effect on the extent of this flaking problem, chipping in electronically structured anvils can lead to short-circuiting between the electronic pathways of the structures and must be minimized. Low-angle bevels next to the culet can be shown to enhance the lifetime of edges and electronic structures.

(1) Burchard et al. (1999), Bull. Liason SFMC, 11, 106. (2) Burchard et al. (2000), Berichte der DMG, Beih. z. Eur. J. Mineral., 12, 28. (3) Zaitsev et al. (2001), Phys. Stat. sol. (a) 185, 159-64. (4) Shen et al. (1992), in: HP Research: Applic. to Earth and Planetary Science (Terra Scientific Publishing Company, Tokyo, 1992), 61-68.

V51A-0980 0830h POSTER

Structural Environments of Chloride Ions in Silicate Glasses: Cl-35 NMR Results.

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Chloride is an important minor anion in many silicate magmas, primarily because of its role in magmatic volatiles and in the vapor-phase transport of metals. Cl and other halogen ions are also of key importance in some technological glasses, especially photochromic materials. However, little direct spectroscopic evidence is available to constrain the structural and chemical environments of Cl in these systems.

Cl-35 NMR is often considered to be "difficult" because of the relatively low resonant frequency of the nuclide and the very large values of quadrupolar coupling constants reported for organic compounds (with highly asymmetric C-Cl bonding) from nuclear quadrupolar resonance. In contrast, in more symmetric environments in inorganic materials, we have found that Cl-35 NMR spectra can be readily observable. In a series of Na-, Cs-, and Ba-silicate and aluminosilicate glasses with 0.05 to 3 wt % Cl, Cl-35 peaks obtained by MAS at 14.1 and 18.8 T fields are roughly Gaussian in shape and much narrower than the wide total chemical shift range for the nuclide, meaning that structural information is readily obtainable. New data on a few key crystalline model compounds helps to interpret such results. Isotropic chemical shifts (relative to 1 M aq. NaCl) and quadrupolar coupling constants for the following Cl environments are: halite (Cl-Na₆, -46 ppm, 0 MHz); sodalite (Cl-Na₄, -124 ppm, 0 MHz); CsCl (Cl-Cs₈, +110 ppm, 0 MHz); BaCl₂ (Cl-Ba₄, +124 ppm, 3.5 MHz; Cl-Ba₅: +219 ppm, 4.0 MHz); AlCl₃ (Cl-Al₂: peak maximum at +14 ppm). As for analogous anions (O-17, F-19), increasing Cl coordination number shifts peaks to higher frequency for a given ligand type. For the glasses, data collected at 2 fields indicate that the most important contributions to peak widths are chemical shift distributions, not quadrupolar coupling. In Na silicates and aluminosilicates, Cl-35 peak positions are consistent with Cl environments that mostly have 4 Na (and no other) neighbors. In Cs silicate glass, the Cl is coordinated by Cs only, probably with a mean coordination number (CN) of somewhat less than 8; in Ba silicate glass, CN for Cl seems to have a range similar to that in BaCl₂ (4 to 5). We see no evidence for Al-Cl bonding; rough quantitation of peak intensities suggests that if some Cl is "NMR-invisible" because of asymmetric bonding environments (e.g. Al-Cl-Na), this is a minor fraction of the total Cl in the glasses.

V51A-0981 0830h POSTER

Solid-State NMR Study of Metastable Immiscibility in Alkali Borosilicate Glasses

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Liquid-liquid phase separation is a critical issue in controlling and designing the physical properties of borosilicate glasses such as chemical durability, crystal nucleation, and high temperature strength and can provide insight into unmixing in natural magmatic systems as well. It is important to clarify this phenomenon, especially the immiscibility boundaries, which can be difficult to determine by conventional methods. High resolution NMR can provide a sensitive probe for the observation of phase separation in glass systems. In the M₂O-B₂O₃-SiO₂ system (M= Li, Na, K), we have used oxygen-17 MQMAS (Multiple Quantum Magic Angle Spinning) technique to explore changes in connectivities between SiO₄, BO₃ and BO₄ units, based on changes in populations of bridging oxygens, such as B-O-B, B-O-Si and Si-O-Si, and of non-bridging oxygens. We have also used boron-11 MAS and MQMAS to quantify populations of borate units with varying first shell coordination and connectivity to other network units, e.g., "ring" vs. "non-ring" BO₃ groups.

In a series of alkali borosilicates of the same stoichiometry, the population of Si-O-B oxygen for the Li glass is significantly lower than that for Na and K borosilicates. This implies that the Li glass has a greater degree of phase separation at a submicroscopic scale as expected from phase diagrams. O-17 MQMAS NMR is also useful in determining the effect of quenching rate and annealing temperature on the degree of phase separation. In the Na borosilicates, a reduced concentration of Si-O-B in compositions within the immiscibility region suggests that even optically homogeneous glasses have small-scale heterogeneity. In the B-11 MAS and MQMAS studies, the ratio of BO₃ to BO₄ does not change with annealing. The non-ring BO₃, however, converts to ring BO₃ with annealing, which increases the degree of phase separation. In the study of Na₂O-B₂O₃-SiO₂ glasses with different Na contents, Si-O-B(III) and Si-O-B(IV) as well as B-O-B(III) and B-O-B(IV) can be distinguished by O-17 MQMAS NMR for the first time. At least two BO₄ species were found in the B-11 NMR study. These semi-quantitative results can provide a further understanding of the glass structure.

V51A-0982 0830h POSTER

Observational and Theoretical Analysis of Shock Waves Associated with Vulcanian Explosions.

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Numerous Vulcanian explosions occurred in August, September and October 1997 at the Soufriere Hills volcano in Montserrat. Some of these events exhibited spherical regions of atmospheric condensation that moved rapidly away from the vent ahead of the erupting mixture. These regions indicated the passing of an atmospheric shock wave generated by the sudden decompression of the volcanic conduit. Like a theoretical shock tube, the instantaneous rupture of the nearly-solid conduit cap resulted in a series of compression waves which rapidly coalesced into a normal shock wave and apparently traveled at supersonic speed into the atmosphere. It is assumed that at the same time, a fragmentation wave traveled into the over-pressured conduit at the local speed of sound. We have compared 1-D theoretical shock-tube predictions of initial shock wave velocity, predictions of shock wave attenuation, and axisymmetric, multi-phase simulation results to video tape observations. One-dimensional shock tube calculations (assuming a cap of membrane thickness and an overpressure of 10 MPa) placed vent shock wave Mach numbers between 3 and 5, with the average equivalent to 1400 m/s-1. The same model also estimated shock strength (ratio of pressure behind the shock to pressure ahead of the shock) between 10 and 25. Assumed overpressure in the conduit, ratio of specific heats, and sound speed of the gas/magma mixture in the conduit greatly affected theoretical results. Axisymmetric,

multi-phase numerical models of the Vulcanian explosions generated semi-circular regions of pressure disturbances that moved away from the vent at very high velocities, generally consistent with the character of shock waves.

V51A-0983 0830h POSTER

Yield Stress of Periclase at High Pressure and Low Temperature

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Magnesiowustite (Mg,Fe)O is a significant constituent of the Earth lower mantle. In a follow-up investigation of the rheological properties of MgO periclase as an analog for magnesiowustite, one powder specimen of MgO (micrometric grain size) has been investigated at pressures up to 10 GPa and temperatures ranging from 25°C to 300°C. The experiment was performed in a multi-anvil (SAM85, DIA-type) high-pressure apparatus, with boron epoxy as pressure medium and a BN capsule enclosing the specimen. Temperature was measured with a W3%Re-W25%Re thermocouple situated next to the sample, while the cell pressure (NaCl Deckers scale) and the stress in the sample (diffraction peak broadening, a review in Weidner, 1998) were monitored by using in-situ synchrotron X-ray diffraction at the superconductor wiggler beam line of the NSLS facility (Brookhaven, NY). The run product was investigated by Transmission Electron Microscopy (TEM) using a Jeol 200 CX microscope.

From the X-ray diffraction data, we infer that periclase exhibits at room temperature a transition from elastic to plastic deformation at differential stresses higher than 3 GPa. A yield stress value of just over 4 GPa was measured under these conditions. Slight sample relaxation over time was also observed during heating at 300°C. Although the specimen average grain size was larger than typically 150 nm during the run, the run-product exhibits a very small average grain size (about 40 nm measured by X-ray diffraction), which suggests that nano-cracking occurred in the highly stressed material during decompression. Investigation of the run product by TEM confirms the X-ray diffraction data. Most crystals exhibit, indeed, nanometric sub-domains and numerous defects. Among these defects, the expected <110> {110} slip systems have been identified and seems to dominate the deformation at high pressure and low temperature, although cleavage along the {001} planes may also have occurred at low pressure during decompression.

Weidner (1998) Rheological studies at high pressure, in Ultrahigh-pressure mineralogy: Physics and chemistry of the Earth's deep interior, R. J. Hemley Ed., Reviews in Mineralogy, vol.37, Mineralogical Society of America, Washington D.C., pp.493-524.

V51A-0984 0830h POSTER

Structure and Chemistry of Grain Boundaries in Deformed, Olivine + Basalt and Partially Molten Lherzolite Aggregates: Evidence of Melt-free Grain Boundaries

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Olivine grain boundaries in quenched samples of deformed olivine + basalt and partially molten lherzolite aggregates were analyzed with various electron microscopy techniques to test for the presence of very thin (0.5-10 nm) intergranular melt films. (i) The structure of the boundaries was investigated using high-resolution transmission electron microscopy (HRTEM). Although a small fraction of grains are separated by relatively thick (~1 μm) layers of melt, HRTEM observations reveal that most of the remaining boundaries do not contain a thin amorphous phase. However, due to the anisotropy of the olivine-melt interfacial energy, melt often extends 1 to 2 μm from a triple junction into

an adjoining grain boundary before the boundary becomes tight, giving an effective dihedral angle of only $\sim 2^\circ$. (ii) The chemistry of olivine-olivine grain boundaries was analyzed using nano-beam analytical scanning transmission electron microscopy (ASTEM) with a probe size of < 2 nm. Ca and Ti segregate to grain boundaries forming enriched regions < 4 nm wide. Al segregation was observed only in the lherzolite sample. Si is not enriched at the grain boundaries in either sample type, demonstrating that chemistry of the grain boundaries is different from that of the melt phase. Combined with the HREM results, the ASTEM analysis indicates that these segregations do not represent very thin grain boundary melt films. Additionally, if a thin melt film exists along all of the grain boundaries, as reported for similar samples by other groups, the rock should be weakened significantly. Creep experiments on the partially molten rocks analyzed in this study reveal little weakening even at melt contents up to 4 vol%, consistent with our observations of melt-free grain boundaries.

V51A-0985 0830h POSTER

Diamond anvil cell investigation of lattice strains and preferred orientation in iron at high pressure and temperature.

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High pressure and high temperature investigations on bcc and hcp iron have been performed using radial x-ray diffraction in the diamond anvil cell. The technique used in previous experiments (Mao et al. Nature, 1998, Wenk et al. Nature, 2000) have been further refined in order to use monochromatic x-ray beam and angular dispersive detectors. This allows us to investigate in great detail the variations in d-spacing and intensity of diffraction as a function of sample orientation and relate them to elasticity, strength, preferred orientation and texture in the sample.

In this study, we investigate the lattice strains and the development of preferred orientation during compression in polycrystalline bcc-Fe and hcp-Fe between 0 and 35 GPa. The bcc phase if found to develop a mixed $<100>$ and $<111>$ fibers texture with compression. At the phase transition, the preferred orientation in hcp-Fe is inherited from the texture in bcc-Fe. With increasing pressure, we observe the development of the texture with dominating (0001) fiber component that was observed in previous experiments (Wenk et al. Nature, 2000). Double-sided laser heating of the sample at the highest pressure is then conducted in order to study the effect of temperature on preferred orientation. Analysis of the variation of the d-spacings with sample orientation can also be used to study the uniaxial stress component and elastic behavior under pressure and we apply it to our sample.

This study proves the feasibility of experimental investigation on elastic behavior, shear strength and deformation mechanisms under pressures and temperatures of the deep Earth.

Mao, H.K., J. Shu, G. Shen, R.J. Hemley, B. Li, and A.K. Singh, Nature, 396, 741-743, 1998 Wenk, H.R., S. Matthies, R.J. Hemley, H.K. Mao, and J. Shu, Nature, 405, 1044-1047, 2000

V51A-0986 0830h POSTER

Elastic constants of fluorite to 9.3 GPa

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Fluorite, CaF₂, represents a model structure for numerous binary compounds. In many respects, it is a nearly ideal material to serve as an internal pressure

calibrant in moderate high-pressure/high-temperature X-ray diffraction experiments. Its equation of state, based on single-crystal X-ray data and the ruby fluorescence scale, has been determined to 9.5 GPa (Angel, 1993). Above this pressure, CaF₂ undergoes a structural transition from cubic to orthorhombic. In order to test the accuracy of the fluorite pressure scale we provide an independent test of its equation of state and elastic properties. The single-crystal elastic constants of CaF₂ (fluorite) have been determined by Brillouin scattering in a diamond anvil cell to 9.3 GPa at 300 K. Acoustic velocities were measured in the (111) plane and inverted to simultaneously obtain the elastic constants and crystal orientation. Only the density at ambient condition was used in the inversion. The high-pressure densities were obtained from the Brillouin data by conversion to isothermal conditions followed by iterative integration of the compressibility curve. The pressure derivative of the bulk and shear modulus determined in this study are 4.78 ± 0.14 and 1.05 ± 0.07 , which differ from some previous low-pressure elasticity measurements. The pressure derivative of the bulk modulus is in agreement with the value from static compression within mutual uncertainties but the standard deviation has been reduced by a factor of 2.5. The elastic constants of fluorite increase linearly with pressure over the whole investigated pressure range. However, at $P \geq 9$ GPa, C11 and C12 show a subtle structure in their pressure dependence while C44 does not. The behavior of the elastic constants in the 9 - 9.3 GPa pressure range is probably related to the onset of a structural transition to a high-pressure orthorhombic polymorph at 9.5 GPa. A single crystal Raman scattering experiment performed in parallel to the Brillouin measurements shows the appearance of new features at 8.7 GPa. The new features are continuously observed to 49.2 GPa, confirming that the orthorhombic high-pressure phase is stable along the whole investigated pressure range, in agreement with a previous X-ray diffraction study of CaF₂ to 45 GPa. The high-pressure elasticity data of cubic fluorite in combination with room-pressure values from previous studies allowed us to determine an independent room temperature compression curve. The comparison of the new compression curve with that derived from X-ray data by Angel (1993) suggests that the accuracy of the fluorite pressure scale is better than 1% over the 0 - 9.3 GPa pressure range.

V51A-0987 0830h POSTER

Orientalional order-disorder phase transition in buddingtonite (NH₄AlSi₃O₈)

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Synthetic ND₄/NH₄-buddingtonite (ammonium feldspar) was studied as a function of temperature by infrared spectroscopy, X-ray diffraction and differential scanning calorimetry. Both ND₄ and NH₄ are found to occupy the M-site in feldspar framework structure. Orientalional order-disorder behaviour of NH₄⁺ is a well-established phenomenon in certain ammonium halides and ammonium salts. In this study, we report the first evidence for an orientational order-disorder phase transition of ND₄ and NH₄ in the 9-fold co-ordination site of buddingtonite. *In situ* low-temperature FTIR (both near infrared and far infrared) and X-ray diffraction has been conducted on buddingtonite from room temperature down to 20 K. The infrared spectra show noticeable changes on cooling. Using the autocorrelation analysis method we find distinct changes in the line width of the Gaussian profile fitted to the central autocorrelation peak upon cooling. The temperature dependence of lattice parameters, determined by X-ray diffraction also shows distinct changes. Low-temperature DSC results indicate a distinct λ -transition in heat capacity. We attribute these observations to the transition of the ND₄⁺ group from an orientational disordered state at higher temperatures to a relatively ordered state at temperatures below a critical temperature of 245 K. The order parameter for the transition appears to follow classical continuous behaviour as a function of temperature.

V51A-0988 0830h POSTER

The pressure-volume equation of state of the high-pressure B2 phase of NaCl

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We report the unit cell volume of the high-pressure B2 phase of NaCl up to 68 GPa measured in the diamond anvil cell with the laser annealing technique and synchrotron radiation. Laser annealing promotes the release of the non-hydrostatic stress in the sample chamber, resulting in a quasi-hydrostatic condition for the sample at high pressures and an associated precision increase in the unit cell volume determination. Since the B2 phase is only stable over 30 GPa, a reference volume is introduced for the Birch-Murnaghan equation of state (EOS) and the general universal EOS. We assumed the reference volume to be the volume of NaCl-B2 at the B1-B2 transition point (27.17 $< \epsilon >$, Bassett et al.1968). The fitted results with the modified Birch-Murnaghan EOS were $P = 31.35 \pm 0.19$ GPa, $K = 137.2 \pm 4.2$ GPa, and $K' = 4.85 \pm 0.35$ using the platinum pressure calibrant (Holmes et al. 1989), and $P = 32.08 \pm 0.19$ GPa, $K = 143.2 \pm 4.2$ GPa, and $K' = 3.94 \pm 0.31$ using the MgO pressure calibrant (Speziale et al. 2001). The fitting results with the modified universal EOS were $P = 31.14 \pm 0.14$ GPa, $K = 143.5 \pm 0.6$ GPa using the platinum calibrant, and $P = 32.15 \pm 0.13$ GPa, $K = 141.0 \pm 0.6$ GPa using the MgO calibrant. The results of the pressure dependence of the bulk modulus will be discussed and compared to those of other materials generally used as pressure media in the diamond anvil cell.

V51A-0989 0830h POSTER

Future Prospects for High-Pressure Structure Determination

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Accurate determination of the structures of Earth materials under the high pressures that they experience within the Earth is essential for understanding the structure and dynamics of the Earth's interior. Furthermore, the new physics that is often revealed in high-pressure experiments can only be interpreted in terms of structure.

The unit-cell volumes of crystals at high pressure can now be determined by X-ray diffraction to an order of magnitude better precision than 15 years ago, as a result of the combination of a number of technical developments (e.g. Angel et al., 2001). By contrast, far less progress has been made in improving the quality of refinements of crystal structures from single-crystal diffraction data collected at high pressures. As a community we are therefore in the position that we can detect small anomalies in the evolution of unit-cell parameters with pressure, yet we are unable to determine the corresponding changes in bond lengths and angles within the structure. We believe that our understanding of single crystal diffraction within the diamond-anvil cell is now sufficiently developed that the development of new data collection and data reduction techniques will yield improvements in single-crystal structure refinements to match those we have seen over the past 15 years in unit-cell parameter determination. Some of these methods will be discussed and an analysis of their potential contribution to improvements in precision of refined structures will be made.

Angel, Downs, Finger (2001). Chapter 16 in *MSA Reviews in Mineralogy*, vol 41.

V51A-0990 0830h POSTER

In Situ Investigations of Ion Exchange Processes in Microporous Materials

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The mechanism by which ions exchange in microporous and layered solids, such as zeolites and clays for example, has important implications in areas as diverse as soil fertility and environmental remediation. A detailed characterization of the ion-exchange pathway, the structural consequences of ion exchange and the specific sites involved in the course of exchange, is desirable. A probe that is both time- and structure-sensitive allows resolution of which specific sites are involved, along with the effects of different

cation types on the uptake and release of ions. In order to discern the mechanism of ion exchange, it is necessary not only to observe the course of the reaction, which can now be done routinely using energy dispersive X-ray diffraction at synchrotron sources, but also to collect dynamic diffraction data of sufficient quality to allow structure refinement using Rietveld structure refinement techniques. This at present requires the collection of monochromatic data. Tradeoffs between time-resolution, peak-to-background discrimination and structural resolution are often required and depend on the problem at hand. We have developed a number of strategies for in situ ion exchange techniques that probe both structural and kinetic information from dynamic solid media. Examples include investigations of the site-specific ion-exchange mechanism in zeolite LSX using a combination of ex situ and in situ time-resolved synchrotron X-ray powder diffraction. Iterative Target Transformation Factor Analysis (ITFA) and Rietveld structural refinements. Measurement of competitive ion depletion curves showed that the newly synthesized gallosilicate TsG-1 is more selective for Sr than mineral clinoptilolite, and the structural pathway of Sr-exchange in TsG-1 was monitored by in situ and ex situ synchrotron X-ray powder diffraction. In those cases where full structure refinement is desirable using less than optimal powder diffraction data, we found it necessary to first obtain excellent models from partially and fully ion exchanged materials, preferably from single crystal data. These allow the setting of realistic constraints on interatomic distances to supplement data with high time-resolution.

V51B MC: Hall D Friday 0830h

Geomaterials: Experimental Mineralogy and Petrology

Presiding: C Mandeville, American Museum of Natural History

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New D-H and ^{18}O - ^{16}O Fractionation Factors for Serpentine and Talc From 250 to 450°C

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D-H and ^{18}O - ^{16}O fractionation factors for serpentine and talc in 3.2 wt.% NaCl solutions have been determined from 250 to 450°C, 0.5Kb. The purpose of this study was to provide new experimental data for stable isotope fractionation in the talc-water system and to resolve the longstanding discrepancy between experimental and field-based hydrogen isotope fractionation factors for serpentine. Fractionation factors for talc were determined by reacting stoichiometric amounts of brucite and quartz with fluids enriched and depleted in D and ^{18}O . Stable isotope exchange between solid and fluid was nearly 100% during talc synthesis by this process. The resulting D-H fractionation factors between talc and water are -47 ± 6 and -31 ± 4 at 350 and 450°C, respectively. For ^{18}O - ^{16}O the fractionation factors are 6.5 ± 0.5 , 1.7 ± 0.6 , and 0.4 ± 0.1 at 250, 350, and 450°C, respectively. These results for ^{18}O - ^{16}O are in good agreement with various empirical and theoretical predictions but our value at 250°C is significantly more positive. For the serpentine experiments, separate runs were performed with lizardite and chrysotile in the presence of fluids enriched and depleted in D and ^{18}O . Lizardite was recrystallized to fibrous chrysotile at 250 and 350°C and the data suggest that D-H exchange was affected by kinetic fractionation during this process. Similar effects were not observed for ^{18}O - ^{16}O exchange during lizardite recrystallization or in runs performed with chrysotile. The extent of D-H exchange in the chrysotile experiments varied from 73 to 89% for run times up to 225 days. In contrast, the extent of ^{18}O - ^{16}O exchange was much less with only 19% exchange observed at 450°C after 45 days of reaction. Our measured ^{18}O - ^{16}O serpentine-water fractionation factors are 3.1 ± 0.8 , 0.0 ± 1.1 , and 3.1 ± 1.1 at 250, 350, and 450°C respectively. The corresponding values for D-H are -32 ± 14 , -29 ± 8 and -20 ± 1 . These experimental values for D-H fractionation are in excellent agreement with the original field-based estimates of Wenner and Taylor (1973).

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Experimental Investigations on the Variation of the Water Content of Antigorite and Resulting Geodynamic Implications for Subducting Processes

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The serpentine-variety antigorite is proposed to be the predominant phase for carrying large amounts of water into the upper mantle during subduction of hydrated ultrabasic rocks. Water-induced processes within subduction zones, like triggering of partial melting, metasomatic alteration or even intermediate depth seismicity (80-150 km), seem to be strongly associated with the decomposition of antigorite. Antigorite forms a series of discrete compositions, which can be expressed by the general formula $\text{M}_{3m-3}\text{T}_2\text{mO}_5\text{m}(\text{OH})_{4m-6}$ (T = tetrahedral cations like Si, Al; M = octahedral cations like Fe^{2+} , Mg; m = number of tetrahedra in a single chain defined by the wavelength λ). According to Mellini et al. (1987), typical compositions of natural antigorites are in a narrow range and the m-value seems to decrease with increasing metamorphic grade. The aim of this experimental study was to investigate the P,T-dependence of the antigorite polysomatism and its water-content. As starting materials brucite and talc were mixed in the stoichiometric proportions of antigorite with m = 17 plus 20 wt.% additional water. Piston-cylinder and hydrothermal experiments were performed over a wide P,T-range (350-710°C, 0.2-5.0 GPa) in the pure system $\text{MgO-SiO}_2\text{-H}_2\text{O}$. Run products were characterized by X-ray diffraction and by using TEM. For the determination of the a-lattice modulation (and corresponding m-values) of antigorite, lattice fringe spacings were deduced from diffraction patterns of selected (010) sections in the lattice fringe image. Our study indicated that increasing temperature and decreasing pressure of antigorite formation is correlated with a smaller m-value. For the P,T-conditions investigated, the compositional m-range of antigorite is rather narrow (14-18). The change in the crystal structure of antigorite from high to low m-values is combined with a gradual partial dehydration process. Therefore, during an ongoing subduction of serpentine-bearing lithosphere a successively partial dehydration of antigorite might occur. Fluids set free by this process might influence the rheological properties of surrounding rocks: Fluid migration into pores or along interfaces, thus changing the adhesion of the grains, might reduce the effective confining pressure. As a consequence, for a better understanding of rheological processes like e.g. dehydration embrittlement, which is thought to be a possible reason for seismicity within subduction zones, the preceding dehydration process of antigorite has to be considered. Additionally, for any formulation of reactions (e.g. within internally consistent thermodynamic datasets) under the participation of antigorite, the variation of its chemical composition with pressure and temperature has to be considered.

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Dynamics and Structure of Point Defects in Forsterite: ab initio calculations

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OH-bearing fluid inclusions in F92 forsterite samples from peridotite nodule 9206 (Udachnaja kimberlite pipe)[1] were documented recently based on TEM and IR studies. The Fourier transform of diffraction pattern from the inclusions exhibited a pattern, which is interpreted as ordered planar (2H)xMg defects. In this study the structure and dynamics of protons associated with Mg(1), Mg(2) vacancies and interstitial polyhedrons ordered in a (100) plane corresponding to double unit cell periodicity of the forsterite lattice has been investigated by ab initio quantum mechanic calculations. Static structure optimizations and

ab-initio molecular dynamics (MD) simulations have been performed using the CPMD density functional code[2]. The calculations were accomplished with the BLYP-functional utilizing the generalized gradient approximation. Non-local Goedecker-type pseudopotentials[3] have been applied to account for core electrons. Valence electron orbitals were approximated by plane wave expansion up to 70 Ry energy cutoff. The energy of static structures was sampled on 2x2x2 Monkhorst-Pack mesh[4]. During the structure relaxation parameters of an orthorhombic 2x1x2 supercell containing 116 atoms corresponding to $\text{Mg}_2\text{Si}_6\text{O}_{16}\text{H}_8$ hydrous olivine was fixed at experimental values of $a=9.524$ $b=10.225$ and $c=11.988$ relative to the Pbnm space group. Series of NVT-MD calculations were performed at 1000 K on 2x1x1 supercell with 58 atoms using four chain Nose thermostat. Randomly disturbed optimized structures were used as initial configuration for MD runs. The 1ps system equilibration is followed by trajectory production over 5 ps interval. A point energy sampling was applied in all MD calculations. A series of geometry optimizations, starting with various initial position of protons in Mg(1), Mg(2) and interstitial sites were carried out to obtain a structure with the lowest lattice energy. It was found that structures with protons completely located within the M1-polyhedron vacancies have lower energies than any other associated with M2 and interstitial polyhedrons. For protons associated with vacancies several configurations with small energy difference have been found. These configurations suggest a possible binding of the protons to O1, O2 and O3 sites including the formation of water-like HOH complexes. The MD simulations shows that protons can move easily within the vacant polyhedron to form covalent OH bonds at various oxygen sites. The protons initially located in interstitial positions of forsterite lattice were found to migrate in vacant polyhedra.

References [1] Khisina, N.R. & Wirth, R. (2001): Hydrous olivine (Mg,Fe) $_2\text{-xvxSiO}_4\text{H}_2\text{x}$ - a new DHMS phase of variable composition observed as nanometer-size precipitation in mantle olivine. PCMC, submitted [2] Hutter J. et al.: CPMD v. 4.0, MPI fuer Festkoerperforschung and IBM Zuerich Research Laboratory 1995-2000 [3] Goedecker S., Teter M. and Hutter J. (1996) Separable dual-space Gaussian pseudopotentials. Phys.Rev. B, 54(3) 1703-1710 [4] Monkhorst H.J. and Pack D. 1975 Special points for Brillouin-zone integration. Phys. Rev B,13,5188-5192

V51B-0994 0830h POSTER

Crystallization of Skeletal Diamonds from Graphite and Natural Coal in Presence of Hydrous Fluids at P=8 GPa and T=1400-1500°C

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Most metamorphic microdiamonds from crustal UHP rocks of the Kokchetav massive, Kazakhstan are characterized by skeletal-hopper crystals, cuboid-like crystals with cavities "healed over" by graphite, rose-like crystals, and other imperfect morphologies. According to the classical theory of crystal growth at thermodynamic equilibrium, only shapes with a minimum surface energy are stable. Thus imperfect crystallographic forms of most metamorphic diamonds formally may be interpreted as metastable while the presence of other high pressure phases associated with diamond indicates that the rocks have been subjected to UHP metamorphism within the diamond stability field. The classical theory also says that a skeletal-hopper crystal is one that develops under conditions of rapid growth, a high degree of supersaturation and in the presence of impurities.

In contrast to these observations, most experiments on diamond synthesis at high P (5-7.7 GPa) and T (1250 - 1900°C) from graphite (Wang et al., 1999; Hong et al., 1999; Yamaoka et al., 2000) and carbonate material (Pal'anov et al., 1999; Sokol et al., 2000) in presence of fluid phase produced perfect octahedral and cube-octahedral diamond crystals. Advanced analytical research on metamorphic diamonds and their inclusions has demonstrated that they were crystallized from a multicomponent COH-rich supercritical fluid phase, the composition of which suggests intermixture of crustal and mantle components (de Corte et al., 1999; Dobrzhinetskaya et al., 2001; Stockhert et al., 2001). We have recently synthesized imperfect diamond crystals (skeletal-hopper morphologies with effect of etching of the diamond surfaces) from graphite and natural coal + 2% Mg(OH)₂ as a source for fluid phase. Conditions of experiments are: P=8-8.5 GPa, T=1400-1500°C, t=14 to 136 hours. Our experimental data are in a good agreement with similar experiments conducted by Kanda et al. (1984) who showed