where they might be misinterpreted as melting. This is particularly true if high-PT experiment is not supported by information on the structure of the emerging phase. We will present theoretical results which show that Xe [1], Fe [2], and Mo [3] exhibit T-induced s-s transitions. These transitions are in good agreement with experimental data, which, however, was interpreted as melting. Our results allow us to suggest that the stable phase in the Earth inner core is body centred cubic iron not the hexagonal closed packed phase. This interpretation allows us to dismiss the major controversy between the "low" and "high" iron melting temperatures. Since *bcc* iron is less dense than *hcp* iron, the presumable amount of light elements in the core is less than was thought before. The melting temperature of iron in the center of the Earth, when the *bcc* phase is taken into account, is about 6900 K.

1. A. B. Belonoshko, R. Ahuja, and B. Johansson, Molecular dynamics study of melting and fcc-bcc transitions in Xe. *Phys. Rev. Lett.* **87**, 165505 (2001).
2. A. B. Belonoshko, R. Ahuja, and B. Johansson, Stability of the body-centred-cubic phase of iron in the Earth's inner core. *Nature* **424**, 1032 (2003).
3. A. B. Belonoshko, S. Simak, B. Johansson, L. Burakovsky, and D.L. Preston, High-pressure melting of Mo. *Phys. Rev. Lett.* (submitted).

V41B-05 0900h

Kawai-type apparatus equipped with sintered diamond and its application to melting of mantle materials

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Kawai-type (the 6-8 type) of multi-anvil apparatus has been widely used in the mineral physics because of its versatile abilities such as large volume and pressure environment of high hydrostacity. However, it has been realized for last two decades that the maximum attainable pressure is limited to ca. 27 GPa when using tungsten carbide (WC) as anvil material. We have tried to extend capability of Kawai-type apparatus by adopting sintered diamond (SD) cubes of 14 mm edge length with 1.5 or 2.0 mm truncations together with an octahedral magnesia pressure medium. Recently generated pressures of 54 GPa and 40 GPa were confirmed for 1.5 and 2.0 mm truncations, respectively, at room temperature based on the MgO pressure scale. Following above technical innovation, we have carried out melting experiments on peridotite and CI model mantle material up to 35 GPa to examine the hypothesis for crystal fractionation in deep magma ocean in early stage of the Earth's history. Powdered starting material was put directly into a small cylindrical Re heater, which was set in the octahedron with a LaCrO3 sleeve. The sample was heated to ca. 2500° C for 2-3 min at the prescribed load. The quenched products were made to polished sections, which were examined by electron microscopy and then analyzed by the electron probe micro analyzer. In peridotite, ferropericlase (Fp) is the liquidus phase up to about 30 GPa. Both Fp and Mg-perovskite (Mg-Pv), however, coexist on the liquidus at 31 GPa, indicating multiple saturation of these phases. At higher than 32 GPa the front of Fp grains moves back from the liquidus to the slightly lower temperature region and Mg-Pv becomes the liquidus phase. Ca-perovskite (Ca-Pv) crystallizes at a fairly lower temperature than Fp and Mg-Pv at pressures up to ca. 29 GPa. However the crystallization temperatures of Fp and Ca-Pv become closer with increasing pressure, and the former might be only a few degrees higher than the latter at 33 GPa. In CI mantle, on other hand, liquidus phase changes from majorite (Mj) to Fp in pressures of 23-25 GPa. At higher than 28 GPa, Mj and Fp completely disappear in the super solidus region, and the liquidus phase is Mg-Pv followed down temperature by Ca-Pv. Differentiation by crystal fractionation of Mg-Pv, Fp, and Ca-Pv in a deep magma ocean has been examined for a CI chondritic and two peridotitic bulk silicate Earth models, using chemical compositions of theses phases coexisted with melt in peridotite charge at 33 GPa. Mass balance indicates that subtraction of about 40 percent Mg-perovskite and 2 percent Ca-perovskite from a CI chondritic bulk silicate Earth yields a residual melt close to a model fertile upper mantle composition. A crystal layer composed of Mg- and Ca-perovskites would pile up to a depth about 1400 km, and may be characterized as an enriched and possibly heat-producing reservoir by the high capability of Ca-perovskite to accommodate large cations such as La and alkaline elements. For peridotitic bulk silicate Earth models, fractionation would be quite limited, up to 10 percent of Mg-perovskite in addition to trace amount of Ca-Pv.

V41B-06 0915h

Deformation Experiments in the D-DIA Using High-Resolution Monochromatic Diffraction

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Differential stresses in polycrystalline MgO and CsCl samples under controlled axial strain are determined as a function of pressure and temperature in the Deformation DIA (D-DIA: Wang et al., RSI, 74, 3002, 2003) using monochromatic diffraction, with a two-dimensional X-ray detector and X-ray transparent sintered cubic boron nitride (cBN) anvils. Radiographic images and diffraction Debye rings are repeatedly recorded at various pressures during constant strain rate deformation. From the sample length change in the X-ray image, total sample axial strain can be determined. From the distortion of the diffraction rings recorded over the entire 360° azimuth angles, elastic lattice strains can be accurately measured as a function of pressure, temperature, and differential stress. Linear lattice elastic theory is applied to convert lattice strains to differential stress (Singh, J. Appl. Phys., 73, 4278, 1993). The ability of the D-DIA to control differential stress separately from pressure (by deforming the sample while maintaining constant pressure) allows us to establish criteria for detecting yielding and to examine pressure and total strain dependence on yield strength. Analyses indicate that Singh's theory is adequate in describing the stress-strain behavior within the elastic regime. However, as some crystallites begin to yield, stress state becomes heterogeneous on the grain scale, resulting in significant change in the apparent anisotropy factor. This change can be considered as an indicator for the onset of yielding. Such details contain important information on rheology but previously could not be observed in conventional deformation and high-pressure (such as the diamond-anvil cell or multianvil) devices. Work is underway to model the stress distribution in polycrystalline samples after yielding, in order to connect stresses measured at the grain-to-grain level to conventional the force-over-the-area measurements. Our findings also raise questions on previous elastic constant measurements using diffraction, where differential stress levels are expected to be high. These data are likely to be influenced by heterogeneous yielding, in which case the elastic data thus obtained would be erroneous.

V41B-07 0930h

Density Measurement of Silicate Glass by In Situ X-ray Absorption Method

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Density is an important physical property to understand high-pressure behaviors of silicate glass and melt. There, however, have not been adequate methods to determine the density of silicate glass and melt at high pressures and high temperatures. We applied x-ray absorption method to silicate glass with low x-ray absorption coefficient, by using a diamond sample container. We measured the densities of basalt composition glass and Fe-bearing sodium silicate glass up to 5 GPa and 773K using synchrotron radiation. High-pressure x-ray absorption experiments were conducted at BL22XU in SPring-8, where the cubic type multi-anvil press, SMAP180 is installed and a monochromatic x-ray is available. To detect the absorption contrast between silicate and surrounding materials, we used a single crystal diamond ring as a sample container and a boron-epoxy resin as a pressure-transmitting medium. Intensities of incident and transmitted x-ray were measured by ion chambers, in which we used the monochromatic x-ray with 25.13 keV. We can evaluate the density of glass from the x-ray absorption profile along a radial direction of a cylindrical sample, because deformation of diamond ring is very small in this pressure range and x-ray absorption of diamond is lower than silicate. We observed 20-30 % increase of densities of basalt composition glass and Fe-bearing sodium silicate glass along room temperature compression from 0.1 MPa to 5 GPa, and also detected density increase in both silicate glasses with increasing temperature at high-pressure by structural relaxation.

V41B-08 0945h

Vibrational Spectra of Hot Dense Molecular Fluids: Tabletop Apparatus for Probing Planetary Interiors

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Spectroscopic information on simple molecules at high temperatures and pressures are necessary for understanding the interiors of the Jovian planets. These conditions easily exceed 2000K and 10 GPa. We shall demonstrate that it is possible to exceed those conditions (statically) and obtain spectroscopic information on such hot dense fluids. This experimental method requires the use of non-linear spectroscopy and CW laser heating on samples that are under pressure inside a diamond-anvil cell. Spectra are obtained by using a four wave mixing technique: Coherent Anti-Stokes Raman Spectroscopy. The sample heating is accomplished by using an in-situ microscopic tungsten toroid as a laser target. By combining these techniques simultaneously, vibrational spectra with relatively high signal to noise can be obtained despite the enormous thermal background generated by the incandescence of extremely hot laser heated material. Temperatures can be measured not only by fitting the Planck radiation to a graybody, but by the spectroscopic evidence of a Boltzmann distribution of molecules in their excited vibrational quantum levels. Our initial experiments will describe these technical developments and demonstrate their success using nitrogen samples.

V41C MCC: Level 1 Thursday 0830h

Minerals, Melts, and Fluids Posters

Presiding: **M Barton,** Ohio State University

V41C-0303 0830h POSTER

Enthalpies of Mixing in Sodium Silicate Glasses and Relevance to Adam-Gibbs Theory

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Solution calorimetric measurements have been made in 20.1 wt % hydrofluoric acid at 50° C on binary Na_2O-SiO_2 glasses ranging in composition from 0 to 50 mol % Na_2O. The initial calorimetric data for compositions between 20 and 50 mol % Na_2O were highly variable, determined later to be due to the development of Na carbonate on the glass surfaces. However, additional measurements using minimally-ground specimens that had been remelted shortly before the calorimetric dissolutions produced highly reproducible results. After adjustment of the data for glass transition temperature (Richet et al., 1984, J. Amer. Ceram. Soc.), the results show nearly linear ("ideal") behavior of the heats of solution between 50 % Na_2O and 30-35 % Na_2O. However, positive enthalpies of mixing (H_{ex}) are evident in the compositional region between 0 and 30-35 mol % Na_2O, with maximum magnitudes of H_{ex} on the order of 5 kJ/mol relative to 0 and 35 % Na_2O end members. Within the framework of the Adam-Gibbs theory of structural relaxation, viscosity and heat capacity data may be combined to determine configurational entropies of silicate glasses. When applied to sodium silicate glasses (Toplis, 2001, Chemical Geology), positive entropies of mixing (S_{ex}) are calculated for compositions between 0 and 30 mole

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V41C-0304 0830h POSTER

Latent heat release and temperature changes as a result of metastable $(Mg,Fe)_2SiO_4$ phase transitions

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When olivine transforms to wadsleyite or ringwoodite, heat is liberated and the temperature of the mineral assemblage increases. Such temperature increases have an important bearing on a wide range of geophysical problems. In normal mantle, for example, the release of latent heat will affect the width of mantle seismic discontinuities. In subducting slabs, on the other hand, latent heat release can significantly reduce the amount of olivine that can persist metastably. The heat released from metastable $(Mg,Fe)_2SiO_4$ transitions may also cause local superheating in the slabs that could enhance shear instabilities and cause deep earthquakes. Thermodynamic calculations of such metastable reactions indicate that the temperature increases can be 200 K or more, depending on the pressure and temperature conditions, with larger T increases occurring farther from equilibrium. Calculating these temperature changes at equilibrium is straight-forward, as the reactions are reversible and $\Delta G = 0$, so the heat released $Q_{rev} = \Delta H = T\Delta S$. However, under metastable conditions the reactions are irreversible and $\Delta G \neq 0$, thus the heat released $Q_{irr} = \Delta H = T\Delta S + \Delta G$. Estimates of the heat released in geophysical processes have been calculated using constant values of the volume change (usually at STP) and ignoring the temperature dependence of ΔH, which can lead to overestimations of the latent heat release. We have attempted to measure the latent heat released from metastable olivine transformations in a multianvil apparatus. A large 25mm multianvil assembly is used with a 3mm diameter hot pressed sample with a thermocouple inserted into a hole in the sample. The sample is thermally insulated and is adjacent, in the same thermal regime, to a second reference sample also with a thermocouple inserted. The assembly is pressurized with a 5000 tonne press to conditions well into the wadsleyite/ringwoodite stability field and then heated until the sample transforms. While the magnitude of the latent heat cannot be accurately determined, important information can be ascertained on the variation of latent heat release with increasing pressure away from the equilibrium boundary.

V41C-0305 0830h POSTER

Water contents in olivines from spinel peridotites from the sub-arc mantle wedge

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Water contents of olivines in spinel-peridotite xenoliths from Mexico and Simcoe (WA, USA) were measured by FTIR. The xenoliths come from mantle domains that were likely affected by subduction, with the host volcanic centers located at various distances from the trench. O-H vibration peaks for most of the high-forsterite content olivines are in the 3400-3600 cm^{-1} range only. One Mexican sample, however, has its main O-H peaks in the lower wavenumber range of 3100-3400 cm^{-1}, a feature so far only reported in experimentally annealed olivines. The two ranges of O-H peaks indicate that hydrogen can enter 2 different sites (defects) in the olivine structure, probably depending on the environment (fluids, depth, temperature) of crystallization and on any later re-equilibration of the mineral. Calculated water contents in olivine range from 12 to 111 ppm H_2O, and correlate positively with those of clinopyroxenes and orthopyroxenes from the same samples. The water content of the sample with low wavenumber peaks lies on the correlation if only its high wavenumber O-H peaks are taken into account. The calculated water contents of the whole-rock peridotites range from 34 to 195 ppm H_2O. As is the case for pyroxene water contents, those of olivine correlate positively, though roughly, with indices of melting (e.g. bulk-rock aluminum content), and correlate negatively with Fe^{3+}/(Fe total) ratios in spinel and oxygen fugacities calculated from them. These correlations indicate that although H behaves as an incompatible element in these minerals during partial melting, the main control of H incorporation in their structure is the oxidation state of the peridotite. The anhydrous phases of the mantle wedge, a typically oxidized environment, thus appear to incorporate very little water from fluids or melts from the slab that may transfer through it to feed volatile-rich highly explosive volcanoes lying above.

V41C-0306 0830h POSTER

Carbon on Quartz Grain Boundaries: Continuous Films versus Isolated Plates

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Piston-cylinder experiments on quartzites containing a small amount of carbon were conducted at 1.0-1.4 GPa and 850-1500°C in order to assess the microstructure of graphite along grain boundaries in deep crustal materials. In one series of experiments, polished 3mm diameter single-crystal quartz discs were coated with ~50 to 150 nm of evaporated carbon or 500 to 1000 nm of alcohol-based carbon paint. Stacks of these were subjected to high P-T conditions for durations ranging from 5 minutes to 10 days. Observations from our earlier experiments suggested that the coatings become discontinuous with time at high temperature. However, more recent observations show that coated disc boundaries contain a dark, interconnected material: those subjected to lower temperatures and shorter durations exhibited continuous films; those run at higher temperatures for longer durations contained thicker, yet still interconnected dendrite and plate structures. In contrast, relatively fine-grained synthetic quartzites produced at similar conditions typically do not contain continuous films. Quartz powder with an initial grain size between 75-150 μm, coated with 30-50 nm of evaporated carbon, was subjected to 850-1300°C for durations ranging from 1 hour to 6 days. Only very short runs at low temperatures contained irregular boundaries still darkened by a connected film; longer duration and higher temperature quartzites exhibited texturally-equilibrated quartz grains accompanied by isolated small opaque carbon plates located along grain corners, edges, and grain boundaries. Identical features are seen in additional quartzite materials constructed in graphite cylinders using uncoated powdered silica glass or smaller quartz crystals (<22 μm) taken to 1000°C and 1.4 GPa for 14 days. The results suggest that carbon may remain as a connected surface, at least metastably, on silicate mineral boundaries in the absence of grain boundary movement. With grain growth, carbon diffuses along boundaries, accumulating in plates along boundaries, edges, and corners, presumably to reduce the surface energy of the system. The behavior of carbon in a given grain boundary may depend on the lattice misorientation of that boundary.

V41C-0307 0830h POSTER

Calibration of a new Model for Estimating the Density, Coefficient of Thermal Expansion, Sound Speed, and Compressibility of Multicomponent Silicate Liquids at Reference Pressure

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Ghiorso (2000, EOS 81[48], F1295) proposed a new equation of state for molten silicate liquids. This equation is designed to facilitate the extrapolation of reference pressure volumetric data to pressures in the Earth corresponding to the base of the mantle transition zone. Extrapolation is performed with a minimal number of adjustable parameters and avoids the singularities and instabilities associated with the Birch-Murnaghan and Vinet equations when these are applied to silicate melts. Here, we calibrate reference pressure (10^5 Pa) parameters for the proposed silicate liquid equation of state from literature data on measurements of densities and sound speeds of molten liquids and from volumetric measurements on supercooled liquids obtained at their glass transition temperatures. A model for the temperature- and compositionally-dependent, reference-pressure volume (density) in the system K_2O-Na_2O-CaO-MgO-FeO-NiO-CoO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2 is obtained for liquids with CaO mole fraction < 0.5. Precision of data recovery is 0.55% for Fe-absent liquids and 0.95% for Fe-bearing liquids. Internally consistent expressions for the reference pressure compressibility and its temperature dependence are formulated from a calibration of sound speeds in molten liquids. A model for the temperature- and compositionally-dependent relaxed sound speed in the system K_2O-Na_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2 is obtained. Precision of data recovery is 1.7%. In contrast to previous workers, we find that effect of pressure on the volume of silicate melts (*i.e.* dV/dP) is more accurately assessed by first calibrating a model equation for the speed of sound and subsequently using this calibration to calculate a value for dV/dP, rather than estimating dV/dP for each experimental datum from the sound speed and modeling the derived quantity directly. Linear mixing relations for model parameters are utilized in calibrations of both the density and the sound speed with the addition of a quadratic composition term in Na_2O and SiO_2 required to accurately reproduce sound speed measurements. The resulting mixing relations for dV/dP at the reference pressure are weakly non-linear. The mathematical structure of the equation of state renders the volume of mixing a non-linear function of composition at elevated pressure.

V41C-0308 0830h POSTER

An Ultrasonic Frequency Sweep Interferometer For Sound Speed Measurements On Liquids At High Temperature And Pressure

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One of the most direct methods for obtaining melt compressibility is through measurements of sound speed via acoustic interferometry. This technique may be applied to silicate melts by either varying the path length or the frequency of the acoustic wave through the melt. To date, only the variable path length (VPL) technique has been applied, which restricts measurements to atmospheric pressure owing to the requirement of mechanical movement of the upper buffer rod. This, in turn, precludes the study of volatile-bearing liquids at pressure and a systematic study of how melt compressibility varies with pressure. We have developed a frequency sweep (FS) interferometer that can be applied at high pressure, which is based on frequency spectrum analysis on mirror reflection waves from high-temperature liquids. First, a theoretical acoustic model for a rod-liquid-rod (RLR) interferometer is proposed and solutions to the resultant wave equations are obtained. The solutions demonstrate that only two kinds of non-dispersive waves exist within the upper buffer rod. They have computable group velocities and waveform patterns that are entirely dependent on the material and diameter of the buffer rods. Experimental tests verify the theoretical model and indicate that buffer rods made of molybdenum metal and > 1.9 cm diameter are ideal for sound speed measurements in silicate melts with the FS interferometer. On the basis of the theoretical acoustic model, a mechanical assembly and signal-processing algorithm was designed to implement the FS interferometer. A very short pulse (e.g. 1 microsecond) encompassing a range of frequencies that span about 1 MHz is sent down the upper buffer rod and the first two mirror reflections from the liquid are collected and stored. Because they have the same waveform and have 180^o phase difference, Fourier spectrum analysis can be performed to find the frequency response function of the two reflections, which is related to the sound speed and thickness of the melt. From the obtained frequency response function, the sound speed is calculated. We have applied this newly designed FS interferometer to two liquids with well-known sound speeds from the literature: NaCl liquid at 930^o C and 1026 ^{o} C and a sodium aluminosilicate liquid at 1436 ^{o} C. Sound speeds were measured for these liquids at three center frequencies (4.5 MHz, 5.0 MHz, and 5.8 MHz). Our results are less than 0.6 % off the literature values and demonstrate the accuracy and precision of the FS interferometer. The principal advantage of the FS interferometer over the VPL method is that it requires no physical intervention or mechanical movement of the micrometer-transducer-rod assembly during a measurement. Thus, the FS method has considerable promise for adaption to high-pressure conditions in an internally-heated pressure vessel.

V41C-0309 0830h POSTER

Molar Volume of Lanthanide-Bearing Silicate Melts

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The lanthanides are of crucial importance in igneous petrology since they are sensitive indicators of the processes involved in the petrogenesis of magmas. One of the primary goals of igneous petrology is the development of thermodynamic models that can accurately predict the crystal-melt phase equilibria in a magma and produce the observed chemical diversity of igneous rocks. The development of such models requires a reliable thermodynamic database which includes volumetric data available for both major and trace element oxide liquids.
Efforts have been made to extend the volumetric database of silicate melts on a variety of multicomponent systems for the most naturally abundant oxides. However, experimental data on other significant oxides, such as lanthanides, are lacking. Therefore, in order to fill this gap and to provide a new volumetric dataset, which will allow the available models in the literature to be extended to lanthanide-bearing liquids, the molar volume of lanthanide-bearing silicate melts has been determined through high-temperature density measurements using the Pt-based double-Archimedean method.
In this paper, we present density measurements obtained in air for various lanthanide-bearing silicate melts (either Na-disilicate or one-atmosphere anorthite-diopside eutectic containing different amounts of one lanthanide oxide). The present results suggest that the addition of lanthanide leads to an increase in density of the melt. In addition, the melt density at a given lanthanide content increases with increasing atomic number, with the exception of La. This volumetric dataset allows a first estimation of the partial molar volume of each lanthanide oxide liquids (i.e., the partial molar volumes calculated at 1550 K for the investigated lanthanide oxides range from 15 to 23 cm^3/mol for Tm_2O_3 and Pr_6O_{11}, respectively).

V41C-0310 0830h POSTER

Cl-35 and F-19 MAS NMR Studies on Silicate and Aluminosilicate Glasses Containing Multiple Volatile Species.

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Cl-35 magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra have been collected at 14.1 and 18.8 T fields to determine the atomic scale structural environments of Cl in Ca- and Na-silicate and aluminosilicate glasses. Data, in addition to that previously presented, suggest that in mixed modifier (Ca-Na) silicate glasses, a large portion of Cl is in a mixed coordination environment (coordinated by both Ca and Na). Relative peak positions, however, suggest a slight preference for Cl to coordinate Na over Ca. Calculated quadrupolar coupling constants (C_Q) increase as Ca/(Ca+Na) increases, indicating that the Cl site is on average more asymmetric at higher Ca/(Ca+Na) ratios. In a series of sodium aluminosilicate glasses containing both water and Cl, data previously presented show a shift to higher frequency NMR signal with increasing water content while C_Q remains constant. This change in observed frequency suggests Cl is not directly associated with H_2O in the samples and rather that the shift reflects a slight change in the average Cl coordination environment. Current work on a similar series of calcium aluminosilicate glasses promises to further elucidate the interaction of Cl and water in these glasses. While the addition of water has a significant effect on the environment of Cl in the glasses studied, the effect of F on the coordination environment of Cl in these glasses is much less pronounced. Previous work on F-containing mixed modifier silicate glasses has shown that F demonstrates a preference to coordinate higher field strength modifier cations. Preliminary ^{35}Cl MAS NMR data suggest that the addition of F appears to slightly order the Cl environment, as evidenced by a slight narrowing of the peak. Conversely, in ^{19}F data collected at 9.4 T, there is little to no noticeable effect on the environment of F with the addition of Cl in the compositions studied. The current ^{19}F data do show a larger preference for Ca over Na coordination than previously reported.

V41C-0311 0830h POSTER

Direct Observation and Finite-Difference Modelling of the Dynamics of two Immiscible Melts

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The dynamics of two immiscible melts at a temperature of 1450 K was experimentally observed by time-resolved neutron radiography and compared with two-dimensional finite-difference calculations. Neutron radiography, which is the time-dependent measurement of neutron absorption, allows to observe a large melt volume in situ and real time. This feature was utilised to observe an initially layered sample which consisted of a dense brass disc overlying a silicate melt contained in a crucible. When heated a single brass drop slowly formed and fell through the silicate melt to finally cover the container bottom. The known experimental parameters (viscosity and density differences between the two melts, sample geometry) were used as input parameters in the numerical calculations. The finite-difference calculations reproduced the experimental observations. This implies that surface tension, which was not included in the model, only has a minor effect on the melt dynamics in the system we investigated. Dynamic neutron radiography has been used here for the first time to study melt dynamics, and the results obtained clearly show that this is a method which can give unique insights into the behaviour of silicate melts without having to resort to model systems.

V41C-0312 0830h POSTER

New igneous thermobarometers based on plagioclase + liquid equilibria

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Calculation of the pressures (P) and temperatures (T) at which minerals grow is crucial to our understanding of igneous processes. Thermometers based on plagioclase + liquid equilibria represent some of the earliest and most long-standing attempts at determining the conditions at which igneous minerals form. In spite of this attention, though, the issue of error on predicted values of temperature has only rarely been addressed. Lacking estimates of error, the usefulness of such models is limited. To address the issue, several recent thermometers and plagioclase saturation surface models were tested for their ability to recover T from their calibration data, and predict T from experiments not used for calibration (tests data). Pre-1990 models, which tend to rely heavily on early anhydrous 1-atm experiments, tend to perform poorly. More recent calibration efforts by Sugawara, (2001) and Ghiorso et al. (1995, 2002) provide much better results for their calibration data at T > 1100 ^oC, but do not perform as well at T < 1050 ^oC for both test and calibration data, and mixed results are evident for hydrous and high SiO_2 liquids. To narrow the magnitude of T uncertainty, a new plagioclase-liquid thermometer was calibrated: $10^4/T(K)=68.8-0.86\ln[An/(Ca^{liq}(Al^{liq})^2(Si^{liq})^2)] + 179.2[Al^{liq}] - 113.3[Al^{liq}/(Al^{liq}+Si^{liq})]$ -7.92[AbAn] -0.0613[P(kb)] $-91.6[Ca^{liq}Al^{liq}]$ $-155[Si^{liq}] + 110.3[Si^{liq}]^2 - 149[Al^{liq}]^2$ In order to predict pressure, a barometer was also developed: $P(kb)= -42.2 + 0.0494[T(K)] + 0.0116[T(K)\ln[(AbAl^{liq}Ca^{liq})/(AnNa^{liq}Si^{liq})]] - 382.3[Si^{liq}]^2 + 514.2[Si^{liq}]^3$ -19.6ln[Ab] $-139.8[Ca^{liq}] + 287.2[Na^{liq}] + 163.9[K^{liq}]$ In these models, T is in Kelvins and P is in kbar. An and Ab are the fractions of anorthite and albite in plagioclase, calculated as cation fractions: $An = CaO/(CaO+NaO_{0.5}+KO_{0.5})$ and $Ab = NaO_{0.5}/(CaO+NaO_{0.5}+KO_{0.5})$. Terms such as Al^{liq} refer to the cation fraction of $AlO_{1.5}$ in the liquid. Errors on these models are comparable to those for clinopyroxene thermobarometers: In the first equation, R = 0.96 and the standard error of estimate (SEE) is 33 K; for the second equation, R = 0.94 and the SEE is 1.77 kbar. These models successfully recover mean pressures for experimental data that are not used for calibration, and are furthermore able to recover near-1-atm P estimates for volcanic rocks from Kilauea, Hawaii, which are thought, based on field and petrographic evidence (C. Thornber, pers. comm.), to have crystallized very near the surface.

V41C-0313 0830h POSTER

Phlogopite Thermometer Calibration and Use: Magmatic History and Processes in the Roman Potassic Province

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Previous investigations have shown that the partitioning of titanium between melt and phlogopite is temperature-dependent (e.g. Tronnes et al., 1985; Righter and Carmichael, 1996). For many compositions of the Roman Potassic Province, a Ti-in-phlogopite geothermometer is useful over a large crystallization interval and has the advantage of being independent of pressure. Righter and Carmichael (1996) present a single geothermometer of the form
$\ln D\ TiO_2\ phl/liq = a/T + b$
where D is wt.% TiO_2 in phlogopite/wt.% TiO_2 in glass, T is in Kelvins, and a and b are constants. Our investigation indicates that titanium partitioning into phlogopite is lower in peralkaline melts than in metaluminous and peraluminous melts. These results are consistent with previous experiments which show that the activity coefficient of TiO_2 is decreased in peralkaline melts (Hess, 1995). We have calibrated two new geothermometers. For peraluminous and metaluminous compositions:
(1) $\ln D\ TiO_2\ phl/liq = 16200/T - 11.02$; $r^2 = 0.85$.
This geothermometer was calibrated using data from our experiments on Agnano Monte Spina trachytes and the metaluminous and peraluminous data used by Righter and Carmichael. For peralkaline compositions:
(2) $\ln D\ TiO_2\ phl/liq = 15180/T - 10.8$; $r^2 = 0.90$.
This geothermometer was calibrated with our experimental data from 79 A.D. Vesuvius compositions and the data of Guo and Green (1990). The molar $(Na_2O+K_2O)/Al_2O_3$ ratios of these compositions are 1.0 and 1.3 respectively; we have not yet investigated higher degrees of peralkalinity. These geothermometers constrain the pre-eruption temperatures of materials from the Roman Potassic Province. Geothermometer (1) gives a temperature of 929^oC for Layer B1 and 938^oC for Layer D1 trachytes of Agnano Monte Spina. These temperatures agree with water-undersaturated (CO_2-bearing) phase equilibria experiments on these compositions. The peralkaline geothermometer (2) gives a temperature of 857^oC for the white pumice of the 79 A.D. Vesuvius eruption; this agrees with phase equilibria obtained from water-saturated experiments. For the gray pumice of 79 A.D. Vesuvius, we calculate a temperature of 924^oC. This temperature is similar to that obtained from phase equilibria data if it is assumed that hornblende, sanidine, and leucite were not part of the pre-eruption phenocryst assemblage but instead were added during syn-eruptive mixing with phonolite. In contrast, the original geothermometer of Righter and Carmichael (1996) overestimated Vesuvius temperatures by 60-65^o; phase equilibria experiments suggest that phlogopite had not even begun to crystallize at these temperatures. Thus our new calibrations are more accurate for a broader range of compositions.

V41C-0314 0830h POSTER

Application of Olivine-Spinel Fe-Mg Thermometers to Olivine - Cr-Spinel Pairs in a Shallow Tahitian Basanite Dike, and a Comparison with 1-atm Experimental Data

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Application of spinel-olivine empirical and theoretical thermometers has mainly been confined to plutonic rocks, although spinel-olivine pairs are also common in basaltic (broadly defined) volcanic rocks and in shallow mafic intrusions (dikes and sills). In this work we have applied olivine spinel Fe-Mg thermometers to samples of a mantle xenolith-bearing basanite dike collected near Papeete, Tahiti. This leucite-normative basanite is notable for presence of a suite of mantle-derived ultramafic nodules (dunites, wehrlites and lherzolites), a relatively rare occurrence on Tahiti that probably reflects very rapid ascent. The basanite contains abundant olivine, titanaugite, plagioclase and titanomagnetite phenocrysts in a very fine-grained, and occasionally glassy, matrix. Zoned olivine phenocrysts (Fo88 cores to Fo60 rims) commonly include small euhedral to subhedral spinel inclusions that range from Mg-chromite to aluminous Ti-magnetite, depending on core-to-rim location within olivine. Systematic

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variations in composition of spinel and adjacent olivine record entrapment during the magmatic crystallization interval from near-liquidus (> 1300 C) to near-solidus (ca. 1125 C) temperature. Three published olivine-spinel Fe-Mg thermometers (Roeder et al, 1979; Sack and Ghiorso, 1991; Jianping et al., 1995) were used to evaluate the T dependence of olivine-spinel Fe-Mg partitioning in analyzed pairs. Calculations show that the olivine-spinel pairs undoubtedly record thermal evolution of the basanite magma during crystallization, however all thermometers appear to underestimate absolute crystallization temperatures. This is particularly evident for the final stages (at lower T) of the co-crystallization of the olivine-spinel pairs, probably due to significant concentrations of the usp end member in the most fractionated magmatic spinels (approx. 70 mol% usp). Ti is not taken into account in calibrating two of the thermometers (Roeder et al. and Jianping et al.) and apparently is not fully accounted for in the spinel solid solution model (Sack and Ghiorso). A direct test of calculated T is possible due to a set of 1-atm crystallization experiments done on the basanite some years ago (in collaboration with E. Stolper). Experimental runs contain olivine microcrystals containing spinel inclusions, and both minerals were analyzed. T calculated using the three thermometers was compared with the known T of each crystallization experiment. Data show approximately linear relationships between Ti content and T- underestimation for all 3 thermometers.

V41C-0315 0830h POSTER

Composition of Olivine, Melt Redox State, and Oxygen Fugacity

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The compositions of ferro-magnesian silicates in equilibrium with melts are a function of oxygen fugacity. This was demonstrated experimentally in the case of olivine by Roeder and Emslie (1970). In principle, therefore, the composition of coexisting olivine and melt (with total Fe as FeO) allows melt redox state and hence oxygen fugacity to be calculated if the equilibrium distribution of Mg and Fe between olivine and melt is known. It has been found that the expression given by Gee and Sack (1988) accurately describes this distribution over a wide range of liquid compositions, so that melt redox state and oxygen fugacity can be calculated from the compositions of olivine-melt pairs. Oxygen fugacities have been calculated from published data for olivine-melt pairs produced in 160 experiments at 10^5 Pa at known oxygen fugacities (from 3 log units below to 7.6 log units above QFM) over a range of T from 1080 to 1339^{O}C. Melt compositions in these experiments include tholeiitic and alkali-olivine basalts, picrites, andesites, and highly alkaline lavas (nephelinites, leucitites, ugandites). Forsterite compositions of olivines range from 0.98-0.55, whereas melt Mg-no's range from 0.75-0.25 (all Fe as FeO). There is excellent correlation (0.99) between calculated and experimental values. The maximum difference between calculated and experimental values is about 0.5 log units, but the average uncertainty (calculated at the 1-sigma level) is 0.24 log units. The results indicate that the expression given by Kress and Carmichael (1991) better describes the relationship between melt redox state and oxygen fugacity than that given by Kilinc et al. (1983). The results suggest that oxygen fugacities can be retrieved from coexisting olivine-melt pairs in natural samples. However, the non-linear relationship between olivine composition, melt ferric-ferrous iron ratio, and (log) oxygen fugacity indicates relatively large uncertainties at oxygen fugacities more reducing than about one log unit below QFM. In addition, it is not clear that this method works for Fe-rich liquids (Mg-no's less than about 0.3). On the other hand, the method does provide a rigorous test for equilibrium between experimentally produced olivines and melts.

V41C-0316 0830h POSTER

Experimental Study of the Effects of Dissolved Sulfur on Olivine-Liquid Ni Partitioning Behavior

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The partitioning of Ni between olivine and a silicate melt is best described in terms of the Nernst partition coefficient, D_{Ni} which is equal to (wt % Ni)^{oliv} / (wt % Ni)^{melt}. Ni in a silicate melt may partition into olivine according to the following reaction NiO^{melt} + $Fe_2Si_{0.5}O_2{}^{oliv}$ = $Ni_2Si_{0.5}O_2{}^{oliv}$ + FeO^{melt}. In the presence of dissolved S, the oxide species in the melt may react via the following reactions FeO^{melt} + 0.5 $S_2{}^{melt}$ = FeS^{melt} + 0.5 $O_2{}^{melt}$ NiO^{melt} + 0.5 $S_2{}^{melt}$ = NiS^{melt} + 0.5 $O_2{}^{melt}$ Thus the abundances of FeO and NiO in the melt and, therefore, the value of D_{Ni} between olivine and a silicate melt are a function of both fS_2 and fO_2 in the melt. Because natural magmas may contain significant amounts of dissolved S, those values of D_{Ni} determined in sulfur-free systems may not be applicable to natural magmas. To address the extent to which D_{Ni} may be a function of dissolved S content, a series of one-atmosphere crystallization experiments were conducted on a moderately evolved MORB lava to which was added 10 % (by weight) powdered San Carlos olivine (MgO = 10.9 wt. %, Ni ~ 300 ppm). All experiments were conducted at 1245^o C where approximately 5-10 volume % olivine (Fo_{88}) coexisted with melt. fO_2 was maintained at a constant value of $10^{-9.5}$. fS_2 was varied from 0 to $10^{-1.9}$, the latter being well below the theoretical sulfide saturation point. Over this range of fS_2, the dissolved S content in the melt increased from 0 to 480 ppm and the value of D_{Ni} decreased from 8 to 2.4. These results confirm a strong dependence of D_{Ni} on the amount of dissolved S in the melt and suggest that experimentally determined D_{Ni} values in sulfur-free systems should be used with caution.

V41D MCC: 3006 Thursday 1020h

Birth, Growth, and Death of Magmatic Arcs: Comparisons Among Arcs in Different Settings IV *(joint with T)*

Presiding: **K Klepeis,** University of Vermont**; J P Davidson,** University of Durham

V41D-01 1020h INVITED

Thermal Evolution of the Deep Roots of a Magmatic Arc, Fiordland, New Zealand

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Reconstruction of detailed thermal profiles and histories in magmatic arcs is crucial for understanding arc development and evolution, because deformation, metamorphism, crustal melting, and a wide range of physical properties are temperature dependent. Fiordland, New Zealand contains a rare exposure of the deep roots of a Mesozoic magmatic arc, and provides an exceptional opportunity to develop high-resolution cooling histories through its middle and lower crust. The ca. 120 Ma granulite-facies Western Fiordland Orthogneiss is a > 10 km thick batholith dominated by dioritic rocks. New U-Pb thermochronologic data in rocks within the upper part of the Western Fiordland Orthogneiss exposed in Doubtful Sound record post-magmatic cooling through the 650-600^{o}C closure temperature of titanite at ca. 113 Ma. Subsequent slower cooling below 400^{o}C is recorded by rutile from the Western Fiordland Orthogneiss at ca. 74 Ma. The upper contact of the Western Fiordland Orthogneiss is defined by the Doubtful Sound extensional shear zone, with mid-Paleozoic metasedimentary cover of the Deep Cove Gneiss of the Tuhua Sequence in the hanging wall. A calcsilicate within the Deep Cove Gneiss immediately above the shear zone yields metamorphic titanite with a U-Pb date of ca. 113 Ma. This suggests new metamorphic titanite growth during heating of the cover sequence associated with emplacement of the Western Fiordland Orthogneiss. Additional U-Pb thermochronologic data from the base of the Western Fiordland Orthogneiss will allow us to better evaluate the cooling history across the entire thickness of the batholith. The integration of these thermal histories with structural and metamorphic data through this middle and lower crustal profile will provide a unique multi-dimensional view of the evolution of this magmatic arc.

V41D-02 1035h

Space-Time Variations in Lower Crustal Rheology and Thermal Structure and its Effects on the Evolution of Arc Crust

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Studies of magmatic arcs in different settings have shown that the rheology and thermal structure of the lower crust are extremely heterogeneous and can change quickly during cycles of magmatism and crustal melting. However, determining the length and time scales of these variations, and their effects on crustal evolution are especially problematic. We present results from a deeply eroded Cretaceous arc exposed in Fiordland, New Zealand that reveal the presence of steep thermal gradients and rheological contrasts in the lower crust (~45 km paleodepth)on length scales of ~100 km^2. Metamorphic and geochronologic data collected from near Milford Sound suggest that part of the lower crust experienced rapid cooling from 750^{o}C<T<850^{o}C to T=650-700^{o}C following a period (126-120 Ma) of mafic-intermediate magmatism and lower crustal melting. Cooling was aided by the thrusting of relatively cool pre-existing crust below hot, partially molten new crust and by the efficient extraction of melts out of the lower crust. Simple thermal models of conductive heat loss suggest that the thermal pulse accompanying magmatism near Milford Sound was short-lived (a 3-4 m.y. duration)and had decayed to temperatures of T=650-700^{o}C by ~116 Ma. These models are in accordance with metamorphic ages obtained using U-Pb dates on zircon from pegmatite and tonalite dikes. However, less than 100 km to the south of Milford Sound, U-Pb zircon ages and metamorphic data suggest that lower crustal temperatures there remained at T=800^{o}C until ~108 Ma. These observations indicate that the thermal structure and rheological transitions linked to magmatism and the partial melting of lower crust were much more spatially heterogeneous and transient than previously believed. These variations created localized hot spots in the lower crust that affected deformation patterns during cycles of extension and contraction within the arc. Hot weak zones preferentially developed large (1 km thick) extensional shear zones that thinned the lower crust at ~108 Ma. Structural relationships and geochronology indicate that these lower crustal shear zones formed simultaneously with extensional core complexes and narrow rift basins at mid-upper crustal levels. In contrast areas that were relatively cool at ~108 Ma lack extensional structures and preserve older contractional shear zones that thickened the crust. The Fiordland setting shows that the development of localized hot spots in the lower crust strongly influences deformation partitioning within arc crust. This process helps explain along-strike variability in arc structure, including the development of highly localized zones of extension in the upper crust.

V41D-03 1050h

Generation and Evolution of Lowermost Crust of an Arc: Examples From Fiordland, New Zealand

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Questions regarding the composition, structure and rheology of the lowermost crust continue to arise due to the acknowledgement that heterogeneity, both spatially and temporally, is the rule rather than the exception in most studied examples. To better understand the origin of lowermost crust in a magmatic arc setting, we are using Fiordland, New Zealand as a natural laboratory. Rock exposures in southwest NZ once formed the ancient Gondwana margin and now represent exhumed crustal levels of 50 km depth within the magmatic arc. In the Fiordland block, we find that the lowermost crust is heterogeneous, particularly in terms of heat and rheologic behaviour. Studies point to several elements which compose the lowermost arc crust and suggest that its heterogeneity resulted from the relative contributions of three components: (1) lower crust generated by the injection of mafic, mantle-derived partial melts and the addition of cooler mafic material through collision and arc building; (2) modification of lower crustal composition by tectonically burying supercrustal material; (3) compositional modification of the lowermost crust and arc crust by in-situ melting and remobilization of crustal-derived partial melts. Integration of field studies with targeted partial melting