

area is limited only in eastern side, which probably results from higher rock alteration by the hydrothermal activity. Eleven heat flow data across the hydrothermal site indicate anomalously high ($>10W\Lambda(m^2)$), high (ca. $4W\Lambda(m^2)$) without hydrothermal activity, and low (ca. $0.2W\Lambda(m^2)$) at the center, the eastern side and the western side of the hydrothermal site, respectively. All the data show that the hydrothermal area has different features between the SW and NE sides, and we will present a model to explain these features.

V72B MCC: Hall C Sunday 1330h Phase Equilibria, Partitioning, and Transport Posters

Presiding: C A Geiger, Universitt Kiel

V72B-1307 1330h POSTER

Phase relations of a carbonaceous chondrite at lower mantle conditions

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The refractory element ratios of Earth's mantle are close to carbonaceous chondrite values. One of the ideas on Earth's bulk composition is that the Earth is made of carbonaceous chondrite-like materials, but the redox state of Earth is closer to that of Enstatite chondrite than carbonaceous chondrite. We do not know exactly when and how the reduction event was occurred at proto Earth. Therefore, it is important to considering differentiation process of early earth that the phase relations of mantle composition are investigated under variable Fe/FeO conditions at high pressures. Allende meteorite (CV chondrite) is applicable to one of the oxidized model of the proto earth, whereas the most reduced model is Peridotite and Metal. We report the phase relations of Allende meteorite in the pressure range from 22 to 30 GPa, at 1600-2300 °C. We use natural Allende meteorite as starting material. The Kawai type multi-anvil apparatus was used for the present experiments. The truncated edge length of the anvil was 2 mm. We use two kinds of heating element, LaCrO₃ and Re. LaCrO₃ heater was used for sub-solidus experiments, and Re heater was used for melting experiments. Pressure calibrations were made at high temperatures using il-pv phase transition, Al₂O₃ content of Pv determined by in situ X-ray diffraction measurements with the Jamieson's Gold scale [1]. The micro-area X-ray diffractometer and EPMA were used for phase identification and compositional analysis of run products. The liquidus phase changed from garnet to Mg-perovskite at about 24.5 GPa, and magnesio-wüstite remained second liquidus phase. The solubility of mafic components in Ca-perovskite in Allende composition is higher than that reported on Peridotite bulk composition. The Ca/(Ca+Mg+Fe) ratio of Ca-perovskite is 0.6 in Allende experiments, whereas that is 0.9 in Peridotite experiments [2]. Our result suggests that chemical differentiation process could change with FeO contents of magma ocean.

References [1] Jamieson et al., in *High-Pressure Research in Geophysics*, edited by S. Akimoto and M. H. Manghnanani, pp. 27-48, CAPJ, Tokyo, 1982. [2] Hirose, K., *J. Geophys. Res.*, 107, 2002.

V72B-1308 1330h POSTER

The High Pressure Stability of K-Cymrite and Phases in the System Or-H₂O

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The sinks for and processing of LIL elements, such as potassium, and water in Earth's mantle are important to the planets evolution, crustal recycling, and the production of mantle melts. Sanidine hydrate or K-cymrite (KAlSi₃O₈·nH₂O) is an example of a crystalline phase for which a hydrous phase is more stable at high pressure than the anhydrous counterpart (e.g., sanidine). A multi-anvil synthesis study has been carried out to delimit the upper pressure stability of K-cymrite (Kcym) using two starting compositions: 1) gel-Or₉₇Qtz₃ and 2) natural sanidine (adularia)

Or₉₇Ab₃ - each with equimolar H₂O (charges sealed in welded Pt capsules) over the range 4.5 to 12 GPa and 1000 to 1300 °C.

Consistent with Massone (1995) and Thompson et al. (1998), Kcym is stable at 4.5 GPa in the assemblages Kcym+silica+melt (1) or Kcym+Jd+melt (2) across the temperature range. Kcym reacts to K-wadeite (K₂Si₄O₉) + kyanite + silica + H₂O or melt at 1000 °C and ~6 GPa; the reaction boundary has positive slope of ~2.5 MPa/°C and is similarly placed to the anhydrous reaction sanidine ⇌ K-wadeite + kyanite + silica (Yagi et al., 1994). The next reaction occurs at ~9 GPa where KAlSi₃O₈-hollandite (Khol) forms at the expense of K-wadeite + kyanite + silica. However, a phase with KAlSi₃O₈ stoichiometry but low oxide total, therefore undoubtedly hydrous, also typically occurs with Khol up to ~11 GPa and 1200 °C; it is presently under investigation to determine what structure type it has (stuffed-Khol, Kcym, or ?).

A melt component appears over a large range of conditions from 4.5 to ~7.5 GPa and 1000 °C to 10 GPa and 1200 °C which may be attributable to both thermal gradients in the multi-anvil charges and discontinuous states of hydration in the charge. The melt volume increases with an increase in temperature and a decrease in pressure on the phase diagram. Melts are enriched in both SiO₂ and H₂O (by low oxide totals in microprobe analyses) and Na₂O and BaO in system-2 experiments. Melt is dominant at the hot portions of the charge but a clear melt-solid boundary is absent.

These experiments demonstrate that K-cymrite and perhaps another hydrous KAlSi₃O₈ polymorph can exist over a broad range of conditions at high pressure and should be important to crustal recycling or potassium interactions in the mantle lithosphere and deeper in the mantle if bulk compositions permit.

V72B-1309 1330h POSTER

Aluminum Substitution in MgSiO₃ Perovskite: Confirmation of Multiple Mechanisms by NMR Spectroscopy

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The substitution of Al into MgSiO₃ perovskite has significant effects on this minerals properties, but the structure of the solid solution remains incompletely constrained. To test mechanisms in which Al substitutes on "B" (Si) sites, creating corresponding oxygen vacancies, we have synthesized perovskites of nominal composition Mg(Si_{0.9}Al_{0.1})O_{2.95} at 1600 °C and 27 GPa. High-field (14.1 and 18.8 T) Al-27 NMR spectra show three main features: a broad peak ("A") whose width and shift with field are consistent with a disordered, distorted site with a chemical shift (cs) of about 7 ppm and quadrupolar coupling constant (CQ) of 7.5 MHz; a narrow peak ("B") with cs of about +6 ppm and CQ of about 1 MHz, and a third, smaller, peak ("C") with cs of about +15 ppm and CQ about 2 MHz. Peak A is probably due to Al in possibly partially collapsed A sites with coordination number of six or higher; peak B is probably due to Al in octahedrally symmetric B sites not associated with O vacancies. Peak C has more than twice the area of peak A, indicating a preference for B sites in this composition and thus necessitating O vacancies for at least global, if not local, charge balance. Peak C is likely to represent Al in B sites adjacent to such vacancies. Although its cs is rather low for AlO₅, it is not far from the value of 18 ppm for the trigonal bipyramidal site with unusually long Al-O bonds in SrAl₁₂O₁₉. The relatively low intensity of peak C suggests that most O vacancies are not ordered next to Al in B sites, but are disordered among most or all O sites in the structure. The entropy generated by both cation and vacancy disorder thus must be included in any accurate model of the thermodynamics of this phase. In Al-bearing perovskites with excess Mg/Si, as is probably most relevant to the lower mantle, an oxygen vacancy mechanism is thus likely to be important, allowing the possibility of enhanced diffusivities and water content. At the same time, charge coupled-substitution with Al in A sites also plays a role. The NMR data rule out the "brownmillerite" structure as a likely MgAlO_{2.5} end-member, as no AlO₄ is observed.

V72B-1310 1330h POSTER

A genesis of carbonatitic melt within eclogite

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Recently, the number of studies for investigation of fluid or melt inclusion in diamond and other mantle minerals has been rapidly, mainly due to progress of analytical instrument. Anderson et al (2001) and Coltorti et al. (2001) showed that CO₂-rich fluid and carbonatitic melt are the major component among the inclusions and their transport would have profound effects in magmatism, metasomatism and others. The several lines of evidences indicate the existence of some recycled carbon. Some metasomatic agent is considered to have originated from recycle carbonates in the arc system (Papua New Guinea; McInnes and Cameron 1994) and in hot spot (Hauri et al. 1993). Hoernle et al. (2002) discussed that the carbonatite magma in the Cape Verde Islands originated from the subducted carbonate sediments.

Yaxley (1999) carried out experiments in the 60 wt.% eclogite + 40 wt.% CaCO₃ system at 3.0-3.5 GPa. He showed that in the partial melting of carbonated eclogite, the first melt coexisting with calcite is carbonatitic.

In order to understand the role of carbonate-bearing eclogite in the upper mantle, we determined phase relations in the system 90 wt.% MORB-10 wt.% CaCO₃ experimentally at 2.7-8.0 GPa and 800-1300 °C. The solidus temperature decreases from ca. 1200 °C at 3 GPa to ca. 950 °C at c.a. 4 GPa dramatically due to the appearance of dolomite below solidus. At 3.5-4.0 GPa, calcite is stable in solidus and carbonatitic melt is produced. With increasing pressure to 8 GPa, dolomite saturated solidus temperature increase up to c.a. 1200 °C. Melt reacts with garnet and changes its composition from dolomite to calcite with increasing temperature.

In the subduction zone with relatively cold oceanic lithosphere with carbonate sediments, carbonate is stable at least up to 8 GPa. On the other hand, subducted hot oceanic plate may produce carbonatitic melt, which will cause metasomatism in the lithosphere overlying wedge mantle and high-pressure metamorphic rocks. Because solidus temperature of dolomite eclogite is 300-400 °C lower than carbonated lherzolite (1330 °C), partial melting of dolomite eclogite is not rare in the upper mantle and possibly account for the origin of carbonatitic magma and their common role as metasomatic agents.

V72B-1311 1330h POSTER

Opx-Cpx Trace Element Partitioning in Mid-Ocean-Ridge Melting Residues

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We have obtained major (EPMA) and trace (SIMS) element mineral compositions on a suite of plagioclase- and vein-free abyssal peridotites (AP) exposed at the ocean floor along mid-ocean ridges. In terms of their melting history, they cover the entire AP compositional spectrum from very fertile compositions (Cr# spinel ~0.12, Yb_N ~10, (Ce/Yb)_N ~0.2) to highly depleted (Cr# spinel ~0.58, Yb_N ~1) (N denotes CI-chondrite normalized). At this stage we have measured trace elements in cpx and opx (mostly 3-6 analyses per grain) for 10 representative samples in order to address the following questions: (1) do large opx porphyroclasts reveal trace element zonation that can support a disequilibrium melting hypothesis as predicted by REE diffusion experiments [1]? (2) Are opx and cpx in equilibrium? (3) How well do the measured data agree with literature partition coefficients?

(1) With the exception of 1 sample, all opx do not show trace element zonation within analytical error. This suggests that LREE diffusion rates in opx at solidus conditions are faster than predicted from laboratory diffusion experiments on diopsides. Significant core-rim variations in cpx (which have generally smaller grain size) have not been observed either in any of our plagioclase- and vein-free peridotites (n ~80). (2) The general trace element pattern of cpx is mimicked by

opx. This is particularly important for two modally depleted samples, in which the LREE in cpx have been enriched ($(\text{Ce}/\text{Yb})_N > 1$). We interpret this enrichment as a late-stage refertilization (i.e. at relatively low T) of a previously depleted harzburgite by percolating exotic melts. Given that no significant core-rim variations have been observed, opx must have attained equilibrium LREE concentrations with this melt. (3) We calculated $\text{Kd}(\text{cpx}/\text{opx})$ from $\text{D}_{\text{cpx}/1}$ and $\text{D}_{\text{opx}/1}$ determined by experiments as well as handpicked cpx-opx isotope dilution data from Tibetan ophiolites, and compared these to our AP data. For the HREE our $\text{Kd}(\text{cpx}/\text{opx})$ is similar to literature data ($\text{Yb}_N \sim 4$, $\text{Er}_N \sim 8$), and little variation exists between the individual samples. Towards the LREE variation increases and the measured Kds are higher than those calculated from literature D-data (avg $\text{Ce}_N \sim 60$), whereas good agreement exists between the AP and Tibetan pyroxene data. Further analyses are required to confirm these observations.

[1] van Orman, J. (2002) EPSL 138, 1-20.

V72B-1312 1330h POSTER

Garnet/silicate Liquid Partitioning in Mafic Lithologies

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It is well-recognized that mafic lithologies such as eclogite in the upper mantle may affect the geochemistry of basalts, but this influence depends in part on the mineral/melt partitioning of the phases in such pyroxenitic domains. Recent studies of garnet (grt) partitioning behavior [Van Westrenen *et al.*, *G³, 2000GC000133*] indicated that differing grossular content in peridotitic and eclogitic garnets may have a significant influence. Peridotitic grt is Ca-poor ($X_{\text{Ca}} \sim 0.05-0.2$), whereas eclogitic grt may have $X_{\text{Ca}} > 0.2$, which may increase compatibility of tetravalent HFSE (Zr, Hf and Ti) relative to REE, thus potentially making high REE/HFSE ratios a unique indicator of garnet eclogite sources. Our previous work established that at 2-3 GPa typical recycled oceanic crust is $\sim 80\%$ clinopyroxene (cpx) and $\sim 20\%$ garnet ($X_{\text{Ca}} \sim 0.18-0.23$). The cpx are Al-rich and have significant M²-site vacancies, lowering overall absolute D-values for 3+ and 4+ cations, thus enhancing the relative role of grt, despite its low modal abundance. Owing to the lack of published partitioning data in this critical grt composition range, we performed experiments at 3.0 GPa and 1360 – 1390°C, yielding grt ($X_{\text{Ca}} \sim 0.16-0.21$) coexisting with Al-rich cpx and andesitic liquid ($\sim 57 \text{ wt.}\% \text{ SiO}_2$). Experimental run products were analyzed by LAM-ICP-MS, using a 193 nm ArF excimer laser with repetition rates of 10 Hz for glasses (30-60 micron spots) and 5 Hz (4-30 micron spots) for grt and cpx. Ablation was carried out in pure He, mixing Ar to the carrier gas between ablation chamber and the mass spectrometer. Our preliminary results differ little for grt between $X_{\text{Ca}} \sim 0.16$ and 0.21. Overall, Ti is little affected by the increase of Ca in grt (it $D_{\text{Ti}} = 0.27-0.29$) and Ti, Zr and Hf remain moderately incompatible, in contrast to the compatible behavior predicted previously. Melting calculations with our new data show that melts derived from eclogite (80% cpx, 20% grt) and peridotite (60% ol, 22% opx, 10% cpx, 8% grt) differ little in Zr/Hf or Nb/Ta ratios, but eclogite-derived melts show clearly elevated Hf/Sm and Zr/Yb ratios. D_{Ti} and D_{U} (0.001-0.002 and 0.008-0.01, respectively) are smaller than previously measured, with large values of $D_{\text{U}}/D_{\text{Ti}}$. This suggests that partial melts of eclogite may potentially produce large ²³⁰Th excesses, but only if melt separation occurs at porosities <1%.

V72B-1313 1330h POSTER

The Behavior of Rare Earth and Other Trace Elements During Laboratory Melting of the Mantle at 1.0 GPa.

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Earlier piston-cylinder experiments in our laboratory produced a collection of mantle melting run products that have now been analyzed by ion probe for selected REE, Ti, Cr, Rb, Sr, Y, Zr, and Nb. Starting materials consisted of five fertile to intermediate, hercynitic to wehrilitic mixtures of natural ol, cpx, opx, and sp handpicked from fresh xenoliths. Samples were run in graphite-lined Pt capsules and the melt was separated from the residual minerals into a layer of vitreous carbon spheres (VCS) thus circumventing the problems of Fe-loss and quench modification of the melt. Major element compositions of all phases were determined previously by electron microprobe and least-squares inversion of these data yielded modes for all run products. The bulk starting materials were analyzed for trace and major elements by ICP-MS and-ES at Boston University. The principle goals of the study were to evaluate whether the trace element data support the conclusion reached previously from the major element data that these run products represent very close approaches to equilibrium, and to evaluate whether the glass data set could be inverted to yield meaningful mineral/melt kds.

With few exceptions, we were unable to get good data from the crystalline phases, primarily because of their small sizes or very low trace element abundances. However, the glass phase in 32 run products (representing Fs from 2-50 wt. percent) yielded excellent data that were remarkably homogenous from spot to spot and varied sensibly with changing melt fraction. Forward modeling using our modes and Co values in conjunction with published kds for ol, cpx, opx, and sp (Kelemen *et al.* EPSL 120: 111-134, 1993) yield calculated trace element abundances that generally agree with our measurements to within 10-30 percent, about the precision of the ion probe measurements, given the small beam diameter we employed. However, our attempts to run the inverse problem using our measurements, modes, and Co values to invert for the mineral/melt kds yielded generally unreasonable results. This suggests that our 32 mass balance constraints are not sufficiently independent, given the error in our measurements, to isolate the partitioning behavior of the different residual minerals.

V72B-1314 1330h POSTER

A Multicomponent Model for the Non-Arrhenian Temperature Dependence of Viscosity of Anhydrous Melts.

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Newtonian viscosities of multicomponent liquids ranging from basanite through phonolite and trachyte, to dacite have been investigated by the use of concentric cylinder viscometry ($10^{*}10$ to $10^{*}5$ Pas) and micro-penetration methods ($10^{*}8.5$ up to $10^{*}12$ Pas) at 1 bar pressure. Regressions of the combined (high and low temperature) viscosities were performed using the 3-parameter Tammann-Vogel-Fulcher (TVF) equation. This parameterisation forms the basis for a new non-Arrhenian modeling approach presented here that is capable of reproducing viscosity data over a wide compositional range. To that end a chemical parameter, modifiers, simply defined as the sum of the Ca, Mg, Mn, half of the total Fetot, Na and K mole oxides, found proportional to the NBO/T structural parameter, served as input to the solution. A relationship between the chemical composition of the multicomponent defined in terms of the mole fraction of network modifiers or the network formers, as we defined here, yields to remarkably good predictive tool for the calculation of the viscosity of multicomponent silicate melts. This parameterisation is proposed as the first reliable model for multicomponent non-Arrhenian Newtonian viscosity of silicate melts.

V72B-1315 1330h POSTER

Viscosity Measurement of the Fe-FeS melt under High Pressure using a High-Speed X-ray CCD camera

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An X-ray radiography technique is a very powerful tool to observe various physical phenomena under

high pressure. This technique with synchrotron radiation is very useful for the falling sphere viscosity measurement, because it enables the direct observation of the sinking process and determination of the reliable viscosity coefficient. The experimental system has been installed on a large-volume multi-anvil apparatus (SPEED-1500) in the BL04B1 beamline at the Spring-8 in Japan. The strong synchrotron X-ray beam passes through the sample, and its radiographic images from the YAG fluorescence screen are monitored by a CCD camera. A metal marker sphere (Pt sphere with a diameter of 100-150 μm) is embedded in the upper part of the sample within the high pressure cell, and real-time images of the process of the sphere sinking in the melt are captured and recorded in a personal computer. Up to now, viscosity measurements using this method have been carried out, but for very low viscosity melt, the reliable viscosity coefficients have not been obtained due to the restriction of the image capturing time of CCD camera ($> 30 \text{ ms/image}$). In this study, we designed a new X-ray radiography system combining with a high-magnification lens and a high-speed CCD camera ($< 4 \text{ ms/image}$), and applied it to the Fe-FeS melt under high pressure and temperature. The Fe-FeS melt is important outer core material and its viscosity has been thought to be very low under high P-T conditions. Recent high pressure radiography measurements of the Fe-FeS melt have showed the low viscosity values ($< 10^{-2} \text{ Pa s}$), however, the accuracy is not so good, because a very few capturing images have been obtained for determining the viscosity values. We have tested a new X-ray radiography system for the Fe-FeS melt, and obtained its reliable viscosity values up to 5 GPa.

V72B-1316 1330h POSTER

The Nature of Polymerization in Silicate Glasses and Melts: Solid State NMR, Modeling and Quantum Chemical Calculations.

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Silicate melts are among the dominant constituents of the upper mantle and crust. The full understanding of atomic scale disorder is essential to the macroscopic properties of the melts such as viscosity and configurational thermodynamic properties. Recently, we quantified the various aspects of the extent of disorder in charge-balanced silicate glasses (non bridging NBO)/T=0) using solid state NMR and theoretical analysis, which allowed the degree of randomness of these systems to be determined in terms of the degree of Al-avoidance and degree of phase separations (Lee and Stebbins, *Geochim. Cosmochim. Acta.* 66, 303).

Quantitative estimation of the framework connectivity and the atomic structures of depolymerized silicate melts (NBO/T>0), however, are still poorly known and framework cations and anions have often been assumed to be randomly distributed. Here, we explore the extent of disorder and the nature of polymerization in several binary and ternary silicate glasses with varying NBO/T using O-17 NMR at varying magnetic fields of 7.1, 9.4 and 14.1 T in conjunction with quantum chemical calculations. We also quantify the extent of intermixing among non-framework cations in mixed cation glasses, and calculate corresponding configurational thermodynamic properties.

Non-random distribution among cations is clearly demonstrated from the relative populations of oxygen sites and the variation of distribution of structurally relevant NMR parameters with NBO/T from O-17 3QMAS NMR. The proportion of NBO (Na-O-Si) in Na₂O-SiO₂ glasses increases with NBO/T. Its chemical shift distribution decreases about 18 % from NBO/T of 0.7 to 2, suggesting a reduced configurational disorder around NBO with Na contents.

Preferential interactions among framework cations are further manifested in peralkaline Ca- and Na-aluminosilicate glasses where depolymerization of networks selectively occurs at Si rather than Al tetrahedra, forming Na-O-Si or Ca-O-Si. The result is consistent with our quantum chemical calculations based on density functional theory where the silicate chain with Al-NBO has energy penalty of about 108 kJ/mol compared with the cluster with Ca-O-Si. The degree of Al avoidance (Q) among framework units in Na-aluminosilicate is larger than that in Ca-aluminosilicates, as recently observed for fully polymerized glasses. On the other hand, Q varies with NBO/T. The above results support the significant chemical order in silicate glasses that leads to considerable mixing among framework units.

The degree of intermixing among non-framework cations in mixed-cation glasses has remained controversial. The population of each Na-NBO in Ca-Na and Ba-Na mixed cation silicate glasses is smaller than the prediction given from random distribution of these cations, and thus supports the preference for dissimilar pairs of cations, which could explain a decrease in diffusivity in these melts.

In this study, we provide new insights into the structure of silicate glasses with varying NBO/T, highlighting more complete, atomic-level understanding on the dynamic processes in silicate magmas.

V72B-1317 1330h POSTER

H₂O diffusion in dacitic glasses and melts

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Understanding H₂O diffusion in magma is crucial to the understanding of bubble growth, magma degassing and volcanic eruptions. H₂O diffusion in rhyolitic melts has been investigated extensively, but not for other melt compositions. In addition to rhyolitic eruptions, there are many explosive dacitic eruptions (such as the 1980 eruption of Mount St. Helens, the 1991 eruption of Pinatubo and Unzen). Modeling dacite degassing requires H₂O diffusion data. Here we report the first study of H₂O diffusion in dacitic melts.

Starting hydrous dacitic glasses containing 0.7 to 2.5 wt% total dissolved H₂O (H₂O_t) were synthesized at 1250°C and 5 kbar in an internally heated pressure vessel at the Universität of Hannover. Composition of anhydrous dacitic glass is similar to Unzen dacite (SiO₂ 65.16, TiO₂ 0.66, Al₂O₃ 16.36, FeO 4.16, MgO 1.96, CaO 5.07, Na₂O 3.95, K₂O 2.69). Dehydration experiments were conducted in two rapid quench cold seal pressure vessels at an Ar pressure of ~1 kbar and 507-637°C for 11 h to 20 days. Concentrations of water species in dacitic melts before and after experiments were determined using FTIR spectroscopy and the calibration of Ohlhorst et al. (2001). Starting samples were homogeneous in water contents within 5% relative except for samples with ~0.8 wt% H₂O_t (up to 19% relative). Molecular CO₂ contents were determined using FTIR and calibration of Fine and Stolper (1985).

The diffusivity of water in dacitic melts is proportional to H₂O_t at low H₂O_t (<1.5 wt%) but depends on H₂O_t exponentially at higher H₂O_t, similar to the behavior in rhyolitic melts. Hence diffusion mechanism in dacite is inferred to be similar to that in hydrous rhyolitic melts where molecular H₂O is the diffusing species. Water diffuses slower in dacitic melts than in rhyolitic melts by about one order of magnitude at ~0.8 wt% H₂O_t. For example, at 608°C and 0.99 kb, $D(\text{H}_2\text{O})$ is ~0.013 μm²/s in dacite and 0.13 μm²/s in rhyolite for ~0.8 wt% H₂O_t (Zhang and Behrens, 2000). As a side product, CO₂ diffusivity can also be obtained from our experiments. CO₂ diffuses slower than H₂O. For samples with ~0.8 wt% initial H₂O_t at 637°C, CO₂ diffusion profile can be fit using an error function with a diffusivity of ~0.006 μm²/s, which is similar to the diffusivity of CO₂ (0.003 μm²/s) in anhydrous rhyolitic melts (Watson, 1994) and that of Ar in rhyolitic melt (0.0075 μm²/s) with similar water contents.

V72B-1318 1330h POSTER

Effect of Water on the Structure of Melts and Glasses Along the Join NaAlSi₃O₈- NaBSi₃O₈

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In the present study we combined complementary spectroscopic techniques such as NMR, Raman and infrared spectroscopy to investigate structural variations associated with B/Al substitution in a series of glasses along the join reedmergerite-albite (NaBSi₃O₈-NaAlSi₃O₈). Since natural B-rich melts are commonly associated with hydrous granitic magmas or aqueous fluids, we focused in particular on the structural effects of water dissolution.

Glasses with five different compositions along the join reedmergerite-albite (Rd-Ab) were studied

(Rd100, Rd75Ab25, Rd50Ab50, Rd25Ab75, and Ab100, in mol%). Hydrous glasses containing 0.5 to 8 wt% water were synthesized at 2 kbar and 1000 - 1100 °C in TZM rapid quench autoclaves. Dry glasses were prepared at similar conditions (2 kbar, 1100 °C, rapid quench) in order to minimize possible effects of different synthesis conditions on the glass structure. All glasses were analyzed with IR, Raman and NMR spectroscopy.

The results show that B incorporates in the glasses as both, tetrahedral BO₄ and trigonal BO₃ groups. The B-speciation strongly depends on the anhydrous melt/glass composition and on the water content. Since ²⁷Al NMR data demonstrate that Al is solely present in tetrahedral coordination, the presence of BO₃ indicates the presence of non-bridging oxygens (NBO) as in a fully polymerized glass all the B-atoms will be in tetrahedral coordination. Near-infrared spectroscopy indicates important changes in the water speciation upon B-incorporation with a new hydroxyl-related band developing at 4730 cm⁻¹. Furthermore, the variations in the spectra indicate that with increasing B-content at constant total water content the concentration of structurally bonded hydroxyl groups increases at the expense of molecular H₂O. For example, at a total water concentration of 4 wt%, pure Rd-glass contains about 50% more water as hydroxyl groups than pure Ab-glass. The peak at 4730 cm⁻¹ could be due to B-OH complexes, however the exact nature of such complexes cannot be deduced from the present data and needs further investigation. In-situ IR spectroscopy of the melts at high P and T using a hydrothermal diamond-anvil cell demonstrates the conversion of H₂O to hydroxyl groups with increasing temperature.

V72B-1319 1330h POSTER

Fluorine-19 NMR Study of the Environment of Fluorine in Silicate and Aluminosilicate Oxyfluoride Glasses.

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Using a compilation of F-19 NMR chemical shift values for crystalline model compounds, we have explored the local fluorine environment in several silicate and aluminosilicate oxyfluoride glasses. The F-19 MAS NMR spectrum of the Mg-silicate glass consists of a broad peak centered at ~170 ppm, which encompasses the F-Mg(3) environments (where 3 is the number of Mg neighbors) of crystalline MgF₂ (-195 ppm) and phlogopite (-175 ppm). The predominant environment in the glass is consequently assigned to F-Mg(n), where n indicates an unknown number of nearest neighbors. The magnesium aluminosilicate glass spectra all consist of a major feature at about -175 ppm and a shoulder at approximately -145 ppm. Based on the model compound data, the shoulder lies in the region attributed to Al-F-M2+ sites, and it was observed that glasses with a higher Al/Mg ratio featured extra intensity in the high-frequency shoulder. The shoulder is consequently assigned to Al-F-Mg(n), while the major feature is attributed to F-Mg(n) sites. This indicates that Mg is decidedly more effective in bonding to fluorine than either Ca or Ba in aluminosilicate glasses, following the trend established in our previous work on the Ba- and Ca-aluminosilicate glasses (the higher field strength modifier cation is more effective in competing with Al). Fluorine preferentially bonding with the modifier cation over aluminum has, to our knowledge, never been previously observed in aluminosilicate glasses.

Spectra for Na-La-silicate glasses are characterized by an extremely wide peak (hundreds of ppm) and a relatively narrow peak at ~220 ppm. The narrow peak at ~220 ppm is assigned to F-Na(n) due to its proximity to the chemical shift of F-Na(6) (-225 ppm, from crystalline NaF). The small relative area of the F-Na(n) peak indicates a pronounced preference for F-La bonds over F-Na bonds, which is consistent with the findings of the previously discussed aluminosilicates. The massive, broad feature encapsulates the region described by the mixed fluorine environments of crystalline NaLaF₄ (-30 to -63 ppm), and has therefore been assigned to a wide variety of fluorine environments, consisting of F-La bonds in a mixed environment with some number of F-Na bonds. In order to explore La-F clustering we have employed echo experiments, which can provide information about F-F distances. In the Na-La-silicates, the broad feature decays much faster than the F-Na(n) peak, indicating a shorter F-F distance in the sites associated with La. This is not consistent with random anion distribution but can be easily explained by the formation of fluorine-rich clusters. This may provide insight into the mechanism for the onset of crystallization in glass ceramics.

In the long echo-time experiments on the Na-La-silicate glasses, the intensity of the broad feature was virtually gone, and the intensity of the F-Na(n) peak was largely decreased. This allowed us to clearly observe another peak centered at ~140 ppm. This is near the peak found for the Si-F-Na(2) structure (-152 ppm)

in the model compounds. Further examination of the original one-pulse spectra revealed the presence of this peak in small quantities in all compositions. Its relative intensity (about 2 percent of the total intensity) is comparable to that of Si-F-Ba(n) and Si-F-Na(n) bonding found in the fluorine-containing Ba-silicate and Na-silicate glasses (respectively) from our previous studies. This suggests that Si-F bonding is independent of composition and may be an intrinsic characteristic of fluorine-containing silicate glasses.

V72B-1320 1330h POSTER

Cation Diffusion in Fluorapatite

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Diffusion of manganese and uranium has been characterized in natural and synthetic fluorapatite under dry conditions. The source of diffusant for Mn experiments were mixtures of ground synthetic or natural fluorapatite and MnO powder, heated in sealed silica glass capsules prior to diffusion anneals. Mn experiments were run by sealing source and apatite in silica glass capsules under vacuum, and annealing capsules in 1 atm furnaces for times ranging from thirty minutes to a few months, at temperatures from 650 to 1050°C. The Mn distributions in the apatite were profiled by Rutherford Backscattering Spectrometry (RBS). The following Arrhenius relation is obtained for Mn diffusion in natural Durango fluorapatite, for diffusion parallel to c:

$$D_{Mn} = 5.4 \times 10^{-7} \exp(-288 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ sec}^{-1}$$

Mn diffusion normal to c appears to be similar to diffusion parallel to c, and diffusivities in natural and synthetic fluorapatite are the same within experimental uncertainties.

Uranium diffusion experiments were run with a U-doped microcrystalline apatite source, made through solid-state reaction of UO₂, CaF₂ and Ca₃(PO₄)₂ under buffered (NNO) conditions. The source and apatite specimens were loaded into Pt capsules, then sealed under vacuum in silica glass capsules with a solid buffer (NNO). Preliminary results over the temperature range 1150-1250°C yield the following Arrhenius relation:

$$D_U = 1.4 \times 10^{-2} \exp(-511 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ sec}^{-1}$$

Diffusivities of Mn are comparable to those of Sr (Cherniak and Ryerson, 1993), and slightly slower than Pb (Cherniak et al., 1991) in apatite. The ionic radii for divalent Mn, Sr, and Pb are 0.90, 1.21 and 1.23 Å, respectively, in 7-fold coordination (Shannon, 1976), and 1.00, 1.31, and 1.35 Å in 9-fold. The similar diffusion rates for Sr and Mn, despite their significant differences in cationic radii, suggest that cation size does not exert strong influence on diffusion of divalent cations in apatite, a finding consistent with that observed for the trivalent REE.

Cation charge, however, does seem to more significantly influence diffusivities in apatite. U diffusion is about 4 orders of magnitude slower than Mn diffusion, and about 2 orders of magnitude slower than REE diffusion (Cherniak, 2000). Further, these results suggest that the activation energy for U diffusion is significantly higher than those for divalent cations or trivalent REE.

Cherniak et al. (1991) *GCA* 55, 1663-1673; Cherniak and Ryerson (1993) *GCA* 57, 4653-4662; Cherniak (2000) *GCA* 64, 3871-3885; Shannon (1976) *Acta Cryst.* A32, 751-767.

V72B-1321 1330h POSTER

Grain-scale permeability of texturally equilibrated rocks continued: synthetic amphibolite.

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Permeability was measured on synthetic, monomineralic aggregates of fluorotremolite, which may be useful analogs for amphibole-dominated rocks in the lower crust. Tremolite aggregates were synthesized in the presence of tremolite-saturated 4M HF, with fluid fractions (φ) ranging from 0.03 to 0.22, at 950°C and 1.4 GPa for 120 hours in piston-cylinder apparatus. Permeability of the quenched and dried materials was measured at near-atmospheric conditions and scaled to a grain-diameter of 1 mm. At low fluid fractions, the tremolite aggregates were substantially less permeable than synthetic quartzites and marbles produced using a similar technique. Materials with φ less than 0.04 did not exhibit detectable permeable flow for periods exceeding 168 hours. Above φ = 0.04, the relationship between permeability (k) and porosity is approximated

by the following: $k = d^2 \times (\phi - 0.04)^3 / 270$. At $\phi = 0.22$, permeability was similar to that of synthetic quartzite.

Scanning electron images of polished sections revealed elongate fluorotremolite crystals with random orientation and an average mean sectional diameter of 10 microns. Pores within these materials were extensively faceted (>90%). Apparent intersections between pore walls averaged 46 degrees, but the small number of curved walls precluded assessing the dihedral angle. Therefore, the exact nature of the pore network is not known, but we suspect that the large degree of faceting limits pore connectivity at low ϕ , reducing permeability relative to other texturally equilibrated, fluid-bearing rocks.

V72B-1322 1330h POSTER

Grain Boundary Chemistry in Mantle Rocks

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We show that the same elements segregate to olivine grain boundaries in both natural rocks and synthetic aggregates. We conclude that this chemical segregation is an energetically favorable phenomenon that will influence the physical and chemical properties of mantle rocks. Two natural samples with unaltered and tight grain boundaries were chosen. One is an ultramylonite from Balmuccia peridotite in the Ivrea Zone. The other is a basaltic rock with olivine phenocrysts from Kilauea, Hawaii. Two olivine phenocrysts often contact one another forming straight and long grain boundaries. Two synthetic aggregates, one composed of olivine + diopside and the other of olivine + anorthite, were synthesized. The diopside and anorthite powders were mechanically mixed with dried San Carlos olivine powder and subsequently isostatically hot-pressed inside an Fe jacket at 1373 K and 300 MPa in a gas-medium apparatus. Some of the hot-pressed samples were annealed at 1373 K and room pressure. Scanning-transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM/EDX) profiling was used to determine the chemical compositions of olivine grain boundaries. In this study, we used a Philips CM200 TEM/STEM equipped with a Schottky field emission gun (FEG) and operated at 200 kV to obtain a probe size (full width at half maximum) of 1.3-1.4 nm. The profiles across every grain boundary exhibited similar chemical features. The primary features are 1) significant Ca enrichment, 2) weak Si and Mg depletion, and 3) weak to significant Al and Ti enrichment. Both the enrichment and the depletion are restricted to a zone <5 nm wide along the grain boundaries. The Ca concentration in the grain boundaries is positively correlated with that in the grains. Segregation can result from kinetic and thermodynamic effects. In nature, a decrease in the solubility of specific elements in the grains during cooling of a rock can cause segregation. However, the effect cannot explain the segregation in synthesized samples, since they were quenched. Elements with ionic radii different from that of its host are likely to stay at grain boundaries to minimize strain energy. This behavior explains the segregation of elements such as Ca, which has a much larger radius than Mg in olivine. Differences in the vacancy formation energy between a cation and an anion can cause segregation and result in a build up of space charge at grain boundaries. To compensate for this space charge, aliovalent elements such as Al can segregate to the grain boundaries.

V72B-1323 1330h POSTER

Thermal Conductivity of Amorphous Geomaterials at Magmatic Temperatures: Review, Theory, and New Experimental Results.

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Of all the transport properties of silicate melts and glasses, thermal conductivity remains the most poorly known despite its significance regarding both the transport of heat between magma and its surroundings and the petrologic evolution of open magmatic systems. The dearth of experimental conductivity data arises from the intrinsic difficulty of the experiments due to the confounding effects of convective heat transport

and radiative transport, the latter which becomes important at high temperature (T). Although the volumetric absorption of radiation can be treated using the extinction coefficient, ϵ_{ex} , defined as the inverse of the photon mean-free path, l_{ph} , the simultaneous treatment of the absorption, emission and scattering of radiation in a nonisothermal experiment may be complex. Additional complexity arises due to the dependence of l_{ph} on wavelength, λ . For example, for low-FeO silicate glass, $l_{ph} = 0.2$ m ($\epsilon_{ex} \approx 5m^{-1}$) at $\lambda = 0.4\mu m$, whereas for $\lambda = 8\mu m$, $l_{ph} = 0.002$ m ($\epsilon_{ex} \approx 500m^{-1}$). In natural systems, the optical thickness, $\epsilon_{OT} \equiv \epsilon_{ex}L$ is large and the thick-medium approximation is justified since $\epsilon_{OT} \gg 1$. Under this assumption the radiant conductivity ($k_R = 16/3\sigma_{SB}n^2T^3l_{ph}$) may be defined where the radiant heat flux is proportional to the temperature gradient as is the case for phonon conduction. We have undertaken a critical compilation of experimental results in order to separate the effects of the radiant (k_R) and phonon (k_P) conductivity in amorphous (molten and glassy) silicates and to understand the role of structural disorder on phonon conduction. Because the radiative conductivity (k_R) is $\propto T^3$, experimental values of the apparent or total thermal conductivity ($k_T = k_R + k_P$) plotted against T^3 enable one to separate approximately the effects of radiation from phonon conduction in some instances. This approach enables one to estimate wavelength integrated extinction coefficients since the radiative heat flux is inversely proportional to the mean (wave-length integrated) extinction coefficient. In contrast, the phonon conductivity (k_P) derives from two sources: phonon interaction and scattering due to structural disorder. Above the Debye temperature, C_p of a melt is constant; k_P is \propto to the mean free path between atomic collisions (Λ) which in turn varies inversely to the number of excited phonons ($\propto T$). Hence, $k_P \propto 1/T$. Near the Debye temperature, C_p decreases as T decreases and k_P is less than expected from 1/T dependence. At very low temperature, even though few phonons are excited Λ does not increase without limit because of structural disorder. Additionally, $C_p \propto T^3$ and so k_P is an increasing function of T. Finally, we present new experimental measurements of the thermal conductivity for supercooled amorphous geomaterials using a transient method and minimize radiative conductive effects using large volume (5×10^{-5} m³) samples (L ~ 0.04 m). The radiant contribution to the thermal conductivity is small in this apparatus for liquids characterized by mean (wave-length integrated) extinction coefficients $> \sim 200$ m⁻¹.

V72B-1324 1330h POSTER

High-Temperature Density of Lanthanide-Bearing Silicate Melts

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The lanthanides are of interest in the geosciences, despite usually occurring as minor or trace elements in rock-forming minerals although they can be essential constituents of some minerals. In general, they are partitioned more extremely than major elements making them more sensitive indicators of the petrological processes that occur. Therefore, they are a powerful tool in order to trace the processes involved in the petrogenesis of magmas, in the thermodynamical modelling to accurately predict the crystal-melt phase equilibria in a magma. 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 multi-component 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, we are conducting density measurements on various lanthanide-bearing silicate melts.

In this paper, we present density measurements obtained in air for various lanthanide-bearing silicate melts (from cerium to lutetium including lanthanum). 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 preliminary 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 cm³/mol for Tm₂O₃ and Pr₆O₁₁, respectively). High-temperature density measurements on new compositions are in progress in order to determine the partial molar volume of lanthanide oxide liquids more accurately.

V72B-1325 1330h POSTER

Molecular Ordering and Dynamic Deformation of Hydrogen Bonding Network in Liquid Water over a Wide Density Range

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Water is the most important volatile component in the Earth's mantle and crust, and its anomalous properties are directly related to the complex network of hydrogen bonds formed among water molecules and the structural and dynamic changes to this network due to variation of thermodynamic conditions. Thus, to predict and understand such issues as the effects of pressure, temperature and proximity to mineral surfaces on the properties of natural fluids, it is essential to have quantitative, molecular-level understanding of the relations between the structure and properties of water. Here we investigate the effect of density on the local ordering and the dynamic deformation of the fundamental tetrahedral structural units formed by each water molecule with its four nearest neighbors in the H-bonding (HB) network of pure water. Molecular dynamics computer simulations were performed for 8 systems at a temperature of 280 K and densities from 0.85 to 1.20 g/cm³, corresponding to situations from highly stretched to highly compressed states of the HB network. An orientation order parameter (q) is used to quantify the tetrahedrality of the network. At a given density the range of q for individual structural units is large. The degree of orientational ordering is in strong linear correlation with the total interaction energy of the central molecule with its four nearest neighbors. Less energy is required to decrease ordering in the stretched range than in the compressed range of densities. The translational order of water molecules is reflected in the radial distribution functions (RDFs). In the stretched systems, the RDFs for water molecules with lower q values are similar to those with higher q . In the compressed systems, the RDFs for molecules with higher q are similar to those of the stretched systems, but with the average position of the second nearest neighbors shifted from 4.5 to 4.0 Å. However, the RDFs for the molecules in the compressed systems with lower q values are completely different and lack any distinguishable second-neighbor signature. The typical time for the transition of a molecule from a highly ordered state (high q) to a low ordered state changes from 0.2 to 1.0 ps with decreasing density. In contrast, typical residence times for a molecule in a local structural neighborhood are in the range 2.0-5.0 ps. The nearly order of magnitude difference between these two correlation times indicates that a water molecule with its four nearest neighbors as a group continuously undergoes "breathing" motions until it diffuses away from its neighbors.

V72B-1326 1330h POSTER

Molecular H₂O-Silicate Interactions

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Water plays a fundamental role in natural dissolution, precipitation and sorption processes. However, relatively little is understood about the chemical and physical interactions that take place between H₂O and crystalline silicates at the molecular level. An understanding of the interactions between bulk H₂O and a mineral surface requires a description of the bonding, especially the role of hydrogen bonding. In order to address this issue, we are studying the behavior of H₂O molecules that are incorporated in the inner surfaces of different silicates such as beryl (Al₂Be₃Si₆O₁₈·H₂O), cordierite (Mg₂Al₄Si₅O₁₈·H₂O) and bikaite (Li₂Al₂Si₄O₁₂·2H₂O) using polarized single-crystal IR and Raman spectroscopy.

In beryl and cordierite two general classes of H₂O are present in small structural cavities located along infinite channels parallel to [-001]. The molecules are isolated from each other and can be described as the "zero-dimensional case". The H₂O internal stretching and bending vibrations can be measured for both classes. Class I involves a single, virtually free H₂O molecule having very little interaction with the silicate

framework. It is dynamically disordered and its internal vibrations are similar in energy to those of H₂O vapor, with an O-H bond energy of about 45 kJ/mole. External librational modes are located around 200 cm⁻¹ and translational around 10 cm⁻¹. In contrast, class II H₂O bonds to an alkali cation located in the six-membered tetrahedral ring through the lone-pair of the O atom. At about 5 K the H-bonding with the framework is roughly 1 kJ/mole.

In the zeolite bikaite, the H₂O molecules occur in infinite channel ways parallel to [010] and they build a hydrogen-bonded H₂O chain that has been termed 'one-dimensional ice'. The molecules in the chains are ordered, whereby one H atom per molecule is not bonded and the second is hydrogen-bonded to a neighboring H₂O molecule. The hydrogen-bonded O-H stretching bands in the Raman spectra show little line broadening, which is untypical for many hydrogen-bonded systems. With increasing temperature, hydrogen bonding between the H₂O molecules weakens and H₂O ultimately diffuses out of the channels by 620 K.

V72B-1327 1330h POSTER

Experimental determination of the solubility of natural wollastonite in pure water up to pressures of 5.0 GPa

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The solubility of natural, near-end-member wollastonite (>99.5% Ca₃Si₃O₉) has been determined at temperatures from 400 to 800°C and pressures between 0.8 and 5.0 GPa in piston-cylinder apparatus with the weight-loss method. The reproducibility was monitored by performing several experiments under constant conditions. Run durations needed to reach constant weight loss were determined by varying run times at constant pressure and temperature conditions. To allow experiments above pressures of 3.5 GPa we have developed a new type of gold capsules, which also minimizes the water lost during the sealing and initial pressurization.

Chemical analysis of quench products and the fact that no additional solid phases formed during dissolution indicate that wollastonite dissolves congruently in the above pressure-temperature range. Additional experiments in a hydrothermal diamond anvil cell confirm these results on the basis of optical and raman characterization. Traces of iron in the natural wollastonite starting material leads to the formation of minor amounts of 10 µm sized andradite crystals. We also observed that the oriented growth of wollastonite-II from the wollastonite-I crystal. The phase transition from wollastonite-I to wollastonite-II requires no more than a few minutes at 3.5 GPa and 700°C.

The molality of dissolved CaSiO₃ equivalent varies between 0.015 and 1.344 and increases systematically with both temperature and pressure up to 3.0 GPa. Above 3.0 GPa the starting material reacts to the high-pressure modification wollastonite-II. The solubility of wollastonite-II appears to be lower and relatively pressure-independent in the given temperature range. For pressures above 0.5 GPa, the solubility of wollastonite can be fitted to the following equation (T in Kelvin) $\log m_{\text{woll(aq)}} = 8.10 + (-13594.92)/T + 4492411.90/T^2 + 10.31 \log r_{\text{H}_2\text{O}}$.

From this it follows that, for a given pressure and temperature, the molality of dissolved CaSiO₃ equivalent is up to an order of magnitude lower than that for pure SiO₂ (1). The solubility of calcite (2) is similar to wollastonite at 500°C but is two times less at 800°C.

(1) Manning, Geochim. Cosmochim. Acta 58, 1994; (2) Caciagli & Manning, Eos. Trans. AGU, 82(47), 2001.

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Zircon: Free Energy of Formation of Aqueous Solubility Measurements at High T and P

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We measured the silica solubility at 800 °C, 12 kbar, of small (~0.5 mg) limpid euhedral zircon crystals grown by a flux-melt method (Hanchar et al., Am.

Min., 86, 667, 2001). Incongruent solution occurs according to $\text{ZrSiO}_4 = \text{ZrO}_2 + \text{SiO}_2, \text{aq}$. Zircon lost ~0.1 mg after exposure of 1-2 mg of zircon to ~32 mg H₂O in welded Pt envelopes for 90-120 hr in piston-cylinder apparatus using NaCl-graphite furnaces. The average solubility was 0.0645±0.007 molal (m), or a mole fraction (X_G) of 0.00116. Reversibility was established by rerunning the baddeleyite-coated zircons with a fluid initially slightly SiO₂-oversaturated, as determined by the forward experiments, resulting in weight gains of the composite crystals. Similar runs on sintered ZrO₂ compacts yielded spontaneous surface nucleation and growth of zircons up to 1 mm. Concentrations were corrected for a small, measured solubility of ZrO₂ (0.001 m). Nonideality of aqueous silica was calculated assuming that SiO_{2, aq} consists of a mixture of monomers and dimers (Zotov and Keppler (Chem. Geol., 184, 71, 2002; Newton and Manning, GCA, in press). Our zircon solubility and that of quartz at the same conditions (X_G=0.02634, Manning, GCA, 58, 4831, 1994) give activity coefficients at the two concentrations of 0.730 and 0.255, respectively. The activity coefficients and concentrations yield the free energy of formation of zircon from the oxides at 800 °C, 12 kbar of -18.46±0.96 kJ/mol, which translates to -11.91±0.96 kJ/mol at 800 °C, 1 bar. Our value is compatible with previous estimates based on experiment (Schulring et al., Am. Min., 61, 166, 1976) and high-T oxide-melt calorimetry (Ehlison and Navrotsky, J. Am. Ceram. Soc., 75, 1430, 1992), but is four times more precise than these estimates.

V72C MCC: 270 Sunday 1330h

Lessons Learned From Santa Maria/Santiaguito, Guatemala: Implications of Long-Lived Silicic Eruptions I (joint with S)

Presiding: B Cameron, University of Wisconsin, Milwaukee; A Harris, University of Hawaii

V72C-01 1330h

Santa Maria and Santiaguito: a Superb Field Volcanological Laboratory

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One of three actively erupting volcanoes in Guatemala, Santa Maria/Santiaguito has been the site of geological work for more than 100 years and is still a magnet for scientists. Santa Maria's 1902 crater offers unusual access to its gradually changing sequential eruptive products over the past 25 ka. Preservation of composite cone lavas and fragmental deposits is excellent. The mixed magma plinian 1902 eruption has well preserved fall deposits over much of western Guatemala and Southern Mexico and spans a compositional gap from basaltic andesite to dacite. The Santiaguito dome activity has been continual since 1922 with an oscillating eruption rate. A variety of eruption styles have been observed, including endogenous dome extrusion, exogenous block lava flows, block and ash flows, lahars and floods and frequent (several times a day) small vertical ash eruptions. The volcano is accessible by ground routes which are no more than a few hours walk at relatively low altitudes from good roads, and including an unusual summit perspective. There is a long context of field observations there, enabling long term studies of dome phenomena to be placed in a context. There is a volcano observatory and an active observer who provides daily observations. Monitoring efforts are planned to improve. The morning weather is usually clear, in spite of a climate that has frequent fog, and this aids in both ground and satellite remote sensing observations. The volcano has active fumaroles and a gas plume with unusual chemistry. A geothermal drill site near Zunil, a few km NE of Santa Maria offers insight into the subsurface geology. The volcano is located upslope from the Boca Costa, an extraordinarily productive area of commercial agriculture which has a growing population and provides important foreign exchange income for Guatemala. So the volcano's future activity and the associated ever changing volcanic hazards of the area are a priority for government agencies. URL: <http://www.geo.mtu.edu/volcanoes/santamaria/>

V72C-02 1345h INVITED

The Soufriere Hills Volcano, Montserrat, is log logistic

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The Soufriere Hills Volcano, Montserrat, experienced a remarkable episode of activity in September-October, 1997. During this period, 75 vulcanian explosions generated plumes that commonly rose between 5 to 15 km a.s.l. accompanied by pyroclastic flows. Repose intervals between vulcanian explosions varied from 2.77 to 33.7 hrs, with a median repose interval of 9.0 hr and mean of 9.6 hr. During the eruption, this narrow range of repose intervals was used in a practical way to provide qualitative forecasts of volcanic hazard. We analyzed repose intervals for these 75 vulcanian explosions and discovered they fit a log logistic distribution with > 99% confidence. This comparatively simple, two parameter model accounts for departures from a classical material failure model (Weibull distribution) at long repose intervals, and serves as the basis for improved hazard forecasts. The crucial differences between Weibull, and log logistic probability models for volcano repose interval are illustrated by comparing their hazard functions. For Weibull distributions the hazard increases indefinitely; the volcano must erupt explosively eventually and as time increases the probability of an eruption in the next time interval becomes much greater. In contrast the log logistic hazard function goes through a simple maximum. We note that largest magnitude eruptions in the time series, deduced from column height estimates and seismic explosion amplitudes, correlate with the peak in the log logistic hazard function. The excellent model fit is explained in terms of two competing processes operating in the upper conduit on different time scales. Gas bubble pressure increases with time due to exsolution and due to rheological stiffening of magma of magma following an abrupt decompression caused by a previous explosion. Once bubble gas pressure exceeds the tensile strength of the magma an explosion occurs a material failure model that should follow a Weibull distribution. However, this process is inhibited by depressurization of gas bubbles due to development of permeability and gas escape. Under these conditions, the timing of vulcanian explosions is expected to follow a log logistic distribution, with the exact timing of individual explosions governed by random variation in the material strength of the magma. Because key parameters in the probability density function have bases in the physical properties of the magma, we suspect that the log logistic survivor function should be applicable to hazard forecasts for vulcanian explosions at other silicic domes.

V72C-03 1400h INVITED

Observations of Santiaguito's Eruptive and Passive Emissions

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In January of 2002, geoscientists from the U.S. and Guatemala made a series of geophysical measurements and observations of Santiaguito volcano, Guatemala. The current activity includes low-level degassing from summit fumaroles, pyroclastic eruptions approximately every 1-2 hours with plume heights typically less than 2km, numerous rockfalls, and a slowly advancing lava flow. Our studies are focusing on providing baseline information and constraints for modeling conduit and eruption processes.

On January 11, digital video of the Santiaguito summit was taken continuously for six hours, during which time 6 explosive eruptions of varying sizes occurred. From Santa Maria's summit, we were able to observe the dome surface within Santiaguito's summit crater.