the measured isotope abundances to differ from the purely kinetic mass fractionation line. Although some of this effect may be caused by 'Si-H' interferences, the intensities of these species alone cannot account for the differences observed between cone geometries. The internal mass fractionation lines that we measure do not agree with the certified values for Si isotope reference materials based on spiked fluorination gas-source mass-spectrometry measurements. For the international NIST NBS-28 isotopic reference material we obtain a δ^{29}Si isotope value that is over 4 $^{o}/_{oo}$ lighter for the given $^{30}Si/^{28}Si$ ratio. Unfortunately, we also observe differences in the relative isotope composition between NBS28, IRMM017 and IRMM018 from those previously measured, suggesting significant heterogeneity of the standards. Clearly, there is need for interlaboratory collaboration to define suitable isotopic reference materials. Cardinal et al., 2003, Journal of Analytical Atomic Spectrometry 18(3): 213-218

V51K-08 1205h

High Mass Resolution Plasma Mass Spectrometry of Cr Isotopes

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Natural mass dependent fractionation of Cr isotopes (masses 50, 52, 53 and 54) is associated with redox reactions (Ellis et al., 2002). In reduced aqueous solutions, chromium (VI) is converted to insoluble chromium (III), which is accompanied by a 3 permil isotope effect. Thus the isotopes of Cr may have wide applicability in the earth sciences as a tracer of redox conditions in the solid earth, oceans and atmosphere over time. Our approach for measuring Cr isotopes utilizes the resolving power of the Finnigan Neptune operated in high mass resolution mode. Using a small diameter, high resolution entrance slit and wide diameter collector slits, flat-topped peak shoulders representing the un-interfered Cr isotopes can be located during a mass scan on the low mass side of composite, interfered peaks. Setting the collectors and magnet field to measure on these peak shoulders, near the high mass edge of the Faraday collector, clips the interfering ion beam preventing it from entering the collector. The largest plasma-generated interference is 40Ar14N on mass 54, comprising about 18 percent of the ion bean intensity in a 1 ppm Cr solution. Molecular interferences on the other isotopes of Cr are less than 0.1 percent, and are negligible in >10ppm Cr solutions. All experiments utilize the Finnigan stable introduction system and a PFA microflow nebulizer. Preliminary results show that about 4 permil of the ArN interference on mass 54 remains despite the peak shoulder measurement. This may be due to peak tailing from the ArN interference, which is a composite peak with an additional interference on the low mass side that is part of the HNO3 blank, and may accentuate tailing of the 54Cr peak. The 4 permil effect is easily removed by performing a blank subtraction. Normalized to a 50/52 ratio of 0.051859, we obtained ratios of 0.113452 and 0.028223 on 53/52 and 54/52, respectively, in 3 to 10 ppm solutions. Results thus far show that a reproducibility of better than +/-50 ppm (2 standard deviations) on the 53/52 ratio is easily achieved from Cr solutions of 3 to 10 ppm. To measure natural Cr isotope variations in nature requires sample-standard-bracketing or double spike addition to correct for instrumental mass fractionation. Experiments with a 50-54 double spike are currently underway, and these results will also be reported. Ellis et al., Science, V. 295, p. 2060

V51L MCC: 3008 Friday 1020h

Kinetic and Rheologic Controls on Transport and Eruption of Magmas II

Presiding: **A Soule,** University of Oregon**; A Whittington,** University of Missouri-Columbia

V51L-01 1020h

Decompression Pattern and Vesiculation Texture of Magma: Preliminary Results of Decompression Experiments Using IHPV With Decompression Speed Controller

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Decompression experiment is an important way to understand vesiculation processes during eruptions. We have installed an internally heated pressure vessel with "decompression speed controller". Our apparatus has two stronger points as follows: (1) high-temperature (>900 C) experiments are possible; (2) smooth decompression is possible at various decompression rates (ca. 10 MPa/s $\sim$ 0.0001 MPa/s). The latter is expected to overcome the difficulty on step-like decompression (e.g., Gardner et al., 1999) that pulsative change in decompression rate at each decompression step could cause another influence on kinetics of vesiculation. Using the apparatus, we are conducting a series of decompression experiments on the 2000 eruptive product (low-K dacite) of Usu volcano, Japan. Firstly, the influence of the decompression patterns was compared: (a) single-step, (b) multi-step (5 steps), (c) smooth. The pressure was decreased from 98 MPa to 50 MPa at a constant temperature 900 C after two days of homogenization. The initial water content is 4.0 wt.%, slightly above the saturation at the initial pressure. For the average decompression rate of 0.003 MPa/s, vesicularity is 31% for (a), 27% for (b), and 20% for (c), and the water content in matrix glass is 2.3±0.4% for (a), 2.4±0.5% for (b), and 2.7±0.6% for (c). These difference are probably caused by the difference of the duration at the final pressure (e.g., the longest in (a)). The BSD (bubble size distribution) plot shows exponential for (c), and power-law for (a) and (b). This can be interpreted as follows: at the smooth decompression, both nucleation and growth occurred "continuously"; at the step-like decompression, nucleation occurred pulsatively at the "step(s)", and growth occured during the following "plateau". Secondly, the experimental results with various (smooth) decompression rates were compared to the natural product. The product is characterized by high water content (ca. 2.5 wt.%; Miyagi et al., 2001) in matrix glass, so that we have proposed that the water content was "frozen" (fixed) at a much deeper level (ca. 2$\sim$3km) than the proposed aquifer (several tens to hundreds meters in depth) (Tomiya et al., 2001). The product is also characterized by many small bubbles (less than several tens of microns in diameter). Our decompression experiments show that high decompression rate causes high water content in matrix glass and domination of small bubbles (the slope of BSD plot is steep). Thus, the characteristics of the 2000 product of Usu volcano can be explained by a high decompression rate during its ascent.

URL: http://staff.aist.go.jp/a.tomiya/tomiyae.html

V51L-02 1035h

The Permeability of Volcanic Rocks: Experimental Data, Modelling and Textural Influence

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The gas permeability of volcanic rocks may influence eruptive processes. The transition from a quiescent degassing dome to rock failure (fragmentation) is likely to be influenced by the rock's permeability, which affects the speed by which a gas overpressure in vesicles is reduced in response to decompression. Using a modified setup of the fragmentation bomb we measure unsteady-state gas flow through porous samples at a high initial pressure differential. After sudden decompression above the rock cylinder, pressurized gas flows through the sample. Two pressure transducers record the pressure signals above and below the sample, whereas the exponentially decreasing trend in the lower space delivers the basis for the permeability determination. To explain the pressure evolution in the high-pressure chamber we developed a transient filtration model that takes into account compressibility of the gas phase, non-linear friction law and gas removal from the chamber through the porous sample. The recorded pressure drop at the upper transducer was used as a boundary condition at the top of the sample. Using the lower end of the pressure curve the linear permeability of the sample was calculated to get the best fit to the data at low pressure drops. Then the non-linear term was added to get the best fit for the whole time interval of the experiment. It was found that the best non-linear fit for the data occurs when the friction coefficient is inversely proportional to the square root of the Reynolds number. The coefficient also depends on the porosity of the sample as a power law function. Measured permeability data show roughly a logarithmic relationship between porosity and permeability. An influence of the pore spaces texture on the degassing behavior of the rock is evident. Our preferred interpretation of the results is a combination of two different but overlapping effects; we propose that at low porosities, gas escape occurs predominantly through microcracks or elongated micropores, whereas at higher porosities, the influence of vesicles becomes progressively stronger as they form an increasingly connected network.

V51L-03 1050h

Phase Equilibria and Kinetic Crystallization Experiments on the Inyo Domes Rhyolite

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Textural characterization of volcanic materials is a common approach used to decipher the conditions of magma ascent, prior to and during eruption. Such an approach is based on the well-established link between magma devolatilization and crystallization. Understanding of the functional relations between degassing and the kinetics of feldspar crystallization has advanced through experimental decompression of natural rhyolitic materials (e.g., Hammer and Rutherford, 2002), thus allowing comparisons between natural and synthetic textures to be used as a geospeedometer. Similar parameterizations of the growth of mafic silicates in silicic melts are sparse, and kinetic information (e.g., growth and nucleation rates) on the crystallization of pyroxene in rhyolitic melts are completely lacking. In light of the common presence of clinopyroxene in groundmass glasses of intermediate volcanic rocks and the abundance of this phase in microlite populations of many pyroclastic and effusive obsidians, we investigate the kinetics of clinopyroxene crystallization in response to isothermal decompression of the Inyo rhyolite. Isothermal decompression experiments are conducted on the low-Ba member of the Inyo rhyolite at H_2O-saturation, 750°C, Pi=200 MPa, and NNO+1; initial conditions are guided both by previous studies and new constraints on the H_2O-saturated stability regions of the natural mineral paragenesis determined by phase equilibrium experiments run over broad ranges in P (200 to 50 MPa) and T (700 − 900°C). Decompression paths involve an equilibration period (4-7 days) followed by multiple-step pressure drops of equal size (16 to 30 MPa) and duration, to varying final pressures (167 to 4.4 MPa). Integrated decompression rates vary from 0.045 MPa/min to 0.004 MPa/min, corresponding to total run durations ranging from 3 to 24 days. The observed crystallization sequence is: Fe-Ti oxide, cpx, biotite, plagioclase. In 3 and 6 day runs, clinopyroxene exhibits both low number densities ($<10^7/cm^3$), and average size (l 4 microns); such textures are indistinguishible from those produced in phase equilibrium experiments at initial P and T. By contrast, longer duration runs (12 and 24 days) produce significant shifts in the number and size distribution of clinopyroxene. In 12 day runs, pyroxene number increases by a factor of 9 over the initial value ($<10^7/cm^3$), while the mean crystal length increases by approximately 3 microns over the decompression interval. These textural shifts, combined with the temporal scale of experiments, imply an average nucleation rate of approximately $9x10^1/cm^3s^1$ and a growth rate of about $3x10^{-6}/s^1$. Clinoyroxene number densities in natural Inyo obsidians exceed experimentally-produced values by up to 3 orders of magnitude, suggesting that the undercoolings imposed by the current experiments were insufficient to induce large degrees of supersaturation required for rapid and ubiquitous microlite nucleation. Size distributions however, match well between experiment and nature. The experimental calibration of clinopyroxene growth rate may therefore provide a valuable tool for constraining time scales of magma ascent where detailed measurements of crystal size can be made.

V51L-04 1105h

Shear Rate Dependence of the Pāhoehoe to 'A'ā Transition

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The surface morphology transition from pāhoehoe-to-'a'ā on basaltic lava flows can be used to interpret the emplacement conditions of solidified flows and predict the behavior of active flows. Investigations of this phenomenon have emphasized either the mechanical properties of the solidified crust (e.g., Kilburn, 1981), or the rheologic properties of the liquid interior

(e.g., Peterson and Tilling, 1980). In the latter, the boundary separating pāhoehoe and ‘a‘ā is represented qualitatively by an inverse relationship between apparent viscosity and shear rate. Recent investigations of the rheology dependence of the transition have revealed a critical crystallinity range at which pāhoehoe transforms to ‘a‘ā of $\phi = 0.18$ to 0.35 that can vary between flows. Here, we extend this approach to investigate the shear rate dependence of the pāhoehoe-to-‘a‘ā transition. We use a suspension of corn syrup and rice to represent lava with crystals. Suspensions of varying particle concentration ($\phi = 0.15$ to 0.40) are sheared in a Couette rheometer over a range of constant shear rates (0.1 to 2.0 s^{-1}). We describe three deformation regimes, clumping, shear zone formation, and fluid failure that produce changes in the suspension microstructure and lead to shear localization. The deformation mechanisms are imaged with digital video and quantified by tracking individual particle paths. In the presence of cooling, these shear localization may be the mechanism by which ‘a‘ā flow surfaces form. We find that the onset of each regime follows the expected inverse relationship between shear rate and suspension viscosity. We expect that the results of these experiments apply to the thermal boundary layer of a flow and thus bridge the distinct approaches taken to investigate this phenomenon. The results of these experiments can contribute to more detailed lava flow modeling and better assessment of flow dynamics from solidified lava flows.

V51L-05 1120h

Solubility of H_2O in Rhyolitic Melts at Low Pressures

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Reversal experiments of H_2O solubility in synthetic haplogranitic and natural rhyolitic melts were conducted at 700 − 1200°C and 0.098-25 MPa. H_2O contents were determined using Fourier transform infrared spectroscopy. When temperature decreases from 1000 to 700°C, the solubility of H_2O increases from 0.100 to 0.124 wt% at 0.098 MPa, from 0.99 to 1.36 wt% at 11 MPa, and from 1.46 to 2.17 wt% at 25 MPa. At 6 MPa, the solubility of H_2O increases from 0.63 to 0.77 wt% from 1200 to 850°C. Using these data and those from the literature for a total of 203 measurements, an empirical solubility model for pure H_2O fluid has been constructed for rhyolitic melt and takes the following expression: $w=(354.97P_w^{0.5}+9.585P_w-1.5095P_w^{1.5})/T+0.0012365P_w^{1.5}$, where w is water contents in wt%, $P_w=X_w^f P$ (in MPa) where X_w^f is the mole fraction of H_2O in the fluid, and T is in K. This empirical model has a 2σ relative uncertainty of 10% and is applicable to 700 − 1200°C and 0-500 MPa. It also applies to H_2O solubility in mixed H_2O-H_2 fluid at total pressure ≤300 MPa (that is, the presence of H_2 in the fluid does not affect H_2O solubility). An empirical model for mixed H_2O-CO_2 solubility is developed and consists two equations: $w=(354.97P_w^{0.5}+9.585P_w-1.5095P_w^{1.5})/T+0.0012365P_w{}^{1.5}+P_{CO2}(-0.0001102P_w^{0.5}-1.341\times10^{-5}P_w)$, $CO_2=(7507P_{CO2}-1.86P_{CO2}^2)/T+0.905P_w^{0.5}P_{CO2}+P_{CO2}(-785.3P_w^{0.5}-40.85P_w+2.291P_w^{1.5})/T$, where w is water content in wt%, CO_2 content is in ppm by mass, $P_w=X_w^f P$ and $P_{CO2}=X_{CO2}^f P$ (in MPa), where X_w^f and X_{CO2}^f are the mole fraction of H_2O and CO_2 in the fluid, and T is in K. The above equations are applicable to 700 − 1200°C and total pressure of ≤500 MPa. The 2σ relative uncertainty is 13% for the H_2O equation, and 25% for the CO_2 equation. Both empirical models are recommended for the modeling of volcanic eruptions and magma chamber dynamics.

V51L-06 1135h

Influence of halogens (F, Cl, Br, I) on lava rheology.

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Degassing of halogens from magma is an important constraint on the nature and efficiency of volatile degassing in subvolcanic systems. Fundamental information on the transport properties of halogens in melts and the melts containing halogens are required for the quantification of models dealing with disequilibrium degassing based on halogens abundances in quenched volcanic glasses. The shear viscosities of melts in the system Na-Fe-Si-O-Br-I have been determined over a wide range of temperatures (1200-400 °C) at 1 atm pressure in air. The compositions are based on the addition of Fe2O3, FeBr3 and FeI2 to a base melt composition corresponding to sodium disilicate (Na2Si2O5). Viscosities were determined using concentric cylinder and micropenetration methods and measurements span the range of 100.5 to 1011 Pa s. The chemical compositions of these melts have been analysed after viscometry determinations. The iron is fully oxidized under the conditions of the viscometry. Although Bromine and iodine are highly volatile elements in silicate melts, levels of bromine and iodine over 1 wt.% have been stabilized in these melts, presumably assisted by the presence of ferric iron. Although some volatilisation occurs during the original synthesis of these samples none occurs during viscometry. The anionic substitutions Br2O-1 and I2O-1 have very small influences on the viscosity of these melts. These effects are similar to the influence of Cl2O-1 substitution. As a consequence, minor to major element abundances of Br and I in strongly peralkaline undersaturated volcanic rocks are not likely to have a significant influence on melt viscosity. These results lead us to infer low values of diffusivity for Br and I in volcanic melts. Thus disequilibrium degassing involving Br and I is highly likely.Implications of these these putative diffusivities of Br and I in explosive volcanism will be discussed.

V51L-07 1150h

Experimental Temperature-X(H_2O)-Viscosity Relationship for Peraluminous Leucogranites, and Comparison With Synthetic Silicic Liquids

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Viscosities of liquid albite ($NaAlSi_3O_8$) and a peraluminous Himalayan leucogranite have been measured between $10^{9.0}$ and $10^{13.8}$ Pa.s for water contents between 0 and 3.4 wt.%. This leucogranite is the first naturally occurring liquid composition to be investigated over the full range of T-X(H_2O) conditions that may be encountered in both plutonic and volcanic settings (rhyolites of near-identical composition are known from Peru).
At typical magmatic temperatures of 750 °C, the viscosity of the leucogranite is $10^{11.0}$ Pa.s for the anhydrous liquid, dropping to $10^{6.5}$ Pa.s for a water content of 3 wt.% H_2O. For the same temperature, the viscosity of liquid $NaAlSi_3O_8$ is reduced from $10^{12.2}$ to $10^{6.3}$ Pa.s by the addition of 1.9 wt.% H_2O. Combined with published high-temperature viscosity data, these results indicate that water reduces the viscosity of $NaAlSi_3O_8$ liquids to a much greater degree than that of natural granitic liquids. Furthermore, the viscosity of $NaAlSi_3O_8$ liquid becomes substantially non-Arrhenian at water contents as low as 1 wt.% H_2O, while that of the leucogranite appears to be near-Arrhenian to at least 3 wt.% H_2O. Therefore the viscosity of hydrous $NaAlSi_3O_8$ liquid does not provide a good model for natural granitic or rhyolitic liquids, especially at lower temperatures and water contents.
Qualitatively, the differences can be explained in terms of configurational entropy theory because addition of water should lead to higher entropies of mixing in simple model compositions than in complex natural compositions. This hypothesis also explains why the water reduces magma viscosity to a larger degree at low temperatures, and is consistent with published viscosity data for hydrous liquid compositions ranging from $NaAlSi_3O_8$ and synthetic haplogranites to natural samples. Therefore predictive models of magma viscosity need to account for compositional variations in more detail than via simple approximations of the degree of polymerization of the melt structure.

V51L-08 1205h

Non-Arrhenian Multicomponent Melts Viscosity: Extension of the Model.

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Viscosity exerts a strong control on many magmatic and petrological processes on micro- and macroscopic scales. Furthermore, knowledge of such a property gives important constraints for structural theories of silicate melts. Giordano and Dingwell (GD)[1] recently described the viscosity of a large number of silicate melts coping a wide compositional range, on the basis of an empirical parameter (SM), sum on a molar basis of the network modifying cations. That model does not consider the contribution of the iron oxidation state to influencing the viscosity. Here, this is rectified. In this experimental study we have doubled (over 700 data) the number of viscosity determinations input into the model provided by [1] extending the compositional basis to further rhyolitic, trachytic, moldavitic, andesitic, latitic, pantelleritic, basaltic and basanitic melt compositions. The effect of Fe^{2+}/Fe^{3+} on viscosity has been expressly examined. The temperature-dependence of the new liquid compositions have been investigated at high temperature (1050-1600°C) and low temperature (616-860°C) by using a concentric cylinder apparatus and the micropenetration technique, respectively. Fe^{2+}/Fe^{3+} ratio has been determined by combining a wet chemistry technique (potassium dichromate titration) with microprobe analysis for each sample, before and after the high and low-T viscometry. Viscosity parameterization along the lines of the GD model, and incorporating the constraint that the high-T viscosities converge to a common value [2], reveal very good agreement with those calculated by [1]. Explicit redox influences appear to be small. [1] D.Giordano, D.B. Dingwell, 2003. Earth Planet. Sci. Lett. 208, 337-349; [2] J.K. Russell, D. Giordano, D.B. Dingwell, 2003, Am. Mineral. 88, 1390-1394.

V52A MCC: Level 1 Friday 1330h

Light Element Geochemistry: Insights Into High-Temperature Processes III Posters

Presiding: **A J Kent,** Oregon State University**; F von Blanckenburg,** Institute for Mineralogy, University of Hannover

V52A-0415 1330h POSTER

Hydrogen Isotope Fractionation in the System Brucite-Water at 3GPa

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Upper mantle rocks are depleted in D by $80^o/_{oo}$ relative to the oceans. As water is recycled through the upper mantle-hydrosphere system over geologic time, the offset between mantle and ocean is likely created by fractionation of isotopes during hydration of the oceanic crust and subsequent partial dehydration of subducted material. To understand how δD of the slab is modified during subduction, we need to know fractionation factors for hydrous mantle minerals at pressures and temperatures relevant to subduction. The

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