since July 7. Remarkable earthquake swarm including five earthquakes more than M5 is stretching to Kozushima Island from Miyakejima Island. From the rapid ground deformation detected by continuous GPS measurements at Miyakejima Island on June 26, magma intrusion models of two or three dikes are discussed in the south and west part of Miyakejima volcano by Irwan et al.(2003) and Ueda et al.(2003). They also estimate dike intrusions are propagated from southern part of Miyakejima volcano to western part, and finally dike intrusion is stretching to 20 km distance toward Kozujima Island. From the ground deformation detected by GPS daily solution of Nation-wide dense GPS network (GEONET), some dike intrusion models are discussed. Ito et al.(2002) estimate the huge dike intrusion with length of about 20 km and volume of 1 km3 in the sea area between the Miyake Island and Kozu Island. (And) Nishimura et al.(2001) introduce not only dike but also aseismic creep source to explain the deformation in Shikinejima. Yamaoka et al.(2002) discuss the dike and spherical deflation source under the dike, because of no evidence supported large aseismic creep. They indicate a dike and spherical deflation source model is as good as dike and creep source model. In case of dike and creep, magma supply is only from the chamber under the Miyakejima volcano. In dike and spherical deflation source model, magma supply is from under Miyakejima volcano and under the dike. Furuya et al.(2003) discuss the gravity change of Miyakejima and they conclude that the magma supply from the chamber under Miyakejima volcano is too small to explain the dike intrusion. In order to discuss the local ground deformation, Nagoya University additionally operates the local GPS network of single frequency receivers at seven sites in Kozujima, Shikineshima and Niijima. Form the vertical deformation detected on local GPS network, northward tilting is observed in Kozujima. We used Genetic Algorithm (GA) for search the model parameter of dike intrusion and fault. GA is an attractive global search tool suitable for the irregular, multimodal fitness functions typically observed in nonlinear optimization problems. We discuss mechanism of Miyakejima - Kozujima event in detail using data of 20 GPS sites near field by GA. The results suggest that magma intrusion system of the dike between Miyakejima and Kozujima changes on August 18 when a large volcano eruption occurred. Until August 18 the activity of creep fault is high and after then deflation at the point source just under the dike is active.

V51J-0413 0830h POSTER

Was Miyakejima undergoing subsidence before the 2000 caldera collapse? JERS1 InSAR results: 1992-1998

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Miyakejima volcano is a basaltic strato volcano island on the eastern edge of the Philippine Sea Plate, and was undergoing a number of eruption activities over the past centuries. In July-August 2000, the Miyakejima volcano underwent a caldera collapse, prompting many modern geodetic and geophysical measurements (e.g., Geshi *et al.* 2002; Furuya *et al.* 2003). The observation results on the pre-caldera-collapse stages are, however, limitted. Were there any precursory secular subsidence before the collapse? Though Miyazaki (1990) reported a secular subsidence at the Miyakejima, using leveling technique, there are no documented reports, to my knowledge, which employed radar interferometry to examine the ground displacements at Miyakejima. Here I will report on the results derived from the radar interferometry at Miyakejima volcano. I chose JERS-1 data (L-band HH) for the analysis, so that I could get rid of the loss of coherence; most of the Miyakejima is covered with vegetation. To remove the topographic fringes as well as to re-estimate the spatial baseline data (Rosen *et al.* 1996), I employed 10-meter resolution digital elevation map derived by Geographical Survey Institute, Japan. I could generate 24 differential interferograms at the time of writing this text. However, I do not yet recognize any significant "signals" that can be discriminated with the atmospheric "noise". There appears to be no specific subsidence pattern, which are detected in a number of other volcanos in the world (e.g., Lu *et al.* 2002; Yarai *et al.* 2002; Okuyama *et al.* 2002). I am going to show a stacked interferogram like that in Fujiwara *et al.* (1998) and to examine the existence of volcanic signals.

V51J-0414 0830h POSTER

Crustal Deformation of Iwojima Volcano Detected by SAR Interferometry and GPS Observations

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Iwojima volcano is located in the Izu-Bonin islands arc, about 1250 km south of Tokyo. Small phreatic eruptions occurred more than 15 times in Iwojima volcano since 1889. Crustal deformation has occurred on a remarkable scale at the volcano. We tried to comprehend the deformation field of Iwojima volcano by SAR interferometry and campaign GPS observation. We processed 20 different pairs of JERS-1 SAR data spanning 1992 to 1998. The concentric circular fringes around Motoyama, northeastern Iwojima Island, can be seen at most interferograms. The line of sight (LOS) displacement at the center of Motoyama was increasing constantly. In Chidoriga-hara, the southwestern Iwojima Island, the fringes patterns of the interferograms were not constant but changed episodically. We have started the GPS campaign observation since August 2002. The observation stations have been observed at 3 months interval. The shrinking of Motoyama and the inflation of Chidoriga-hara were detected by GPS observations. The largest horizontal displacement of above 7cm was observed near the Chidoriga-hara during August and November 2002. The stations around Motoyama have displaced constantly. In contrast, the speed of displacements around Chidoriga-hara is not constant but decreasing with time. These features of deformation appeared by GPS campaign observations is similar to interferograms from JERS-1 InSAR. We constructed a preliminary model for the deformation field of Iwojima. The deformation field can be explained by two sources, a deflation source beneath the center of Motoyama and a tensile fault beneath Chidoriga-hara. The location and the volume change rate of the deflation source estimated from GPS observations (-0.7×10^7m^3/year, 3.0km depth) is near the deflation source which are estimated from JERS-1 InSAR (-0.4-1.5×10^7m^3/year, 1.5-3.0km depth).

V51K MCC: 3006 Friday 1020h

Light Element Geochemistry: Insights Into High-Temperature Processes II

Presiding: **W Bach,** Woods Hole Oceanographic Institution**; T Elliott,** University of Bristol

V51K-01 1020h

Ab initio molecular orbital calculations for boron isotope fractionations on boron acids and borates

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Based on the studies of Hemming and Hanson (1992) and Palmer et al. (1987), the stable B isotopic composition (d11B) of carbonate has been used as a pH-indicator to reconstruct the paleo-pH value of seawater and the paleo-CO2 in the atmosphere (e.g. Palmer and Pearson, 2003; Sanyal et al., 2000; etc.). This promising approach is based on the basic isotope exchange reaction between B(OH)3 and B(OH)4-:
10B(OH)3 + 11B(OH)4- – 11B(OH)3 + 10B(OH) (1) The isotopic fractionation coefficient K for the above reaction is hence very important for building the relation between pH and d11B composition. However, for a long time, there has been only one calculated value given by Kakihana et al., (1977), which K=1.0194 at 25°C. Unfortunately, Kakihana et al. used a theoretical method to calculate this value without specifying its details. Hence we indeed don't know how accurate this value is. Recently, Oi (2000, 2001) has calculated the K value again by using the ab initio molecular method and a simple scaling method. His calculated K value is 1.0260. Compared to 1.0194 provided by Kakihana et al., this difference already can cause a change in predicted pH of at least 0.5 pH unit. Oi (2000) also suggested a wrong approximation method for the K values for polyboric acids and polyborates. Hence we think a careful re-calculating on this issue is needed. We calculate the isotopic fractionation K value by different approaches: the water-cluster and the simple scale factor method Oi has used. We also extend the calculations for polyborates and polyboric acids, which are important in some cases. Our results show the K value should be about 1.025 to 1.027 based on our water-cluster model. Our calculations on different temperatures and on 4-coordinated B in silicates (such as the BO4(Si(OH)3)4- cluster) can let us easily explain many experimental results.

V51K-02 1035h INVITED

Fractionation of Boron (and Lithium) Between Hydrous Fluid and Silicate Melt: Diffusion, Contamination, and Orphaned Experiments

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We have measured the isotopic fractionation of boron between hydrous fluid and basaltic and rhyolitic melt using boron rich (approx. 2000 ppm B) anhydrous starting glasses. The results showed that heavy boron was preferentially partitioned into the fluid, even at high temperatures. We are now attempting reversal experiments by equilibrating B-rich hydrous fluid with B-poor silicate melts. A rhyolitic run product most recently recovered (100MPa, 900C, 48 hours) was mounted in epoxy and analyzed by SIMS for H, Li, B, and B isotopes. At the fluid-melt interface, boron concentrations were influenced by B-rich phases on the meniscus presumably quenched from the fluid. At distances of 10 to 100 microns from this interface the boron concentration dropped from approx. 600 ppm to 9 ppm, respectively (the initial B content of the rhyolite) while the H content was constant (3.2 wt.%) throughout. The boron isotope ratios become lighter with decreasing B content. This experiment 1) shows that the diffusion of boron is slow (<1E-13m2/s), but is >10000x faster than in anhydrous systems, and 2) confirms that hydrous silicate liquids concentrate the light isotope of B compared to hydrous fluid. We have also examined older experiments (performed for other purposes) to see if the boron and/or lithium contents and isotope ratios of these melts (equilibrated with hydrous fluids) can help us understand the high-temperature behavior of these light elements. For example, our earlier experiments measuring boron isotope fractionation between Li-rich (3400 ppm Li) macusanite rhyolite and hydrous fluid also show significant Li loss to the fluid allowing the determination of a fluid melt partition coefficient (D(Li) fl/melt) of 1.7 at 500 MPa. However, experiments on MORB glass containing initially 6 ppm Li reveal a gain of 1000 ppm Li during the run. Similar contamination of piston cylinder and internally heated experiments have been observed for boron as well as lithium. For example, in a study of D and H diffusion in rhyolite melt by (1), a lithium profile was also observed, with an implied diffusion coefficient near 1E-11m2/s. In contrast to these experiments, the above study on rhyolite showed a slight decrease in Li content in the melt implying a D(Li) fl/melt of 0.5 at 100 MPa. This Au capsule was cleaned in HF followed by sonication in a degreasing solvent, thereby minimizing light element contamination. Capsules from earlier experiments (Au, AuPd, AgPd) that were not degreased all show extreme light element contamination. Complementary experiments on boron fractionation between andesite and hydrous fluid are in progress. (1) Stanton, T. (1990) PhD Thesis, ASU.

V51K-03 1050h INVITED

Stable Chlorine Isotopes in Ocean Crust Processes

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The study of natural variations of Cl isotopic composition in ocean crustal rocks has large potential to further our understanding of geochemical cycling of volatiles and elements soluble in saline aqueous solutions. Studies of oceanic basalt suites to date confirm that Cl abundances are highly sensitive to the addition of saline components - either from addition of subduction-related volatile fluxes in back-arc basins

and volcanic arcs or via interaction between magmas and Cl-rich seawater-derived components during melting, magma storage and transport. Recent data suggest that δ^{37}Cl is much more variable in the marine environment than originally thought, with strongly negative δ^{37}Cl values (down to -7.5 $^{o}/_{oo}$) in marine pore waters and positive values (up to +7 $^{o}/_{oo}$) in hydrothermal fluids from oceanic spreading centers. Moreover, mantle-derived magmatic rocks reveal large variations in δ^{37}Cl (-3 to +11 $^{o}/_{oo}$), reflecting mantle heterogeneity as well as assimilation of exogenic Cl by crystallizing magmas. The large isotopic variation in low-Cl basalts has been explained by isotopic heterogeneities of the mantle, with very light δ^{37}Cl values in rocks from the southwest Chile Ridge that have island arc geochemical affinities and heavy δ^{37}Cl values in Reykjanes Ridge samples (Stewart, 2000, PhD Thesis, Duke University). The inference is that a slab-flux carries a negative δ^{37}Cl signature while recycled ocean crust in mantle plumes carries a strongly positive δ^{37}Cl signature, although this is not well constrained at present. Preferential release of isotopically light Cl from the dewatering sediments is suggested by pore water data from the Barbados and Nankai accretionary prisms with δ^{37}Cl values down to -7.5 $^{o}/_{oo}$ (Ransom et al. 1995, Geology, 23, 715). Volcanic fumaroles also appear to have negative δ^{37}Cl values. If this is the case then residual Cl in the subducting slab should become isotopically heavier as ^{35}Cl is preferentially released in the shallow subduction zone. The depleted MORB mantle is believed to have a δ^{37}Cl between 4 and 7 $^{o}/_{oo}$, similar to C1-chondrite (Magenheim et al., 1995, EPSL, 131, 427). MORB with high Cl and Cl/K tend to have δ^{37}Cl close to 0 $^{o}/_{oo}$, which has been explained by contamination of basaltic magmas with seawater-derived Cl. However, the most evolved ferrobasalts and andesites from oceanic spreading ridges have negative δ^{37}Cl values, down to -1.7 $^{o}/_{oo}$ (Magenheim, unpublished data). Together with data for oceanic gabbros, the δ^{37}Cl-[Cl] data for these highly evolved rocks form a trend that could be explained by an AFC-like process, although the fact that the trend extends to negative δ^{37}Cl values cannot be reconciled with batch mixing of magma and salt or brine. Rather, it indicates that ^{35}Cl is preferentially incorporated into the magma and may be related to diffusive exchange between Cl in brine pools above the melt lens of an axial magma system. A more comprehensive global dataset as well as spot analyses of Cl isotope ratios by IMP-SIMS (e.g., of melt inclusions) and the combination of δ^{37}Cl with other stable isotope systems (B, Li, O, H) are required before these tentative models for global chlorine cycling and crustal assimilation at spreading ridges can be rigorously evaluated.

V51K-04 1105h INVITED

Advantages of Secondary Ion Mass Spectrometry (SIMS) for Stable Isotope Microanalysis of Trace Light Elements

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SIMS has several general advantages for the determination of light stable isotopes occurring at trace element concentrations in natural samples. Ion microprobe SIMS instruments sputter nanogram quantities of material from a well defined, micrometer-sized analytical crater. The extremely small quantity of sample extracted allows analysis of very small objects, such as igneous melt inclusions. Sputter ionization of many light elements (e.g.; Li, B, S, Cl) is efficient enough ($\gg$1%) to allow precise determination of isotope ratios at elemental concentrations as low as 1 - 100 ppm. Primary bombardment of the sample is performed in close proximity to the initial extraction optics of the mass spectrometer, enabling very stable control of the ionization process. Consequently, instrumental mass fractionation (IMF) can be maintained at a very consistent and reproducible level. In situ SIMS microanalysis has a particular advantage for samples where the elemental concentration is less than that which would provoke chemical blank problems during preparation of the purified samples necessary for other types of mass spectrometry. B isotopes. Use of SIMS for the determination of $delta^{11}$B is simplified because compositionally diverse matrices are amenable to calibration for IMF with a single standard; usually a high silica glass containing 100s - 1000s ppm total B[1].This attribute is particularly convenient in subduction-related volcanic systems, where tephra sequences may contain a wide spectrum of major element chemistries. The combination of δ^{11}B and trace element microanalyses has been particularly valuable in these same systems. For example, the inverse correlation of δ^{11}B with LILE/Nb ratios in Neogene fallout tephra was used to infer the contribution of a metasomatized mantle wedge to the Izu Arc Front volcanics[2]. Li isotopes. For Li, IMF is more dependent on matrix chemistry, requiring a well-determined suite of standards. IMF may also drift in response to elemental mobility under ion beam charging. Nevertheless, Li ionizes (as Li+) with extremely high efficiency under O- bombardment ($\gg$10%). With careful attention to calibration and sputtering stability, δ^{7}Li may be quantitatively determined in glass or silicate mineral samples containing as little as 1 ppm total Li. Contrasting aqueous solubility behavior makes δ^{7}Li a valuable complement to δ^{11}B in the study of processes involving high temperature hydrothermal fluids. Cl isotopes. δ^{37}Cl is readily amenable to SIMS microanalysis in a variety of matrices, due to the vigorous ionization of Cl (as Cl-) under bombardment by positive primary ion beams such as Cs+. Determination of δ^{37}Cl in glassy matrices requires using a Normal Incidence Electron Gun (NEG) to compensate for sample charging. A series of well-typified standards are also essential to calibrate for IMF, which can vary up to 10 per mil relative between basaltic and rhyolitic matrices[3]. However, precise determinations of δ^{37}Cl are possible for glasses or silicate minerals with as little as 100 - 200 ppm total Cl. Further, certain natural fluids (e.g., seawater or submarine hydrothermal vent fluids) can be prepared by evaporation/integration with conductive binders, and then sputtered directly for SIMS analysis. In this manner, δ^{37}Cl can be determined in microliter fluid aliquots, containing as little as 1 microgram of total Cl[4].

[1]Chaussidon, M. et al, 1997, GSNL 21(1), 7-17; [2]S.M.Straub and G.D.Layne, 2002, EPSL, 198, 25-39; [3]A.V.Godon et al, 2001, EOS, 82(47), F1392; [4]W.Bach et al, 2002, EOS, 83(47), V61B-1367.

V51K-05 1120h

Why is the Ocean Heavy?

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The hydrogen isotopic ratio of the oceans (δD=0$^{o}/_{oo}$) is heavier than that of the bulk Earth (δD=-40$\pm$20$^{o}/_{oo}$) and the upper mantle (δD=-75$\pm$5$^{o}/_{oo}$). To investigate the process responsible for making this isotopic difference between the oceans and the Earth s interior, we have calculated forward models of water exchange between the mantle and the surface through Earth history. We use two functions for oceanic crust production through time: (1) proportional to radioactive heat production (low mantle overturn rates) and (2) proportional to the square of the heat production (high overturn rates). The volume of the mantle exchanging with the surface is varied from the upper mantle (above 660 km) to the whole mantle. The calculations start with all the water initially present in the mantle. Early rapid degassing is required to satisfy constraints given by xenon isotopes. Fluxes of mantle degassing at mid-ocean ridges and regassing at subduction zones must approach steady state for at least the Phanerozoic, as constrained by near-constancy of continental freeboard during this time. In our calculations, degassing of one ocean mass is achieved rapidly (in $\sim$1 Ga), except in the case of whole mantle convection at low overturn rates, in which case the xenon and freeboard constraints are not met. Calculated δD of the ocean also reaches steady state after the first Ga. The constancy of the D/H ratio of the ocean through time is consistent with δD profiles of modern to Jurassic oceanic crust and ophiolites of variable age. Results are insensitive to assumptions about initial distributions of water; i.e., they also hold if all water is initially at the surface or if there is large initial isotopic disequilibrium between the surface and the mantle. Model results show that the ocean/upper mantle difference in δD is set by fractionation at subduction zones, reflecting vigorous exchange between the two reservoirs. They also require that dehydration of subducted altered oceanic crust (δD=-40$^{o}/_{oo}$) is accompanied by a decrease of 35$\pm$5$^{o}/_{oo}$ in δD. This places a strong constraint on the dehydration process and the residual hydrous phases carrying water into the mantle. Our calculations strongly suggest that both the upper mantle and oceans have been profoundly affected by recycling of water and that water in the upper mantle is dominated by a recycled component. They also may imply that oceanic basalts with high δD relative to typical MORB have a larger component of primordial H_2O.

V51K-06 1135h

Magnesium Isotopes in the Earth and Moon by Laser Ablation MC-ICPMS

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Magnesium isotopes potentially offer new insights into a diverse range of high temperature processes ranging from evaporation and condensation in the solar nebula, to melting and metasomatism in the mantle, and hydrothermal circulation. For example, volatility-related Mg isotopic variations of up to 10 per mil/amu occur in early nebular phases that are interpreted as evaporation residues, and surprisingly large variations (up to 3 per mil/amu) have been reported recently for the terrestrial mantle. We have measured the Mg isotopic compositions of olivine phenocrysts from primitive ocean island and island arc picrites, and Apollo 12 mare basalts by laser ablation multi-collector ICPMS to investigate possible source effects in the mantle, and to search for evidence of temperature-dependent isotopic fractionation during formation of the Moon. Analyses were obtained with a Neptune MC-ICPMS operated in medium resolution mode, and an excimer laser (5 Hz, 50 micron spot diameter, 80 mJ/pulse). 26Mg was measured at an off-center peak position to avoid interference from 12C-14N. Replicate analyses of mantle olivines demonstrate an analytical precision of better than 0.2 per mil/amu (1 sigma stdev) using the standard-unknown bracketing method. Picritic olivines (Fo88-90) from Hawaii and Vanuatu show a range in Mg isotopic composition of about 0.5 per mil/amu relative to San Carlos olivine. No systematic differences that could be related to variations in source composition or extent of melting were found. In contrast, olivines from Apollo 12 picritic mare basalts show an apparently larger range of isotopic compositions of about 1.5 per mil/amu. The measured Mg isotope ratios of these phenocrysts vary systematically to heavier values with decreasing Fo content, from +0.2-0.4 per mil/amu (relative to San Carlos olivine) in the most primitive phenocrysts (Fo70-75) to +1.5 per mil/amu in the most evolved olivines (Fo45-50). To examine the possibility that the apparent isotopic variations in the lunar olivine actually reflect a composition-dependent analytical effect, we measured the Mg isotopic compositions of experimentally crystallized olivines with a similar range of major element compositions (Fo50-90) and prepared from a common starting material. These results demonstrate a matrix effect of approx. +0.3 per mil/amu per 10 Fo units, which reproduces the range of compositions observed in the lunar samples. The trend to heavier apparent Mg isotopic compositions with increasing iron content in the olivine is consistent with a space-charge effect in the MC-ICPMS, although an ablation-related mechanism is also possible. When corrected for matrix effects, the Mg isotopic composition of the Moon is identical to the Earth's mantle, placing strong constraints on any volatility-related fractionation that could have occurred during formation of the Moon.

V51K-07 1150h

Assessing Kinetic Mass Fractionation of Si Isotopes Measured by High Resolution MC-ICP-MS.

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The introduction of silicon into a MC-ICP-MS via a desolvating nebuliser system is a recently developed method to measure Si isotope abundances with high precision and accuracy (Cardinal et al., 2003). Silicon is the most abundant rock-forming element. This technique allows for the investigation of Si isotope fractionation between different mineral phases in terrestrial and extra-terrestrial materials. Understanding the distribution of Si isotopes between different terrestrial reservoirs and thus the Si isotope terrestrial mass-balance is fundamental for the development of Si isotopes as a tracer of biogeochemical cycles. Furthermore, like oxygen and magnesium, Si has three stable isotopes, such that mass-dependent and -independent processes can be assessed. However, a terrestrial mass fractionation line has yet to be characterized for Si isotopes. The measurement of Si isotopes by MC-ICP-MS is limited by large isobaric interferences, particularly on mass 30, which can only be separated at a mass-resolution of at least $\sim$1500. On the high resolution Nu1700 MC-ICP-MS these interferences can all be separated, and we are thus able to measure all three isotopes ^{28}Si-^{29}Si-^{30}Si isotopes directly. A range of standards and natural samples have been measured which define a single, purely kinetic mass fractionation line (e.g. a slope of 0.5092 for measured ln(^{30}Si/^{28}Si) versus ln(^{29}Si/^{28}Si)). However, not only do different cone geometries cause different mass-fractionation factors but the standard wide-angle cones also cause

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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