

Mineral-Hosted Melt Inclusions How do we read the stories they have to tell?

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Welcome to Mineral-Hosted Melt Inclusions: How do we read the stories they have to tell?

The study of mineral-hosted melt inclusions traces its origins all the way back to the mid-nineteenth century. In 1857, Henry Clifton Sorby recognized that the presence of "glass cavities" demonstrates that the host crystals had a magmatic – rather than an aqueous – origin and used this observation to argue that granite is the product of fusion rather than precipitation from a fluid. Today, these small pockets of silicate melt entrapped within growing mineral grains are used to study everything from mantle heterogeneity to pre-eruptive magmatic volatiles and the oxidation state of the upper mantle. The information recorded in melt inclusions is unique because entrapped melts are physically shielded from most interactions with the external environment by the host mineral. Melt inclusion studies require careful sample preparation, application of state-of-the-art analytical methods, and meticulous attention to potential artifacts related to post-entrapment processes. As analytical techniques progress and our understanding of post-entrapment processes evolve, it is important that the rapidly growing melt inclusion community periodically assess the state of the field.

Over the next two days, fifteen invited speakers will discuss the state of our knowledge with respect to mineral-hosted melt inclusions. Topics range from the origin and fidelity of mineral-hosted melt inclusions to the application of state-of-theart micro-analytical techniques to quantify their compositions. Each talk will be followed by a discussion session intended to promote interaction among all the attendees. One objective is to develop guidelines for publication of data from melt inclusion studies to be summarized in a collegial manuscript that the organizers will submit for publication shortly after the workshop. As the workshop progresses, it is instructive to remember the words used by Sorby to close his 1857 address before the Geological Society of London: "I argue that there is no necessary connexion between the size of an object and the value of a fact, and that, though the objects I have described are minute, the conclusions to be derived from the facts are great."

Anne-Sophie Bouvier, Glenn Gaetani, Estelle Rose-Koga, and Paul Wallace Co-organizers

Program

10 August - Friday

Location: Clark Lab Building, Room 507

5:00-8:00 pm

Icebreaker

11 August - Saturday

Location: Clark Lab Building, Room 507

7:30-8:30 am	Breakfast
8:30-8:45 am	Introduction
8:45-9:45 am	Keynote: Leonid Danyushevsky, University of Tasmania
	Trapping of, and post-entrapment processes in, the melt inclusions; reheating experi- ments with melt inclusions; and Fe-Mg exchange in melt inclusions in olivine.
9:45-10:00 am	Discussion led by Roger Nielsen, Oregon State University
10:00-10:30 am	Bob Bodnar, Virginia Tech
	Selection and characterization of melt inclusions: The first step in a melt inclusion study
10:30-10:45 am	Discussion led by Roger Nielsen, Oregon State University
10:45-11:00 am	Coffee break
11:00-11:30 am	Katherine Kelley, University of Rhode Island
	The thing you do last: Trace element analyses of melt inclusions by LA-ICP-MS
11:30-11:45 am	Discussion led by Horst Marschall, Goethe Universität Frankfurt
11:45-12:15 am	Graham Layne, Memorial University
	Secondary Ion Mass Spectrometry (SIMS) for In Situ Microanalysis of Melt Inclusions
12:15-12:30 am	Discussion led by Horst Marschall, Goethe Universität Frankfurt
12:30 – 1:30 pm	Lunch
1:30-2:00 pm	Alex Nichols, University of Canterbury, New Zealand
	Using FTIR to analyse dissolved water and carbon dioxide in melt inclusions
2:00-2:15 pm	Discussion led by Peter Michael, University of Tulsa

11 August - Saturday (continued)

2:15-2:45 pm	Lowell Moore, Virginia Tech
	Fluid bubbles in mineral-hosted melt inclusions
2:45-3:00 pm	Discussion led by Peter Michael, University of Tulsa
3:00-3:15 pm	Coffee break
3:15-3:45 pm	Margaret Hartley, University of Manchester
	XANES analyses of mineral-hosted melt inclusions: redox evolution in magmatic systems
3:45-4:00 pm	Discussionled by Muriel Laubier, Université Clermont Auvergne
4:00-4:30 pm	Yves Moussallam, Institut de Recherche pour le Développement
	Redox change during magma ascent; Observations and implications
4:30-4:45 pm	Discussion led by Muriel Laubier, Université Clermont Auvergne
4:45-8:00 pm	Posters
Evening free	

12 August - Sunday

Location: Clark Lab Building, Room 507

8:00-9:00 am	Breakfast
9:00-9:30 am	Terry Plank, Lamont Doherty Earth Observatory, Columbia University
	Diffusion of water through olivine: implications for melt inclusion flaelity
9:30-9:45 am	Discussion led by Mike Garcia, University of Hawaii
9:45-10:15 am	Megan Newcombe, Lamont Doherty Earth Observatory The melt inclusion record of the countdown to eruptions
10:15-10:30 am	Discussion led by Mike Garcia, University of Hawaii
10:30-10:45 am	Coffee break
10:45-11:15 am	Kei Shimizu, Carnegie Institution for Science Partial degassing and regassing of CO ₂ in CO ₂ undersaturated mid-ocean ridge basalts
11:15-11:30 am	Discussion led by Oded Navon, Hebrew University
11:30-12:00 pm	Janne Koornneef, Vrije Universiteit Amsterdam Combined Sr-Nd-Pb isotope analyses of individual melt inclusions to reveal extreme source heterogeneity
12:00-12:15 pm	Discussion led by Oded Navon, Hebrew University
12:15– 1:15pm	Lunch
1:15-1:45 pm	Jay Thomas, Syracuse University Making melt inclusions: an experimental approach to study syn- and post-entrapment compositional modifications
1:45-2:00 pm	Discussion led by Emily Johnson, New Mexico State University
2:00-2:30 pm	Ayla Pamukcu, Woods Hole Oceanographic Institution Melt inclusion faceting: What - and how - can we learn from melt inclusion morphologies?
2:30-2:45 pm	Discussion led by Emily Johnson, New Mexico State University
2:45-3:00 pm	Coffee break
3:00-3:30 pm	Madison Myers, Montana State University Inferring magma ascent timescales and reconstructing conduit processes in rhyolitic explosive eruptions using diffusive losses of hydrogen from melt inclusions
3:30-3:45 pm	Discussion led by Julie Roberge, ESIA-Ticoman, Instituto Politecnico Nacional
3:45-5:00 pm	Summary & outline of the consensual guidelines to study MI
5:15 pm	Large passenger bus available for trip back to Boston will depart from Clark Lab, and drop off at the Goldschmidt venue, the Hynes Convention Center.

Abstracts – Oral Presentations

Trapping of, and post-entrapment processes in, the melt inclusions; reheating experiments with melt inclusions; and Fe-Mg exchange in melt inclusions in olivine.

Leonid Danyushevsky, University of Tasmania

The presentation will provide a brief overview of the underlining principles of the melt inclusions technique, including trapping mechanisms of melt inclusions, the nature and causes of the postentrapment modification to the phase and chemical compositions of melt inclusions, and the behaviour of melt inclusions in reheating experiments.

This will be followed by a detailed discussion of Fe-Mg exchange between melt inclusions in olivine with their host phenocrysts as a function of cooling rate and extent of fractionation during magma crystallisation. Cooling of an inclusion after trapping results in crystallisation of olivine from the trapped melt, forming an olivine rim on the walls of the inclusion. In the case of fractional crystallisation when the composition of the host phenocrysts does not change, the forming rim is progressively enriched in Fe and depleted in Mg, i.e., its forsterite component is decreasing, resulting in a compositional gradient within the rim. The existence of this compositional gradient causes re-equilibration of the inclusion with its host. This re-equilibration is achieved by diffusion of Fe out of, and Mg into the

initial volume of the inclusion. This leads to a rapid decrease in Fe content of the residual melt inside the inclusion, a process referred to as "Fe-loss" by Danyushevsky et al. (2000). Conversely, if an olivine grain containing a melt inclusion is heated over the temperature of inclusion entrapment, host olivine around the inclusion would melt, increasing the Mg# of the melt inside the inclusion and resulting in disequilibrium between the melt and host olivine. This leads to reequilibration of the melt with the host, which is achieved by diffusion of Fe into, and Mg out of the melt inside the inclusion. This leads to a rapid increase in Fe content of the melt, a process that can be referred to as "Fe gain."

Known values of the diffusion coefficient for Fe-Mg inter-diffusion in olivine allow for calculations of residence time of individual phenocrysts within the magmatic system from the time of entrapment of inclusions to the onset of rapid cooling on eruption. Implication of the derived residence times of individual phenocrysts to the dynamics of magmatic plumbing systems will be discussed.

Selection and characterization of melt inclusions: The first step in a melt inclusion study

Robert Bodnar, Virginia Tech

The validity of interpretations based on data from melt inclusions depends on the extent to which the inclusions record and preserve the composition of the melt at the time of trapping. Moreover, use of melt inclusion data in petrogenetic modeling requires an understanding of the temporal relationships between the inclusions and other physical and geochemical features of the magmatic system. Here, we will summarize various protocols for selecting and characterizing melt inclusions, and examine consequences of failure to understand temporal relationships of melt inclusions to each other on petrogenetic interpretations.

The thing you do last: Trace element analyses of melt inclusions by LA-ICP-MS

Katherine Kelley, University of Rhode Island

Advances in micro-analytical geochemical techniques have, over the last two decades, increased the breadth of data and consequently the utility of melt inclusion studies as windows into magmatic systems. Since the late 1990's, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become an established and preferred method for determination of trace element abundances in melt inclusions and their host minerals. Other micro-analytical methods (e.g., electron microprobe, ion microprobe, synchrotron X-ray spectroscopy) may also deliver comparable trace element data, but LA-ICP-MS remains the most rapid and inexpensive of these methods and covers the largest range of elements. The destructive nature of the method, however, remains a key disadvantage, which is why this kind of analysis is usually the last to be done on a melt inclusion.

This presentation will provide a tutorial in the basics of LA-ICP-MS methods, with particular emphasis on trace element analyses of glass inclusions and their host minerals. We will compare different approaches to data handling, and assess the quality of LA-ICP-MS data against whole-rock ICP-MS trace element data. We will further explore some examples of studies that make use of trace element data in melt inclusions to probe a variety of petrological processes.

Secondary Ion Mass Spectrometry (SIMS) for In Situ Microanalysis of Melt Inclusions Graham Layne, Memorial University

SIMS is now well recognized as a versatile tool for melt inclusion analysis. In addition to quantitative trace element and volatile (e.g., H₂O, S, Cl, F, CO₂) analysis, a specific strength of SIMS is sub-per mil precision and reproducibility for a wide variety of light stable isotope ratio determinations.

In general a lateral spatial resolution of 10 μ m (with sputtered pit depths of less than a few μ m) may be achieved for individual analyses (total sample size < 10 ng). In situ SIMS microanalysis is thus compatible with the size range of many melt inclusion populations. Samples commonly require only simple preparation of a flat polished surface that exposes the melt inclusions, thus preserving information on both host minerals and textural context - although samples and mounting media must be compatible with the ultra-high vacuum of the SIMS sample chamber. A thin conductive layer, usually Au, is applied to the sample surface to mitigate charging during analysis. Balanced electron flooding may also be required if using Cs⁺ primary ion beams.

SIMS instruments are designed to resolve the complex mass spectra of secondary ions produced by the ion beam sputtering of solid materials. SIMS also inherently accumulates a time-resolved depth profile, allowing the selective elimination of signals from defects or micro inclusions. Specific challenges that need to be addressed for quantitative SIMS analysis of melt inclusions include; 1) Provision of well characterized matrix-specific reference materials for the calibration of instrumental mass fractionation (IMF), 2) Elimination of sample surface contamination and other exotic contributions through pre-sputtering and other means. This is especially important for the analysis of CO₂ or δD , and 3) Calibration of accuracy and stability of ion detectors (multiple array or single) over an adequate dynamic range. This can be especially important for stable isotope determinations on trace element analytes (e.g., δ^7 Li, δ^{11} B, δ^{37} Cl).

Using FTIR to analyse dissolved water and carbon dioxide in melt inclusions

Alex Nichols, University of Canterbury, New Zealand

Transmitted light micro-Fourier-transform infrared spectroscopy (FTIR) has been widely used to undertake in-situ analysis of dissolved water and carbon dioxide in silicates, including melt inclusions. Its advantages are that it is relatively cheap, easy to use, non-destructive during analysis, and can measure volatile speciation. However, there are various drawbacks. Preparing inclusions for analysis is destructive, difficult and laborious; typically, you have to prepare a sample wafer in which the inclusions are exposed and polished on both sides. Inclusion thickness and a composition-specific molar absorption coefficient are required. Thickness is difficult to measure and a range of molar absorption coefficients have been constrained for similar compositions, both of which introduce uncertainty. Over the last decade several developments have occurred to circumvent these issues. I will outline some of these, which include using spectral interference fringes to measure thickness at the analyzed spot, attempts to simplify sample preparation by analyzing through the host crystal, analyzing in reflected light and using microattenuated total reflectance. An explanation for the range of molar absorption coefficients for a given composition will be provided, together with the method to constrain an accurate value. I will also outline how micro-FTIR can provide insight into future melt inclusion research, applying synchrotron radiation, mapping and imaging capabilities.

Fluid bubbles in mineral-hosted melt inclusions

Lowell Moore, Virginia Tech Department of Geosciences

Melt inclusions (MIs) are mixtures of glass, fluid, and/or minerals that occur within crystals which trapped droplets of melt during growth within volcanic or magmatic systems. As such, MIs are particularly useful for constraining the volatile abundances of pre-eruptive melts which degas during eruption. However, internal processes of cooling, crystallization, and decompression within MIs typically cause volatiles to exsolve from the melt into a separate fluid bubble. As a result, it is necessary to account for fluid bubbles that have formed within MIs when determining the volatile content of the trapped melt.

A range of methods have been developed to account for bubbles within MIs. In some cases, the inclusionbearing host mineral may be experimentally heated to the temperature at which the inclusion contains only a single, homogeneous melt and then rapidly quenched so that the MI contains only a glass. Alternatively, the bulk volatile content of naturallyquenched MIs which contain only glass and a bubble may be determined by analyzing each phase individually (e.g., using Raman and ion probe microanalyses), and then applying a mass balance calculation. For such glassy MIs, the amount of fluid that has exsolved into the bubble may also be estimated based on the composition of the glass and host mineral phases and known volatile-melt solubility relationships.

The Raman mass-balance approach requires significantly less time and fewer resources compared to the experimental approach, but it is less precise because of uncertainty associated with the mass balance calculation. Other challenges associated with this approach include quantifying volatile abundances in carbonate and other volatile-bearing daughter phases on the surface of the bubble and identifying instances of MI decrepitation and heterogeneous entrapment.

XANES analyses of mineral-hosted melt inclusions: redox evolution in magmatic systems

Margaret Hartley, University of Manchester

Co-authors: Oliver Shorttle, John Maclennan, Marie Edmonds, Yves Moussallam

Mineral-hosted melt inclusions have long been exploited for their capacity to retain chemical information about a magma's history, from mantle source through crustal storage to eruption at the surface. The redox evolution of magmatic suites can theoretically be tracked using X-ray absorption nearedge structure (XANES) spectroscopy at the iron and sulfur K-edges to measure the oxidation state of melt inclusions. However, melt inclusions have been shown to be permeable to fast-diffusing elements such as hydrogen, and their retention of initial oxygen fugacities may be similarly diffusion-limited. Iron and sulfur in basaltic glasses are also susceptible to photooxidation or reduction when exposed to radiation. To what extent are melt inclusions reliable archives of redox changes in volcanic plumbing systems?

Olivine-hosted melt inclusions in rapidly quenched tephra samples from the 1783 AD Laki eruption,

Iceland, appear to preserve the redox conditions of their pre-eruptive magma. However, the melt inclusions behave as open systems with respect to magma mixing and degassing. Mantle-derived redox heterogeneity present at the time of inclusion trapping has been overprinted as melt inclusions approach equilibrium with their external environment. Similarly, melt inclusions from glassy lava selvages are more reduced than their tephra-hosted counterparts: they have approached equilibrium with their carrier lava, which has been reduced by sulfur degassing. The decoupling of melt inclusion archives of fO2, major and trace element chemistry masks associations between fO2, magmatic differentiation and mantle source heterogeneity – unless the assembly of diverse magmas and their melt inclusions is rapidly followed by eruption. Nonetheless, melt inclusions can be used to confirm relative differences in mantle oxidation state between different magmatic systems.

Redox change during magma ascent; Observations and implications

Yves Moussallam, Université Clermont Auvergne, Laboratoire Magmas et Volcans, IRD, France

Co-authors: Clive Oppenheimer, Nial Peters, Margaret Hartley, Ian C. Schipper, Bruno Scaillet, Marie Edmonds, Phil Kyle

The oxidation state of volcanic gases dictates their speciation and hence their reactivity in the atmosphere. It has become increasingly recognized that the oxidation state of a magma can be strongly affected by degassing. The oxidation state of gases will equally be impacted and the composition of gases emitted by volcanoes will therefore be function of the magma degassing history. This presentation will show results from volcanoes where the oxidation state of the magma has been tracked during degassing using Fe X-ray absorption near-edge structure spectroscopy (XANES) on extensive suites of melt inclusions and glasses. At all locations we found that a strong reduction of Fe is associated with magma ascent. At Erebus this reduction is greatest, corresponding to a fall in magmatic fO2 of more than two log units. We propose that sulfur degassing can explain the observed evolution of the redox state with ascent and show that forward modeling using initial melt composition can successfully predict the composition of the gas phase measured at the surface.

Diffusion of water through olivine: implications for melt inclusion fidelity

Terry Plank, Lamont Doherty Earth Observatory of Columbia University

Co-Authors: Elizabeth Ferriss, Megan Newcombe, Anna Barth, Erik Hauri

rising and water diffusing out of melt inclusions through the host crystal and into the degassing melt. The ability of melt inclusions to retain water

Volcanic eruption starts a race between magma

concentrations from the storage region to the surface depends on magma winning the race. The requisite rise speed is set by the diffusivity of water through the host mineral. For olivine, the rate of water loss is highly uncertain, with published measurements varying by 5 orders of magnitude. In order to address this problem, we have conducted the first laboratory experiments that dehydrate natural, oriented olivine crystals (a San Carlos olivine and a Kilauea Iki 1959 phenocryst, at 1 atm, 800-1000 °C and NNO-2.6). We use the whole-block method [1], which allows a finely-resolved time series of H profiles in all 3 crystallographic directions by FTIR. Both crystals lose water at a rate intermediate between protonpolaron (p-p) and the proton-Mg-vacancy (p-v) rates [2], with diffusion along [100] more than 10x faster than along [001]. Diffusivities between p-p and p-v are consistent with bulk diffusivity inferred

from previous experiments on melt inclusion reequilibration through unoriented olivine, as well as our own data on water zonation in untreated olivine phenocrysts. Such rapid diffusivity (logD ~ -10.5 m_2/s at 1050 °C) means that significant water loss from olivine-hosted melt inclusions may occur in hours, for phenocrysts that are 10 times bigger than their melt inclusions and for a partition coefficient for H₂O in olivine ~ 0.001. Such timescales (hours) are thought to be typical of strombolian eruptions that yield scoria commonly sampled for melt inclusion studies. Thus, one can't always assume the fidelity of melt inclusions, and knowledge of magmatic temperature, decompression rate and inclusion, host and clast size are critical parameters to document in any melt inclusion study.

[1] Ferriss et al. 2015 [2] Kohlstedt & Mackwell 1998

The melt inclusion record of the countdown to eruptions

Megan Newcombe, Lamont-Doherty Earth Observatory

Co-authors: Alexander S. Lloyd, David Ferguson, Youxue Zhang, Anna Barth, Erik Hauri, Terry Plank

We have constrained syneruptive pressuretemperature-time (P-T-t) paths of magmas using a combination of short-timescale cooling and decompression chronometers. Thermal histories of olivine phenocrysts in the last few seconds to hours of eruption can be constrained using concentration gradients of MgO inside olivine-hosted melt inclusions (MIs), produced in response to syneruptive cooling and crystallization of olivine on the inclusion walls. We have applied this technique to the study of MIs erupted by arc and ocean island volcanoes, including the sub-Plinian 1974 eruption of Fuego volcano; the 1977 fire-fountain eruption of Seguam volcano; and episode 1 of the 1959 Kilauea Iki firefountain eruption.

Of the eruptions studied so far, MIs from Kilauea record the highest syneruptive cooling rates (~103–104 °C/hr) and the shortest cooling durations (~100–101 s). The largest MIs (radii up to 170 μm) from the Kilauea and Seguam fire fountain eruptions exhibit long plateaus of approximately constant MgO across their centers, suggestive of ascent through the conduit at an approximately constant temperature (or a period of shallow magma stalling) prior to fragmentation. The high cooling rates inferred for Seguam and Kilauea Iki are consistent with air quenching over 10s of seconds upon fragmentation and eruption. MIs from Fuego record the lowest cooling rates (~102–103 °C/hr) and longest cooling durations (~102–103 s) of the studied eruptions.

The average cooling rates of MIs from the studied eruptions are negatively correlated with magma decompression rates as determined from volatile gradients in melt embayments. Our magma P-T-t constraints are in agreement with thermodynamic models that show that the dominant driver of cooling in the conduit is adiabatic expansion of a vapor phase. A corollary of these models is that, in order to drive syneruptive cooling, the magma must ascend rapidly enough to prevent significant melt-vapor segregation and crystallization.

Partial degassing and regassing of CO2 in CO2 undersaturated mid-ocean ridge basalts Kei Shimizu, Department of Terrestrial Magnetism, Carnegie Institution for Science

Co-authors: Alberto Saal, Erik H. Hauri, Michael R. Perfit, Roger Hékinian

Studies of natural and experimental samples have demonstrated that CO₂ is a highly incompatible element during mantle melting. Thus, ratios such as CO₂/Ba in CO₂ undersaturated depleted mid-ocean ridge basalts (D-MORBs) have been used to estimate the CO₂/Ba ratio and carbon content in Earth's upper mantle. One potential issue with this approach is the effect of partial degassing and mixing of near fractional melts on the CO2/Ba ratios. Matthews et al. [Earth Planet. Sc. Lett. 480, 1-14, 2017] presented a partial degassing and mixing model, where near fractional melts of the mantle degas and mix in magma chamber within the crust or mantle. If CO2 undersaturated D-MORBs are generated through such process, their average CO₂/Ba ratio would underestimate that of the mantle source.

Here, we report the compositions of olivine-hosted melt inclusions and glasses from the Siqueiros and Garrett transform faults. The melt inclusions are CO2 undersaturated and highly depleted in incompatible trace element contents with CO₂/ Ba ratios of 113±48 and 86±40 for the Garrett and Siqueiros melt inclusions, respectively. We evaluate if the model by Matthews et al. (2017) can reproduce the composition of the melt inclusions. We find that, while the partial degassing and mixing model can explain the observed range in CO₂/Ba ratio of the melt inclusions, the Pearson's correlation coefficients between CO₂/trace element and 1/trace element ratios of the model does not match those observed in the Siqueiros and Garrett melt inclusions. Instead, the Pearson's correlation coefficients for Siqueiros melt inclusions may suggest that the partially degassed CO2 is re-dissolved into higher degree melts prior to mixing. Therefore, there is no net degassing of CO2 from the primitive magma represented by the Siqueiros melt inclusions; and hence, their average CO₂/Ba ratio may provide a reliable estimate of the CO₂/Ba ratio of their mantle source.

Combined Sr-Nd-Pb isotope analyses of individual melt inclusions to reveal extreme source heterogeneity

Janne Koornneef, VU Amsterdam

Co-authors: Igor Nikogosian, Lisa Hageman, Maximilian Berndsen, Manfred van Bergen, Pieter Vroon, Gareth Davies

Melt inclusions (MIs) in primitive magmatic minerals record far greater geochemical variability than host lavas and more fully reflect the heterogeneity of magma sources. Radiogenic Isotope analyses of such primary MIs in olivine provide a direct means to determine the presence of recycled crustal or sediment components at depth. To date, use of multiple isotope systems (Sr-Nd-Pb) on small (<300 μ m) melt inclusions was hampered by analytical limitations, but improved techniques now allow analyses of individual MIs.

Combined ultra-low blank wet chemistry and thermal ionisation mass spectrometry (TIMS)

techniques using 10e13 Ω resistors mounted in the feedback loop of Faraday cup amplifiers were developed that permit isotope analyses of 2 ng Sr, 100 pg Pb and 30 pg Nd. Compared to default 10e11 Ω , use of 10e13 Ω resistors results in a 10-fold improvement of the signal-to-noise ratio and more precise data for small ion beams.

We present coupled Sr-Nd-Pb isotope data on individual MIs from Italy's subduction setting that confirm that we can discriminate the presence of source components that are not resolved by bulk lava compositions. Where Sr and Nd isotope ratios largely overlap with the hosts, Pb isotope ratios show extreme variability towards two different unradiogenic end-members. The exotic unradiogenic Pb compositions requires derivation from a system that lost U with respect to Pb in an old metamorphic event and is typical for lower continental crust.

We infer the presence of components from Variscan or older basement that were emplaced into Italy's upper mantle by either delamination, sediment recycling, subduction erosion and/or slab detachment processes that acted during the complex geodynamic evolution of the Western Mediterranean. The capability to obtain isotope ratios in individual melt inclusions now permits revealing previously unrecognised mantle contaminants and allows unravelling better how geodynamic processes affect subduction recycling.

Making melt inclusions: an experimental approach to study syn- and post-entrapment compositional modifications

Jay Thomas, Syracuse University

Melt inclusions (MI) are routinely used to study magmatic processes. Important outstanding questions remain concerning the reliability of MI to provide information on pre-eruptive melt compositions. Observed compositional variations in suites of natural MI may reflect changing conditions within an evolving magma, or compositional variability may reflect (1) entrapment of unrepresentative (boundary layer) melt adjacent to a growing crystal, and/or (2) various post-entrapment modifications. Studies of natural melt inclusions have not resolved these questions unequivocally due to uncertainties concerning their complete PTX history. Experimental and analytical methods were designed to determine if MI are representative of the 'far-field' melt, and evaluate the significance of post-entrapment modifications that may alter MI compositions. Experiments were performed in piston-cylinder devices from 0.5 to 2 GPa and 700 to 900°C in the haplogranite (rhyolite)-H2O-

CO₂ system to produce melt and, in the case of volatile-saturated experiments, fluid inclusions (FI) in quartz. Starting materials and experimental PT conditions were adjusted to produce melts with prescribed CO2 and H2O concentrations. Inclusions were synthesized in quartz by fracturing and acid etching quartz wafers to produce a polycrystalline material with embayments ~15-20 µm wide that penetrated well into the interior of quartz wafers. Prepared quartz wafers were placed into capsules so that they were surrounded by melt at run conditions. During the experiments, aqueous fluid- and meltfilled embayments were trapped as FI and MI. Melt inclusions range up to 50 µm in diameter and display a wide range of shapes that are commonly observed in natural specimens. Water, CO2 and major element compositions of MI are essentially identical to the far-field melt. Efforts to experimentally induce postentrapment modifications to MI compositions are ongoing.

Melt inclusion faceting: What – and how – can we learn from melt inclusion morphologies?

Ayla Pamukcu, Woods Hole Oceanographic Institution

Co-authors: Guilherme A. R. Gualda, Mark L. Rivers, Veronique Le Roux, Glenn A. Gaetani, Alfred T. Anderson Jr.

Melt inclusions (MI) are key sources of information on magma evolution and storage. Efforts to extract such information from MI has primarily focused on their compositions; however, MI morphologies can also be mined. Namely, at magmatic temperatures, MI change shape in a prescribed way over time – from round to faceted – through dissolution and re-precipitation; thus, the degree of MI faceting can be a measure of crystallization timescales. Combining faceting times with textural and compositional data from MI and crystals can also provide constraints on parameters such as crystal growth and magma recharge/mixing rates. Determining faceting times requires careful characterization of MI textures. Optical measurement of critical parameters (size, shape, position) results in relatively crude estimates; thus, we have developed x-ray tomographic (XCT) methods to better quantify these features in 3D. During image processing, we define a 3D convex hull that encases an MI and fit an equal volume ellipsoid to it. We compute the volume moved in faceting, used in the faceting time calculation, as that of the ellipsoid protruding from the hull. We also assess the size and position of MI in crystals. For quartz-hosted MI, where glass-host density contrast is low, synchrotron-based propagation phase contrast XCT is used to enhance object edges, and image processing is performed using edge detection rather than grayscale thresholding. Preliminary work on olivine-hosted MI, where glass-host density contrast is greater, suggests desktop XCT systems may work for studying these systems. We determined quartz crystallization times and growth rates in three large-volume systems (Bishop Tuff, Oruanui, Ohakuri-Mamaku). Results suggest short timescales (101-103 a), akin to those from other methods, and average quartz growth rates of 10-12 m/s. We are now undertaking heating experiments to establish a faceting calibration for olivine-hosted MI, where the rate-limiting diffuser is unknown.

Inferring magma ascent timescales and reconstructing conduit processes in rhyolitic explosive eruptions using diffusive losses of hydrogen from melt inclusions

Madison Myers, Montana State University

Co-authors: Paul J. Wallace, Colin J.N. Wilson

We have developed a hydrogen diffusion-based method in quartz to interrogate conduit processes during initial explosive phases from three calderaforming events: (1) the episodic Oruanui eruption, Taupo NZ (530 km³, 25.4 ka), (2) the continuous Bishop eruption, Long Valley (650 km³, 0.77 Ma) and (3) the episodic Huckleberry Ridge eruption, Yellowstone (2500 km³, 2.08 Ma). Quartz-hosted melt inclusions for all eruptions exhibit coherent trends for major and trace elements (e.g. Al₂O₃, Nb, U, Rb). However, in the Oruanui and Huckleberry there is significant variability in measured H₂O (2.6-5.8 wt% and 1.0-4.5 wt%, respectively). In contrast, melt inclusions from the first two fall layers of the Bishop Tuff yield a narrower range (4.0-5.8% H₂O, with 90% at 4.5 to 5.8 wt.%). We infer that the H2O scatter reflects diffusive losses, occurring during slow magma ascent or partial stalling within the conduit at lower pressures. Using a diffusion model, we estimate that 84% of Huckleberry Ridge and 61% of Oruanui melt inclusions experienced modification from storage H2O conditions, with most inclusions requiring 1-5 days of slow ascent towards the surface. In contrast, only 33% of melt inclusions from the initial Bishop fall layer experienced diffusive losses, implying that most of the magma spent less than a day in transit in the conduit system. These differing results are attributed to differences in internal magma overpressure and regional stresses acting upon the magmatic systems.

Abstracts – Poster Presentations

Evidence for exsolved fluid at depth from melt inclusions in a basaltic sub-Plinian eruption at Sunset Crater volcano

Chelsea Allison, Cornell University

Co-authors: Kurt Roggensack and Amanda B. Clarke

Sunset Crater volcano (AZ, USA) is an alkali basalt scoria cone that produced a sub-Plinian eruption ca. 1085 AD. Primary melt inclusions (MIs) in free olivine crystals from the tephra deposit have dissolved volatile contents of 0.5 wt% to 1.5 wt% H2O and 1,200 ppm to 3,000 ppm CO2. MI vapor bubbles were measured by Raman spectroscopy, calibrated with synthetic CO2 inclusions, to determine total CO2 content. Calculations constrain bubble volume from post-entrapment MI shrinkage and crystallization to <3 vol% in these samples. Approximately 1/3 of MIs with no signs of decrepitation contain larger bubbles that likely include co-entrapped exsolved fluid. Total MI CO₂ contents (dissolved CO₂ plus bubble) reach 6,500 ppm. Large MI bubbles contain the most CO₂, consistent with co-entrapped fluid. The CO₂ dissolved in the magma at MI entrapment ranges up to ~4500 ppm, indicating depths of ~10 km to 18 km. The co-entrapped vapor suggests a bubbly magma and significant overpressure at depth, which likely drove rapid magma ascent to produce the sub-Plinian eruption. Characterization of MI vapor bubbles not only yields important information about total volatile contents of magmas, but also provides physical constraints on eruptive processes.

Control of magma decompression rate on the explosivity of basaltic eruptions

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Magma decompression rate plays a crucial role in modulating the dynamics of explosive basaltic eruptions. This control is imparted through the kinetics of crystallization and bubble nucleation, rheological changes, and dynamics of the multiphase flow. We explore whether the transition from VEI 2 to 3 intensity could be the result of an increase in magma decompression rate. To constrain decompression rate, we exploit the incomplete diffusive re-equilibration of water through olivine. In order to isolate the effects of decompression rate from other controls on eruption style, we focus on two eruptions at the same volcano; the 1992 (VEI 3) and 1995 (VEI 2) eruptions of Cerro Negro, Nicaragua.

Olivine-hosted melt inclusions (MIs) show a negative correlation between MI size and diffusive water loss, as predicted for diffusive re-equilibration. We develop a 1D numerical model of diffusion from the MI through the host olivine, coupled with a degassing model in the magma, and find that the 1995 olivines ascended five times slower on average than those from the 1992 eruption. MIs from both eruptions extend to comparable maximum H₂O and CO₂ contents (~ 4.75 wt.% H₂O, ~ 600 ppm CO₂), suggesting similar magma source conditions.

The largest uncertainty in our modelling comes from the six order of magnitude range in hydrogen diffusivity from the literature. Some of this variation is due to effects of anisotropic diffusion, while the rest is likely due to a range in olivine composition, particularly Fe content. To better constrain the diffusivity relevant to our system, we perform dehydration experiments on oriented cuboids of Cerro Negro olivine. We find diffusivities intermediate between those measured on natural olivine from San Carlos and Kilauea Iki and the fast 'proton-polaron' mechanism. Using our diffusivity, we find that the 1992 magma ascended from 15 km in ~3 hours, while it took the 1995 magma ~15 hours.

Pliocene–Quaternary intraplate magmatism in Anatolia: Insights from melt inclusions and mineralogy

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Pliocene–Quaternary intraplate magmatism occurs in different parts of Anatolia with contrasting tectonic regimes, related to the continental collision of Africa and Arabia with the Eurasian plate. We present a detailed study of olivine-hosted melt inclusions (MI) and (near-)liquidus phases (olivine phenocrysts and chromian spinel inclusions) in mafic alkaline lavas from volcanic centers in western (Kula), southerncentral (Ceyhan-Osmaniye) and southeastern Anatolia (Karacadağ), aimed at exploring the makeup and origin of intraplate magmatism within these geodynamically distinct settings. CaO, NiO), spinel (Cr#, Mg#) and MI (major and trace elements) reveal heterogeneity in primary melts and contributions of compositionally distinct end-members in the magma sources of each of these Anatolian volcanic centers. Estimated P–T conditions of primary melt generation in mantle domains are not uniform and, in agreement with the geochemical signatures of the melts, substantiate marked differences between sources and melting regimes. Our results suggest that interplay between upwelling asthenospheric mantle, facilitated by extensional processes, and spatially variable overlying lithospheric mantle created the compositional spectrum of intraplate-type primary melts throughout Anatolia.

Compositional variations in coexisting olivine (Fo,

Zircon-Hosted Melt Inclusions in Porphyry Systems

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Co-authors: Jon Blundy, Brian Tattitch, Cam McCuaig, Chris Hawkesworth

Porphyry copper deposits (PCDs) are magmaticallyderived geochemical anomalies that concentrate economic quantities of metals in the crust. It is generally agreed that PCD formation requires highly fractionated hydrous arc magmas, oxidised conditions and the exsolution of magmatic volatile phases (MVPs) which extract Cl, S and metals from the magma, leading to ore precipitation. Corrosive magmatic-hydrothermal fluids associated with porphyry intrusions frequently destroy primary mineral assemblages and alter whole-rock compositions. This has resulted in a significant gap in our understanding of the metal and volatile budgets of the parental porphyry magmas prior to MVP exsolution. Zircon is ubiquitous in evolved porphyry intrusions, and with its refractory nature and insolubility in acidic fluids, it makes an ideal host for melt inclusions. We have recently identified abundant glassy and crystalline melt inclusions (1-200µm) in zircons from porphyry intrusions in Chile. We propose that melt inclusions in zircon represent vestiges of the porphyry melt and may be analysed to establish the initial magmatic volatile contents, chemistry and intensive parameters of these parental magmas. To our knowledge, there are currently no publications on the use of zircon-hosted melt inclusions in the context of PCDs, but these inclusions are promising recorders of processes occurring during the magmatic stages of PCD evolution.

Magma composition and role of volatile degassing in Deccan Large Igneous Province: A melt inclusion approach

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Co-authors: Richard E. Ernst, Gajananrao Jadhav The Deccan LIP constitutes one of Earth's largest continental flood basalt provinces (Glišović and Forte, 2017). The inclusions are crystalline, glassy, with or without a shrinkage bubble, usually distorted, due to pressure changes inside the inclusion (Wallace et al. 2015). Inclusions are enriched in TiO₂ (3.68 to 0.08 wt%) and FeO (18.3 to 2.63 wt%). SiO₂ ranges from 43.4-66.8 wt%. Al₂O₃ ranges from 9.7-22.4wt % and MgO 18.3-1.6. EPMA measurements demonstrated the presence of daughter crystals, such as magnetite and titanomagnetite. Volatile concentrations were measured by FTIR, show a wide variable range of volatiles (up to 2 wt% H2Ototal and 1808 ppm CO2). Compositions are affected by diffusion, e.g. precipitation of host, resulting in the high Al2O3. Melt inclusions showed evolved melt with the aggregated crystals indicating that formation of these Fe-Ti oxides has occurred in an aqueous condition. Daughter mineral assemblages (titanomagnetite, and magnetite) promotes the diffusion of hydrogen.

Glišović P and Alessandro M. Forte (2017) Science 355, 613–616 Wallace et al. (2015) American Mineralogy 100, 787-794

Dukono, the predominant source of volcanic degassing in Indonesia, sustained by a depleted Indian-MORB

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Located on Halmahera island, Dukono is among the least known volcanoes in Indonesia. A compilation of the rare available reports indicates that this remote and hardly accessible volcano has been regularly in eruption since 1933, and has undergone nearly continuous eruptive manifestation over the last decade. The first study of its gas emissions, presented in this work, highlights a huge magmatic volatile contribution into the atmosphere, with an estimated annual output of about 290 kt of SO2, 5000 kt of H2O, 88 kt of CO2, 5 kt of H2S and 7 kt of H2. Assuming these figures are representative of the longterm continuous eruptive activity, then Dukono is the current most prominent volcanic gas discharge point in Indonesia and ranks among the top-ten volcanic SO2 sources on earth. Analyses of major, trace and

volatiles elements from melt inclusions especially indicates that this voluminous degassing output from Dukono is sustained by a depleted Indian-MORB (I-MORB) mantle source. This latter is currently undergoing lateral pressure from the steepening of the subducted slab, the downward force from the Philippine Sea plate and the westward motion of a continental fragments along the Sorong fault, leading to high fluid fluxes to the surface. Over the course of Dukono eruptive activity, the magma reservoir has changed from a less differentiated source that fed the past voluminous lava flows to a more evolved melt that sustained the current ongoing explosive activity.

Oldoinyo Lengai natrocarbonatite derives from classical calciocarbonatite: a melt inclusion study

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Carbonatites are rare magmas containing almost no silica; their igneous counterparts represent the main rare earth element deposits in production. No consensus exists on their origin, genesis and evolution. Oldoinyo Lengai (Tanzania) is the only active carbonatite volcano, but the alkalirich natrocarbonatites it erupts are unique among the >500 reported fossil carbonatite occurrences. Here, we use exceptional 3-phase melt inclusions from cognate cumulates—sampling the active Oldoinyo Lengai magma chamber during the 2007–08 sub-Plinian explosive eruption—to track the carbonatite presence within the plumbing system, and to eventually quantify its composition at depth. We show that although natrocarbonatites are emitted at the Oldoinyo Lengai summit, more classical calciocarbonatites are present at magma chamber depth, consistent with rare natrocarbonatites deriving from calciocarbonatites by further magma differentiation. We present the first direct measurements of major and trace element partition coefficients between natural coexisting carbonate and silicate melts. Partitioning behaviour and recent experiments support our conclusion that natrocarbonatites derive from calciocarbonatites by fractionating Ca-rich, Na-poor phases. Natrocarbonatites are highly unstable at surface conditions, and were likely erupted (but not preserved) in association with fossil calciocarbonatites worldwide, and Oldoinyo Lengai can be considered as representative of other carbonatite systems.

Iron isotope fractionation in olivine-hosted melt inclusions as an indicator of mantle oxygen fugacity

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Many studies have demonstrated that arc basalts are more oxidized (QFM -0.5 to +4) than MORBs (QFM-1.2 to ~ QFM; [1-6]). However, the oxidation state of the sub-arc mantle is still debated. On the one hand Kelley and Cottrell [2, 3] suggest that variations in the Fe³⁺/Fe^{Tot} ratio measured in basaltic glasses and olivine-hosted melt inclusions from mid-ocean ridges and arcs could be explained by the sub-arc mantle being more oxidized than the mantle beneath ridges. On the other hand, Mallmann and O'Neill [7] and Lee et al. [8] proposed the use of other fO₂ proxies, namely V/Sc and Zn/FeTot ratios in lavas and suggested that the oxidation state of the MORB mantle could not be distinguished from that of the mantle wedge. In a study of synthetic glasses ranging from basaltic to rhyolitic compositions, Dauphas et al. [9] have demonstrated that iron isotope fractionation is mainly controlled by redox (Fe³⁺/Fe^{Tot}) and polymerization

of silicate melts. In the present study and for the first time, iron isotopic compositions (⁵⁶Fe/⁵⁴Fe) were measured by SIMS in olivine-hosted melt inclusions from various arc, OIB and MORB localities. The results obtained with this technique, along with Fe³⁺/ Fe^{Tot} ratios obtained by XANES on the same set of melt inclusions, are used to constrain the oxidation state of primary magmas formed in these different geological settings and their mantle source.

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Determining magma ascent rates from diffusive D/H fractionation in olivine-bosted melt inclusions

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The depths at which magmas are stored, their preeruptive volatile contents, the nature of degassing (i.e. open- versus closed-system), and the rates at which they ascend to the Earth's surface are interrelated, and exert important controls on the dynamics of volcanic eruptions. Of these variables, magma ascent rates are particularly difficult to quantify due to a lack of geospeedometers applicable to processes occurring on timescales ranging from hours to days. We developed a new approach to determining ascent rates on the basis of D/H fractionation associated with diffusive H2O loss from olivine-hosted melt inclusions (MIs). During ascent, the host magma degasses which, in turn, drives diffusive loss of H from MIs. Preferential loss of H - relative to the more slowly diffusing D - leads to increasing D/H with decreasing H2O concentration in the MI. The extent of diffusive H2O loss and D/H

fractionation is primarily a reflection of ascent time, the nature of degassing, and melt inclusion size. This approach was used to determine the ascent rate for hyaloclastite from Hut Point Peninsula, Antarctica. All inclusions are glassy and contain vapor bubbles. Total CO₂ was determined by summing CO₂ in the included glass and in the vapor bubble (VB). The volumes of MIs and VBs were determined by X-ray microtomography, and the density of CO2 within each VB was determined using Raman spectroscopy. The included glass was analyzed for volatiles and D/H by secondary ion mass spectrometry. Entrapment pressures calculated on the basis of total CO2 and maximum H₂O using the MagmaSat solubility model indicate a depth of origin of ~24 km - in good agreement with the seismically determined depth of the Moho beneath Ross Island. Results from finite difference modeling are consistent with closed system degassing and an average ascent rate of $\sim 0.5 - 2.0$ m/s.

Assessing Historical Parental Magma Compositional Variations at Kīlauea Volcano, Hawaii

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Co-author: Marc Norman

Two hundred years of magmatic history are preserved by lava and tephra from Kilauea's historical summit eruptions. Whole-rock data show large and systematic compositional and isotopic variations during the last two centuries from 1820 to 1924, when the summit suddenly and violently collapsed. Thereafter, a reversed geochemical trend has continued for 80 years, including the 35-year-old Puu 'O'o eruption. Melt inclusions in relatively primitive olivine (forsterite, Fo 85-90) were examined to determine the cause of these trends (e.g, magma mixing or systematic parental magma changes). These rapidly-quenched samples show minimal post-entrapment re-equilibation with host olivine. The melt inclusions from a single lava trap a remarkable range in major and trace element compositions, much larger than recorded in the erupted lava during the last 200 years, although inclusions within individual olivines show a limited

range. The range of melt inclusion compositions in high Fo olivine record primary magmatic variation, especially for major and trace element ratios (e.g., CaO/Al2O3, Nb/Y, La/Yb). These results indicate that magma supplying Kilauea changes rapidly (over less than a decade) and that its source has small-scale mantle heterogeneities. These short-term magma compositional variations are buffered by the summit magma chamber but preserved in melt inclusions from high Fo olivine. The rapid and overall systematic nature of these temporal geochemical variations indicate that summit eruptions are fed from a simple, relatively small reservoir that is being continuously fluxed with new, mantle-derived magma. The rate of compositional variation during the last two hundred years is directly correlated with magma-supply rate and the estimated degree of melting. Magma supply rate and the degree of melting are probably controlled by the scale of source heterogeneity within the Hawaiian plume.

δD Variations In Olivine-hosted Melt Inclusions Due to Post-Entrapment Processes: A Case Study From Baffin Island Picrites

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Water concentrations and δD values obtained from olivine-hosted melt inclusions are routinely used to estimate the amount of H₂O and the δD of the upper mantle. However, olivine-hosted melt inclusions do not necessarily retain a record of the original H2O conditions, due to post-entrapment processe such as diffusive loss or gain of H⁺ (Gaetani et al., 2012, Bucholz et al., 2013). Recently, new analyses of melt inclusions from Baffin Island (Hallis et al., 2015) reported H2O contents ranging from 576 to 1964 ppm and light δD values between -97‰ and -218%, together with a negative H₂O- δ D correlation. Such correlation was interpreted as an indication that the inclusions dehydrated before the eruption, either via H+ migration from the melt to the olivine, or via degassing. The most depleated value (-218‰) was suggested to be the most indicative of the isotopic composition of H in the mantle, and interpreted as the indication of the presence of

an heterogenous mantle tapping a deep, primitive, undegassed source. We analysed melt inclusions and their host olivines from two samples from the same locality as presented in Hallis et al. We report H2O content between 530 and 1243 ppm and δD values between -96 and -112‰ for the melt inclusions, and olivine H₂O content between 1 to 17 ppm, consistent with analyses of olivines from MORBs-type basalts. Our data show no negative correlation between water content and δD , althought they are consistent with the majority of the non-depleted δD and low H₂O contents reported in Hallis et al. We cannot confirm nor refute the extremely light δD value presented by Hallis et al., however we discuss the possibility, based on results from hydration experiments, that the light δD values and the negative H₂O- δD correlation observed by Hallis et al. could have been caused either by pre-eruptive hydration-induced H⁺ diffusion, or by post-eruptive molecular water diffusion, due to hydration of the olivines by meteoric water.

Chemical and isotopic compositions of melt inclusions from the Faroe Islands

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Melting of the proto-Iceland Plume produced the intra-plate lavas of the Faroe Islands (1-3). The basaltic rocks from the Faroe Islands follow a liquid line of descent (Ol-chromite-Cpx-Plag) and are not modified by crustal assimilation during magma evolution. The middle lava series, the so-called Malinstindur Formation, contains picrite flows with up to 50% olivine (Ol), and thus formed by accumulation of Ol (3). Whole-rock and Ol-hosted melt inclusions (MI) from this formation along with samples from the younger Enni Formation were analysed for their major element, trace element and Sr isotope composition. Melt inclusions are influenced by post-entrapment crystallisation of Cpx and chromite. However, their comparatively depleted, but homogenous trace-element compositions overlap those of the host lavas, specifically those of the 'low-Ti' group (3, 4).

Strontium isotope compositions of MI in Ol, which have been grouped by their Fo contents (Fo93-85, in 1 mol. % Fo bins), reveal large variations within this single lava flow. This variation in ⁸⁷Sr/⁸⁶Sr increases with decreasing Fo, suggesting progressive melt mixing during magmatic differentiation. The total variation in Sr isotope ratios in the MI population covers 50 % of the variation recorded in the erupted lavas but is slightly biased towards the radiogenic end of the spectrum.

1 Gariépy et al. 1983. EPSL 63. 2 Holm et al. 2001. Chem.Geol. 178. 3 Søager & Holm 2011. Chem. Geol. 280. 4 Millett et al. 2017. Lithos 286-287.

Reconstructing initial CO2 contents of magmas using carbon isotopes in melt inclusions

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Melt inclusions (MIs) are often used to estimate the volatile evolution of magmas as they ascend and degas. Volatiles with high solubility (H2O) and/ or low (below saturation) concentrations (S and Cl), remain dissolved to low pressures. Hence, there is plenty of opportunity for MI formation during ascent. In contrast, CO2 is less soluble, and some natural concentrations are high enough to saturate at much greater depths, well before MIs are captured. This early stage of volatile loss is not recorded, leading to an underestimate of the importance of CO2 in the system. Even when the primitive CO2 content is captured there are problems of bubble formation post-entrapment. As MIs fail to capture the early degassing history, an alternative way to estimate initial CO2 concentrations is using carbon isotopes. Carbon isotopically fractionates during degassing, resulting in an isotopically heavier fluid (13C-rich) and a light melt (¹²C-rich), where the magnitude of fractionation is controlled by the fractionation factor (Δ). Based on new experimental data, we derived a model for Δ which varies with pressure and XCO₂, leading to extreme values of Δ up to 16 ‰, in contrast to previous data which had a constant Δ of 2 – 4 ‰. We analysed the CO₂, H₂O, and δ^{13} C of MIs from Rangitoto, New Zealand, and Etna, Italy, and model their evolution during degassing to estimate their initial CO2 contents. We assess the effect of bubble formation on the δ^{13} C of MIs and its impact on δ^{13} C modelling.

Tracing fluid variations across the Kamchatka arc: melt inclusion volatile contents and B isotopes

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Co-authors: M.C.S. Humphreys, I.P. Savov, T.G. Chruikova, C.G. Macpherson

We present a new suite of volatile and trace element contents (e.g. H₂O, CO₂, S, Cl, F, Li, Be, B, Nb, REEs), and δ^{11} B signatures of primitive olivinehosted melt inclusions from 10 volcanoes of the Kamchatka arc. The volcanic centres investigated span the total length and width of the arc, and encompass the Eastern Volcanic Front (EVF), Central Kamchatka Depression (CKD), and the extreme back-arc Sredinny Ridge (SR). We also present the first primitive melt inclusion data for Bakening (up to 4 wt.% H₂O, >2000 ppm CO₂, >2500 ppm S, and 1300 ppm Cl) and Shiveluch volcanoes, and in combination these samples provide us with robust spatial constraints to track variations in subduction zone fluid chemistry and fluxes between the distinct tectonic locations.

The euhedral and naturally glassy melt inclusions are primarily derived from Fo90-75 olivine crystals extracted from rapidly quenched mafic scoria, minimising the potential for post-entrapment modification. However, a suite of crystallised inclusions from lava flows were rehomogenised using either an internally heated pressure vessel or a Vernadsky heating stage. Geochemical analyses of the inclusions were conducted through a combination of EPMA, SIMS, Raman, and LA-ICP-MS techniques.

Na/K and S/H2O ratios of fluid inclusions in Pinatubo harzburgite xenoliths

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Fluid inclusions in the Pinatubo harzburgite xenoliths have compositions of Na73K27 according to LA-ICP-MS. This is more K-rich than those of aqueous fluid components in the Mariana Trough basalts (Na82K12, Stolper & Newman 1995, EPSL) and H2O-rich slab components in Mt. Shasta basalts (Na77K23, Grove et al. 2002, CMP), and between two H2O-rich components estimated from olivine melt inclusions from Mt. Shasta (Na70K30 of melt or supercritical fluids components and Na87K12 of aqueous fluids components, Le Voyer et al. 2010, J Petrol).

Sulfate ions and gypsum and/or anhydrite crystals were found in the Pinatubo fluid inclusions.

Sulfur contents in the fluid inclusions are <5mg S in 1g water, which are within a range of those in serpentinites (Alt et al. 2012 EPSL). Olivinehosted melt inclusions in arc basalts show a positive correlation between water contents and Fe³⁺/ Fe²⁺ ratios (Kelley & Cottrell 2009 Science). The presence of sulfate ions in the Pinatubo aqueous fluid inclusions supports the correlation. Current estimate of S content in the aqueous fluids in forearc is much lower than that in melt inclusions in Mt. Shasta basalts (20-600mg S in 1g water; Le Voyer et al. 2010, J Petrol). This indicates that slab-derived fluids beneath sub-arc contain larger amount of S than in the Pinatubo fluid inclusions or that sulfur can be enriched from source mantle through its partial melting rather than addition by the slab-derived fluids.

Redox sensors applied to olivine-hosted melt inclusions

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Co-authors: Marion Gaborieau, Nathalie Bolfan-Casanova, Juliette Maurice

The study of primitive olivine-hosted melt inclusions has allowed a better understanding of petrogenetic processes and mantle source regions. These unique samples may also provide a means to link the redox state in primary magmas to that in their mantle source. Arc magmas are more oxidized than midocean ridge magmas [1], likely because the mantle source region of arc magmas has been modified by oxidized and fluids from the subducting slab. However, whether the variations in $Fe^{3+}/\Sigma Fe$ of magmas from various environments arise owing to differences in mantle fO2 or to differentiation processes such as crystallization and degassing is still a matter of debate [2]. Alongside this scientific debate, $Fe^{3+}/\Sigma Fe$ ratios in primitive melts also show discrepancies between values derived from different analytical methods (wet chemistry, XANES and Mössbauer spectroscopy) that clearly need to be resolved [3]. Here we combine different fO2 proxies in an attempt to carefully reconstruct mantle source

fO2 from the compositions of highly primitive olivine-hosted melt inclusions from mid- ocean ridge, hot spot and arc settings. These fO2 proxies include Fe³⁺/ Σ Fe measurements and trace element proxies that rely on the experimental calibration of the partitioning behavior of multivalent cations such as V, Cu and S as a function of fO2.

In particular we will compare fO₂ values derived from the V oxybarometer [4] with direct measurements of the oxidation state of Fe. A careful assessment of the differentiation and melting processes and their effects on fO₂ proxies will be carried out in order to reveal the link between redox state in melts and that of their mantle source. This work will provide an evaluation of the robustness of the various oxybarometers when applied to melt inclusions.

 Kelley & Cottrell (2009), Science 325, 605–607.
 Gaillard et al. (2015), Chem. Geol. 418, 217-233. [3] Berry et al. (2018), EPSL 483, 114-123. [4] Mallmann & O'Neill (2013), J. Pet. 54, 933-949.

Sulfur degassing and magma oxidation state at Mount St. Helens (WA) and Augustine (AK) Volcanoes

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Authors: A. Lerner, P. Wallace, C. Thornber, P. Kelly, M. Coombs, C. Mandeville

Redox changes associated with magmatic sulfur (S) degassing can potentially change magma fO₂, which in turn can affect phase stability, S solubility, and further degassing. We test whether S degassing and fO₂ are linked in oxidized arc systems by undertaking a combined EPMA and μ XANES study of Mount St. Helens and Augustine volcanoes.

We analyzed matrix glass and melt inclusions from the 1980 and 2004-2008 eruptions of Mount St. Helens and the 2006 eruption of Augustine. Sulfur in melt inclusions ranges from 40 - 340 ppm in Mount St. Helens samples and from 80 - 2600 ppm in Augustine samples, reflecting S degassing during stages of magma ascent and storage. At Mount St. Helens, µXANES melt inclusion measurements show a relatively narrow range of S speciation, and fO₂ determinations largely overlap fO₂ estimates from Fe-Ti oxides (Δ NNO 0 to +1). Augustine melt inclusions, in contrast, record a wider range of S concentrations and substantially more reduced melt fO₂ (Δ NNO +0.2 to +1.2 via μ XANES) than determined by Fe-Ti oxides (Δ NNO +1 to +2.5). Augustine melt inclusions generally become more oxidized with lower S contents, suggesting that S degassing may cause oxidation in this sulfur-rich system. Mount St. Helens is very S-poor overall and does not show such a relationship between S and fO₂ changes.

In summary, we find that magmatic oxidation may be linked to S degassing, and that pre-eruptive fO₂ conditions may be substantially different from fO₂ recorded by Fe-Ti oxides.

Low D/H in Baffin Island Melt Inclusions: Primordial Water or Diffusive Hydration? Peter Michael, University of Tulsa

Fundamental questions remain concerning the timing, source, and delivery of water to the condensing Earth, and whether any part of the Earth retains primordial water. Discovery of low-Deuterium melt inclusions from Baffin Island lavas that were previously shown to have primordial noble gas signatures prompted Hallis et al. (2015) to conclude that there is primordial water in Earth, and that it was derived from the solar nebula by adsorption. But there is abundant experimental evidence for the mobility of hydrogen through olivine that shows how melt inclusions may be unreliable indicators of initial H2O contents and H-isotope ratios. The low H2O contents of the Baffin Island melt inclusions make them particularly susceptible to rehydration, which would produce inclusions with

higher H₂O and low D/H. I show several different physical mechanisms by which rehydration could occur. For example, mixing of diverse liquids just prior to eruption (Fig. 1a). In Fig 1 b., inclusions equilibrate with surrounding liquid, but D diffuses slower than H, leading to low- δ D, depleted inclusions (e.g., Hauri, 2002).

Hallis, L.J., et. al. (2015) Evidence for primordial water in Earth's deep mantle. Science 350, 795-797.

Hartley, M.E., et al. (2015) Diffusive over-hydration of olivine-hosted melt inclusions. Earth Planet. Sci. Lett. 425, 168-178

Hauri, E. (2002) SIMS analysis of volatiles in silicate glasses, 2: isotopes and abundances in Hawaii melt inclusions. Chem. Geol. 183,115

Using the Cameca IMS 1280 SIMS at WHOI to measure volatile concentrations and hydrogen isotopic compositions within melt inclusions and glasses of variable composition Brian Monteleone, Woods Hole Oceanographic Institution

Co-author: Glenn Gaetani, WHOI

Secondary Ion Mass Spectrometry (SIMS) is a minimally destructive micro-analytical technique that is ideal for measuring volatile concentrations (CO₂, H₂O, F, S, Cl) and hydrogen isotopic compositions of mineral hosted melt inclusions and volcanic glasses. Primary (¹³³Cs⁺) beam focusing on the IMS 1280, when combined with secondary beam aperture application, allows for high quality analysis of most (e.g. bubble-, crack-, and mineral-inclusion free) melt inclusions as small as 10µm in shortest dimension. Typical precision on individual volatile concentration measurements is <3% for CO2 (2RSD) and <2% (2RSD) for H₂O, F, S, and Cl. Bootstrap regression analysis on a calibration of multiple in-house basaltic glass standards yields typical accuracy of <5% 2 sigma for all volatiles. Recent developmental work has led to a substantial reduction in measured volatile backgrounds, with typical concentration measurements on volatile free materials (suprasil,

synthetic forsterite) yielding <2µg/g CO₂, <4µg/g H2O, and <0.2µg/g for F, S, and Cl (at spot sizes > 30 µm). Further standard development will be geared toward matrix-matching common host minerals (e.g. olivine, pyroxene), thus enabling precise and accurate measurement of nominally anhydrous host minerals to allow for improved partition coefficient determination. Work on intermediate and felsic standards has shown a marked matrix effect on calibrations for CO2 and H2O with measured ratios of ¹²C/³⁰Si decreasing with increasing SiO₂ wt% and ¹⁶O¹H/³⁰Si decreasing with increasing H₂O content in more silicic glasses. However, no such matrix effect exists for F, Cl, and S (Hauri et al, 2002). Hydrogen isotopes are measured on the IMS 1280 at high mass resolving power (MRP >8500), with the ratio of oxides $({}^{16}O^2D/{}^{16}O^1H)$ serving as a proxy for D/H. High MRP analysis of basalt and rhyolite standards at variable H2O concentrations shows no discernable matrix effect with increasing SiO2 or H₂O concentration.

The effect of slab-derived sulfur on the sulfur content, metal content, and oxidation state of primitive magmas in the Southern Cascades

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Arc magmas are oxidized relative to MORB, but the causes of this oxidized signature are uncertain. This study uses primitive olivine-hosted melt inclusions from the tephra of basaltic cinder cones in the Southern Cascades to investigate the role of slab-derived sulfur in the oxidation state, sulfur content, and chalcophile element behavior of primitive arc magmas. We integrate evidence for a hydrous slab component in Lassen primitive magmas from previous work [1] with evidence from major element, trace element, and chalcophile element concentrations in addition to fO₂ values from XANES analysis.

Sulfur concentrations in individual melt inclusions range from 883 to 2043 ppm. Cu, Zn, and Sn

concentrations in melt inclusions range from 17 to 167 ppm, 65 to 124 ppm, and 0.5 to 1.5 ppm, respectively. Minimum fO₂ values inferred from S XANES range from QFM + 0.8 to QFM + 1.5. The fO₂ values for the different cinder cones correlate with S/Dy and Sr/Nd values and are consistent with the addition of oxidized, sulfur-carrying slab material to the Lassen sub-arc mantle. A subset of fO₂ melt inclusions contain small immiscible sulfide blebs. The sulfur contents of melt inclusions from these samples are close to sulfur concentrations predicted by sulfur solubility models [2,3], indicating the melts were near or at sulfide saturation during entrapment.

[1] Walowski et al. (2016) EPSL 446, 100-112. [2] Fortin et al. (2015) GCA 160, 100-116. [3] Jugo et al. (2010) GCA 74, 5926-5938.

Evidence of different lithology sources and metasomatic agents under Ecuadorian volcanoes

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We studied olivine-hosted melt inclusions from Sangay and Puñalica volcanoes, located in the southern termination of the Ecuadorian arc. The 30-150 µm melt inclusions were homogenized before we analyzed them under SEM, ICP-MS and SIM instruments for major, trace and volatiles composition, respectively. Two different lithologies (a peridotite and an amp-bearing clinopyroxenite) are needed to explain the major oxide variation of our melt inclusions. We also recognized two distinctive slab components that metazomatized the Ecuadorian sub-arc mantle. We propose that the different nature of the slab component is related to a distinctive thermal regime along the Benioff zone. We also state that Grijalva fracture zone, which enters in subduction in front of the Ecuadorian arc, is under Puñalica volcano allowing the increasing in volatile content (mainly F and Cl) in Puñalica melt inclusions.

The analysis of high density fluid microinclusions in diamonds and garnet

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The analysis of inclusions that are smaller than 1 μ m is challenging, but when they are present in large numbers, a wealth of information may be collected on their composition. Microinclusions in diamonds are analyzed for their mineralogy and volatile content (TEM, FTIR and X-ray diffraction), major (EPMA) and trace elements (LA-ICP-MS) and isotopic composition. The transparent diamond matrix allows identification of water, carbonates, silicates and phosphates by IR spectroscopy. TEM finds these phases + halides as secondary multi-phase assemblages that formed during the cooling, at the surface, of a uniform high-density fluid (HDF) trapped by the diamonds during their growth in the

mantle. The EPMA provides the bulk-composition of individual subsurface inclusions and reveals variation between four endmembers: a saline HDF, a high-Mg carbonatitic HDF and a continuous array between silicic and low-Mg carbonatitic HDF. LA-ICP-MS reveals two main trace-element patterns: "Planed" and "Ribbed" with negative anomalies in alkalis and the HFSE. Sr and Nd isotopes reveal derivation form the asthenosphere as well as old enriched lithosphere.

Recently we found silicic fluids in microinclusions in eclogitic garnets. The determination of their major elements is complicated because of the garnet matrix. We find that the trapped material is similar to the silicic to low-Mg carbonatite HDFs in diamonds, attesting to the involvement of HDFs in mantle metasomatism.

The compositional consequences of natural and experimental diffusive re-equilibration on plagioclase hosted inclusions

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Interpretation of compositional information from melt inclusions requires that we understand the degree to which the melt inclusions represent the melt present at the time of entrapment. Our work focuses on plagioclase hosted melt inclusions from plagioclase ultraphyric basalts (PUB). This includes time series experiments on inclusion homogenization which document progressive partitioning of CO₂ into the vapor bubble as a function of time and the diffusive exchange of both major elements and trace elements. Such changes can be attributed to the relaxation of the plagioclase structure during the heating of the crystal. Such relaxation is similar in type to that described by Schiavi et al (2016) for olivine - but take place on a much longer time scale (4 days vs 30 minutes).

Diffusive exchange manifests itself in both the experiments and in the naturally occurring megacrysts. In the experiments, profiles within the megacrysts leading up to the inclusions exhibit diffusion profiles for rapidly diffusing elements (e.g. Mg). Such profiles are present for 4 day run times but not for experimental run times of 30 minutes. In the megacrysts, some exhibit a relative narrow range of composition for rapidly diffusing elements (e.g. Sr) than for slow diffusing elements (e.g. Ti, Ce). However, local equilibrium appears to be maintained based on the fact that the ratio of trace elements between the MI and the host are similar to experimentally determined partition coefficients.

Reconstructing the CO2 contents of bubble-bearing, olivine-hosted melt inclusions

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Melt inclusions provide a means to probe the depth and volatile content of magma. However, post-entrapment processes can lead to volatile exsolution (importantly CO₂) into vapor bubbles inside inclusions. Methods to reconstruct entrapped CO2 contents yield inconsistent results. To reconcile the inconsistencies, we conducted homogenization experiments and bubble growth experiments. Homogenization experiments, in which inclusions were heated and vapor bubbles were resorbed, were conducted on inclusions from Seguam and Fuego volcanoes using a piston cylinder apparatus (~1150 °C, ~700 MPa, 2 hrs) with a KBr matrix and brucite as a water source. Most of the resultant inclusions are homogeneous. In each sample, CO₂ and S contents are correlated, defining S-CO₂ degassing paths. CO2 contents of unheated inclusions from the same samples were previously reconstructed using Raman addition (RA; Moore et al., 2015), and we have corrected CO₂ with two computational approaches:

the ideal gas law (IGL; Shaw et al., 2010) and a bubble growth model (BG; Riker, 2005). Relative to our empirical degassing paths, IGL results are offset to higher CO2 or lower S, while RA and BG results overlap but tend to be offset to lower CO2 or higher S. The discrepancies are attributed to CO2 because S contents of heated and unheated inclusions overlap. IGL may overestimate CO2 because CO2 diffusion cannot keep pace with bubble growth during rapid cooling upon eruption. Minute amounts of carbonate on the bubble interior may cause RA to underestimate CO2. BG discrepancies might relate to diffusive loss of H+ from unheated inclusions and uncertainties (e.g., temperature) involved with the calculation. Results will also be presented on Vernadsky heating stage experiments, conducted to observe bubble growth during cooling and diffusive loss of H+. Our ultimate goal is to use targeted homogenization and bubble growth experiments to create a more accurate calculation for restoring entrapped CO₂ contents.

The contribution of bubble-hosted mineral phases to the volatile content of melt inclusions estimated by 3D Raman imaging

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Volatile abundances in magmas control the style, dynamics and intensity of volcanic eruptions. Reliable assessment of pre-eruptive conditions and degassing budget depends on correct estimation of the original volatile contents of magmas. Phenocryst-hosted melt inclusions (MI) record the volatile contents of the magma at the time of MI entrapment. During magma ascent and eruption, bubbles often form inside MI due to pressure drop and cooling. Recent studies have shown that up to 40-90% of the CO₂ initially contained in MI is sequestered inside bubbles [1]. In addition to a fluid phase, bubbles often contain solid phases crystallized on the bubble wall. Raman spectroscopy measurements indicate that the volume of these solid phases (mainly carbonates and sulphates) relative to the fluid phase may be important. We present a method to identify the different phases filling inclusion-hosted bubbles and to quantify the volume of the solid phases using 3D Raman imaging. The method is applied to the study of olivine-hosted MI of basanitic and basaltic compositions erupted from different volcanoes. The accuracy and the limits of the method are examined by performing 3D Raman imaging of bubbles in silicate glasses synthesized in the laboratory. The contribution of bubble-filling mineral phases to the MI volatile content is quantified and discussed.

[1] Wallace et al. (2015) Am Mineral 100, 787-794.

The role of melt-rock interaction on the CO2/Ba ratio of depleted MORBs

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Carbon content of the depleted upper mantle has been estimated using CO₂/Ba in depleted midocean ridge basalt (D-MORB) melt inclusions and glasses that are undersaturated in CO₂. One of the potential issues with this approach is the effect of melt-plagioclase chemical interaction on the CO₂/ Ba ratios in D-MORBs. Assimilation of plagioclasebearing rocks into MORB has been shown to affect their Ba (and Sr and Eu) concentrations, implying that such a process may also affect their CO₂/Ba ratio. In this study, we report on the compositions of olivine-hosted melt inclusions and glasses from the Siqueiros and Garrett transform faults. The melt inclusions are CO₂ undersaturated D-MORBs with highly depleted incompatible trace element compositions. Subsets of melt inclusions from both transform faults show signatures of assimilation of plagioclase such as significant increases in Al2O3 and decreases in FeO with decreasing MgO, positive Sr anomalies, and low Nb/Ba. CO2/Ba ratios significant ranges of 113±48 and 86±40 for the Garrett and Siqueiros melt inclusions respectively. We model assimilation fractional crystallization of plagioclase into the D-MORBs. These models reproduce the range in CO₂/Ba ratio and trends between CO₂/Ba, Nb/Ba, and Nd/Sr as well as between Al₂O₃, FeO, and MgO observed in the melt inclusions. Hence, chemical interaction with plagioclase may affect the CO₂/Ba ratio in D-MORBs, and care should be taken to evaluate this effect using Nd/Sr and Nb/Ba ratios.

Comprehensive volatile analyses of ~30 µm melt inclusion using SIMS

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We developed in-situ analyses of volatile contents, hydrogen and sulfur isotopes of basaltic glass using IMS-1280HR at Kochi Institute, JAMSTEC. Series of standards were prepared including synthetic and natural basaltic glasses to cover the broad ranges of volatile contents in basaltic glasses reported to date. H₂O and CO₂ concentrations of the standard glasses were determined by FTIR, and concentrations of F, Cl, and S were determined by ion chromatography following pyrohydrolysis (Shimizu et al., 2017, Geochem. J. 51, 299-313). Hydrogen and sulfur isotope ratios were determined by TCEA/IRMS and IRMS, respectively at Tokyo Institute of Technology. For the in-situ analysis of volatile contents and sulfur isotope, defocused Cs beam (~0.5nA) of ~10µm was used, but for hydrogen isotope, we used larger defocused beam (~5nA, ~15µm). Secondary ions of volatile elements were detected by an axial EM using a magnetic peak switching method to determine volatile contents. For analyses of D/H (³⁴S/³²S) ratios, ¹⁶OH (³²S) and ¹⁶OD (³⁴S) were measured in multi-detection mode with a Faraday cup and an axial EM, respectively. Each measurement time is ~6 minutes. Precision for D/H and ³⁴S/³²S ratios are ±5‰(2sd) (H₂O>1wt%) and ± 0.6 ‰ (S>1000ppm), respectively. Our developed analyses of rapid, accurate, and high spatial resolution can determine multi-elements and isotopes of volatiles in a single small melt inclusion (Figure 1).

A high carbon content of the Hawaiian mantle from olivine-hosted melt inclusions

Jonathan Tucker, Carnegie Institution for Science

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Quantification of CO₂ in melt inclusions is complicated by the ubiquitous presence of vapor or "shrinkage" bubbles. We measured exsolved vapor bubble CO₂ by a volumetric method, and dissolved CO₂ by SIMS, in order to reconstruct total melt inclusion CO₂ concentrations in >400 Hawaiian melt inclusions. Unlike a similar method by Raman spectroscopy, our method accounts for the presence of cryptic carbonates, which may sequester much of the vapor bubble CO₂.

We find that vapor bubbles often contain ~90% of the inclusion's CO₂. Importantly, we demonstrate that addition of vapor bubble CO₂ to dissolved CO₂ results in ~50% uncertainty in total melt inclusion CO₂, primarily due to melt inclusion geometry. This same uncertainty is also applicable to Raman studies. Therefore, due to this uncertainty, large numbers of samples must be measured in order to accurately capture population statistics.

Based on our data set, we estimate that parental melts from five Hawaiian volcanoes have between 0.24 and 1.1% CO₂, with mantle sources between 130 and 490 ppm CO₂. The average mantle source of the five volcanoes has 315 ppm CO₂, suggesting that the Hawaiian plume is significantly more C-rich than the MORB mantle. The high CO₂ concentration of the Hawaiian plume could either be due to deeply subducted surficial C, retention of juvenile C, or both.

Diffusive Re-Equilibriation of Plagioclase-Hosted MIs and their Host: Insights from Analytical Data, Modeling, and Experiments

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Interpretation of compositional information from melt inclusions requires that we understand the degree to which the melt inclusions represent the melt present at the time of entrapment. Our work focuses on plagioclase hosted melt inclusions from plagioclase ultraphyric basalts (PUB). This includes time series experiments on inclusion homogenization which document progressive partitioning of CO_2 into the vapor bubble as a function of time and the diffusive exchange of both major elements and trace elements. Such changes can be attributed to the relaxation of the plagioclase structure during the heating of the crystal. Such relaxation is similar in type to that described by Schiavi et al (2016) for olivine - but take place on a much longer time scale (4 days vs 30 minutes).

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Hydration induced hydrogen isotope fractionation in olivine-hosted melt inclusions: an experimental study

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Olivine-hosted melt inclusions from mantle-derived lavas have been used to investigate the hydrogen isotopic composition (D/H) of the Earth's deep reservoirs, which are key to understanding the origin of water on Earth (Hallis et al., 2015). However, experimental studies have demonstrated that olivinehosted melt inclusions show open system behavior for water (Gaetani et al., 2012). Significant hydrogen isotope fractionation can occur in melt inclusions during diffusive dehydration or hydration of the host olivine. As H2O in the melt inclusion re-equilibrates with the external magma, deuterons diffuse through host olivine slower than protons. In such cases, a negative correlation develops between water contents and D/H ratios in some olivine-hosted melt inclusions. To quantify this process during olivine hydration, which could occur when the carrier melt is mixed with a more hydrous melt just prior to eruption, hydration experiments were performed on olivines from Puu Mahana, Hawaii. The melt inclusions in these olivines have initially low water contents (0.27 to 0.39 wt.%) and relatively large variation of δD^{VSMOW} values (-65 to -104‰). Olivines were held at 300 MPa and 1200°C in pure distilled water ($\delta D^{VSMOW}=0$) for 30 min, 60 min, and 90 min. All run products were analyzed for H2O concentrations and D/H ratios by SIMS on the Cameca 1280 ion microprobe at WHOI. The hydrated melt inclusions have increased water contents (0.39 to 1.47 wt.%) and decreased δD values (-100.3 to -178.6%) as hydration progresses, and a negative $H_2O-\delta D$ correlation was produced. Additionally, in each run, negative correlations have been found between water contents and MI sizes and between δD values and olivine sizes. Our hydration experiments well reproduced the hydrogen isotope fractionation trend produced by a numerical olivine hydration model (Qin et al., 1992) based on the same olivine geometry and a hydrogen diffusivity of 6.16×10⁻¹² m²/s at 1200 °C (parallel to [001]).

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MINERAL-HOSTED MELT INCLUSION

Small pockets of melt entrapped within growing mineral grains (mineral-hosted melt inclusions) are commonly used to study everything from mantle heterogeneity to preeruptive magmatic volatiles. The information recorded in melt inclusions is unique because entrapped melts are physically shielded from most interactions with the external environment by the host mineral. Melt inclusion studies require careful sample preparation, application of state-ofthe-art analytical methods, and meticulous attention to potential artifacts related to post-entrapment processes. As analytical techniques progress and our understanding of post-entrapment processes evolve, it is important that the rapidly growing melt inclusion community periodically assess the state of the field.





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