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# Subduction Factory: Understanding the role of water flux in arc systems

Central America and Izu-Bonin-Mariana Subduction zones

Erik Hauri<sup>1</sup>, Alison Shaw<sup>2</sup>, Glenn Gaetani<sup>2</sup>, Terry Plank<sup>3</sup>, Katherine Kelley<sup>4</sup>, Jennifer Wade<sup>3</sup>and Julie O'Leary<sup>1</sup>

<sup>1</sup>Carnegie Institution of Washington, <sup>2</sup>Woods Hole Oceanographic Institution, <sup>3</sup>Boston University, <sup>4</sup>University of Rhode Island

#### Introduction

The stability of liquid water on the Earth's surface, and its introduction into the mantle at subduction zones, has had an impact on the evolution of our planet in ways that transcend fields of study in traditional Earth science. The presence of liquid water is generally regarded as a prerequisite for the sustenance of life as we know it, and discoveries in micro-



Figure 1. Distribution of volcanoes, and average Ba/La and  $H_2O$  (wt%) for samples from each volcano, along the Izu-Bonin-Mariana (IBM) and Central American arcs.  $H_2O$  data come from melt inclusions, while Ba/La ratios come from both whole rocks and melt inclusions. Ba/La ratios are used as proxies for the presence of a slab-derived hydrous fluid; maximums in Ba/La suggest the largest quantity of hydrous fluid beneath the northern Izu islands (Oshima volcano) and northwest Nicaragua (Cerro Negro). The extremes in IBM  $H_2O$  contents occur in samples from Maug volcano (lowest  $H_2O$ ) and NW Rota seamount (highest  $H_2O$ ), which both have low Ba/La and are at opposite ends of the Mariana arc where increased curvature in the strike of the subduction zone results in oblique subduction. Maximum  $H_2O$  contents in Central America occur at Cerro Negro, which has the highest Ba/La. Data summarized from Elliott et al. (1997), Taylor & Nesbitt (1998), Roggenack et al. (2001), Walker et al. (2003), Sadofsky et al. (2004), Wade et al. (2006, 2007), Benjamin et al. (2007), Shaw et al. (2004, 2006) and K. Kelley (unpublished data).

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biology over the past two decades have made clear the wide range of surficial and deep-sea environments within which single-celled organisms can thrive. The presence (ancient or modern) of living things on other planetary bodies is an open question that has profound scientific and sociological implications, and its ultimate resolution will very likely be tied to the presence of water.

Back home on our own planet, water has an influence on the Earth's convective engine that is no less significant. The active plate tectonic cycle that now characterizes the surface expression of mantle convection depends critically on the strong impact that water has on the strength of mantle and crustal rocks. One need look no further than Venus or Mars to imagine how different Earth's tectonics would be on a dry one-plate planet without subduction zones. Beneath the plates, water influences mantle convection to a degree that belies its abundance; as little as 150 ppm H<sub>2</sub>O (by weight) is sufficient to lower the viscosity of the mantle by three orders of magnitude below that of dry mantle (Hirth and Kohlstedt, 1996). In the upper 150 km of the mantle, the melting point drops by 200-300°C upon addition of as little as 0.1% of H<sub>2</sub>O (Gaetani and Grove, 1998; Grove et al., 2006), permitting cold mantle beneath subduction zones to melt when it would otherwise never melt in the absence of water. Upon reaching the Earth's surface, a magma's potential for explosive and violent eruption depends almost entirely on its water content. Because of its strong influence on convection, and the location and style of surface volcanism, the origin, distribution and influence of water in the mantle are among the most important issues in all of Earth science.

### Water in the Upper Mantle

Advancing our understanding of water in the mantle requires both field-based and experimental approaches. US and international support of oceanographic expeditions to recover submarine lavas has been crucial to this effort; because subaerial lavas quickly lose their water during eruptive degassing, only lavas quenched to glass under the confining pressure of seawater have a chance of retaining their original pre-eruptive  $H_2O$ . Studies of water in mid-ocean ridge basalts (MORB) show that the upper mantle contains 100-200 ppm  $H_2O$  (Michael, 1988; Dixon et al., 1988; Michael, 1995; Danyushevsky et al., 2000; Saal et al., 2002), and that sections of mid-ocean ridge influenced by hotspots can contain more (up to 1000 ppm  $H_2O$ ) (Dixon et al., 1997; Dixon et al., 2002; Simons et al.,

## Arcs and back-arc basins overlie the most water rich regions of the upper mantle.

2002; Asimow et al., 2004). High-pressure experimental studies demonstrate that this amount of water is less than the amount required to saturate common upper mantle minerals (olivine, pyroxenes, garnet) (Hirschmann et al., 2005; Hauri et al., 2006; Mierdel et al., 2007), so we can say with some confidence that solidstate convection, rather than aqueous fluid flow, is the dominant mode of water transport within the upper mantle beneath mid-ocean ridges and hotspots. However, arcs and back-arc basins overlie the most water-rich regions of the upper mantle (up to 12,000 ppm H,O) (Danyushevsky et al., 1993; Stolper and Newman, 1994; Kelley et al., 2006; Langmuir et al., 2006). It is thus very likely that in some regions, the mantle is locally saturated in H<sub>2</sub>O, and supercritical hydrous fluids are active in transporting water and other elements from the subducting slab to the mantle wedge.

These studies and others have made clear that water abundances in the upper mantle are heterogeneous, and this is due to the continuous introduction of water into the convecting mantle at suduction zones. Central goals of the Subduction Factory initiative of the MARGINS program are to constrain the flux of water entering the mantle, the amount of water leaving the mantle wedge via magma generation and transport, the amount of water retained by the slab and transported into the deep mantle beyond the zone of arc magma generation, and the role of this water in upper mantle magma generation.

## Melt Inclusions: IBM and Central America

To this end, on-going field-based and experimental efforts are improving our understanding of water in subduction zones. Various field campaigns were launched in 2003-2006 to recover air-fall scoria from arc volcanoes in the Izu-Bonin-Mariana (IBM) and Central American subduction zones, with the goal of obtaining glassy melt inclusions that could be used to study the systematics of water and other volatiles dissolved in arc magmas (Fig. 1). Melt inclusions are tiny volumes of magma (typically  $<200 \ \mu m$  diameter) that are trapped within growing crystals prior to magma eruption (Fig. 2). Although many lava samples had been collected from both IBM and Central America prior to these field efforts, almost all of the existing samples were from massive lava flows, which are generally poor samples for melt inclusion studies: this is an endemic sampling problem at all arcs. Lava flows cool slowly, which can permit H<sub>2</sub>O to diffuse out of melt inclusions after eruption (Hauri, 2002). Air-fall scoria cools to a solid within seconds after eruption, and this has the effect of quenching even very H<sub>2</sub>O-rich melt inclusions into glass that can be readily analyzed by microbeam methods.

Recovery and analysis of melt inclusions is a laborious process, with the most informative geochemical data coming from populations of at least 10-15 inclusions from each individual hand sample. Inclusion-bearing olivine crystals are first hand-picked from the larger olivine population, which is often only a few percent of the total sample mass. The selected crystals are polished to expose each inclusion, which is then sequentially



Figure 2: Melt inclusions in olivine (Fo75-82) extracted from a scoria sample from the Mariana islands. The largest inclusion is 100 µm across.

analyzed by ion probe methods (SIMS) for volatile contents, electron probe for major elements, and then SIMS or laserablation ICP-MS for trace element abundances. Inclusions of sufficient volume can also be analyzed in-situ for certain isotope systems (D/H, B, Sr, Pb). Each inclusion is subsequently examined by SEM to screen for inclusions that may be devitrified, and the sizes of the inclusions and any vapor bubbles (when present) are measured. A final melt composition is determined by adding back the H<sub>2</sub>O and CO<sub>2</sub> contained in the vapor bubble, and any olivine that may have grown on the interior wall of the inclusion.

To date, over 650 melt inclusions have been recovered and analyzed from more than 20 subaerial and submarine volcanoes in the IBM arc (Shaw et al., 2004, 2006). The melt inclusions span an enormous range in H<sub>2</sub>O, from 0.2 wt% up to 6 wt% in melt inclusions with significant CO<sub>2</sub> concentrations, reaching as high as 1000 ppm in some inclusions. The data reveal two significant observations regarding the behavior of water in the IBM subduction zone. First, the average H<sub>2</sub>O contents for each volcano in the Mariana arc are inversely related with their TiO<sub>2</sub> content (Fig. 3a), a feature that is also characteristic of Mariana backarc basin basalts (Stolper and Newman, 1994; Kelley et al., 2006; Langmuir et al., 2006). This inverse relationship is the result of the role of water in depressing the mantle melting point, so that regions of the mantle with more H<sub>2</sub>O will melt to a higher degree, resulting in a dilution of incompatible elements in the magma that are insoluble in  $H_2O$ -rich fluid (i.e. TiO<sub>2</sub>).

Equally interesting, however, is that the magmatic  $H_2O$  contents are not correlated with elements that are highly soluble in water-rich fluids, such as potassium (Fig. 3b). In subaerial rocks, the abundances of water-soluble trace elements (including elements such as boron and barium) are often used as proxies for the presence and amount of fluid liberated from the subducting slab (Elliot et al., 1997; Taylor and Nesbitt, 1998). The Mariana arc melt inclusion data make clear the dubious nature of such an inference at IBM; Ba/La is not well correlated with magmatic  $H_2O$  in



Figure 3: Volcano-averaged TiO,, K,O and Ba/La versus  $H_2O$  for melt inclusions from the Izu-Bonin-Mariana arc and Mariana Trough. Abundances are corrected for fractional crystallization until the melt composition is in equilibrium with Fo90 olivine. (A) Inverse correlation of TiO, and H<sub>2</sub>O indicates high extents of melting in regions with higher  $H_2O$ , resulting in a dilution of  $TiO_2$  contents. (B) The presence of slab-derived fluids is well correlated with fluid-soluble trace elements in the back-arc Mariana Trough, but trace elements are decoupled from  $H_2O$  in the arc proper. (C) Ba/La ratios are decoupled in both IBM and Central America, despite being well-correlated in Mariana Trough melt inclusions.

melt inclusions from the arc, although a good correlation is observed for melt inclusions from the back-arc Mariana Trough (Fig. 3c). It thus appears likely that specific metamorphic dehydration reactions are at work to fractionate  $H_2O$ from other trace elements in the vicinity of the slab-mantle interface.

The IBM results contrast markedly with the results from the Central American arc. In Central American arc magmas, very clear along-strike correlations exist among trace elements (i.e. Ba/La), isotopes (<sup>10</sup>Be,  $\delta^{18}$ O) and depth to the slab beneath the volcanic front (Morris et al., 1990; Morris et al., 2002; Walker et al., 2003; Eiler et al., 2005). However, prior to 2004 only Cerro Negro volcano in Nicaragua had been investigated for its melt inclusion H<sub>2</sub>O content (Roggensack, 2001). In the past three years, melt inclusions have been recovered and measured from Arenal and Irazu volcanoes in Costa Rica (Wade et al., 2006; Benjamin et al., 2007) as well as several others (Sadofsky et al., 2004), and it appears that among these volcanoes H<sub>2</sub>O is well correlated with trace element proxies of slab fluids.

## Experimental Calibration of "H<sub>2</sub>O in Cpx" Hygrometer

Melt inclusions are not ubiquitous in arc settings, and this reality has thus far limited the number of volcanoes that have been studied for their water contents. However, high-pressure experimental studies of H<sub>2</sub>O partitioning between pyroxene and basaltic melt (Aubaud et al., 2004; Hauri et al., 2006) have provided a solution to this dilemma that can be used in any arc setting. The addition of H<sub>2</sub>O adds complexity to melting experiments at high pressures and temperatures; the composition of the experiment must be carefully chosen to match the composition of mantle minerals and melts, the capsule containing the experiment must limit the loss of water and iron from the melt, the furnace used to heat the experiment must minimize thermal gradients during heating, and the high-pressure press must be designed for fast quenching

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rates upon conclusion of the experiment (Gaetani and Grove, 1998; Grove et al., 2006). The experimental heating schedule must strike a careful balance between the long times required for chemical equilibrium and the danger of H diffusion out of the experiment. After recovery of the capsule, electron probe analysis of the minerals and melt are used to assess homogeneity of phase compositions and construct a mass-balance against the starting composition in order to screen experiments against loss of H<sub>2</sub>O. Only those experiments that pass this gauntlet can be used for examining mineral-melt H<sub>2</sub>O partitioning by SIMS.

The experimental results show a clear dependence of the pyroxene-melt H<sub>2</sub>O partition coefficient with Al<sub>2</sub>O<sub>3</sub> content of pyroxene, indicating a substitution of H<sup>+</sup> and Al<sup>3+</sup> replacing Si<sup>4+</sup> in the pyroxene mineral structure (Hauri et al., 2006). This observation has permitted the determination of magmatic H<sub>2</sub>O contents even in degassed arc lavas, using careful SIMS measurements of the H<sub>2</sub>O content of pyroxene phenocrysts (Wade et al., 2007). The magma's  $H_2O$  content is then calculated by dividing the pyroxene H<sub>2</sub>O content by the pyroxene/melt partition coefficient, taking into account the variation of pyroxene-melt H2O partitioning as a function of pyroxene composition (Fig. 4). For this method to work, rapidlycooled scoria samples are still preferred, yet this method permits a determination of magmatic H<sub>2</sub>O even in samples that contain no melt inclusions. Magma water contents determined by the "H<sub>2</sub>O in pyroxene" hygrometer on scoria samples agree very well with melt inclusion measurements from the same samples (Wade et al., 2007), and further support the coherence between H<sub>2</sub>O abundances and trace element proxies of slab fluids in Central America (Fig. 1).

#### **Future Directions**

The difference in  $H_2O$ -trace element coherence at IBM and Central America make it clear that these two arcs process subducted water differently; we cannot make simple extrapolations about the behavior of water to other arcs worldwide until we have a better grasp on the underlying processes that fractionate H<sub>2</sub>O from lithophile trace elements in subduction zones. The reasons for this dichotomy in the two MARGINS focus areas are not yet clear, but may relate to differences in mantle wedge heterogeneity, subduction zone tectonic geometry and its influence on wedge convection, the age of the subducting slabs and their alteration history, convergence rate, slab dip angle, and/or differences in the compositions (and associated prograde metamorphic reactions) of the down-going sedimentary sections. Whatever the cause, the location of interest appears to be restricted to the mantle directly beneath the arc. Back-arc lavas and melt inclusions from the Mariana Trough show very good cor-



Figure 4: (A) Pyroxene/melt partition coefficients for  $H_2O$  as a function of tetrahedral Al content of pyroxene, in H<sub>2</sub>Oundersaturated melting experiments (Hauri et al., 2006). This correlation indicates a coupled substitution of aluminum and hydrogen for silicon. (B) H<sub>2</sub>O content (ppm) of clinopyroxene phenocrysts from Arenal volcano (Wade et al., 2007). The H<sub>2</sub>O content of the melt is calculated from the cpx H<sub>2</sub>O content divided by the Al-dependent  $H_2O$  partition coefficient calculated from the correlation in (A). The results for Arenal are consistent with the maximum  $H_2O$ contents of Arenal melt inclusions (Wade et al., 2006).

relations between  $H_2O$  and water-soluble trace elements like  $K_2O$  and Ba/La, but these correlations break down in melt inclusions from the arc proper (Fig. 3).

Further measurements along-strike in Central America, and across-strike at both arcs, are required to help illuminate the major processes at work that transport H<sub>2</sub>O through the mantle wedge in different ways, and will also be key in "closing the loop" on volatile- and trace-element flux balance calculations that are presently underconstrained. However, the promise that these future studies hold is critically dependent on our ability to conduct land- and ocean-based field expeditions to recover melt inclusions from both sub-aerial and submarine samples. At the same time, the insight gained from magmatic H<sub>2</sub>O contents will always depend on our ability to conduct high-pressure experiments that can be used to predict the behavior of H<sub>2</sub>O at all pressures, temperatures and compositions relevant to the subduction process.

We are at the early stages of an era of rapid progress in our understanding of water in the Earth's interior. Further studies have the potential to reveal the role of water in other fields of interest, which include constraining interpretations of seismic velocity structure beneath arcs, for determining the efficiency of water transport past subduction zones and into the deeper mantle, for understanding the origin of magmatic water in hotspots, the distribution of water in the Earth's transition zone and lower mantle, and the ultimate cosmochemical origins of water that was delivered to the Earth during planetary accretion. But as we learn more about water in the Earth's interior, we will also reach a greater appreciation for how much we truly don't know about the most influential molecule on the planet.

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