

# Prediction of magmatic water contents via measurement of H<sub>2</sub>O in clinopyroxene phenocrysts

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## ABSTRACT

**Water is fundamental to magma genesis, evolution, and eruption. Few direct measurements of magmatic H<sub>2</sub>O exist, however, because rocks found at the surface have extensively degassed upon eruption. Olivine-hosted melt inclusions provide a standard approach to measuring volatiles in undegassed magma, but many volcanic deposits do not contain melt inclusions large enough for analysis (>30 μm), or olivine at all. Here we use an Al<sup>IV</sup>-dependent partitioning relationship to calculate magmatic H<sub>2</sub>O from direct measurements of H<sub>2</sub>O in clinopyroxene phenocrysts. We test this approach using phenocrysts from four arc volcanoes (Galunggung, Irazú, Arenal, and Augustine) that span the global range in H<sub>2</sub>O contents as measured in olivine-hosted melt inclusions (from 0.1 to 7 wt% H<sub>2</sub>O). The average and maximum magmatic H<sub>2</sub>O contents calculated from the clinopyroxene measurements agree within 15% of the melt inclusion values for most of the samples. The evolutionary paths recorded in H<sub>2</sub>O-Mg# variations overlap in some clinopyroxene and olivine-hosted melt inclusion populations, and in others, the clinopyroxenes record a larger portion of the liquid line of descent or a different portion of the magma system. Thus, the use of phenocrysts to estimate magmatic H<sub>2</sub>O contents creates a new and powerful tool in igneous petrology and volcanology.**

**Keywords:** clinopyroxene, partition coefficient, water, melt, subduction zones.

## INTRODUCTION

Nominally anhydrous minerals such as pyroxene and olivine can incorporate small amounts of water into their crystalline structures (100–1000 ppm H<sub>2</sub>O by weight), and these minerals are important reservoirs of water in the upper mantle (Bell and Rossman, 1992; Hirschmann et al., 2005). Nominally anhydrous phenocrysts that grow from wet magmas should also contain H<sub>2</sub>O in their structures. For example, the partition coefficient of H<sub>2</sub>O in clinopyroxene (cpx) relative to melt is generally >0.01 (Aubaud et al., 2004; Hauri et al., 2006), predicting >100 ppm H<sub>2</sub>O in cpx in equilibrium with melt of 1 wt% H<sub>2</sub>O. Given that arc magmas typically have >>1 wt% H<sub>2</sub>O (Wallace, 2005), and that detection limits by secondary ion mass spectrometry (SIMS) and Fourier transform infrared spectroscopy (FTIR) can be <10 ppm H<sub>2</sub>O (Koga et al., 2003), cpx phenocrysts have great potential as useful recorders of magmatic water content, in a greater variety of volcanic rocks than those that yield rare and tiny melt inclusions for volatile analysis (e.g., Anderson, 1979; Sisson and Layne, 1993; Sobolev and Chaussidon, 1996; Cervantes and Wallace, 2003). We initiated this study to test the feasibility of the phenocryst-based approach.

## SAMPLES AND METHODS

Clinopyroxene phenocrysts were chosen from four volcanic deposits that span the global range in water concentrations (Wallace, 2005) as measured in olivine-hosted melt inclusions: the A.D. 1983 eruption of Galunggung volcano, Java (<1 wt% H<sub>2</sub>O; Sisson and Bronto, 1998;

Kelley et al., 2004); the A.D. 1723 eruption of Irazú volcano, Costa Rica (~2–3 wt% H<sub>2</sub>O; Benjamin et al., 2007); the ~930 yr B.P. ET3 (AR-19) tephra of Arenal volcano, Costa Rica (3–4 wt% H<sub>2</sub>O; Wade et al., 2006); and a Pleistocene eruption of Augustine volcano in the U.S. Aleutian Islands (~4–7 wt% H<sub>2</sub>O; Zimmer, 2008). To minimize the potential for H loss by diffusion, all samples studied were rapidly quenched during eruption, including scoria lapilli for the Costa Rican deposits, a small bomb at Galunggung, and a basaltic hyaloclastite at Augustine.

The cpx phenocrysts from all four deposits are from a similar size fraction, ranging from ~500 to 1300 μm at the longest axis. Phenocrysts with abundant melt or mineral inclusions were avoided, as were grains broken during handling or eruption. Clinopyroxenes were analyzed by ion microprobe at the Carnegie Institution of Washington, after polishing and mounting in indium metal in order to minimize the H background (generally <4 ppm; Hauri et al., 2006). Water concentration was determined from <sup>16</sup>O<sup>1</sup>H/<sup>30</sup>Si measured in multiple ~10 μm spots (centered within 50 μm × 50 μm rastered pits) in each cpx. H<sub>2</sub>O calibrations were based on natural pyroxene standards, following protocols in Koga et al. (2003) and Hauri et al. (2006), and as outlined in the GSA Data Repository<sup>1</sup>. Uncertainties on individual spot measurements are ~15% (2σ external precision over multiple sessions) and ~33% (2σ accuracy due to current interlaboratory differences in cpx standards values). All of the melt inclusion volatile measurements (referenced above) were also made at Carnegie using the same ion probe and with calibration strategies consistent with those used for the cpx analyses.

## COMPOSITIONAL VARIATION WITHIN PHENOCRYSTS

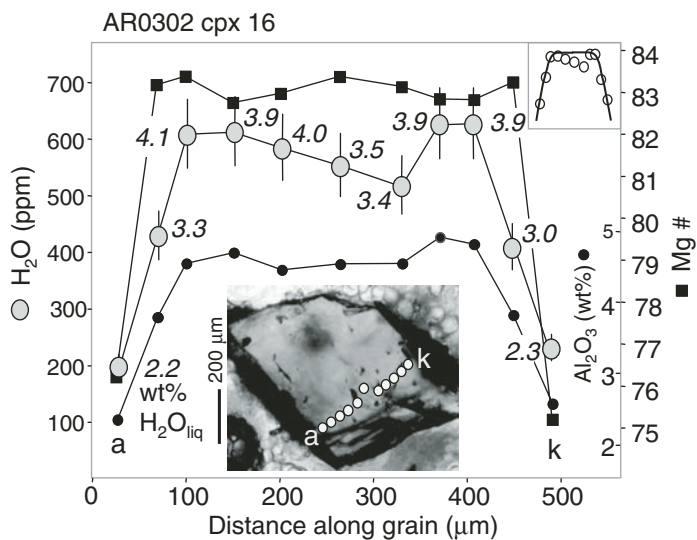
H<sub>2</sub>O contents in the clinopyroxenes range from ~40 to 1200 ppm, the lowest being in Galunggung cpx, and the highest in Arenal cpx, although there is significant variation within each population and within individual grains. In many grains, H<sub>2</sub>O is lowest near the rim, and highest near the center of the grain. This is to be expected, as the solubility of H<sub>2</sub>O in magmatic liquids decreases dramatically with decreasing pressure, and so there is a strong potential for H loss to vapor as melt and crystals ascend. Given the fast diffusion of H in cpx (as high as 1 × 10<sup>-10</sup> m<sup>2</sup>s<sup>-1</sup> at >1000 °C; Woods et al., 2000; Hercule and Ingrin, 1999), there also could be significant diffusion of H out of the grain during ascent and/or cooling.

In order to evaluate variations within a single grain, we measured a H<sub>2</sub>O profile across a cpx grain from Arenal volcano (Fig. 1). The water concentration is fairly uniform in the grain interior (588 ppm H<sub>2</sub>O ± 44 ppm standard deviation, sd), but falls to ~200 ppm in the outer 100 μm of the grain. Such zonation could be caused by diffusive loss of H from the crystal. Fitting a one-dimensional diffusion model to this profile with the diffusivity cited above (Fig. 1) predicts a duration of 8 s, which would lead to an unreasonable ascent rate of 875 m/s (see Cashman, 2004), assuming eruption from a depth of 7 km, based on the maximum melt inclusion trapping pressure of 2 kbar (in Wade et al., 2006). This result is consistent

<sup>1</sup>GSA Data Repository item 2008206, cpx data set, and detailed discussions of 1) calibration of the SIMS for analysis of H<sub>2</sub>O in cpx, 2) mechanisms of water partitioning in cpx, and 3) calculations of errors in magmatic water estimates, is available online at [www.geosociety.org/pubs/ft2008.htm](http://www.geosociety.org/pubs/ft2008.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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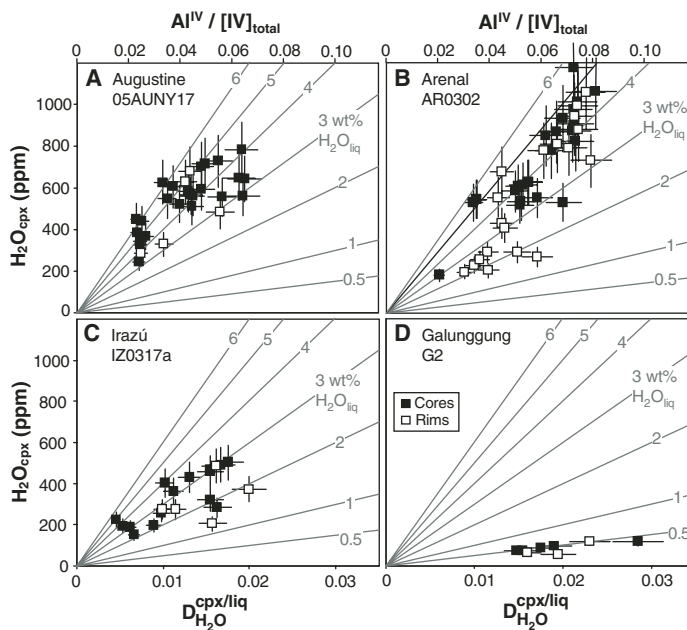
**Figure 1.** Compositional variations across clinopyroxene (cpx) grain (from a to k, inset photo). Profile is across complete section of grain, from glassy rim to glassy rim; crystal subsequently broke in the long direction. Error bars reflect 15% ( $2\sigma$ ) uncertainty on H<sub>2</sub>O measurements; values listed at each point are content,  $C_{\text{H}_2\text{O}}^{\text{liq}}$  calculated using the Al<sup>IV</sup>-dependent partition coefficient,  $D_{\text{H}_2\text{O}}^{\text{cpx/liq}}$  of Hauri et al. (2006). Upper inset shows H<sub>2</sub>O diffusion model (equation 2 in Plesier and Luhr, 2006), where  $D_{\text{H}_2\text{O}} = 1 \times 10^{-13} \text{ m}^2/\text{s}$ , after ~2 h of ascent at a rate of 1.0 m/s. Data and discussion of errors are in the Data Repository (see footnote 1).

with recent observations from mantle xenoliths that suggest that a lower diffusivity for H in cpx than that in olivine,  $<10^{-12} \text{ m}^2/\text{s}$  (Plesier and Luhr, 2006; Demouchy et al., 2006). Thus, the lab-based diffusion rates cited above (measured mostly in gem-quality diopsides) may not be appropriate. If an ascent rate of ~1 m/s is used (Szczek et al., 2006), the diffusive time scale would be 2 h (Fig. 1, inset), which would require H diffusivity in cpx of  $10^{-13} \text{ m}^2/\text{s}$ , consistent with the xenolith observations. Thus, it may be possible to use H diffusion profiles in cpx to calculate magma ascent rates, although further work is needed both in determining H diffusive mechanisms in natural cpx, and in measuring H<sub>2</sub>O profiles in oriented crystals to account for anisotropic diffusivities.

Despite the potential for diffusive loss, the H<sub>2</sub>O zonation shown in Figure 1 may have other causes, such as crystal growth zoning. Support for this comes from the similarity between H<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> zonation (Fig. 1), which is expected from the strong relationship between Al and  $D_{\text{H}_2\text{O}}^{\text{cpx/liq}}$  (where  $D = \text{partition coefficient}$ ) (Hauri et al., 2006; Grant et al., 2007), but not consistent with the expected contrasting diffusivities for H and Al in pyroxene. Another argument against widespread diffusive loss of H from grains is a lack of correlation between H<sub>2</sub>O and grain size. In some cases, H<sub>2</sub>O contents are higher at the crystal margin than the interior (e.g., grain 23 from IZ03–17a) and this makes sense given the zonation of Al within the crystal, but not with a diffusive mechanism. So while diffusive processes may affect H<sub>2</sub>O concentrations in some grains, especially at crystal rims, it is not the main driver of H<sub>2</sub>O variation in the samples studied as a whole. Instead, we interpret most H<sub>2</sub>O zonation to be the result of crystallization and degassing of the magma upon ascent.

### CALCULATING MAGMATIC WATER CONTENTS FROM CLINOPYROXENE

The H<sub>2</sub>O contents of magmatic liquids ( $C_{\text{H}_2\text{O}}^{\text{liq}}$ ) are calculated from the H<sub>2</sub>O contents measured in cpx ( $C_{\text{H}_2\text{O}}^{\text{cpx}}$ ), by dividing by the partition coefficient ( $D_{\text{H}_2\text{O}}^{\text{cpx/liq}} = C_{\text{H}_2\text{O}}^{\text{cpx}}/C_{\text{H}_2\text{O}}^{\text{liq}}$ ). We use a modified form of the relationship in Hauri et al. (2006) to estimate  $D_{\text{H}_2\text{O}}^{\text{cpx/liq}}$  as a linear function of the fraction of the tetrahedral site occupied by Al ( $\text{Al}^{\text{IV}}/[\text{IV}]_{\text{total}}$ ), calculated at each SIMS spot from adjacent (within ~20 μm) electron microprobe

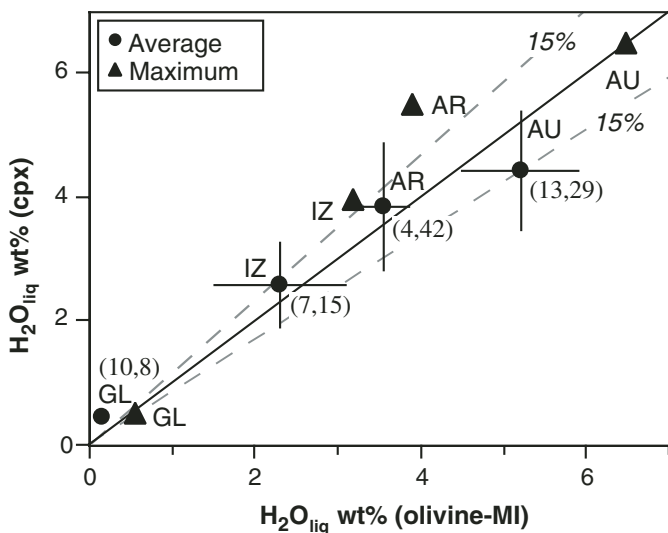


**Figure 2.** H<sub>2</sub>O and Al concentrations in clinopyroxene (cpx) from four volcanic deposits. Open symbols are analyses within 100 μm of the crystal rim; solid symbols are in crystal interior. Partition coefficient ( $D$ ) for H<sub>2</sub>O between cpx and liquid is calculated from  $\text{Al}^{\text{IV}}/[\text{IV}]_{\text{total}}$  (fraction of tetrahedral site occupied by Al), after Hauri et al. (2006). Lines of constant slope give H<sub>2</sub>O concentration in magmatic liquid. Error bars reflect 10% uncertainty on  $D$ , and 15% uncertainty on external precision of H<sub>2</sub>O measurements. Concentration data, analytical methods, partitioning relationship, cation assignments, and error estimates are in the Data Repository (see footnote 1).

analyses of major elements in the cpx (see the Data Repository for full details and discussion of errors). The resulting  $D_{\text{H}_2\text{O}}^{\text{cpx/liq}}$  values vary from 0.005 to 0.03, with significant variation occurring within the cpx population of a given sample (Fig. 2).

The predicted H<sub>2</sub>O concentrations in coexisting magmatic liquids are given by lines of constant slope on a plot of  $C_{\text{H}_2\text{O}}^{\text{cpx}}$  versus  $D$  (or  $\text{Al}^{\text{IV}}/[\text{IV}]_{\text{total}}$ ). This diagram (Fig. 2) has the advantage of illustrating magmatic water predictions directly from actual measurements of H<sub>2</sub>O and Al in the cpx. For some of the volcanic samples, H<sub>2</sub>O and Al concentrations in the cpx correlate, as would occur for a characteristic H<sub>2</sub>O content in the magma. For example, most of the cpx cores from Arenal predict 4–5 wt% H<sub>2</sub>O in the magmatic liquid, even though absolute values of  $C_{\text{H}_2\text{O}}^{\text{cpx}}$  and  $\text{Al}^{\text{IV}}/[\text{IV}]_{\text{total}}$  vary by more than a factor of two (Fig. 2B). Many of the cpx rims from this sample overlap with core composition, again providing evidence against diffusive loss of H<sub>2</sub>O at grain rims. A separate population of Arenal rims predicts the lowest H<sub>2</sub>O contents in the sample (1.5–2.5 wt%), which may reflect rim growth after ascent and degassing of the magma. Similar coherence exists in  $C_{\text{H}_2\text{O}}^{\text{cpx}}-\text{Al}^{\text{IV}}$  for the Irazú sample (with a dominant population at  $3.0 \pm 0.5 \text{ wt}\% \text{ H}_2\text{O}$ ; Fig. 2C) and the Galunggung sample (with 0.3–0.5 wt% H<sub>2</sub>O; Fig. 2D), with some rims plotting with cores, and others representing the minimum  $C_{\text{H}_2\text{O}}^{\text{liq}}$  in the sample. Most Augustine cpx cores predict  $C_{\text{H}_2\text{O}}^{\text{liq}}$  of 4–6 wt%, including the separate population of high Mg# cpx (~87) that has very low  $\text{Al}^{\text{IV}}/[\text{IV}]_{\text{total}}$  (~0.022).

Figure 3 illustrates how these H<sub>2</sub>O concentrations predicted from the cpx correspond with those measured in melt inclusions trapped within olivine from the same samples. There is significant agreement in population means and maxima. For example, the average of all the Arenal melt inclusions in sample AR0302 is  $3.6 \text{ wt}\% \text{ H}_2\text{O} \pm 0.3 \text{ 1 sd}$  (Wade et al., 2006), which is within the average of that predicted from the entire cpx population (including rims):  $3.9 \pm 1.0 \text{ wt}\% \text{ H}_2\text{O}$ . Likewise, the means for the Irazú and Augustine cpx and melt inclusions are within their standard deviations. While Galunggung cpx predict signifi-

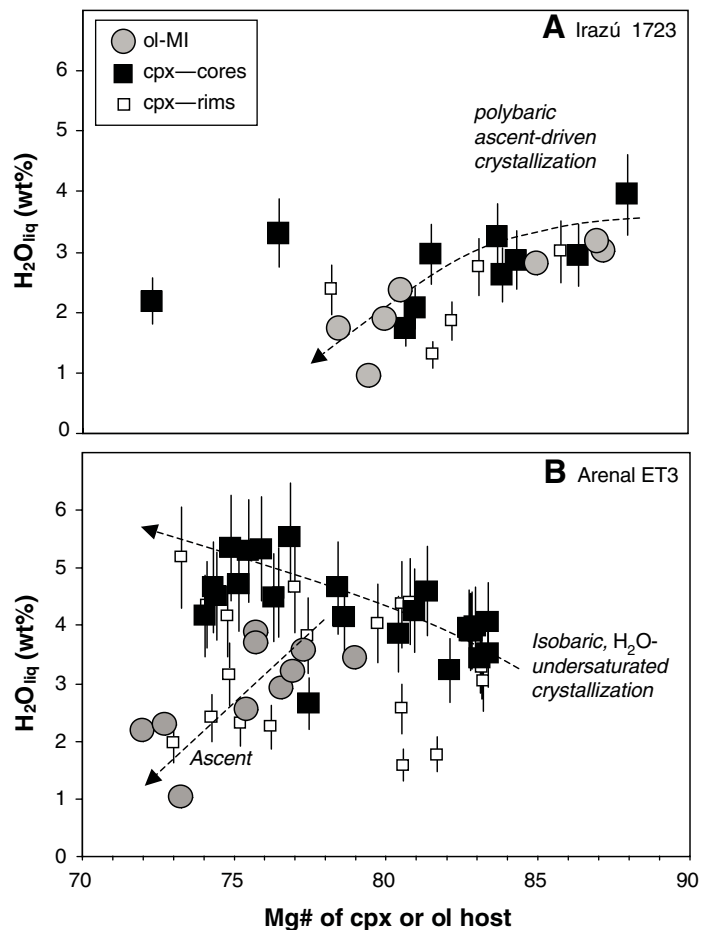


**Figure 3.** Comparison of  $H_2O$  measured in olivine-hosted melt inclusions (MI) versus  $H_2O$  calculated from clinopyroxene (cpx) measurements from Augustine (AU), Arenal (AR), Irazú (IZ), and Galunggung (GL) volcanoes. Cpx-based averages ( $\pm 1$  standard deviation, sd) and maximum values in each sample are from this study (Data Repository; see footnote 1). Averages include rims, but exclude  $H_2O$  calculated from cpx with  $<0.02 Al^{IV}/[IV]_{total}$ , which is outside the range used to determine partition coefficient D (Hauri et al., 2006). MI data are reported elsewhere (05AUNY17, Zimmer, 2008; AR0302, Wade et al., 2006; IZ03-17a, Benjamin et al., 2007; Gal-G2, Kelley et al., 2004), and shown here as averages ( $\pm 1$  sd) and maximum values in each sample. All MI concentrations are corrected for olivine addition until in equilibrium with host olivine. Parentheses give number of MI analyzed, number of analyses within cpx.

cantly higher  $H_2O$  ( $0.45 \pm 0.08$ ) than the melt inclusions ( $0.12 \pm 0.06$ ), the difference is small in an absolute sense ( $0.33$  wt%  $H_2O$ ). It is also relevant to consider maximum  $H_2O$  values, which in many cases is taken as the best estimate of pre-eruptive or primary magmatic water contents. In this regard, there is also a close correspondence (within  $0.75$  wt%) between the maximum  $H_2O$  predicted from the cpx and melt inclusions from Irazú, Augustine, and Galunggung (Fig. 3), although Arenal cpx predict higher maximum  $H_2O$  ( $>5$  wt%) than the melt inclusions ( $\sim 4$  wt%). We discuss ways in which the cpx and olivine phenocrysts might record different parts of the magma system, but note here the promising agreement between the two techniques. These tests demonstrate that in many cases, one would be able to estimate the mean and maximum magmatic water contents from a cpx population, that agree within 15% relative of that measured in olivine-hosted melt inclusions (Fig. 3). For samples with little olivine, or rare glassy melt inclusions, cpx could provide estimates of  $H_2O$  contents that might otherwise be impossible to obtain.

#### MAGMA EVOLUTION RECORD IN CLINOPYROXENES

While population means and maxima are useful, individual cpx can provide a record magma conditions along an evolutionary path. As magmas evolve from primary basalts to andesites and dacites, the Mg# of cpx decreases, from a maximum of  $\sim$ Mg# 90 to Mg#  $<70$  in high silica andesites and dacites. Such evolution is present in the Irazú cpx (Fig. 4A), with near primary (Mg# 88) to highly evolved (Mg# 72) compositions. The range in cpx Mg# overlaps almost entirely that in the olivines, and both phenocryst records show a coupled decrease in Mg# and  $H_2O$ , which Benjamin et al. (2007) interpreted as crystallization driven by  $H_2O$  loss during ascent. The very low Mg# cpx ( $<77$ ) do not conform to the overall degassing trend, and may represent foreign phenocrysts derived from older dacites present as inclusions in the A.D. 1723 eruption (Alvarado et al., 2006). Nonetheless, the majority of the cpx record a coherent magma



**Figure 4.** Comparison of clinopyroxene (cpx) and olivine-hosted melt inclusions (MI)  $H_2O$  and Mg# (molar ratio of  $MgO/[MgO + FeO]$ , with all Fe as FeO). A: A.D. 1723 scoria from Irazú. B: ET3 eruption of Arenal. Decreasing Mg# reflects crystallization, where cocrystallizing olivine (ol) and cpx have similar Mg# (within a few Mg# units; Putirka et al., 2003; Putirka, 2005). MI and cpx data and sources as in Figure 3, except all MI from the ET3 eruption of Arenal (Wade et al., 2006) are included here. Error bars reflect 17% ( $2\sigma$ ) uncertainty on water content,  $C_{H_2O}^{cpx}$ , derived by propagating uncertainties in both external precision and partition coefficient, D. Additional uncertainty in the accuracy ( $\sim 33\%$ ) would largely affect cpx and MI data in the same way (Data Repository; see footnote 1).

evolution trend for the A.D. 1723 eruption of Irazú of coupled  $H_2O$  loss with Mg# decrease, like the olivines and melt inclusions they host.

Such coherent trends are not present in all of the samples studied here. There are too few Galunggung cpx measurements to discern a trend, although the cpx Mg#s fill gaps within the olivine melt inclusion host population, and support the unusually low  $H_2O$  contents ( $<0.5$  wt%) inferred for this arc volcano (Sisson and Brontó, 1998). There is an offset in the cpx- and melt inclusion-derived water estimates of  $\sim 0.3$  wt%, which may derive from uncertainties in the cpx  $H_2O$  calibrations or partition coefficients, or from greater diffusive loss of H from olivine. In the Augustine sample, both the cpx and olivine-hosted melt inclusions indicate a wide range in magmatic  $H_2O$  contents, with as much as 2–3 wt% variation in  $H_2O$  at any given Mg#. This is consistent with multiple magma parents inferred from  $H_2O$ - $CO_2$  systematics and trace element variability in Augustine melt inclusions (Zimmer, 2008).

On the other hand, cores of Arenal cpx form a trend of increasing  $H_2O$  with decreasing Mg#, opposite to that observed at Irazú (Fig. 4B), and opposite to that in the olivine-hosted melt inclusions in samples from the same eruption (Wade et al., 2006). Such a path is consistent with isobaric,  $H_2O$ -undersaturated crystallization, where  $H_2O$  increases in the

melt as crystallization proceeds (Anderson et al., 1989). Many of the cpx rims, however, follow a degassing path similar to that of the olivine melt inclusions. Taken together, the cpx and melt inclusions may record different parts of the magma system: the cpx cores growing during cooling-driven crystallization of a magma body at depth, and the cpx rims and melt inclusions from subsequent polybaric ascent. In this example, cpx cores preserve a deeper history of magma conditions than cpx rims and melt inclusions, which may remain open to communication with evolving liquid during decompression and ascent (Blundy and Cashman, 2005).

## CONCLUSIONS

We have demonstrated that clinopyroxene phenocrysts may accurately record the H<sub>2</sub>O content of coexisting melt. The coherence between the pyroxene and melt inclusion methods supports the Al<sup>IV</sup> dependence of  $D_{\text{H}_2\text{O}}^{\text{cpx/liq}}$ , the integrity of melt inclusions as faithful recorders, and the promise of using H<sub>2</sub>O in nominally anhydrous phenocrysts as a new method for estimating magmatic H<sub>2</sub>O contents (from <0.5 to 7.0 wt%). Such a new method is critically needed for volcanic samples that otherwise lack olivine or viable melt inclusions. Moreover, the cpx method may provide a richer context for existing melt inclusion data sets. Because pyroxenes may crystallize over a large range of compositions, they have the potential to record H<sub>2</sub>O variations over a significant part of the magma path from the mantle to the surface. This capability adds to the already recognized potential of pyroxene phenocrysts as sensitive recorders of temperature and pressure of crystallization (e.g., Putirka et al., 2003; Streck et al., 2005), trace element composition (e.g., Yogodzinski and Kelemen, 1998), oxygen fugacity (Toplis and Corgne, 2002), and now water.

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