Final Report for
"Experimental Petrology and Geochemistry of Volatile-Bearing Silicate Melts"
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The focus of this project is the application of experimental petrology and geochemistry to problems in petrology and geochemistry, with particular emphasis on understanding the behavior and properties of the principal volatile components, H₂O and CO₂, and trace elements such as P in magmatic systems.

Part 1. Diffusion of water in silicate melts

The diffusivity of water ($D_{\text{H}_2\text{O}}$, defined in this paper to be the diffusion coefficient of total water, regardless of the details of the speciation) in silicate melts is a useful parameter for understanding physical parameters such as electrical conductivity of magmas and igneous phenomena such as the degassing of magma and explosivity of volcanic eruptions. Over the past several decades, there have been many experimental and theoretical studies of the diffusion of water in silicate melts and glasses. Although there have been many studies of diffusion of water in silicic melts (e.g., Shaw, 1974; Arzi, 1978; Jambon, 1979; Jambon et al., 1992; Delaney and Karsten, 1981; Karsten et al., 1982; Lapham et al., 1984; Persikov et al., 1990; Chekhmir and Epel'baum, 1991; Zhang et al., 1991; Behrens and Nowak, 1997; Nowak and Behrens, 1997; Doremus, 2000; Zhang and Behrens, 2000; Behrens et al., 2004; Liu et al., 2004; Acosta-Vigil et al., 2005; Behrens and Zhang, 2009; Wang et al., 2009), there have been relatively few for such diffusion in mafic and intermediate melts (Zhang and Stolper, 1991; Freda et al., 2003; Behrens et al., 2004; Ni et al., 2013). We have studied diffusion of water in a range of silicate melts from haplobasalt through obsidian in order to better define the relationship between water content ($C_{\text{H}_2\text{O}}$) and water diffusivity and to understand this relationship in terms of the chemical structure of silicate melts.

Experimental samples were generated through a close collaboration with Dr. Eduard S. Persikov of the Institute for Experimental Mineralogy of the Russian Academy of Sciences. A series of diffusion couple and hydration experiments

covering a wide range of water contents (0~4 wt.%; referred to as “large gradient experiments”) of haplobasaltic ($\text{Ab}_{45}\text{Di}_{37}\text{Wo}_{18}$) and haploandesitic ($\text{Ab}_{77}\text{Di}_{19.5}\text{Wo}_{3.5}$) composition had previously been generated. These were studied in detail to understand the sources of error in determining diffusion coefficients (Persikov et al., 2010). We used several methods to determine the variation of diffusivity with water content along the profiles –

1. assuming various functional relationships
 - a. constant $D_{\text{H}_2\text{O}}$
 - b. $D_{\text{H}_2\text{O}}$ proportional to $C_{\text{H}_2\text{O}}$
 - c. $D_{\text{H}_2\text{O}}$ an exponential function of $C_{\text{H}_2\text{O}}$
2. a chemical speciation model assuming that all diffusion takes place through H_2O molecules (constant $D_{\text{H}_2\text{O-molecules}}$) while the hydroxyl groups in equilibrium with them are immobile ($D_{\text{H}_2\text{O-OH}} = 0$); and
3. an empirical technique (modified Boltzmann-Matano; Sauer and Freise, 1962; den Broeder, 1969) whereby we calculated the diffusivity along the profile

In the following description, we highlight results from a second manuscript in preparation (Persikov, Newman, Newcombe, Bukhtiyarov, and Stolper, 2013), only mentioning our results published in our first paper (Persikov et al., 2010).

The first task was to develop a calibration based on major element composition for the measurement of water in silicate glasses by Fourier transform infrared spectroscopy (FTIR). We compared data for various compositions from the literature and combined them into relationships of molar absorptivity (calibration factors for FTIR) with NBO/T (non-bridging oxygens divided by tetrahedral sites; a measure of the polymerization, and therefore physicochemical structure, of the melts) to develop equations for polymerized ($\text{NBO/T} < 0.21$; silicic) and non-polymerized ($\text{NBO/T} > 0.21$; mafic) melts (Fig. 1).

Figure 1. Compositional dependence of molar absorption coefficients in silicate glasses for hydroxyl groups (4500 cm^{-1} band) and molecular water (5200 cm^{-1} band). Solid squares and diamonds indicate molar absorptivities for molecular water and hydroxyl groups, respectively, for the compositions studied here. Plus symbols and Xs indicate molar absorptivities for molecular water and hydroxyl groups, respectively, for similar compositions from Ohlhorst et al. (2001) and Withers and Behrens (1999).

The largest source of error was the choice of functional relationship for $D_{\text{H}_2\text{O}}$ versus $C_{\text{H}_2\text{O}}$ (Persikov et al., 2010). In all cases, it was clear that a constant diffusivity was not the best model to fit the data, as had been shown many times in the literature, but that diffusivity increases with water content. Using all of the results with non-

constant D_{H_2O} , we calculated an average relationship for each of the major element compositions, fitted to an exponential $D_{H_2O} - C_{H_2O}$ relationship. These general exponential equations were able to recreate the measured diffusion profiles within the errors of the measurements and the fits (Persikov et al., 2010). These equations show that diffusivity is higher in the less polymerized haplobasaltic melts than the haploandesitic melts.

Figure 2. Relationship between D_{H_2O} and C_{H_2O} at 1300°C for haplobasalt and haploandesite for the small gradient experiments, showing the comparison with the results from the large gradient experiments from Persikov et al. (2010; lavender) and low C_{H_2O} experiments (orange circles). Proportional and exponential fits to the midpoints of the C_{H_2O} ranges are shown in black and red, respectively, while data for the individual experiments are shown in the multi-colored, shorter curves. Error bars on the data for the midpoints (black dots) reflect the standard deviations of the D_{H_2O} for the range 10-80% of total C_{H_2O} for each experiment.

black proportional fit to D_s for midpoints in C
red exponential fit to D_s for midpoints
lavender general exponential fits from high gradient experiments
(gen exp; only good up to 3 wt.%)

curves are 10 - 80% of the H_2O ranges of individual samples

A set of diffusion samples with small gradients in water content, generally ~1 wt.%, were then made, to cover the range in water content of ~0.5 – 6 wt.% and major element composition (haplobasalt, haploandesite, haplodacite, and obsidian). The goal was to use these experiments to empirically build up the relationship between D_{H_2O} and C_{H_2O} for this wide range of compositions, since D_{H_2O} should be effectively constant over small ranges in water content. Indeed, we have shown that diffusion of water can usually be described by a constant over water content ranges on the order of 1 wt.%. Unfortunately, technical difficulties and experimental uncertainties made it impossible to differentiate among the models that we were evaluating for the haplodacite and obsidian compositions (e.g., diffusion from the bottoms of capsules, experiments run too long, unexplained irregularities in profiles such as

dips in concentrations, etc.). However, the method worked well for the haplobasalt and haploandesite compositions, as shown in Figure 2. The data show that the model of $D_{\text{H}_2\text{O}}$ being proportional to $C_{\text{H}_2\text{O}}$ is not correct, since the proportional fit to the data for the midpoints of the small gradient range of each experiment misses the points with the lowest H_2O contents. The simple speciation model, which requires that $D_{\text{H}_2\text{O}} = 0$ at $C_{\text{H}_2\text{O}} = 0$, similarly cannot describe the relationship. However, exponential fits to the data for both of these compositions fit the data reasonably well. At $C_{\text{H}_2\text{O}} < \sim 3$ wt.%, the exponential fits for the small gradient experiments are consistent with those calculated for the large gradient experiments (Persikov et al., 2010), but the large-gradient curves deviate to high values for $D_{\text{H}_2\text{O}}$ when extrapolated to high $C_{\text{H}_2\text{O}}$ (Fig. 2). Our new experiments constrain the relationship up to 5-6 wt.% H_2O .

Although we did not have a enough experiments for the obsidian composition to constrain the $D_{\text{H}_2\text{O}} - C_{\text{H}_2\text{O}}$ relationship, as mentioned above, we did have a set of experiments at different temperatures but similar $C_{\text{H}_2\text{O}}$ (~ 0.75 wt. %) that was able to define the variation of $D_{\text{H}_2\text{O}}$ with temperature, following an Arrhenius equation (Fig. 3). Our data are for samples generated at 700 – 1200°C at 20 MPa. They are very consistent with the data from Zhang and Behrens (2000) generated at 403 – 1215°C at 0.1 – 810 MPa and fill in the higher temperature region, validating our general methods.

Figure 3. Arrhenius relationship between $D_{\text{H}_2\text{O}}$ and temperature for obsidians from this study compared with those from the literature.

From our D-C work, we realized that looking at the very low water-content range could unambiguously differentiate an exponential relationship from the proportional and speciation models. At very low water contents, the diffusion coefficient should be a finite value if the governing relationship is exponential. If the value of the diffusion coefficient continues to decrease essentially to zero with decreasing $C_{\text{H}_2\text{O}}$, then the D-C relationship must be either a proportional one or one controlled by the simple speciation model. A refinement of the speciation model that we must consider is whether $D_{\text{H}_2\text{O}-\text{OH}}$ is truly zero, or if it has a finite value that also may be dependent on water content. Graduate student Megan Newcombe has been working on this issue in basaltic glasses (Newcombe et al., 2011, 2012). Her experiments on haplobasalt of a similar composition (An₃₆Di₆₄) to the other haplobasaltic experiments show that the diffusion coefficient at much lower water contents, down to < 50 ppm, is essentially the same as that for 0.2-0.5 wt.% (Fig.

2top, orange circles). The diffusivity has leveled out to $2\text{--}3 \times 10^{-10} \text{ m}^2/\text{s}$, similar to the value found by Zhang and Stolper (1991) for basaltic glass from the Juan de Fuca Ridge. Therefore, $D_{\text{H}_2\text{O}}$ can be described by an exponential function of $C_{\text{H}_2\text{O}}$. As mentioned above, the simple speciation model with OH groups being totally immobile ($D_{\text{H}_2\text{O-OH}} = 0$) is not supported by our data. However, if $D_{\text{H}_2\text{O-OH}}$ is a function of $D_{\text{H}_2\text{O-molecules}}$, such as $D_{\text{H}_2\text{O-OH}} = 0.15 \cdot D_{\text{H}_2\text{O-molecules}}$, then we can describe all of the data. Ni et al. (2013) proposed a model for finite, constant, $D_{\text{H}_2\text{O-OH}}$ for a haploandesitic composition, which described diffusion at low water contents in samples with a large total range of $C_{\text{H}_2\text{O}}$. The experiments at very low $C_{\text{H}_2\text{O}}$ extend this model by defining $D_{\text{H}_2\text{O-OH}}$ to be an exponential function of $C_{\text{H}_2\text{O}}$.

Another important conclusion that has come out of this work is the development of a relationship between viscosity and diffusion of water in silicate melts. Since water is so important to magmatic and volcanic processes, such as reducing melting temperatures and contributing to explosive volcanic eruptions, it can be important to understand its movement within melts even in compositions for which diffusion coefficients have not been measured. We have found that the diffusivity of water is related to viscosity by a log-log relationship, following the Stokes-Einstein and Eyring equations. Our results for the large gradient experiments are consistent with experiments from the literature, which show that one relationship fits mafic, non-polymerized melts, while another describes silicic, polymerized ones:

$$\begin{aligned} \log D_{\text{H}_2\text{O}} &= -8.87(\pm 0.13) - 0.578(\pm 0.047) \cdot \log \eta && \text{--depolymerized melts} \\ \log D_{\text{H}_2\text{O}} &= -9.65(\pm 0.06) - 0.269(\pm 0.009) \cdot \log \eta && \text{--polymerized melts} \end{aligned}$$

where η is viscosity in Pas, and $D_{\text{H}_2\text{O}}$ is the total diffusivity of H_2O in m^2/s (Persikov et al., 2010). Our small gradient experiments fit these same relationships, within the

Figure 4. Relationship between $D_{\text{H}_2\text{O}}$ and viscosity determined by the small gradient experiments. The black line is the least squares best fit for the more mafic, depolymerized compositions, and the red line is for the polymerized compositions.

errors of the fits. The intersection of the fits (Fig. 4) for the polymerized and depolymerized compositions at $\log \eta = 2.1 \pm 0.3$ matches the composition of the transition between polymerized and depolymerized melts derived by plotting activation energy of viscous flow versus NBO/T (Persikov, 1991, 1998) of $\log \eta = 2.4 \pm 0.1$. By reproducing these relationships independently, we have demonstrated the robustness of this very important method of calculating the intrinsic property of water diffusivity in melts of different compositions (including water content) representing a wide range of temperature and pressure conditions.

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Part 2. The focus of this part of the project is the study of the zonation of P and other elements in olivines. Using electron microprobe, we have characterized the complex (and often oscillatory) phosphorus zoning in natural olivines from basalts, andesites, dacites, komatiites, and igneous meteorites. We generated similar P, Al, and Cr zoning in olivines grown experimentally at 1 atm with cooling rates of 1-30°C/hr in a synthetic Hawaiian basalt. We have also been studying the relative chemical diffusivities of Ti, Cr, Al, and P in olivine.

Here we present some of the salient research results of this portion of the grant. We start with a paper that has been published and then proceed to four manuscripts that are finally nearing completion.

1. Milman-Barris, Beckett, Baker, Hofmann, Morgan, Crowley, Vielzeuf, & Stolper (2008) *Contributions to Mineralogy and Petrology* 155, 739–765.

Complex zoning patterns in phosphorus have been observed in olivines from terrestrial komatiites, basalts, andesites, and dacites and from an SNC (Martian) meteorite. These features are decoupled from zoning in divalent cations; for example, P₂O₅ contents vary from below the detection limit to up to 0.2–0.4 wt. % over length scales of a few microns with no detectable variations in forsterite content. The P zoning patterns take various forms including (i) P-rich crystal cores with skeletal, hopper, or euhedral shapes; (ii) thin, widely spaced, concentric P-rich zones, especially near crystal rims, and various other types of oscillatory zoning; (iii) structures suggesting resorption of the P-rich zones and replacement by P-poor olivine; and (iv) sector zoning. Melt inclusions (and to a lesser degree, spinel inclusions) are usually located near P-rich zones but are nearly always in contact with low-P olivine that sometimes crosscuts features in nearby P-rich zones. Crystallization experiments on high-MgO, model Hawaiian basalt compositions at constant cooling rates (15-30 °C/hr) produced olivine with many comparable zoning features, demonstrating that they can form by crystal growth during simple cooling histories. Al and Cr zoning is correlated with P zoning in the experiments and in natural crystals to similar or lesser extents.

We infer that P-rich zones in experimentally produced and natural olivine reflect incorporation of P during rapid growth of the olivine and that the complex zoning patterns primarily record variations in crystal growth rate. The typical correlations of Al and Cr with P could reflect either coupled substitutions and/or kinetic controls on their partitioning as well. Crystal growth rate has undetectable effects on the incorporation of the common divalent cations into olivine, so the complex zoning patterns in P, Al, and Cr are superimposed on normal Fe/Mg zoning. The frequent occurrence of high-P zones in the cores of olivine phenocrysts may reflect undercooling of the liquid followed by nucleation and a pulse of rapid crystal growth.

We infer that oscillatory zoning in P generally reflects intrinsic factors whereby variable and oscillating growth rates occur without external forcings such as magma

mixing, variable cooling rates, and variations in the P content of the magma, since we generate such features in our simple cooling experiments. However, some of the variations in P content from core-to-rim in natural olivines probably do reflect external forcings: for example, thin, concentric high-P zones that often occur near crystal rims plausibly reflect eruptive processes (e.g., mixing, cooling, depressurization) that lead to transiently high crystal growth rates. Determination of the dependence of P incorporation into olivine on growth rate could provide a new tool for determining time scales of crystal growth and/or variations in the P content of the magma.

In agreement with previous studies of rare natural phosphoran olivines (e.g., with up to ~10 wt. % P_2O_5), we suggest that high-P olivine resulting from rapid crystal growth rate is out of equilibrium with the melt from which it formed. Although such high-energy olivine is probably metastable under these conditions, P diffusion in olivine is expected to be very slow, and thus when P-rich olivine is not in contact with melt it can persist over geological time scales. However, when it is adjacent to melt, the high-energy, P-rich olivine dissolves in the melt and then reprecipitates as low-P olivine. This may explain (i) the characteristic halos of low-P olivine around melt inclusions and around some spinel inclusions, which often form in association with melt inclusions; (ii) the dissolution from within of skeletal P-rich cores observed in the experiments and in some natural olivines; and (iii) the crosscutting by low-P olivine of features defined by high-P olivine. The fact that such crosscutting features are observed in our experiments indicates that this process can occur on time scales of hours.

Although P, Al, and Cr are highly correlated in our experiments and in natural olivines with short high-temperature residence times, it is more common, particularly in phenocrysts, for Cr zoning to be less intense than P zoning and for Al zoning to be weak to absent. Although in some cases this may reflect decoupling of Al and/or Cr incorporation into olivine from that of P (e.g., in the olivines from andesites and dacites), we suggest that in relatively primitive basaltic systems this reflects residence times of phenocrysts in hot basaltic magma. We propose that olivines initially grow from basic and ultrabasic liquids with normal zoning in Fe/Mg and other divalent cations, on which is superimposed complex zoning in P, Cr, and Al, largely reflecting variable crystal growth rates. The rapidly diffusing divalent cations then homogenize during residence of the olivine in hot magma, Al and Cr generally only partially homogenize, while fine-scale P zoning is preserved. In contrast, in rims of olivine phenocrysts grown during eruption or magma mixing events, in komatiitic olivines, and in groundmass olivines (i.e., microphenocrysts), all of which have short residence times at high temperature, zoning in divalent cations, Al and Cr, and P is preserved. The inferred order of diffusivities within P-enriched regions of olivine ($Fe, Mg, Ni, Ca \gg Al > Cr \gg P$) suggests an approach to quantifying thermal histories of olivines once the diffusivities have been quantified. Note, however, that this might be difficult because diffusivities may be highly dependent on small differences in olivine composition due to complex and variable substitution mechanisms.

P zoning appears to be widespread in magmatic olivine, revealing detailed histories of crystal growth and providing a stratigraphy in what can appear to be relatively featureless crystals. Since it is preserved in early formed forsteritic olivines that have had prolonged residence times in magmas at high temperatures (i.e., in which zoning in the more common divalent cations has diffused away), P zoning has promise as an archive of information on an otherwise largely inaccessible stage of a magma's history. Moreover, these features can be easily observed with standard electron microprobe techniques. We thus suggest that study of such features will be a valuable supplement to routine petrographic investigations of basic and ultrabasic rocks.

2. Fabbrizio, Baker, Beckett & Stolper (2013) Zoning of major and minor elements in olivine from the Kilauea Iki lava lake, Hawaii (in preparation)

The Hawaiian lava lakes provide natural laboratories to study processes that may occur within small shallow crustal magma chambers (e.g., Wright et al., 1976; Helz, 1987; Barth et al., 1994; Jellink & Kerr, 2001). The detailed monitoring of Kilauea Iki by the USGS, including temperatures within the lake as a function of time and depth and sampling as a function of depth, provides a wealth of information on the crystallization of this $\sim 40 \times 10^6 \text{ m}^3$ magma body. We have studied the zoning of Fe-Mg, Mn, Ca, and Ni as well as that of P, Cr, Al, and Ti in phenocrysts (grains $\geq 0.5 \text{ mm}$ in longest dimension) and microphenocrysts in 15 samples from hole #1 drilled in 1981 (KI81-1); depths of the samples ranged from 45.3 to 93.6 m (maximum depth in the lake is inferred to be $\sim 135 \text{ m}$; Helz, 2009). Preliminary results have been reported in Fabbrizio et al. (2010).

Samples from ~ 44 to 94 m contain glass; SiO_2 and MgO contents range from 70.1 and 1.7 wt% in sample 181 (55.2 m depth) to 52.3 and 6.3 wt% in sample 246 (75 m depth). Based on the Helz and Thornber (1987) glass geothermometer, quench temperatures for the samples with $>2.5 \text{ wt\% MgO}$ (the lower limit of the Helz and Thornber calibration) range from ~ 1140 to 1080°C . Given that the majority of the lava that filled the lake was erupted at a temperature of $\sim 1190^\circ\text{C}$, this implies a zeroth-order cooling rate of $\sim 6 \times 10^{-6} \text{ }^\circ\text{C/hr}$ for samples in the interval between ~ 60 and 90 m (with glass thermometer temperatures of $\sim 1140^\circ\text{C}$).

X-ray maps of and microprobe profiles through olivines from 45.3 to 60.3 m depth show that the grains are zoned with the shallower samples more strongly zoned in Fo content ($\text{Mg}/[\text{Mg}+\text{Fe}]$, atomic) than the deeper samples. For example, olivines from the 45.3 m depth can have core Fo contents ranging from 72-79 and rim values of 68.5-78.5. Compositional zoning is also seen in CaO and MnO (decreasing from core to rim in the case of CaO and increasing in the case of MnO). However, samples from $\geq 64 \text{ m}$ in depth are unzoned in divalent cations.

Based on X-ray intensity maps, all olivines that we examined display P zoning, with a range of features that are similar to those described by Milman-Barris et al.

(2008). Concentric P-rich lineations parallel to the crystal edges can occur as single bands or as two or more regularly spaced bands with similar or variable intensities along individual bands and/or from band to band. Bands can be finely spaced (5-20 μm) producing a fine-scale oscillatory zoning or widely spaced (e.g., many tens of microns) forming concentric P-rich zones. All melt inclusions that we observed in mapped olivines are enclosed in low-P regions cutting or disrupting the P-rich features. X-ray intensity maps for Cr, Al, and Ti sometimes show zoning in these elements that is spatially coincident with the P zoning. Based on ultra-high beam current quantitative line-profiles on a subset of the olivines for which we have X-ray maps, we suspect that zoning in Cr and Al (and perhaps Ti) coincident with P is present more often than would be inferred from our X-ray maps (i.e., the analytical conditions used for some of our X-ray maps, while sufficient to register P variations, were not adequate for capturing zoning in Cr, Al, and Ti). Examples of olivine X-ray maps are shown in Fig. 1.

Figure 1. Selected X-ray maps (P, left-hand column; Cr, middle column; Al, right-hand column) of olivines from the 1981 (hole 1) Kilauea Iki drill core; numbers along the left-hand side of the figure (i.e., 218, 231, and 246) refer to depths in feet; lower case letters (a, b, c...) indicate olivine grains. (These images represent a small subset of the total number of X-ray maps that we have collected on Kilauea Iki lava lake olivines.) Scale bar in all images is 100 μm . Relative pixel intensities between panels are not meaningful, but brighter pixels within a given image indicate higher concentrations of the element in question; gray-scale in each image has been adjusted to highlight features of interest, which are labeled [A], [B], etc. and indicated by red arrows. Locations of quantitative spot analyses are indicated by blue dots; high-beam-current line profiles are indicated by numbered red lines (e.g., 1-1').

218-Ol11: crystal “a” has a well-developed P-Cr-Al-rich band [A] that parallels the euhedral shape of the olivine; note that [A] is interrupted on its left side by two chromite inclusions. Crystal “b” has concentric zonation [B] around a melt inclusion; these bands contain submicron chromite crystals [C] visible in the Cr and Al maps. Crystal “c” shows skeletal banding in P (faintly visible in the Cr map; not visible in the Al map). 231-Ol12: crystals “a” and “b” both show P-Cr-Al concentric bands surrounding a low-P core; note that the bands are associated with submicron chromite crystals (these crystals are also distributed in the interior of the two crystals. 246-Ol14: olivine crystals “b” and “c” display spatially correlated P, Cr, and Al bands (Cr and Al bands are quite faint) [A]. 246-Ol15 crystal “d” shows features that are similar to those displayed by olivines “a” and “b” in sample 246-Ol14.

Based on our ultra-high beam current analyses of 12 olivines (covering depths of 45.3 to 93.6 m), P_2O_5 contents range from ~ 0.005 wt% outside of the P-rich bands to up to ~ 0.19 wt%. TiO_2 , Cr_2O_3 and Al_2O_3 vary from ~ 0.02 to 0.08 wt%, from below the detection limit (~ 10 ppm) to 0.074 wt%, and from below the detection limit (~ 20 ppm) to ~ 0.105 wt%, respectively. The ultra-high beam current analytical conditions that we used were: an accelerating voltage of 15 kV, beam current of 400 nA, and counting times of 200s on-peak. These conditions yielded detection limits for P, Ti, Al, and Cr in the range of 10-20 ppm. Figure 2 shows an example of a line scan across a P-rich zone from an olivine from 66.4 m depth. Note that the peaks of P, Cr, Al, and Ti are nearly coincident, and more importantly, the peaks for Ti, Cr, and Al appear to be slightly broader than that for P. Given the temperature-time history for this sample (which can be estimated from temperature measurements and cooling models for lava lakes; e.g., Ault et al., 1962; Hardee et al., 1981; Hort, 1997; Rüpke & Hort, 2004; Harris, 2008) and the assumption that at time t_0 (corresponding to the filling of the lava lake) compositional bands for all the elements had the same width, then we can estimate diffusion coefficients for Ti, Cr, and Al. The fundamental assumption here is that relative to diffusion of Cr, Al, and Ti, P is immobile. To first-order, this assumption is supported by observation in Milman-Barris et al. (2008). The chilled crust of the lava lake also shows compositional bands in P, Ti, Cr, and Al in the olivine phenocrysts and microphenocrysts and fully characterizing those bands will allow us to use profiles like those shown in Fig. 2 to potentially model, in a semi-quantitative fashion, P diffusion coefficients—if P bands in the olivine phenocrysts in the crust sample are consistently higher and narrower than those in the lake olivine phenocrysts than this difference in morphology can be attributed to diffusive relaxation.

Figure 2. High-beam current line profiles across a high-P zone in an olivine from sample 218 (66m depth); the x-axis units are in microns. Note that, if the Cr, Al, and Ti bands originally had the same width as the P band, the broadening of the Cr, Al, and Ti zones would suggest diffusive equilibration within the lava lake. That is, P zones can potentially be used as inert markers of the initial widths of all of the compositional bands.

3. Hofmann, Baker, Beckett & Stolper (2013) Olivine-liquid partitioning and spatially correlated minor-element zoning in synthetic komatiitic olivines (in preparation).

In addition to our study of minor element zoning in natural komatiitic olivines from Gorgona Island (see section 4 below), we performed both isothermal experiments (between 1500 and 1425°C) and two series of dynamic crystallization experiments (at cooling rates of 5°C/h and 20°C/h from a liquidus temperature of 1510°C down to between 1395 and 1320°C) on a synthetic haplo-komatiite bulk composition in order to evaluate the physical parameters governing incorporation of minor elements in olivines grown from a very MgO-rich bulk composition (BSE photomicrographs and X-ray maps of the 20°C/h run are shown in Fig. 3). The bulk composition for this study was derived from the average bulk composition of two plate spinifex komatiites from Gorgona and then modified such that the major components of the mix were limited to CaO, MgO, Al₂O₃, SiO₂. Because we were interested in comparing the zoning profiles observed in natural komatiite olivines, we added P, Sc (as a proxy for Cr), and Mn to the mix. While we didn't analyze our natural komatiitic olivines for Sc, Sc, unlike Cr, does not exhibit multivalent behavior in silicate melts with varying fO_2 and while somewhat more incompatible than Cr it is much less incompatible than Al in olivine (e.g., Spandler and O'Neill, 2010), and thus it can serve as a proxy for Cr³⁺ under experimental fO_2 conditions where all Cr would be present as Cr²⁺. (These very reduced experiments are described in section 4.) The experiments here were designed to investigate the behavior of Sc, Al, and P

in olivine during dynamic crystallization and to help constrain the equilibrium partitioning of Sc, Mn, and P between olivine and melt ($D^{\text{ol/liq}}$).

The isothermal experiments produced euhedral olivine grains that yielded $D^{\text{ol/liq}}$ values for Mn and Sc that show little to no variation as a function of temperature: 0.26 ± 0.02 to 0.33 ± 0.02 (Mn; 1495 to 1425°C) and ~ 0.12 – 0.13 ± 0.02 (Sc; same temperature range). The slight increase in D_{Mn} with decreasing temperature is consistent with the results of Watson (1977) as are our experimental partition coefficients. The Sc D 's are consistent with the 1300°C results of Spandler and O'Neill (2010). P partitioning shows substantially more scatter with D_{P} varying from 0.32 ± 0.23 (at 1495°C) to 0.16 ± 0.09 (at 1425°C). Not all of the olivines grown in our cooling rate experiments displayed zonations in P and/or Sc. However, the bladed olivines that were produced in this study (Fig. 3) display spatially correlated sector zoning in P and Sc broadly similar to features observed in P and Cr in the Gorgona olivines. No zoning was observed in any of the other elements comprising the experimental starting material in the olivines produced in the cooling rate experiments. Quantitative analyses of olivines from the cooling rate runs showing P-Sc zoning demonstrate a strong linear correlation between P and Sc with a slope of ~ 3 (Fig. 4). This suggests that in the absence of Cr^{3+} , and for Sc concentrations in olivine above ~ 0.0008 cations per four oxygens, Sc and P are involved in a substitution of the type: $3\text{P} + \text{Sc} + 2\Box = 3\text{Si} + 3\text{M}^{2+}$ (where $\Box$ represents a vacancy). For a discussion of bulk compositions that contain Cr, see part 5 below. The results of these experiments demonstrate that Sc and P can show coupled substitutions similar to those shown by Cr and P (see Fig. 9 in Milman-Barris et al., 2008). This in turn means that in our Sc-bearing but P-free cooling rate experiments (see part 4 below) banding observed in Sc could be expected to have been coupled with P if P were present in the bulk composition.

Figure 3. Backscatter electron image and phosphorus, scandium, and aluminum K_{α} X-ray maps of synthetic olivine K-1-3a grown during cooling rate experiment K-1-3 (cooled from 1510°C at 20°C/h). Scale bar shown in panel a is 50 μm and applicable to all panels. **a.** Backscatter FE-SEM image of the crystal. Melt pools appear as lighter gray blebs within the interior of the grain. Feature marked [D] is a crack also visible in other panels. **b.** P K_{α} X-ray intensity map of K-1-3a showing distinct dark “fans” (suggesting lower P content than surrounding, lighter areas) between melt pools [A]; brighter “fingers” [B] appear in between the dark fans [A] and, in some cases (panel c), appear to touch the terminus of some melt pools. **c.** Sc K_{α} X-ray intensity map of K-1-3a showing the same fanning observed in (b). A bright sector [C] appears near the left edge of the crystal; this feature is also visible in P (a). **d.** Al K_{α} X-ray intensity map of K-1-3a showing no discernable zonation within the olivine. The same crack identified in panel a is indicated here [D].

Figure 4. Relationship between Sc and P concentrations expressed as cations per four oxygens in two synthetic olivines produced in the 20°C/h cooling rate experiment. Error bars are one standard deviation based on counting statistics. Best-fit line shown is an unweighted linear regression of all data corresponding to equation: $P = -0.0022 + 2.769 * Sc$ ($r^2 = 0.66$).

4. Hofmann, Beckett, Baker & Stolper (2013) Insight into spinifex textures via cooling rate experiments and zoning of phosphorus and associated elements in natural komatiitic olivines (in preparation).

Komatiites are ultramafic, mostly Archean, igneous rocks that are studied for the potential insights they may yield into melting of the early Earth's mantle. In this study, however, we focus on a representative suite of younger, Cretaceous komatiites from the Colombian island of Gorgona. These rocks are the youngest known komatiites and their olivines, unlike those in their Archean counterparts, are relatively unaltered. Komatiite flows are layered ultramafic units consisting of

olivine and pyroxene in a matrix of dendritic pyroxenes, Cr-rich magnetite, and devitrified glass, the majority of which has been replaced by secondary minerals due to hydrothermal alteration. The brecciated flow top, which displays chilled textures including microphenocrystic olivine, grades downward into a “spinifex zone” consisting of an upper, randomly oriented spinifex zone and a lower plate spinifex zone in which the spinifex olivines grow in elongate bundles subparallel to crystals of the same morphology and perpendicular to the komatiite flow top. In this study, we analyzed a selection of komatiitic olivines from the layered regions of Gorgona komatiite flows in order to evaluate how phosphorus zoning is manifested in olivines displaying a range of growth textures (e.g., microphenocryst, plate spinifex) and how zoning in other minor elements is connected to that of P. Preliminary results are reported in Hofmann et al. (2008)

We observed spatially correlated P, Al, and Cr zoning in 36 of 40 Gorgona komatiitic olivines from three textural units: a jointed flow top, two random spinifex zones, and two oriented plate spinifex zones (Fig. 5-6). Phosphorus zoning is decoupled from or inversely correlated with Al and Cr zoning in one or two of the olivines we examined from each of the three units. Microphenocrysts from the jointed flow top display oscillatory and sector zoning as well as $P \pm Al \pm Cr$ rich cores with boundaries between P-enriched regions and surrounding P-poor regions parallel to the crystal’s grain boundaries. Spinifex olivines from both the random and oriented zones display bands alternately enriched and depleted in P, Al, and Cr parallel to the long dimension of these crystals. Oriented plate spinifex olivines, however, often show a single central high-P band along the a-axis. The absence of elemental zoning (P, Al, or Cr) with hopper or chain morphologies in the spinifex olivines strongly suggests that these grains did not initially grow with these morphologies followed by subsequent growth that “filled in” the voids. Note that many equant non-skeletal olivine phenocrysts (e.g., from Hawaii) display P-zoning that has a skeletal morphology—clearly subsequent growth of these crystals has filled in the initial skeletal structure.

In an effort to reproduce both the morphologies and the distinctive linear zoning in minor elements in olivine that is characteristic (see Fig. 6) of the spinifex texture, we conducted a series of 1-atm cooling rate experiments in a thermal gradient. These runs used a major-element bulk composition and an experimental design similar to that described by Faure et al. (2006), but with the addition minor elements Sc and Mn added to the bulk composition. The work of Faure et al. (2006), involving dynamic crystallization experiments in a thermal gradient, are the only experiments that have reproduced olivine morphologies that are similar to those in the spinifex zone of komatiite lava flows. However, the use of a graphite crucible to hold the silicate melt prohibits including P_2O_5 in the starting mix, since under the reducing conditions imposed by graphite at 1-atm, P is extremely volatile. The three experimental charges in our study were all cooled at 5°C/hr ; however a different thermal gradient was imposed along the ~ 1.5 cm portion of melt in the crucible in each run: $\sim 20^\circ\text{C/cm}$ (run 9), $\sim 15^\circ\text{C/cm}$ (run 10), and $\sim 10^\circ\text{C/cm}$ (run 8). Like the experiments of Faure et al. (2006), the experiments produced elongate (upwards of

½ a cm) non-skeletal olivine crystals. Sc X-ray maps of two grains are shown in Fig. 7. Bright bands in each image denote enrichments in Sc; compare with Fig. 6b, c, h, and i.

Cation-cation plots for Gorgona komatiite olivines reveal strong linear trends between Al and Cr and suggest that Al and Cr enter the olivine crystal lattice in a ~2:1 ratio. Similar observations were previously made by Milman-Barris et al. (2008); therefore, we suggest that the 2:1 Al to Cr substitution may represent a relatively universal zoning feature in olivines that grow from Cr- and Al-bearing melts under terrestrially relevant bulk compositions and redox conditions. Trends in P-Al and P-Cr composition space are nearly vertical in the case of microphenocrysts from the flow top (Fig. 8a), despite the visual confirmation of P zoning being spatially correlated to zoning in Al and Cr (Fig. 5). Random spinifex olivines define two trends in both P-Al and P-Cr space: one that is sub-vertical and one that is sub-horizontal; sometimes, examples from both trends can be found in a single grain (Fig. 8b). With one exception, oriented plate spinifex olivines define a single P-Al and P-Cr trend, which suggests that P is being accommodated into the olivine lattice via a substitution mechanism involving both Al and Cr. The exception is a rare preserved plate spinifex terminus, which records much higher P at low Al and Cr concentrations compared to the other portions of plate spinifex grains; we interpret these data to be suggestive of P incorporation in excess of equilibrium values due to rapid crystal growth.

Figure 5. Phosphorus, Cr, and Al K_{α} X-ray maps of Gorgona olivine microphenocrysts from sample GOR94-19, taken from the jointed flow top of a komatiite flow. Scale bars (only one shown per grain) are 50 μm for all panels. Pixel intensities are meaningful within a single panel with white corresponding to more x-ray counts and black to fewer but differences in intensities between panels are not meaningful because the grayscale in each panel is scaled to emphasize features of interest (labeled [A], [B], etc. and indicated by red arrows). Locations of representative quantitative analyses are indicated by numbered yellow dots. **a.-c.** Equant microphenocryst GOR94-19e has a skeletal core [A] with the same geometrical shape as the overall grain and with correlated, high concentrations of P, Cr, and Al; surrounding this core at irregular intervals are concentric bands high in these elements. There are several melt inclusions, which are surrounded by a region low in P [B], and a small sector [C] that displays correlated Cr and Al anticorrelated with P. **d.-f.** Skeletal microphenocryst GOR94-19g contains multiple melt inclusions in addition to a single spinel inclusion [A]. The spinel inclusion appears bright in P due to differences in the background between P in spinel and P in olivine that are not taken into account in the X-ray maps, which

are not background corrected. The core of the grain contains a region high in Al and Cr [B] that is low in P. Surrounding melt inclusions are regions low in P (e.g., [C]). **g.-i.** Equant microphenocryst GOR94-19h contains a core with the same shape as the rest of the grain [A]; however, the core appears hopper-shaped and surrounds a low P, Cr, and Al center [B]. Angular melt inclusions like [C] exist near grain boundaries in nearly all imaged microphenocrysts.

Figure 6. Phosphorus, Cr, and Al K_{α} X-ray maps of portions of Gorgona olivines in sample GOR94-29, from a random spinifex zone of a komatiite flow. Scale bars are 50 μm for all panels. **a.-c.** Elongate spinifex olivine GOR94-29b displays a central band high in P, Cr, and Al [A] parallel to the grain's long axis. The band bifurcates, with the thicker band thinning to a sharp point in the lower right of the image. **d.-f.** Olivine GOR94-29g, contains multiple lobate internal "regions" demarcated by abrupt changes in P, Cr, and/or Al zonations and X-ray intensity (e.g., [D]). Note that the low-P region [A] has been altered, which is apparent in

the Al map (panel f) but the grain appears continuous and the original zoning is preserved in Cr (panel e). The zone denoted [B] and encircled appears to be a single region based on P (panel d); however, distinct bands [C] are apparent in both the Cr and Al maps that are not visible in P. Banding (that is not parallel to grain boundaries) continues in all three elements close to the termination [E]. **g.-i.** Elongated spinifex olivine GOR94-29h contains a central band [A] elevated in P, Cr, and Al parallel to the grain's long axis. Along the region of the grain marked [B], Al and Cr bands appear to be the same width, but the P band appears to be wider. [C] points to a potential spinifex olivine tip that shows preservation of zoning in both P and Cr; a crack is visible in Al to the left of the arrow denoting [C], and the high intensity Al signal from the surrounding glass makes it impossible to discern the outline of the olivine and suggests that the olivine itself may have undergone alteration, as seen in panels d-f, feature [A].

Figure 7. Sc K α X-ray maps of elongate olivine grains from two cooling rate experiments. Both runs cooled at 5°C/hr; thermal gradient imposed on the graphite crucible in run 8 was ~10°C/cm, in run 10 the thermal gradient was ~15°C/cm. Note the non-skeletal morphology. The very bright regions are quenched glass $\pm$ dendritic pyroxenes. Bright linear bands in both olivine grains are regions enriched in Sc.

Figure 8. Relationship between Al and P (cations per four oxygen atoms) in Gorgona komatiite olivines based on background-corrected electron microprobe analyses. Error bars are one standard deviation of the mean based on counting statistics. **a.** Gorgona microphenocrysts (filled triangles) from GOR94-19, a jointed flow top sample. Also plotted are two sets of Hawaiian microphenocrysts (C7 [filled diamonds] and C4 [open diamonds], as given in Milman-Barris et al. 2008). Equations and correlation coefficients based on unweighted linear regressions are: GOR94-19 (dashed line): $P = -3.302e-5 + 0.1314 * Al$ ($r^2 = 0.16$); global Hawaii (solid line): $P = -0.003 + 3.856 * Al$ ($r^2 = 0.74$). **b.** Al vs. P in olivines from Gorgona random spinifex sections GOR94-43 (filled circles) and GOR94-29 (open circles).

5. McCanta, Beckett & Stolper (2013) Zonation of phosphorus and other minor elements in olivine: An experimental study (in preparation).

The origins of P zonation in olivine were investigated through a series of 1-atm dynamic crystallization experiments performed near the QFM buffer on a variety of basaltic bulk compositions over a range of cooling rates (1-30°C/h) and maximum melting temperatures. Starting materials were doped with variable amounts of P, Sc, a trivalent transition element, and Cr in order to examine possible interactions among these elements and Al in olivine. Our results are reported in McCanta et al. (2008a,b; 2009; 2011).

Oscillatory and sector zoning of P in olivine is present in all P-bearing experiments and oscillatory zoning of olivine is present even in P-free experiments. X-ray maps for P, Cr, and Fe for a suite of experimentally produced olivines for a variety of cooling rates are shown in Fig. 10. Note that oscillatory zoning of P and Cr is present in all of the run products and, indeed, it is also present for all maximum melting temperatures we examined on four Cr- and P-bearing bulk compositions. The universal development of oscillatory zoning in olivine from experimental samples that were subjected only to constant temperature soaks (i.e., isothermal experiments) or a soak at a maximum temperature followed by cooling at a constant rate indicates that such zoning in natural samples cannot be ascribed to changing magmatic conditions without additional information. Intrinsic processes in the boundary layer of the melt and at the melt-olivine interface can result in oscillatory zoning, even in an otherwise static magmatic system. The presence of oscillatory zoning in P-free olivine suggests that the process producing the zoning does not require the presence of high field-strength cations.

The more rapidly cooled experiments we conducted (15° and 30°C/hr), as well as those taken initially to superliquidus temperatures, exhibit predominantly skeletal or dendritic olivine morphologies. More slowly cooled, subliquidus runs (1-10°C/hr) are more equant.

Figure 9. Cations of P in olivine produced in dynamic crystallization experiments as a function of cations of Sc.

We conducted experiments on one Sc-doped bulk composition; most Sc substitutes independent of P but up to half participates in a coupled substitution with P in a roughly 5:3 ratio (see Fig. 9) suggesting reactions of the type $5P + 3Sc + 4\Box = 5Si + 7M^{2+}$ (where $\Box$ represents a vacancy). However cation sums of Sc+Al+Cr:P in these experiments are consistent with a 1:1 relationship between trivalent cations and P, suggesting the simple substitution $P + M^{3+} + \Box = Si + 2M^{2+}$ and we conclude that this is probably the dominant substitution mechanism in Sc-, P-bearing bulk compositions. In

the absence of Sc, both molar Al-P and Cr-P plots yield much higher slopes ($>\sim 5$), suggesting that the mechanism is different; P-Cr and P-Al relationships are consistent with previous work on Hawaiian bulk compositions (Milman-Barris et al., 2008).

Figure 10. K α X-ray maps of P, Cr, and Fe in 1 atm dynamic crystallization experiments on an olivine-doped Hawaiian basalt held at 1280-1285°C for 3 hours and cooled at various rates to 1150°C.

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Zoning of phosphorus in igneous olivine

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Abstract We describe P zoning in olivines from terrestrial basalts, andesites, dacites, and komatiites and from a martian meteorite. P_2O_5 contents of olivines vary from below the detection limit (≤ 0.01 wt%) to 0.2–0.4 wt% over a few microns, with no correlated variations in Fo content. Zoning patterns include P-rich crystal cores with skeletal, hopper, or euhedral shapes; oscillatory zoning; structures suggesting replacement of P-rich zones by P-poor olivine; and sector zoning. Melt inclusions in olivines are usually located near P-rich regions but in direct contact with low-P olivine. Crystallization experiments on basaltic compositions at constant cooling rates (15–30°C/h) reproduce many of these features. We infer that P-rich zones in experimental and natural olivines reflect incorporation of P in excess of equilibrium partitioning during rapid growth, and zoning patterns primarily record crystal-growth-rate variations. Occurrences of high-P phenocryst cores may reflect pulses of rapid crystal growth following delayed nucleation due to undercooling. Most cases of oscillatory zoning in P likely reflect internal factors whereby oscillating growth rates occur without external forcings, but some P zoning in natural olivines may

reflect external forcings (e.g., magma mixing events, eruption) that result in variable crystal growth rates and/or P contents in the magma. In experimental and some natural olivines, Al, Cr, and P concentrations are roughly linearly and positively correlated, suggesting coupled substitutions, but in natural phenocrysts, Cr zoning is usually less intense than P zoning, and Al zoning weak to absent. We propose that olivines grow from basic and ultrabasic magmas with correlated zoning in P, Cr, and Al superimposed on normal zoning in Fe/Mg; rapidly diffusing divalent cations homogenize during residence in hot magma; Al and Cr only partially homogenize; and delicate P zoning is preserved because P diffuses very slowly. This interpretation is consistent with the fact that zoning is largely preserved not only in P but also in Al, Cr, and divalent cations in olivines with short residence times at high temperature (e.g., experimentally grown olivines, komatiitic olivines, groundmass olivines, and the rims of olivine phenocrysts grown during eruption). P zoning is widespread in magmatic olivine, revealing details of crystal growth and intra-crystal stratigraphy in what otherwise appear to be relatively featureless crystals. Since it is preserved in early-formed olivines with prolonged residence times in magmas at high temperatures, P zoning has promise as an archive of information about an otherwise largely inaccessible stage of a magma's history. Study of such features should be a valuable supplement to routine petrographic investigations of basic and ultrabasic rocks, especially because these features can be observed with standard electron microprobe techniques.

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Introduction

Forsteritic olivines are common as phenocrysts in basaltic lavas and therefore have been intensively studied as

archives of information about their host magmas. However, despite its abundance, olivine's usefulness in this regard has been limited, in part because it is compositionally simple (i.e., olivine is largely a solid solution of forsterite and fayalite, usually with only minor amounts of other cations), but also because early-formed zoning is prone to erasure by rapid diffusion of divalent cations at magmatic temperatures. Thus, information that zoning in these elements might have held about early stages of olivine growth is often largely lost (Nicholls and Stout 1988; Petry et al. 2004; Coogan et al. 2005).

In this paper, we report the discovery of complex zoning patterns of P (frequently coupled with Cr and Al) in natural olivine from several localities and rock types and demonstrate that olivine with comparable features can be generated in simple crystallization experiments. Such zoning, especially in P, appears to be a widespread phenomenon and highly resistant to diffusive relaxation. It should thus be of value in deciphering the otherwise largely inaccessible early crystallization histories of basic and ultrabasic magmas.

Samples and analytical and experimental techniques

Polished sections of olivine-bearing rocks and of separated olivines were studied from basalts (Mauna Kea and Koolau volcanoes, Hawaii; Réunion island; Siqueiros fracture zone), andesites and dacites (Volcán San Pedro, Chile), komatiites (Isla de Gorgona, Colombia; Belingwe greenstone belt, Zimbabwe), and igneous meteorites (martian meteorite ALHA 77005 and the Brenham pallasite). Information on these natural samples is given in Table 1. Images of most are shown in Figs. 1, 2, 3, 4, 5 and representative analyses are given in Table 3. Features of interest are labeled (A, B, etc.); in the text, they are referred to by the figure number followed by the label (e.g., feature B in Fig. 1a is referred to as Fig. 1a[B]). Positions of representative analyzed spots are also shown in the appropriate figures.

Whenever possible, we use standard petrographic terminology to describe the two-dimensional morphologies of P-rich regions in olivine and the nomenclature of Donaldson (1976) to describe olivine growth shapes. There is a continuum of olivine sizes in the samples we studied, but for convenience we refer to ≥ 0.5 mm grains as phenocrysts and 0.1–0.5 mm grains as microphenocrysts. No effort was made to cut sections through crystal centers or in particular crystallographic orientations.

Controlled cooling rate experiments were done on two bulk compositions (Table 2): The first, with 0.16 wt% P_2O_5 , was based on the low- SiO_2 parental liquid for Mauna Kea computed by Stolper et al. (2004); the second

(1.18 wt% P_2O_5) was produced from the first by the addition of Durango apatite. Liquidus temperatures for both compositions were near (but below) 1400°C based on reconnaissance isothermal experiments and MELTS calculations (Ghiorso and Sack 1995). Each experiment was conducted in a vertical 1-atm gas-mixing furnace using an H_2 – CO_2 gas mixture that matched the fO_2 of the QFM buffer (Huebner 1971) at 1,400°C. Experiments were initiated by inserting a ~ 80 mg sample suspended on a Pt loop into the hot spot of the furnace at 1,000°C under flowing H_2 – CO_2 . The sample was then heated to 1,400°C at $\sim 500^\circ C/h$, held for 4 h, cooled at 15 or 30°C/h to $\sim 1,200^\circ C$, and drop quenched into deionized H_2O . The H_2/CO_2 ratio was fixed during cooling, so the fO_2 of the constant-composition gas was ~ 0.3 log units more reducing than QFM at 1,200°C. Run products were studied as polished thick sections. Images of the experiments are shown in Figs. 6, 7 with features of interest and representative analyzed points indicated as described above for the natural samples.

K_α X-ray intensity maps of Al, Ca, Cr, Fe, Ni, S, P, and/or Ti were obtained using the SX100 Cameca electron microprobe at the Université Blaise Pascal and Caltech's JEOL JXA-8200 electron microprobe. The Cameca microprobe was used for preliminary maps, with 512×512 pixel images, a beam current of 100 nA, and dwell times of 100 ms per pixel. Four images were acquired simultaneously, mapping P, Fe, Ni, and either Ca or Cr. P was analyzed with a large PET crystal to improve counting statistics. The JEOL microprobe was used with an accelerating voltage of 15 kV, beam current of 400 nA, beam diameter of 1 μm (excitation volume ~ 1.4 microns across, calculated according to Potts 1987), and pixel spacings of 1–4 μm in sessions lasting up to 62 h. Beam current variations during map acquisition were ≤ 5 nA (generally ~ 1 nA). Five images were acquired at the same time, mapping P, Cr, Al, Fe, and Ti for most samples, and P, Al, Ca, S, and Cr for ALHA 77005. P and Cr were acquired on high-intensity PET crystals. Dwell times of 200 ms were sufficient to detect P zoning in Hawaiian and experimental olivines, but 800 ms was generally required to detect zoning in Cr and Al. The Gorgona olivines had lower P contents and required correspondingly higher dwell times, 1,200–1,800 ms. A few maps used a specialized setup to image low concentrations of Ti, with a dwell time of 1,200 ms and acquisition of Ti K_α X-rays on three spectrometers simultaneously (two PET crystals and the high-intensity PETH) to improve the signal-to-noise ratio. Maps only show X-ray intensity (i.e., neither calibrations nor background corrections were applied).

Quantitative analyses of SiO_2 , TiO_2 , Al_2O_3 , Cr_2O_3 , FeO^* (all Fe as FeO), MnO, MgO, CaO, NiO, Na_2O , $\pm K_2O$, and

Table 1 Description of natural samples

Sample ID	Sample type	Grain ID	Locality	Rock type	Grain type	References/Notes ^a
SR756-14.10	PTS	C1-a	Mauna Kea, Hawaii	Submarine tholeiitic basalt	Phenocryst	1
SR756-14.10	PTS	C1-b	Mauna Kea, Hawaii	Submarine tholeiitic basalt	Phenocryst	1
SR756-14.10	PTS	C3	Mauna Kea, Hawaii	Submarine tholeiitic basalt	Phenocryst	1
SR756-14.10	PTS	C4	Mauna Kea, Hawaii	Submarine tholeiitic basalt	Microphenocryst	1
SR756-14.10	PTS	C6	Mauna Kea, Hawaii	Submarine tholeiitic basalt	Phenocryst	1
SR756-14.10	PTS	C7	Mauna Kea, Hawaii	Submarine tholeiitic basalt	Microphenocryst	1
SR756-14.10	PTS	C11	Mauna Kea, Hawaii	Submarine tholeiitic basalt	Phenocryst	1
SR762-5.25	PTS	C13	Mauna Kea, Hawaii	Submarine tholeiitic basalt	Phenocryst	1
R215-7.2	OS	2	Mauna Kea, Hawaii	Subaerial tholeiitic basalt	Phenocryst	1
R215-7.2	OS	4	Mauna Kea, Hawaii	Subaerial tholeiitic basalt	Phenocryst	1
S500-5b	OS	4	Koolau, Hawaii	Basalt	Phenocryst	2
PB-8-2002	OS	–	Piton Caille, Réunion Island	Basalt	Phenocryst	3
2384-2	OS	12	Siqueiros Fracture Zone	MORB	Phenocryst	4
94-19	PTS	1	Isla de Gorgona, Colombia	Phanerozoic komatiite	Microphenocryst	5
94-1	PTS	1	Isla de Gorgona, Colombia	Phanerozoic komatiite	Spinifex	5
ZS1-1	PTS	1	Belingwe Greenstone Belt, Zimbabwe	Archaean komatiite	Microphenocryst	6
Qcf4	PTS	1p	Volcán San Pedro, Chile	Andesite	Xenocrystic phenocryst	7
Qcf2	PTS	1s	Volcán San Pedro, Chile	Dacite	Xenocrystic microphenocryst	7
ALHA 77005,137	PTS	–	Meteorite	Shergottite	Phenocryst	8
Brenham (10Y)	PTS	–	Meteorite	Pallasite	Phenocryst	9

PTS Polished thin section, OS olivine separate (thick section), MORB Mid-Ocean Ridge Basalt

^a References/Notes: 1. Stolper et al. (2004); 2. Garcia (2002); 3. Collected by N Métrich; 4. Perfit et al. (1996), Saal et al. (2002); 5. Kerr et al. (1996), Kerr (2005); 6. Nisbet et al. (1987); samples from TL Grove; 7. Costa and Chakraborty (2004); samples from F Costa; xenocrysts of basaltic parentage in calc-alkaline host; 8. sample from NASA Meteorite Working Group; 9. Sample from Arizona State University

P₂O₅ in olivine and glass were acquired using Caltech's JEOL JXA-8200 electron microprobe and the P X-ray maps to guide locations. Analyses were done with an accelerating voltage of 15 kV, a 40 nA beam current for olivine (10 nA for glass), and a 1 µm beam diameter for olivine (1 or 10 µm for glass with most done with a 10 µm beam to minimize alkali loss). Synthetic and natural mineral standards included Shankland forsterite (Si in olivine; Mg in olivine and glass); VG2 basalt glass (Si in glass); synthetic TiO₂ (Ti); anorthite (Al, Ca); Cr₂O₃ (Cr); fayalite (Fe); tephroite (Mn); Amelia albite (Na); Ni olivine (Ni); Durango apatite (P); and microcline (K). Counting times and

spectrometer assignments were chosen to minimize errors on P, Cr, and Al, the low-abundance elements of greatest interest in olivine. Data were reduced using a modified ZAF procedure (CITZAF; Armstrong 1988). Acceptance criteria included oxide sums of 100.0 ± 2.0 wt% for olivine and glass and cation sums of 3.000 ± 0.015 per four oxygens and 1.000 ± 0.015 Si + P cations per four oxygens in olivine. A few olivine analyses that met these criteria were nevertheless rejected due to obvious glass contamination (e.g., anomalous Ti and Al). For Al₂O₃, Cr₂O₃, and P₂O₅ in olivine, detection limits and absolute errors (based on counting statistics) were ≤0.01 wt %.

Crystallographic orientations of most olivines were obtained by electron-backscattered diffraction (EBSD) with a LEO 1550VP field emission scanning electron microscope. EBSD patterns were collected with an accelerating voltage of 20 kV, aperture of 60 μm, working distance of 20 mm, and tilt angle of 70°. On each

grain, 2–8 points were analyzed, all of which produced a good indexed solution for forsterite using HKL Channel 5 software, with a mean angular deviation $<1^\circ$. Averaged results are shown as insets in Figs. 1, 2, 3, 4, 5, 6, 7 as equal-area upper-hemisphere projections of the crystallographic axes.

Fig. 1 Phosphorus X-ray maps of Hawaiian olivine phenocrysts. Scale bars are 500 μm for all panels. Relative pixel intensities between panels are not meaningful but brighter pixels within a panel indicate higher P; the greyscale in each image is scaled to highlight features of interest, which are labeled ([A], [B], etc.) and indicated by red arrows. Locations of representative quantitative analyses are indicated by the blue–green numbered points (see Table 3 for analyses). Some regions were mapped at higher spatial resolution than others and some figures are mosaics of images obtained at different resolutions. Crystal orientations based on EBSD are shown as inserts, each containing an upper hemisphere equal area projection of the crystallographic axes along with approximate direction of the normal to the polished surface. In this and other figures, cracks are sometimes visible as irregular or curved, very P-rich features; these are generally readily distinguished from the features of interest to us. **a** Glomerocryst from a Mauna Kea submarine tholeiite (HSDP sample SR756-14.10, crystals C1-a and C1-b). Both crystals have virtually the same orientation based on EBSD measurements. Crystal C1-a has a high-P core in the shape of a relict hopper-shaped crystal [A] built up by concentric bands of high- and low-P olivine (i.e., oscillatory zoning); its limbs are open at one end, enclosing a low-P olivine core [B]. A spinel inclusion [C] is present in the core of the relict crystal, surrounded by low-P olivine, which crosscuts the high-P, oscillatory zoning of the relict crystal. Although quantitative analyses detect no P in any spinel grain, they are slightly bright in this and other P X-ray maps because of differences in background intensities between spinel and olivine. The core of crystal C1-b contains a high-P, skeletal, oscillatory zoned, relict crystal [D] with two low-P chambers [G]. The high-P core of C1-b differs in shape from the core of C1-a, although the outer faces of the relict crystals parallel the rims of the crystals in which they occur in both cases. The relict P-rich cores in both C1-a and C1-b are enclosed in broad, featureless, low-P zones [E]. Three parallel P-rich bands (also rich in Al and Cr; not shown) occur near

the outer rims of C1-a and C1-b [F]; these bands do not extend into the zone in which the two crystals are attached, suggesting they grew after agglomeration, perhaps in conjunction with eruption. Both of the crystals are strained (i.e., they are kink-banded), but the P-zoning patterns are undisturbed. **b** A portion of crystal #4 from Mauna Kea subaerial tholeiite HSDP R215-7.2. This crystal is characterized by thin, concentric, P-rich bands. The individual bands are each roughly constant in intensity, but variable from band to band. The brightest band contains $\leq 5 \mu\text{m}$ melt inclusions [feature A; very bright in P] and is offset at one corner [B]. **c** Phenocryst C6 from Mauna Kea submarine tholeiite HSDP SR756-14.10. This is a composite crystal, with two high-P cores [A] that have outlines paralleling crystal rims; the core nearer the bottom of the image has oscillatory zoning. Both cores are surrounded by a broad, low-P zone, and there are four concentric, evenly spaced bands near the rim of the composite crystal [B] that grew (perhaps associated with eruption) after the two cores had joined into a single crystal. Note the strongly zoned microphe-nocryst in the lower right of the image [C]. **d** Another crystal (C3) from Mauna Kea submarine tholeiite HSDP SR756-14.10. This subhedral crystal has a faint, euhedral to subhedral P-rich core [A] surrounded by a broad, low-P region. The microphe-nocryst [B] is crystal C4 shown in greater detail in Fig. 4a–d. **e** A portion of a glomerocryst (#2) from Mauna Kea subaerial tholeiite HSDP R215-7.2. The small bright dots are pits from ion microprobe analyses. The larger of the two crystals [A] has wispy, feathery, oscillatory zoned, high-P regions in its core [B] surrounded by low-P olivine. This elongate central region is enclosed in faint concentric, high-P bands [C]. The smaller crystal in the lower left of the image [D] has a high-P core, surrounded by a thin, rounded, low-P zone, which is in turn surrounded by curved oscillatory zones. **f** Crystal C13 from Mauna Kea submarine tholeiite HSDP SR762-5.25. Consisting mostly of low-P olivine, this crystal has discontinuous, concentric, high-P bands [A] and curved, wispy, oscillatory “knots” of high-P olivine [B]

Zoning patterns in natural and experimentally produced olivines

P zonation in natural olivines

P_2O_5 contents of the natural olivines range from below detection limit to 0.41 wt% (in ALHA 77005). Zoning in phosphorus, based on X-ray intensity maps, was observed in all olivines we examined except for the Brenham pallasite (consistent with its low P content (0.004 wt% P_2O_5 ; Smith et al. 1983); i.e., less than our detection limit). The P zoning patterns of the natural olivines display a range of features. Examples are shown in the figures and summarized in the descriptions below and in the figure captions.

Phenocryst interiors are frequently unzoned in major and minor divalent cations (Fe, Mg, Mn, Ca, Ni), but all are zoned in P. They often have a zoned P-rich core surrounded by a broad, generally P-poor region (Fig. 1). The outer edges of the P-rich cores typically define euhedral shapes (or euhedra with low-P embayments) and are parallel to the outer edges of the phenocrysts. The P-rich cores display a range of patterns: For example, as shown in Figs. 1a, 2c, 3a, c, some are skeletal (compare

to Fig. 1e, g in Donaldson 1976), with oscillatory-zoned P-rich limbs enclosing P-poor, unzoned “cavities”. In contrast, P-rich cores of the olivines shown in Fig. 1c, d are not skeletal though the core of the olivine shown in Fig. 1c has concentric P banding. Some of the olivine phenocrysts are composite crystals, in which case each of the component crystals has its own P-rich core (e.g., Fig. 1c[A], e[B,D]); the same is true for the glomerocryst in Fig. 1a, composed of two similarly oriented crystals, each of which has its own skeletal, P-rich core. In some crystals, the P-rich central regions are “wispy” or “feathery” (e.g., Fig. 1e[B]), sometimes with no obvious preferred orientation relative to the phenocryst edges (e.g., Fig. 1f[B]). Although the Réunion sample also has a roughly uniform P-rich region near its center (Fig. 2a[A]), the shape is subhedral rather than euhedral, and in contrast to the generally P-poor regions observed outside the cores of the Hawaiian samples, the Réunion sample has relatively wide (100–200 μm), tapering, discontinuous P-rich bands (Fig. 2a[B]) outside the core, some of which roughly parallel the outer edges of the crystal. It is important to reemphasize that none of these P-rich features have any detectable manifestation in the common, divalent constituents of olivine.

Fig. 2 Phosphorus X-ray maps of non-Hawaiian olivine phenocrysts. Scale bars are 100 μm for all panels. Other details are given in the caption to Fig. 1. **a** Composite olivine from Piton Caille, Réunion. This glomerocryst has a prominent subhedral- to anhedral-shaped high-P core [A]. The region between this core and the crystal rim has complex, wavy, tapering oscillations of high- and low-P olivine [B], some of which emanate from a skeletal apex [C]. These features are also seen in Al X-ray maps. Closely spaced, P-rich bands are present near the crystal rim in some places [D]. **b** Xenocrystic olivine from a Volcán San Pedro andesite (Qcf4, Fig. 1p in Costa and Chakraborty 2004). This euhedral crystal has multiple, prominent, P-rich bands [A, B] of variable intensity (between bands and along individual bands) within $\sim 20 \mu\text{m}$ of the crystal rim, all in the region of strong Fe/Mg zoning described by Costa and Chakraborty (2004). Spinel inclusions [C] occur throughout this crystal, but their compositions change abruptly at the location of the brightest P-rich band (i.e., at [B]) from Fe-rich and Al-, Cr-, Mg-poor near the rim to more Fe-poor and Al-, Cr-, Mg-

rich in the interior. Large spinels decorate the crystal “corners” where P-rich zones parallel to adjacent crystal edges would intersect [C], but the P-rich zones actually terminate $\sim 10 \mu\text{m}$ from the spinels. P-rich bands are absent from the interior of the crystal (unzoned in Fe/Mg, Costa and Chakraborty 2004), but there is a faint, “patchy” structure in P-zoning interior to the P-rich bands [D]. **c** Crystal from a mid-ocean ridge basalt from the Siqueiros fracture zone. This olivine has a rectangular, low-P core [A] surrounded by a rectangular region defined by concentric oscillatory zoning in P [B], which is in turn surrounded by a largely featureless, low-P region [C]. The image shows four glass inclusions [D]. All of the inclusions are enclosed in low-P olivine; the three at the top of the image are surrounded by halos of low-P olivine [E] that embay the well-defined rectangular, high-P, oscillatory-zoned region [B]. **d** Xenocrystic olivine Qcf2 from a Volcán San Pedro dacite. This crystal has concentric, high-P bands [A] parallel to the euhedral, outer crystal edges and is partially resorbed, resulting in anhedral crystal edges that crosscut the P-rich bands [B]

Oscillatory zoning in P is a common feature in the olivines we examined. It occurs in several different morphologies and at a range of length scales, often within a single crystal. We distinguish several types of oscillations:

- In some cases, one or more thin (most are 5–10 μm wide; the full range is 3–20 μm) P-rich zones form nearly continuous concentric bands parallel to the crystal edges, clearly outlining edges at different stages in a crystal’s growth. These can occur anywhere within a

crystal (e.g., Fig. 1b[A], e[C]), but are often near the outer edges of phenocrysts (e.g., Figs. 1a[F], 2b[B], d[A]); sometimes, they occur as sets of multiple, regularly spaced bands with similar or variable intensity along individual bands and/or from band to band (e.g., Figs. 1c[B], 2b[A,B], 4a[A]). In crystal interiors, these bands are typically widely spaced (e.g., 50–100 μm apart), but multiple bands near crystal rims are closer together (~ 10 to 50 μm). An interesting example of this is shown in Fig. 1c where two distinct euhedral, P-rich cores are surrounded by four concentric P-rich zones near the phenocryst rim that enclose the two cores, suggesting that the composite crystal continued to grow after the two cores had agglomerated. Figure 1a[F] shows a similar feature: two attached crystals have near-rim concentric zones on their outer faces except where the two crystals meet, again suggesting the crystals continued to grow after agglomerating. An apparently unique example of a thin, concentric, P-rich zone is a 20 μm thick zone in Fig. 1b[A] that is crowded with P-rich melt inclusions ~ 5 μm in diameter. Clark et al. (1986; their Fig. 2b) observed features possibly related to the P-rich bands reported here by Nomarski interference contrast imaging.

- Delicate, often highly regular (i.e., periodic) oscillatory zoning is also often present on a much finer scale (e.g., Figs. 2c[B], 3a[C]). High-P zones in these occurrences are typically 5–10 μm in width and spaced 5–20 μm apart. The P-rich phenocryst cores described above sometimes contain regions of such regular oscillatory zones (e.g., Figs. 1a[A, D], 3c[C]). Figure 3e[B] shows a more complex manifestation of oscillatory zoning in which the oscillatory zoning defines a herringbone structure with feathery or wispy terminations. Based on preliminary microprobe traverses, the oscillations in P described here are in some cases asymmetric (e.g., “saw-toothed”, as is typical for oscillatory zoning in plagioclase; see summaries in Pearce 1994; Shore and Fowler 1996). Although we have focused on examples from phenocrysts, microphenocrysts display oscillatory zoning in P comparable to the features observed in phenocrysts, including relatively widely spaced, concentric P-rich zones (e.g., Fig. 5g[B]) and periodic, fine-scale oscillations (e.g., Figs. 4a[E], 5a[A]).
- A third type of oscillation is illustrated in the Koolau phenocryst shown in Fig. 3c[A]. Here, oscillating, ~ 10 to 20 μm wide bands of higher and lower P are wedge-shaped and/or more diffuse and curved than the previous examples. Wider (100–200 μm), alternating high- and low-P bands in the Réunion phenocryst are also curved, tapering, and diffuse (Fig. 2a[B]).
- Spinifex olivines from the Gorgona island komatiite have oscillatory zones (10–45 μm wide and 10–45 μm

apart) parallel to the long dimension and to the crystallographic *a* axis of the crystal (Fig. 5d[A]). Gorgona komatiitic magmas have low P contents (Kerr et al. 1996; Kerr 2005), and the “high-P” zones of the spinifex olivines in this sample have very low absolute P concentrations (≤ 0.015 wt% P_2O_5 ; i.e., near our detection limit).

The high-P zones and bands display several types of offsets and discontinuities. In some cases (e.g., Fig. 1b[B]), these have no apparent relation to other features, but in general they fall into one of the following categories: (1) P-rich features often terminate in the vicinity of melt inclusions (Figs. 2c[E], 3e[D], 4a[C], e[B]); consequently, P-rich olivine is not usually in contact with the inclusions, which are typically surrounded by a rim of low-P olivine. (2) P-rich bands sometimes terminate close to spinel inclusions surrounded by P-poor olivine (Figs. 1a[C], 2b[C], 3a[D]). (3) P-rich bands are sometimes crosscut by low-P features, suggesting dissolution, in some cases accompanied by reprecipitation events. For example, Fig. 2d[B] shows an example of a partially resorbed olivine in which oscillatory zones terminate at the resorbed crystal boundary. Features suggesting partial replacement of P-rich bands by low-P olivine via a dissolution/reprecipitation process are shown in Fig. 3a[B,E], c[D,F]. In particular, in Fig. 3a, c the wavy/scalloped inner edges of the P-rich “relict” cores appear to have been dissolved away or reacted from within the crystals. Such dissolution-related features are often reported in plagioclases with oscillatory zoning (e.g., Pearce 1994; Shore and Fowler 1996). Clark et al. (1986) describe possibly related features in Nomarski interference images of igneous olivines. (4) Strained olivines displaying kink bands are common in Hawaiian basalts. Generally (e.g., Fig. 1a), P-rich features are undisturbed by the kink banding, but Fig. 1f[A] shows a strained Hawaiian crystal in which P-rich bands are discontinuous in two of the kink-band sectors, perhaps as a result of the deformation leading to the kink bands. (5) Offsets of 5–25 μm occur in the oscillatory bands of martian meteorite ALHA 77005 (Fig. 3e[A]) and probably reflect the effects of shock (all shergottites display varying degrees of shock metamorphism, e.g., Fritz et al. 2005). These offsets do not extend all the way through the crystal and crystal edges are unbroken; prominent cracks in the crystal (Fig. 3e[F]) crosscut and therefore postdate the event(s) that produced the offsets. While the offsets are likely shock induced, the inferred oscillatory zoning of P prior to microfaulting is similar to what we observed in demonstrably unshocked olivines (Figs. 1, 2, 3, 4, 5) and, therefore, the P distribution reflects a normal igneous process and not, as proposed by Edmunson et al. (2005), shock effects.

Some crystals display distributions of P that do not fall into the categories described above, and indeed, it is likely that there are many additional morphologies of P-zoning that we have not yet sampled. For example, the crystal (from a komatiite) shown in Fig. 5a[B] has an elongate triangular region with low P relative to the regions on

either side. Although without the classic hourglass shape (e.g., Strong 1969), this feature may be a kind of sector zoning. As shown experimentally by Pack and Palme (2003), olivine can develop classic hourglass sector zoning. Another P-poor region that may relate to sector zoning is observed in a Hawaiian microphenocryst (Fig. 4e[C]). In

Fig. 3 Phosphorus (a, c, e) and Cr (b, d, f) X-ray maps of olivine phenocrysts from basalts. *Scale bars* (only one shown for each grain) are 100 μm for all panels. Other details are given in the caption to Fig. 1. **a, b** Olivine from a Mauna Kea submarine tholeiite (HSDP sample SR756-14.10, crystal C11). This crystal is characterized by a high P_2O_5 , oscillatory zoned, central rhomb [A] with a ragged core of low-P olivine [B] surrounded by concentric oscillatory P zoning of variable intensity [C]. Two features are of particular interest: (i) A spinel is present at one of the corners of the concentric P zoning ([D], *middle arrow*), but the two P-rich limbs emanating from this corner stop short of the spinel crystal ([D], *top and bottom arrows*; note that the bottom *arrow* terminates in a crack). A similar feature is seen in Fig. 2b[C]. (ii) The features defined by P zoning are only present below the central P-rich rhomb [A]; indeed the upper left corner of the P-rich rhomb is not present. Feature [E] (outlined in *cyan*) defines a wavy boundary between featureless, low-P olivine above and oscillatory zoning below that terminates discontinuously at this boundary. Although faint, the same zoning features can be seen on the Cr image in panel **b** (e.g., the central rhomb is defined by elevated Cr as well as P; [G]). This rhomb is also very faintly visible on the Al map (not shown). The very bright circular regions in the Cr image are spinels. Cracks appear as P-rich features in the P map (e.g., [F]) but these can be distinguished by looking at the Cr map in (**b**). **c, d** Olivine from a Koolau subaerial tholeiite (S500-5b). The crystal has a relict skeletal P-rich zone in its core (its outer edges are at [A] and [F]). There are two types of oscillatory zoning: feature [A]—tapering oscillations emanating from a P-rich axis parallel to the crystallographic *c* direction that appears to define the most rapid growth direction of the crystal in cross-section (shown by a *dashed blue-*

green line [B]); and feature [C]—finer-scale, periodic oscillatory zoning. As with the central rhomb described in (**a–b**), the inner edge of the skeletal P-rich relict crystal is ragged and/or wavy [D], and the core itself [E] is all low-P olivine; this texture suggests that the low-P olivine replaced the high-P skeletal crystal from the inside. An interesting example of the texture of the inner edge of the relict, skeletal P-rich crystal is shown by [F], where the low-P embayment of the inner edge of the skeletal crystal truncates widely spaced, tapering oscillatory zoning. This feature is shown in more detail in Fig. 8 and described in the accompanying text. The same features visible in the P map (**c**) are less intense but clearly visible in the Cr map (**d**, [G]). The most intense features visible in P and Cr may be very faintly visible on the Al map (not shown). **e, f** Olivine from Iherzolitic shergottite ALHA 77005. Olivines in this meteorite are generally thought to be cumulus crystals derived from parental liquids similar to but somewhat more depleted than those that generated the basaltic shergottites (e.g., McSween et al. 1979; Bridges and Warren 2006). The P map (**e**) shows many features seen in other crystals: oscillatory zoning with the high-P zones highly variable in intensity; wispy, feathery terminations of some of the zoned regions [B], which emanate from a somewhat more intense P-rich axis ([E], shown by a *dashed cyan line*); and a halo of low P and Cr olivine [D] surrounding a large melt inclusion [C]. A distinctive feature is the offset of the oscillatory zones along microfaults ([A], shown as *blue lines*), probably related to the shocked nature of this meteorite. The same features are clearly visible in the Cr map (**f**) but none are visible on the Al map (not shown). There are prominent cracks filled with P- and Cr-rich material [F]

both cases, faint oscillatory zoning is superimposed on the P-poor sector. One of the Volcán San Pedro olivines displays an irregular, patchy distribution of P in its core (Fig. 2b[D]). Finally, the strained crystal with discontinuous P-rich zones described above has wispy, sinuous P-rich “knots” (Fig. 1f[B]). This feature may be on a continuum with other feathery or wispy features (e.g., Figs. 1e[B], 3e[B]) that are more clearly associated with crystal orientation or oscillatory zoning.

P-zoning in experimentally produced olivines

Quenched experimental samples consist of olivine (maximum dimension up to ~ 2 mm in section), chromian spinel (<100 μm), and glass. The olivines have a range of morphologies characteristic of rapid crystal growth including hopper-shaped, skeletal, and linked-parallel growth forms, as expected for the moderate cooling rates and high normative olivine contents of the starting materials (Donaldson 1976; Lofgren 1989). All olivines contain irregularly shaped interior melt (i.e., glass) pools, some clearly connected to melt outside the crystal. Spinel (with euhedral to dendritic morphologies) occur both at exterior edges of olivine grains and at the edges of included melt pools. Olivines are zoned continuously from $\sim\text{Fo}_{90}$ in crystal cores to $\sim\text{Fo}_{85}$ at their rims; they are similarly zoned toward interior melt pools. Based on X-ray maps and

quantitative analytical traverses, glass adjacent to olivine exhibits boundary layers (~ 150 to 250 μm wide) in all experiments, although not all experiments display boundary layers in all elements (e.g., a boundary layer in P was only observed in experiment 4); glass adjacent to olivine is variably depleted relative to the far-field glass by up to $\sim 10\%$ in FeO^* , $\sim 20\%$ in MgO , and $\sim 30\%$ in Cr_2O_3 and variably enriched by up to $\sim 10\%$ in Al_2O_3 , $\sim 20\%$ in P_2O_5 , and $\sim 30\%$ in K_2O and Na_2O . Elemental variations in the interior melt pools are similar or even more extreme.

P zoning is observed in olivine in all three dynamic crystallization experiments.

- Figure 6a shows two distinct (though similarly oriented) olivine crystals from experiment 1. The central crystal is elongated left-to-right, approximately perpendicular to the *c* axis, with tapering (up to 10 – 50 μm wide) P-rich (up to 0.06 wt% P_2O_5) and P-poor (<0.01 wt% P_2O_5) bands (Table 3), also elongated left-to-right (Fig. 6a[A]). The second crystal in the lower right contains tapering (up to 10 – 50 μm wide), oscillating P-rich (up to 0.11 wt% P_2O_5) and P-poor (<0.01 wt% P_2O_5) bands (Fig. 6a[D]) and an irregularly shaped, lobate melt pool (Fig. 6a[E]) that (like most melt/glass interfaces in this experiment) is bordered by P-poor olivine (<0.01 wt% P_2O_5). Boundaries between high- and low-P olivine near this melt pool are curved or embayed, often parallel to the outline of the melt pool (e.g., Fig. 6a[C]). Such

Fig. 4 P, Cr, Al, and Fe X-ray maps for olivine microphenocrysts in the groundmass of a Mauna Kea submarine tholeiite (HSDP SR756-14.10). Scale bars (shown in the P X-ray images) are both 50 μm . Melt and/or spinel inclusions are indicated as *small red dots* (some are below the sample surface). Other details are given in the caption to Fig. 1. **a–d** Crystal C4 (see [B] in Fig. 1d). Core-to-rim oscillatory zoning of variable intensity (both along individual zones and from zone-to-zone; [A, E]) is well developed in P and somewhat fainter but still prominent in Cr and Al. The P–Cr–Al-rich patterns are interrupted by a “swiss-cheese” texture in which irregularly shaped, low-P regions (e.g., [B]) are superimposed on the overall concentric zoning pattern. Some of these low-P zones are associated with melt

and/or spinel inclusions (e.g., [C]); but others are not, although nearby inclusions may have been present out of the plane of the section). These complex zoning patterns in P, Cr, and Al are superimposed on a relatively simple, mostly monotonic normal zoning pattern in Fe (i.e., low- to high Fe from core to rim; [D]). **e–h** This crystal (C7) shows features similar to those described for crystal C4, although it is only about half the size: core-to-rim oscillatory zoning in P, Cr, and Al [A] superimposed on normal zoning in Fe [E]; and interruptions in the high-P zones and patterns, sometimes spatially associated with melt and/or spinel inclusions [B]. Distinctive features of the zoning in this crystal include the possible low P–Cr–Al “sector” [C]; zoning in Al and Cr, although still clearly visible, is less distinct than that in P [D]

low-P embayments into high-P olivine regions are characteristic of included melt pools in this experiment (e.g., Fig. 6a[B]). Variations in P in these olivines are independent of the normal zoning in Fe/Mg, which increases monotonically toward boundaries with glass at crystal rims and toward interior boundaries with melt pools.

- Figure 7a shows olivine from experiment 3. The central crystal has a prominent high-P “skeleton” (up to ~ 0.8 wt % P_2O_5 ; 30–165 μm wide; Fig. 7a[F]). Low-P olivine (~ 0.05 to 0.06 wt % P_2O_5 ; Fig. 7a[G]) extends outward from the high-P skeleton toward the crystal rim and inward from the skeleton toward several elongate melt pools (Fig. 7a[D]). The high-P skeleton contains regions of fine oscillatory zoning (3–6 μm wide P-rich bands, separated by 5–7 μm wide P-poor

bands) with banding perpendicular to the apparent growth direction and with diffuse, feathery, or wispy terminations (Fig. 7a[A]); in one region, the oscillating bands are not perpendicular to the apparent growth direction of the olivine (Fig. 7a[B]). The low-P olivine around the interior melt pools shows fine oscillatory zoning patterns at lower levels of P than seen in the high-P skeleton (Fig. 7a[H]). P-rich ridges and knobs or protrusions of high-P olivine into low-P olivine are present close to one melt pool (Fig. 7a[E]), perhaps due to breakdown of the boundary layer during crystal growth. As in experiment 1, most of the olivine in contact with glass is low in P, but there are a few cases of high-P olivine in contact with glass (Fig. 7a[C]). We have not surveyed the full circumferences of the crystals, but analyzed glass in contact with high-P

Fig. 5 Phosphorus, Cr, and Al X-ray maps for olivine crystals from komatiites. Scale bars (shown in the P X-ray images) are 50 μm , other details as given in the caption to Fig. 1. **a–c** Olivine microphenocryst in 94-19 from the polyhedrally jointed upper layer of a Gorgona island komatiite flow. This olivine displays correlated oscillatory zoning in P, Al, and Cr [A] and sector zoning. The prominent sector [B] shows continuation of oscillatory zoning from outside the sector, elevated Cr and Al, and diminished P. The matrix consists of minor olivine, pyroxene, Cr-spinel, and devitrified glass, two portions of which can be seen as apparent inclusions [C] (possibly embayments in three dimensions) within the olivine. The two EBSD determinations did not have identical *b* and *c* axis directions (shown as gray dots on the equal area projections); the averages are shown as black dots. **d–f**

Spinifex olivine in 94-1 from the oriented-plate spinifex zone of a Gorgona island komatiite. Olivines in this zone form branching chains in a matrix of feathery to needle-like pyroxene, minor plagioclase laths, Cr-spinel, and devitrified glass. The olivines display prominent, elongated, correlated oscillatory zoning in P, Al, and Cr [A] parallel to the long dimension of the crystal (i.e., parallel to the *a* axis). **g–i** Olivine microphenocryst from the base of the Belingwe komatiite displaying correlated oscillatory zoning in P, Cr, and Al. The core [A] has a *square* (in cross-section) region of elevated P, Cr, and Al concentrations with a single low-P oscillation, surrounded by a broad region with low concentrations of these elements, and two concentric high P, Al, and Cr bands [B]. The matrix consists of pyroxene, Cr-spinel, and devitrified glass

Table 2 Nominal bulk compositions and run conditions of experiments

	bc#1 (wt %) ^a	bc#2 (wt %) ^{b,c}
SiO ₂	46.80	45.62
TiO ₂	2.00	1.94
Al ₂ O ₃	10.54	10.27
Cr ₂ O ₃	0.23	0.22
FeO*	11.78	11.48
MnO	0.17	0.17
MgO	17.45	17.00
CaO	8.62	9.76
NiO	0.12	0.11
Na ₂ O	1.83	1.79
K ₂ O	0.30	0.29
P ₂ O ₅	0.16	1.18
Sum	100.00	100.00

^a Experiment 1 (bc#1): cooled from 1,400°C to 1,200°C at 15°C/h

^b Experiment 3 (bc#2): cooled from 1,400°C to 1,190°C at 15°C/h

^c Experiment 4 (bc#2): cooled from 1,400°C to 1,190°C at 30°C/h

FeO* is all Fe calculated as FeO

olivine has slightly lower P (~1.1 wt% P₂O₅; 1σ ~0.02 wt%) than glass in contact with low-P olivine (~1.3 wt% P₂O₅). The apparent partition coefficient for P (P₂O₅ in olivine/P₂O₅ in adjacent glass) is ~0.5 for high-P olivine and <0.1 for low-P olivine.

- Figure 7d shows olivine from experiment 4. Most olivine in this experiment is dendritic. The branching olivine extending from the lower left of Fig. 7d has a thin (3–5 μm wide) P-rich band (0.3–0.4 wt% P₂O₅) along its discontinuous central axis surrounded by low-P olivine (~0.1 wt% P₂O₅; Fig. 7d[C]). Oscillatory bands (3–8 μm wide P-rich bands; 3–10 μm wide P-poor bands) parallel to crystal faces are also present (Fig. 7d[B]). One small hopper olivine is sector zoned in P (Fig. 7d[A]), with P₂O₅ contents up to 0.8 wt%. As in experiment 3, glass in contact with high-P olivine in experiment 4 has slightly lower P than glass in contact with low-P olivine (1.2 vs. 1.4 wt% P₂O₅), and the apparent partition coefficient is higher at the contacts between glass and high-P olivine (~0.4 vs. <0.1).

In several respects, P zoning in the experimental olivines resembles that in the natural olivines: (1) With a bulk composition similar to Hawaiian magmas, the experiments generated individual olivines containing high- and low-P regions with concentrations comparable to those measured in natural Hawaiian olivines (up to ~0.1 wt% P₂O₅ in the experimental and ~0.2 wt% P₂O₅ in the natural olivines). (2) The experimental olivines show oscillatory zoning of P similar to that observed in naturally occurring olivines. The broad, alternating, tapering P-rich and P-poor regions

characteristic of experiment 1 (Fig. 6a[A,D]) are similar to such features in phenocrysts from basalts (e.g., Figs. 2a[B], 3c[A]). Likewise, the fine-scale oscillatory zoning in experiment 3, including the wispy terminations of these zones (Fig. 7a[A]), is similar to features observed in natural olivines (e.g., Figs. 1a[A], 2c[B], 3e[B]). However, features comparable to the widely spaced concentric interior P-rich bands (e.g., Fig. 1b[A]) and multiple bands near crystal rims (e.g., Figs. 1c[B], 2b[B]) have not been reproduced experimentally. (3) Possible sector zoning is observed in experiment 4 (Fig. 7d[A]), similar to a feature observed in naturally occurring microphenocrysts (e.g., Fig. 5a[B]). (4) Most (if not all) interior melt pools in the experiments are enclosed in low-P olivine, just as most naturally occurring melt inclusions in olivines have low-P olivine walls (e.g., Fig. 2c[E]). Moreover, the low-P olivine regions adjacent to interior melt pools in the experiments, as in the natural occurrences, sometimes disturb or cut high-P olivine zones. For example, Fig. 8 compares a structure associated with an interior melt pool in experiment 1 with an embayed interior edge of a high-P region of an olivine phenocryst in Koolau basalt S500-5b. This similarity suggests that the low-P olivine in the interior of the Koolau olivine may also have been associated with an interior melt pool.

Coupling of P zonation with zonation in other elements

Although it appears to be independent of Fe/Mg zonation, zoning in P is strongly coupled spatially with that of Cr and Al in the experimental olivines; i.e., P-rich regions are also typically enriched in Cr and Al (Figs. 6, 7). Quantitative electron microprobe data for the experiments indicate that overall P–Al and P–Cr correlations are roughly linear (red symbols in Fig. 9a, b), although variations in P content are much larger than variations in Al and Cr (i.e., the slopes of the P–Al and P–Cr trends are >>1). Al and Cr are highly correlated in the experimental olivines, with a slope of ~0.5 (Fig. 10a). Ti (not shown) is also positively correlated with P, Cr, and Al in experiment 1. However, the correlations break down in the “sector-zoned” crystal in experiment 4 (Fig. 7d–f[A]), in which the P-poor sector is rich in Al. Also, not surprisingly, the highest and lowest P contents of olivines from experiments 3 and 4 are higher than those of olivines from experiment 1, reflecting the ~7 times higher P₂O₅ content of the starting material used in experiments 3 and 4.

Natural olivines also show enrichments in Al and Cr that correlate spatially with the enrichments in P, although the connection between zoning in P, Al, and Cr is more complex than in the experiments. Some natural olivines show spatial correlations among these elements comparable to the experimental olivines (e.g., Figs. 3, 4a–c, 5),

Table 3 Representative analyses of olivine (wt %)

Sample ID	Grain ID ^a	Figure-point ^b	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO*	MnO	MgO	CaO	NiO	Na ₂ O	P ₂ O ₅	Sum
SR756-14.10	C1-a	1a-1	40.73	<0.005 ^c	0.041	0.106	10.76	0.10	48.67	0.22	0.376	NA	0.100	101.11
SR756-14.10	C1-a	1a-2	40.79	<0.005	0.034	0.101	11.02	0.14	48.71	0.22	0.385	NA	0.013	101.41
SR756-14.10	C1-b	1a-3	40.78	<0.02	0.056	0.095	12.27	0.15	47.63	0.25	0.407	0.006	0.100	101.74
SR756-14.10	C1-b	1a-4	40.39	<0.005	0.050	0.099	11.18	0.14	47.93	0.23	0.383	0.007	0.007	100.41
R215-7.2	4	1b-1	40.52	<0.02	0.043	0.095	11.15	0.12	47.73	0.23	0.420	<0.005	0.155	100.48
R215-7.2	4	1b-2	40.63	<0.02	0.038	0.059	11.31	0.15	47.71	0.22	0.390	<0.005	<0.01	100.51
SR756-14.10	C6	1c-1	41.24	<0.02	0.042	0.083	10.29	0.15	49.22	0.23	0.306	<0.005	0.032	101.59
SR756-14.10	C6	1c-2	41.24	<0.02	0.038	0.081	10.21	0.14	49.26	0.24	0.303	<0.005	<0.01	101.51
SR756-14.10	C6-a	1c-3	40.69	<0.02	0.035	0.066	13.30	0.18	46.83	0.28	0.438	<0.005	0.058	101.87
SR756-14.10	C3	1d-1	41.28	<0.02	0.052	0.077	10.11	0.13	49.49	0.19	0.546	<0.005	0.014	101.88
SR756-14.10	C3	1d-2	41.35	<0.02	0.050	0.072	9.86	0.13	49.65	0.20	0.567	<0.005	<0.01	101.87
R215-7.2	2	1e-1	40.52	<0.02	0.044	0.088	11.67	0.14	47.36	0.22	0.391	<0.005	0.125	100.57
R215-7.2	2	1e-2	40.61	<0.02	0.040	0.069	11.82	0.16	47.62	0.22	0.395	<0.005	0.017	100.94
SR756-14.10	C11	3a-1	39.86	0.007	0.046	0.074	12.98	0.17	46.23	0.27	0.413	<0.005	0.180	100.22
SR756-14.10	C11	3a-2	40.09	<0.005	0.039	0.068	12.89	0.17	46.12	0.22	0.433	<0.005	<0.006	100.03
S500-5b	4	3c-1	40.49	<0.02	0.053	0.118	10.66	0.15	48.15	0.19	0.422	<0.005	0.151	100.38
S500-5b	4	3c-2	40.68	<0.02	0.051	0.105	10.58	0.13	48.46	0.18	0.397	<0.005	<0.01	100.58
ALHA 77005	5	3e-1	37.44	<0.02	0.009	0.039	26.78	0.56	34.97	0.31	0.049	<0.005	0.410	100.58
ALHA 77005	5	3e-2	37.71	<0.02	<0.004	0.025	26.99	0.57	35.39	0.21	<0.03	<0.005	0.014	100.91
SR756-14.10	C4	4a-1	39.51	0.017	0.063	0.084	12.73	0.17	45.81	0.28	0.430	<0.005	0.212	99.31
SR756-14.10	C4	4a-2	39.38	0.006	0.038	0.064	14.78	0.18	44.17	0.27	0.378	<0.005	<0.006	99.27
SR756-14.10	C7	4e-1	39.76	0.016	0.057	0.089	12.87	0.18	46.10	0.26	0.449	0.008	0.161	99.96
SR756-14.10	C7	4e-2	39.91	0.010	0.034	0.065	13.42	0.16	45.60	0.31	0.416	<0.005	<0.006	99.92
Gorgona 94-19	1	5a-1	40.23	<0.005	0.111	0.139	10.11	0.15	48.50	0.35	0.413	<0.005	0.029	100.04
Gorgona 94-19	1	5a-2	40.90	<0.005	0.097	0.136	8.53	0.14	50.04	0.33	0.481	<0.005	0.016	100.67
Gorgona 94-19	1	5a-3	40.31	<0.005	0.073	0.104	10.90	0.18	48.14	0.36	0.384	<0.005	0.006	100.46
Gorgona 94-1	1	5d-1	40.81	<0.012	0.074	0.086	12.64	0.19	46.40	0.35	0.367	<0.004	0.010	100.92
Gorgona 94-1	1	5d-2	40.96	<0.012	0.064	0.080	12.02	0.18	46.96	0.35	0.372	0.009	0.006	101.01
Gorgona 94-1	1	5d-3	41.05	<0.012	0.050	0.068	12.63	0.19	46.72	0.34	0.308	<0.004	0.004	101.37
Experiment 1	1	6a-1	39.58	0.030	0.128	0.192	10.79	0.13	47.86	0.26	0.663	<0.005	0.062	99.69
Experiment 1	1	6a-2	40.64	<0.02	0.115	0.176	9.99	0.10	48.90	0.22	0.676	0.008	0.111	100.93
Experiment 1	1	6a-3	40.63	<0.02	0.076	0.147	12.19	0.13	46.97	0.28	0.598	<0.005	<0.01	101.02
Experiment 3	1	7a-1	40.10	<0.02	0.152	0.201	10.31	0.13	48.08	0.30	1.047	0.017	0.768	101.10
Experiment 3	1	7a-2	39.30	0.011	0.141	0.135	13.70	0.12	45.40	0.36	0.619	0.031	0.052	99.87
Experiment 4	1	7d-1	39.98	<0.02	0.145	0.244	12.56	0.13	46.52	0.30	0.944	0.014	0.816	101.66
Experiment 4	1	7d-2	39.95	<0.02	0.077	0.172	13.94	0.14	45.11	0.32	0.759	0.007	0.054	100.54

NA not analyzed

^a See Table 1 for additional information on grains and samples^b Entries refer to the figure panel on which an analysis location is to be found followed by the specific analysis number^c Below the detection limit, which varies from analysis to analysis because of different count times

consistent with the results of Edmunson et al. (2005) who noted an association of elevated Al, Cr, and P in olivine in the martian meteorite ALHA 77005; in others, especially the Hawaiian microphenocrysts (Fig. 4e–h[D]), P, Al, and Cr are correlated, but the boundaries between high- and low-Al and Cr regions are more diffuse than the same boundaries in P. In some of the phenocrysts, Cr correlates with P but zoning in Al is faint or undetectable

(e.g., the three crystals shown in Fig. 3; but in these cases the elevation in Cr₂O₃ content of the Cr-rich zones above the Cr-poor zones, ~0.01 wt%, is significantly lower than the difference between adjacent Cr-rich and Cr-poor regions in the experiments, ~0.03 to 0.1 wt%). The core of crystal C1a shows strong zoning in P (Fig. 1a[A]), weak zoning in Cr, and extremely weak zoning in Al, but the P-rich zones near the rim of the same crystal

Fig. 6 X-ray maps of P (a) and Cr (b) for experiment 1 on bulk composition bc#1 (Table 2). Scale bar is 100 μm . The charge was quenched after cooling from 1,400 to 1,200°C at 15°C/h. The P map shows several features comparable to those seen in natural olivines, including wide, tapering oscillatory zones of alternating high- and low-P olivine [A,D]. Included melt pools (e.g., [E]) are always adjacent to low-P olivine and typically associated with embayments toward the high-P olivine of the boundary between high- and low-P olivine [B]. One such embayment [C] is shown in more detail in Fig. 8. All features in the P map are also observed in the Cr map, and high-P, high-Cr, and high-Al (not shown) regions are highly correlated spatially. There is also a weak positive correlation of P with Ti (not shown)

(Fig. 1a[F]) show correlated zoning in all three elements. In still other crystals (e.g., Volcán San Pedro phenocrysts; Fig. 2b, d), significant P zonation is observed in the absence of detectable features in the X-ray maps for any other element we measured. Finally, sector zoning in the Gorgona microphenocryst (Fig. 5a[B]) is expressed by enhanced Al and Cr concentrations and lower P contents. We emphasize again that Fe, Ca, and Ni do not exhibit zoning patterns correlated with P in either the natural or experimental olivines. It is also important to note that a

lack of observable zoning on an X-ray map does not mean the absence of an element: in particular, concentrations of Cr and Al are almost always above background, and even in grains with featureless Cr and Al X-ray maps, the concentrations of these elements often exceed those of P (Fig. 9).

The complex interrelationships between P–Al–Cr zonation in natural olivines based on comparing X-ray maps of these elements are also apparent in comparisons of quantitative analyses (Figs. 9, 10). For example, individual Hawaiian microphenocrysts fall on well-defined trends in P–Al (Fig. 10b) and P–Cr (not shown), with slopes similar to those observed in the experimental olivines; likewise, these microphenocrysts and olivine from Gorgona komatiite 94–1 fall on well-defined trends in Al–Cr space with slopes of ~ 0.5 , like the experimental olivines (Fig. 10a). Finally, although individual experimental olivines, microphenocrysts, and komatiitic olivines define trends with slopes of ~ 0.5 in Al–Cr space, the data set as a whole falls close to a 1:1 line (Fig. 9c).

Discussion

P contents of igneous olivines: comparison to the literature

Olivines with up to 27 wt% P_2O_5 have been synthesized (Boesenberget al. 2004) and naturally occurring phosphoran olivines are known from pallasitic meteorites (up to ~ 5 to 8 wt% P_2O_5 ; Buseck 1977; Buseck and Clark 1984; Wasson et al. 1999), a carbonaceous chondrite (up to ~ 4 wt% P_2O_5 ; Wang et al. 2006), silicate inclusions within an iron–carbon alloy boulder from Disko island, Greenland (up to ~ 3 wt% P_2O_5 ; Goodrich 1984), and a skarn associated with an intrusive breccia pipe in Pine Canyon, Piute County, Utah (up to ~ 6 wt% P_2O_5 ; Agrell et al. 1998). These natural occurrences are, however, from unusual rocks and environments. Low $f\text{O}_2$ (reflected by the presence of iron-rich metal in the pallasites and Disko island samples), high bulk P_2O_5 , and low silica activity have all been invoked as factors in the formation of these rare P-rich olivines, but a consensus on the major factor is rapid (possibly disequilibrium) growth of olivine from P-rich liquids (Goodrich 1984, 2003; Goodrich and Barnes 1984; Agrell et al. 1998; Boesenberget al. 2004; Tropper et al. 2004; Boesenberget al. 2006).

Maximum P contents reported here for typical terrestrial olivine (up to ~ 0.2 wt% P_2O_5) and martian meteoritic olivine (up to ~ 0.4 wt% P_2O_5) are much lower than those reported for the rare phosphoran olivines referred to in the previous paragraph. There are few analyses of P in typical terrestrial igneous olivines in the literature, but these are

Fig. 7 X-ray maps of P, Cr, and Al for experiments 3 (a–c) and 4 (d–f) conducted on P-enriched bulk composition bc#2 (Table 2). Scale bars are 100 μ m. Experiments were cooled from 1,400 to 1,190°C at 15°C/h (experiment 3) or 30 °C/h (experiment 4), then quenched. The large crystal in experiment 3 (a–c) has a central, high-P skeleton [F], zoned outward toward low-P rims [G] and inward toward elongate melt pools enclosed in low-P olivine [D]. Fine-scale oscillatory zoning in P is observed in several places in this crystal [A, H]. Other features in this crystal include knobs or protrusions of high-P olivine close to an interior melt pool [E] and a region of oscillatory bands [B] where the bands are parallel to the apparent growth

direction (although these may be more closely related to the knobs and protrusions in [E] than to typical oscillatory zoning). Most of the glass is adjacent to low-P olivine (exceptions are at [C]). Most of these features are observable in Cr (b) and Al (c). Images of experiment 4 (d–f) are dominated by an elongate branching, dendritic crystal with a thin P-rich band along its discontinuous central axis surrounded by low-P olivine [C]. Oscillatory banding in P parallel to crystal faces is also present [B]. One hopper olivine is sector zoned in P [A]. Similar features are observed in the Cr and Al images, although the general rule that P, Cr, and Al concentrations are positively correlated breaks down in this sector-zoned crystal

Fig. 8 Comparison of morphologically similar features in P X-ray maps of experiment 1 ([C] in Fig. 6a) and a natural olivine phenocryst from a Koolau basalt ([F] in Fig. 3c). We infer for both that a P-rich band has been resorbed from the interior of the crystal by a melt pool and replaced by low-P olivine, resulting in a

crosscutting relationship between the low-P olivine core and the partially resorbed P-rich band. In the experiment, the included melt pool is still present; in the natural crystal, it is inferred to have been either completely infilled by low-P olivine or not cut by the plane of the section. Scale bar is 100 μ m

Fig. 9 Phosphorus, Cr, and Al concentrations (cations per 4 oxygens) in all analyzed natural and synthetic olivine based on background-corrected wavelength-dispersive electron microprobe analyses. Error bars, where larger than symbol size, are one standard deviation based on counting statistics. **a** P vs. Cr, **b** P vs. Al, **c** Cr vs. Al, the analyses tend to fall near the 1:1 line (shown for reference), but individual crystals with short high-temperature histories define trends with slope ~ 0.5 (see Fig. 10a)

generally about an order of magnitude lower than values for P-rich zones in the olivines we have studied. Anderson and Greenland (1969) reported ~ 0.01 to 0.04 wt% P_2O_5 in Hawaiian phenocrysts and Kent and Rossman (2002) reported 0.046 wt% P_2O_5 in an olivine phenocryst from a Mt. Vesuvius leucite. Analyses of olivines from spinel and garnet lherzolite peridotites (e.g., up to 0.038 wt% P_2O_5 ; Bishop et al. 1978; Delaney et al. 1979; Hervig and Smith 1982; Bell et al. 2004; Witt-Eickschen and O'Neill 2005) are also much lower than our maximum concentrations, but those reported for olivine from a partially melted, metasomatized, apatite-bearing spinel lherzolite (<0.01 to ~ 0.15 wt% P_2O_5 ; Brunet and Chazot 2001) are similar. There are many previous P analyses for olivines from martian meteorites, but with the exception of a chromite-hosted olivine in a melt inclusion (~ 0.75 wt% P_2O_5 ; Goodrich 2003), all are significantly lower than the maximum 0.41 wt% P_2O_5 reported here (ranging from below detection limit to 0.14 wt%; Smith et al. 1983; Gleason et al. 1997; Mikouchi 2001; Barrat et al. 2002; Mikouchi and Miyamoto 2002; Mikouchi et al. 2004; Edmunson et al. 2005; Gillet et al. 2005; Imae et al. 2005; Mikouchi 2005; Beck et al. 2006). Overall, the maximum P_2O_5 contents of ordinary terrestrial and martian meteoritic olivines we measured are higher than expected based on a survey of the literature, but since high P_2O_5 contents typically occupy a small fraction of the exposed surface of any given olivine, it is not necessarily surprising that previous analyses rarely encountered such P-rich regions.

The formation of P-enriched zones in olivine

Our most significant observation is not the somewhat higher than expected P_2O_5 contents of “ordinary” terrestrial and meteoritic olivine, but rather that complex (including oscillatory) zoning of P (even in otherwise essentially compositionally featureless olivines) is typical of igneous olivines. What is responsible for this zonation? One possibility is that the olivines grew from melts whose P_2O_5 contents varied significantly and often abruptly through time, due to magma mixing and/or motion of the olivines (e.g., by settling) from one batch of magma to another (these are examples of “extrinsic” magmatic processes as defined by Shore and Fowler 1996). The fact that low-P olivines in our experiments with higher bulk P contents are higher by roughly the same factor as the bulk compositions confirms that varying P contents in the melt can lead to observable variations in growing olivines. Such processes are known to occur in nature: for example, studies of melt inclusions in olivines indicate that compo-

sitions of the melts from which olivines grow sometimes vary significantly during growth of the olivine and that these differences cannot always be attributed to simple fractionation processes (e.g., Sobolev and Shimizu 1993; Sobolev et al. 2000; Danyushevsky et al. 2004; Kamenetsky and Gurenko 2007). Likewise, rims of olivine phenocrysts can differ abruptly in composition from their cores, recording magma mixing events close to the time of eruption (e.g., Gerlach and Grove 1982; Costa and Chakraborty 2004; Costa and Dungan 2005). However, such mixing processes typically cause significant excursions in concentrations of the divalent cations (and forsterite content) toward olivine rims. Although we observed P-enriched bands in crystal rims strongly zoned in Fe/Mg (e.g., Fig. 2b[A, B]), variations in P_2O_5 are not correlated with those of the divalent cations (as might be expected if each oscillation in P reflected a discrete mixing event).

Fig. 10 Relationships among P, Cr, and Al concentrations in natural and synthetic olivine based on background-corrected wavelength-dispersive electron microprobe analyses (i.e., not based on X-ray maps). Error bars, where larger than symbol size, are one standard deviation based on counting statistics. **a** Al vs. Cr (cations per 4 oxygen atoms) in experimental and natural olivines with short high-temperature histories. Equations and correlation coefficients based on unweighted linear regressions are: Gorgona island komatiite 94-1: $Cr = 0.0007 + 0.43 Al$ ($r^2 = 0.77$); Hawaiian microphenocrysts C4 and C7: $Cr = 0.0008 + 0.51 Al$ ($r^2 = 0.93$); controlled-cooling-rate experiments from this study: $Cr = 0.0019 + 0.48 Al$ ($r^2 = 0.75$). **b** Al vs. P (cations per 4 oxygen atoms) in experimental and natural olivines with short high-temperature histories. Equations and correlation coefficients based on unweighted linear regressions are: Hawaiian microphenocryst C4: $P = -0.0043 + 5.24 Al$ ($r^2 = 0.85$); Hawaiian microphenocryst C7: $P = -0.0041 + 4.19 Al$ ($r^2 = 0.96$); controlled cooling rate experiments from this study: $P = -0.014 + 6.51 Al$ ($r^2 = 0.79$). **c** Al vs. Cr (cations per 4 oxygen atoms) in synthetic and natural olivines; for each crystal, the analyses are normalized to the average for that crystal. For clarity, error bars in Cr/Cr_{avg} , typically $\sim 20\%$, are not shown for Volcán San Pedro. Crystals with short high-temperature histories (e.g., experimentally grown olivines, komatiitic olivines, Hawaiian microphenocrysts) fall approximately on the red line with slope ~ 0.5 . Crystals with prolonged high-temperature histories (e.g., most Hawaiian phenocrysts and Volcán San Pedro) define a vertical field, which we interpret as reflecting diffusive relaxation (illustrated schematically by the black curves), where grains initially zoned in Cr and Al and on the red line first moved roughly horizontally (1→2) and then vertically (2→3), reflecting the faster diffusion of Al than Cr. See text for further discussion

Moreover, we consider it improbable that external events (such as those leading to near-rim excursions in Fe/Mg) could be sufficiently regular and repetitive to account for the observed fine-scale oscillatory zoning in P. Furthermore, our experiments demonstrate that olivines with oscillating P contents can grow during simple linear cooling of a basaltic liquid, and many of the details of zoning observed in natural olivines are reproduced in our experiments. Consequently, we consider it likely that much of the complex variability in P we have observed in natural olivines formed during relatively simple cooling of magmas without oscillatory external forcings (i.e., via “intrinsic” magmatic processes; Shore and Fowler 1996).

The most likely explanation of the regions of elevated P content in our experimentally grown olivines is that they form during periods of relatively rapid crystal growth. Rapid crystal growth could influence the P content of olivine in two ways:

- First, if crystallization is fast but equilibrium partitioning of an incompatible element like P (with a partition coefficient of <0.1 ; Anderson and Greenland 1969; Brunet and Chazot 2001) occurs at the interface, P will become enriched in the adjacent liquid boundary layer, leading to enrichment of P in crystallizing olivine relative to expectations based on the far-field liquid composition (Smith et al. 1955; Albarède and Bottinga 1972; this assumes that the equilibrium partition

coefficient is not strongly affected by other components within the boundary layer). Enrichments of this sort are known to occur, leading for example to crystallization of apatite in the boundary layer adjacent to plagioclase (Bacon 1989). In our experiment 4, we observe boundary-layer enrichment in P adjacent to the growing olivine crystals, and this could thus account for some enrichment of P in growing olivines; however, the melt adjacent to olivine in this experiment is enriched in P by only $\sim 20\%$ relative to the far-field melt, so unless there were transient elevations in P in the boundary layer about an order of magnitude or more than we have observed (or such elevations occur in zones adjacent to the crystals that are narrower than we can resolve; i.e., $<1\text{--}2\text{ }\mu\text{m}$), equilibrium partitioning between P-enriched boundary layers and the growing olivine cannot explain quantitatively the observed elevation in P in the olivines. Moreover, in experiments 3 and 4, P concentrations in melt near both high-P and low-P olivines are similar, so boundary-layer enhancements in P are unlikely to be the sole source of the observed variations unless highly P-enriched boundaries are too narrow for us to discern. Shimizu (1990) rejected equilibrium crystallization from boundary layers as an explanation for oscillatory zoning of incompatible trace elements in augite crystals for similar reasons—the required boundary-layer enrichments were implausible.

- A second process, known as “solute trapping”, becomes important as the crystal growth rate approaches the rate at which a cation in the liquid can diffuse away from the interface (e.g., Aziz 1982; Reitano et al. 1994; Charach and Keizman 1996). Basically, structural incorporation into the crystal lattice (or adsorption onto the surfaces of growing crystals; Dowty 1977) of constituents that cannot “outrun” the moving crystal face leads to elevated concentrations in the growing crystal (Lofgren et al. 2006; Schwandt and McKay 2006). This can be a disequilibrium process and the phenomenological partition coefficient at the interface can approach 1 even if the equilibrium partition coefficient is <0.1 , as it is for P. Such an effect for P is consistent with the experimental data of Goodrich and Barnes (1984), who observed apparent olivine-melt partition coefficients for P as high as ~ 0.4 for rapidly quenched samples, and our results, which suggest values up to ~ 0.5 . Solute trapping has also been documented for other incompatible trace elements in olivine (Kennedy et al. 1993; although Lindstrom (1983) did not detect such an effect in Fe-free olivine). One prediction of the solute trapping hypothesis is that disequilibrium partitioning will be most significant for the slowest diffusing cations in the melt; P is indeed a very slowly diffusing component in silicate melts (Harrison and Watson 1984; Mungall 2002), much

slower than divalent cations, consistent with our observation that complex zoning patterns in P are superimposed on normal Fe/Mg zoning in the experiments and natural samples. Solute trapping of P may also account in part for the correlated Al, Cr, and P enrichments in the experimentally produced olivines: P is incorporated into olivine through solute trapping while Cr and Al may be influenced by a coupled substitution with P (see “[correlations between P, Al, and Cr—the possibility of constraining thermal histories](#)”). Kennedy et al. (1993) attributed incompatible element enrichments in rapidly grown olivine to the trapping of submicroscopic melt inclusions, but this cannot be the case in our experiments because Al/P ratios of P-enriched regions in the olivine are about an order of magnitude lower than in the coexisting liquid in the boundary layer. Finally, P is not always enriched in glass adjacent to olivine in our experiments, and when it is, the enrichment is lower than for incompatible elements such as Na and K that are unlikely to be significantly affected by solute trapping because of high diffusivities in the liquid (Hofmann 1980); this is consistent with elevated partition coefficients for P due to solute trapping at high growth rates. This could also explain our observation that the experiment 3 and 4 glasses in contact with high-P olivine have slightly lower P contents than glass in contact with low-P olivine: i.e., crystallization of P-enriched, rapidly growing olivine results in lower enrichment in P in residual melt than crystallization of lower-P (closer to equilibrium) olivine.

In summary, we are confident that rapid crystal growth is at the root of most P enrichment in igneous olivine. This conclusion is consistent with current interpretations of the extraordinary P contents of phosphoran olivines, which have also been explained by rapid crystal growth (Goodrich 1984; Boesenberg et al. 2004; Tropper et al. 2004; Boesenberg 2006).

The hypothesis that rapid olivine growth is responsible for the development of P-rich zones is consistent with the shapes of “relict” P-rich crystals we observe in the cores of natural olivines. For example, elevated P contents define hopper-shaped and skeletal relict crystals in Hawaiian olivines (e.g., Figs. 1a, 3a, c), and based on morphology alone, these cores undoubtedly reflect an early phase of rapid crystal growth (Donaldson 1976); this provides independent evidence of an association of elevated P contents in the crystals’ cores and rapid crystal growth. Although unanticipated based on the euhedral shapes and uniform Fe–Mg contents of many phenocrysts, rapid initial growth of olivine is easily understood in terms of growth rate and nucleation as functions of undercooling (e.g., see Dowty 1980); i.e., olivine crystallization is delayed by

undercooling but a nucleation event then results in an initial pulse of rapid olivine growth. Evidence of this initial growth is usually erased or obscured by slower overgrowth of olivine as cooling continues and thus has not been previously observed, but based on our observations it may be a common phenomenon in the cooling of basaltic magmas, with the only preserved record being the P-rich, sometimes skeletal cores of olivine phenocrysts.

Fine-scale oscillatory zoning in P, Cr, and Al in olivines

Regular, fine-scale (i.e., of order 10 μm band width and spacing) oscillatory zones observed in experimentally produced and natural olivines plausibly result from crystal growth rate phenomena and their interaction with the adjacent boundary layer. Such oscillatory zoning is a well-known phenomenon in igneous minerals and has been reported previously in terrestrial (Clark et al. 1986) and meteoritic olivine (Steele 1995, in Al and Ti), although not in P (and the oscillations observed by Clark et al. (1986) were only observed using Nomarski interference techniques and could not be connected by them to any compositional manifestation).

There is a large literature on oscillatory zoning and its origin in igneous minerals, especially plagioclase (see reviews by Pearce 1994; Shore and Fowler 1996). Although often attributed to external factors such as variations in temperature or pressure, magma composition, $\text{P}_{\text{H}_2\text{O}}$, etc. (“extrinsic” in the sense of Shore and Fowler 1996), the fact that chemical oscillations occur in our synthetic olivine shows that they can be generated “intrinsically” in igneous systems without being forced by oscillations in such external factors. As applied to our particular case, we envision rapid (and therefore P-enriched) olivine growth depleting the adjacent liquid boundary layer in olivine components, which slows olivine growth, resulting in a low-P olivine overgrowth. Although this would result in a zone of high-P olivine overgrown by low-P olivine, something else must occur to stimulate another phase of rapid olivine growth so as to produce oscillatory zoning. Examples of how non-linearities resulting in oscillatory behavior might be introduced into the system include dependence of growth rate on the composition of the crystalline phase or on the structure of the interface and its temporal evolution, variations in the diffusivities of cations in the melt as a function of liquid composition, time dependence of the degree of constitutional supercooling of the liquid at the crystal interface, and convective instability of the liquid boundary layer (see reviews by Pearce 1994; Shore and Fowler 1996).

Our observations do not help distinguish between models for the formation of oscillatory zoning, but there

are aspects of oscillatory zoning of P in olivine that might ultimately provide broader insights into this phenomenon:

- Individual zones in plagioclases with oscillatory zoning are asymmetric with a characteristic “saw-toothed” shape (see review by Pearce 1994). As stated above, based on preliminary quantitative traverses across regions of oscillatory zoning in natural olivines, P enrichment can also be asymmetric. Full characterization of these features in olivine, especially in the experiments, and their comparison to the extensively studied and modeled plagioclase system may suggest tests of proposed mechanisms for the formation of oscillatory zoning.
- Oscillatory zoning in P, Al, and Cr (and indeed all zoning in these elements, whether or not it is oscillatory) has no manifestation in major element zonation of the olivine; i.e., P zoning is either unaccompanied by zoning in major components or superimposed on gradual, typically normally zoned profiles in Fe/Mg. Clark et al. (1986) and Steele (1986) reported similar decoupling between the oscillations they observed and major element zonation in olivines, as did Vielzeuf et al. (2005) for magmatic garnets. Oscillatory zoning in plagioclase is very different, being defined by major element variations (up to a few tens of mole % anorthite within zones and across boundaries between zones; Pearce 1994). Clark et al. (1986) suggested that major element oscillations of this sort existed during olivine crystal growth, but diffused away during prolonged annealing at high temperatures and the homogeneity in major elements observed in many Hawaiian phenocrysts has been explained in this way (e.g., Nicholls and Stout 1988; Baker et al. 1996; Garcia 1996). However, it is much less plausible for the oscillatory zoning generated in our experiments or in spinifex olivine from komatiites and Hawaiian microphenocrysts (all of which cooled rapidly from magmatic conditions) to have P–Cr–Al-rich oscillations (up to several tens of microns across for the microphenocrysts; see Figs. 4, 5) without associated oscillations in forsterite content if such oscillations ever existed. We conclude that the absence of significant oscillations in Fe/Mg accompanying observed minor element oscillations is a primary feature in olivine. Models along the lines developed for plagioclase should allow the significance of this difference to be explored.
- If details of the growth-rate dependence of P partitioning between olivine and melt could be determined experimentally, P zoning in olivines might provide an approach to quantifying growth rates of natural olivine. This would not only be of general petrological value, but promises a test of available models of oscillatory zoning. Indeed, all

such models require significant time-dependent variations in growth rate in order to explain the oscillations, and oscillations in P in olivine could provide an independent measure of these variations.

- There are several oscillatory structures in the experimentally produced and natural olivines that are not linear in two dimensions (e.g., wispy and feathery structures and “knots”), and experiment 3 has regions of oscillatory zoning with diffuse terminations (Fig. 7a[A]) and regions in which the oscillations are not parallel to current crystal rims (Fig. 7a[A, B, E]). We do not know how these features form or what they signify, but they may ultimately provide insights into the complexities of olivine crystal growth and oscillatory zoning.

The effects of olivine crystallization from restricted melt pools

Melt pools trapped within growing olivines will generally crystallize slowly. If a melt pool is isolated from melt outside the olivine, crystallization on its walls depletes the melt pool in olivine components, thereby slowing the rate of further crystallization. This also applies to melt pools still connected by narrow channels to the near-infinite reservoir of melt outside the olivine (Stewart and Pearce 2004; Blundy and Cashman 2005 describe such occurrences in plagioclase); in such cases, olivine crystallization on the wall of a pool will be slow, rate-limited by the replenishment of olivine components through the narrow channel. We thus expect that walls of melt pools will generally be lined by low-P olivine. This explains the universally low-P interiors of skeletal olivines from our experiments (Figs. 6a[B], 7a[D]). Infilling of skeletal crystals by slowly crystallizing, low-P olivine might also explain the broad, tapering alternations of high- and low-P zones in experiment 1 (e.g., Fig. 6a[A, D]) and morphologically similar oscillations in some natural olivines (e.g., Figs. 2a[B], 3c[A]); we envision rapid growth of a skeleton of high-P bands separated by melt and the infilling of these internal melt bands by slowly crystallized, low-P olivine.

Slow crystallization on the walls of melt pools may contribute to the low-P walls that are the rule for naturally occurring olivine-hosted melt inclusions (e.g., Figs. 2c[E], 3e[D]). Two other factors, however, may also contribute to the low-P olivine walls of most natural melt inclusions: As discussed above, we and others have suggested that rapid growth of olivine generates high-energy (likely metastable), high-P olivine out of equilibrium with adjacent melt (Goodrich and Barnes 1984; Agrell et al. 1998; Boesenberg et al. 2004). If kept in contact with a melt with which it is not in equilibrium, such high-P olivine will tend to dissolve (perhaps contributing to the “nucleation” of melt

inclusions), closely followed by slow precipitation of near-equilibrium, low-P olivine. This could help explain why melt inclusions generally are in close proximity to P-rich olivine, yet nearly all such inclusions are in direct contact only with low-P olivine (see Figs. 2c[E], 4a[C], e[B]). Association of local dissolution of P-rich olivine, precipitation of P-poor olivine, and trapping of melt in cases where compositionally distinct boundary layers are present might explain in part compositional variations among melt inclusions that are not readily explicable in terms of changes in far-field magma compositions (e.g., Ikeda 1998; Danyushevsky et al. 2004). Another factor in the formation of low-P envelopes around melt inclusions could be the migration of melt inclusions by dissolution–reprecipitation in a thermal gradient (Schiano et al. 2006); i.e., melt inclusions within olivines exposed to a thermal gradient dissolve high-P olivine on the high-temperature side and slowly reprecipitate low-P olivine on the low-temperature side. Over time as phenocrysts move and thermal gradients shift, the melt inclusion could generate a low-P halo on all sides. Finally, spinel inclusions in olivine form typically in association with melt inclusions (e.g., see Fig. 8 in Maaløe and Hansen 1982), so it is not surprising to find that in some cases features in olivine around spinels are similar to those around melt inclusions (Figs. 1a[C], 2b[C], 3a[D]).

Low-P regions around both melt and spinel inclusions appear in some cases to crosscut features defined by P-zoning patterns (e.g., Figs. 1a[C], 2c[E], 3a[E]). Such “unconformities” would be difficult to explain by other than a dissolution–replacement process. We also speculate that wispy terminations of regions of oscillatory zoning (e.g., Figs. 1e[B], f[B]) and the herringbone pattern of such terminations in ALHA 77005 (Fig. 3e[B]) in part reflect incomplete replacement of high-P olivine by low-P olivine through proximity of melt to high-energy, P-rich olivine. This could also explain the observation that most fully enclosed (in two dimensions) melt pools in the lower half of experiment 1 as pictured in Fig. 6a are associated with embayments of low-P olivine into a high-P olivine (Fig. 6a[B]). If so, high-P olivine in close proximity to melt can be replaced by low-P olivine on time scales as short as the ~14 h duration of experiment 1. The embayments in experiment 1 are unlikely to have formed in response to thermal gradients as such gradients are very small in these experiments and the embayments are in various directions. One such embayment in experiment 1 is morphologically very similar to the inner edge of a high-P zone in Koolau crystal S500-5b (Fig. 8). We suggest that both features formed similarly by a dissolution–reprecipitation process operating on the wall of a melt pool—first by dissolution of the high-P, skeletal inside wall of the melt pool, followed by slow crystallization of olivine, eventually filling the

melt pool completely with low-P olivine in S500-5b (although there could have been a melt inclusion outside the plane of the section). Goodrich and Barnes (1984) and Boesenberget al. (2004) also observed that high-P olivine in contact with melt was replaced by low-P olivine. The former authors explained this by diffusion of P from the high-P olivine into the melt but we favor a dissolution–reprecipitation process because, as shown in Fig. 2c[B], oscillatory zoning in P with length scales of <10 μm and sharp boundaries between high- and low-P zones persist in close proximity to >10 μm low-P halos around melt inclusions (Fig. 2c[E]); if simple diffusion of P from olivine into the melt inclusions were responsible for the low-P halos, diffusion should also have smeared out the oscillatory zoning far from the melt inclusions.

“Extrinsic” factors in the origin of P zonation in olivine

Our experimentally grown olivines show both wide, tapering oscillatory zonation (Fig. 6a[A, D]) and fine-scale oscillations (Fig. 7a[A, H]) comparable to those in natural olivines but we have not produced features comparable to the concentric, isolated P-rich zones (e.g., Fig. 1b[A]) or the multiple, closely spaced P-rich bands near crystal rims (e.g., Fig. 1c[B]). We cannot rule out that such features might be produced in future experiments, but they could reflect growth of P-rich olivine during rapid crystallization induced by “extrinsic” factors such as rapid changes in temperature, pressure, $\text{P}_{\text{H}_2\text{O}}$, etc., due, for example, to eruption or magma mixing. Such factors have been invoked to explain zoning of divalent cations near rims of olivine crystals (e.g., Nakamura 1995; Costa and Dungan 2005) and oscillatory zoning in plagioclase (see review in Shore and Fowler 1996; and recent work by Blundy and Cashman 2005). If they do reflect external forcings, concentric P-rich zones could provide a tool for monitoring such events in magmas in which olivine is a fractionating phase. This is particularly attractive as an explanation of near-rim oscillations in P, since rapid cooling, depressurization, and degassing, all of which can lead to rapid crystal growth, accompany eruption (Sahagian and Proussevitch 1996; Hort 1998; Métrich et al. 2001). Additionally, some P-rich and P-poor zones could reflect abrupt changes in the P content of the liquid from which the olivine is growing due, for example, to magma mixing events or motion of olivine between low and high-P magmas; if so, the prominent oscillations in P observed near the margins of many natural olivines may also reflect the common association of magma mixing with eruption in addition to the effects on crystal growth rate of the cooling, depressurization, and degassing that accompany eruption.

Substitution mechanisms

It is generally accepted that P^{5+} substitutes for Si^{4+} in the tetrahedral site in olivine. Although tetrahedral vacancies may play a role in charge balancing this substitution: i.e., $5^{\text{iv}}\text{Si}^{4+} = 4^{\text{iv}}\text{P}^{5+} + ^{\text{iv}}\square$ (Self and Buseck 1983; Agrell et al. 1998), studies of phosphoran olivines strongly suggest that at least at high P^{5+} concentrations, charge balance is largely maintained by vacancies in octahedral sites: $2^{\text{iv}}\text{Si}^{4+} + 4^{\text{vi}}\text{M}^{2+} = 2^{\text{iv}}\text{P}^{5+} + 3^{\text{vi}}\text{M}^{2+} + ^{\text{vi}}\square$ (see summary in Boesenberget al. 2004). In forsterite, Al^{3+} and Cr^{3+} form a coupled substitution, with Cr^{3+} in octahedral coordination and Al^{3+} in an adjacent tetrahedron ($^{\text{iv}}\text{Si}^{4+} + ^{\text{vi}}\text{M}^{2+} = ^{\text{iv}}\text{Al}^{3+} + ^{\text{vi}}\text{Cr}^{3+}$) (Bershov et al. 1983; Mass et al. 1995), and Colson et al. (1989) suggested the same mechanism for ferromagnesian olivines. However, Cr^{3+} can also form dimers consisting of a pair of $^{\text{vi}}\text{Cr}^{3+}$ cations associated with an octahedral vacancy ($3^{\text{vi}}\text{M}^{2+} = 2^{\text{vi}}\text{Cr}^{3+} + ^{\text{vi}}\square$) (Gaister et al. 2003), and Papike et al. (2005) suggested, based on ionic radius considerations, that Al^{3+} can also substitute into the octahedral M1 site. Thus, a wide variety of substitution mechanisms is possible.

Although references in the previous paragraph demonstrate that P^{5+} can substitute without significant accompanying Al^{3+} and/or Cr^{3+} and that Cr^{3+} and Al^{3+} can substitute without significant P^{5+} , the strong positive correlations among P, Al, and Cr in our experimentally produced olivines and in several natural occurrences are consistent with coupled substitutions in these cases. Establishing mechanisms for such couplings definitively at the low concentration levels of these cations in our samples is difficult (see the excellent discussion of this in Boesenberget al. 2004), but the Al–Cr–P systematics we observe allow some constraints to be placed on the nature and extent of coupled substitutions in these crystals.

As described in “coupling of P zonation with zonation in other elements”, in the experiments and in some natural crystals thought to have had relatively short igneous histories (e.g., Hawaiian microphenocrysts C4 and C7 and the spinifex olivine from komatiite 94-1), there are linear correlations between Al and Cr, with slopes ~ 0.5 for each crystal (Fig. 10a), consistent with compositional variations along each linear trend resulting from Al substituting together with Cr in a $\sim 2:1$ ratio. However, the lines in Fig. 10a have positive Cr intercepts, suggesting that significant amounts of Cr could be substituting independent of Al. We infer that at least two substitution mechanisms for Cr were operative, only one of which can be confidently assigned to a strong association with Al. Variable Cr intercepts of the best-fit lines in Fig. 10a may reflect factors such as the Cr content of the liquid (e.g., higher for the relatively primitive melt from which the synthetic olivine crystallized and lower for the Hawaiian microphenocrysts,

which crystallized from relatively evolved melts), fO_2 , and/or crystal growth rate. The X-ray maps (Figs. 4, 7) show spatial correlations of Al and/or Cr with P in most of these crystals, and Figs. 9a, b, 10b demonstrate that these correlations are roughly linear. For example, Al is roughly linearly correlated with P with a slope of ~ 5 (Fig. 10b) in the experimental olivines and Hawaiian microphenocrysts; similar correlations are observed for these grains in Cr–P but with higher slopes (Fig. 9a). The high slopes of the best-fit lines in Fig. 10b suggest that only ~ 15 to 25% of the P is associated with Al and/or Cr even when P is fairly abundant (i.e., Cr and Al increase more slowly than P on a cation basis and so cannot account for most of the required charge balance). Additionally, as deduced from Al–Cr correlations shown in Fig. 10a, large non-zero intercepts for Al (Fig. 10b) imply that much of the Al substitutes into olivine independent of P; the same is true for Cr. No P-related correlations are observed for olivine from komatiite 94-1 (Fig. 10b), reflecting the bulk rock's extremely low P content. If a correlation does exist for this grain, it must involve a very low slope and can account for little of the Al and Cr budgets (i.e., virtually all Al and Cr substitute into the olivine independently of P).

It is not possible to deduce definitively how the correlations described in the previous paragraph constrain atomic level substitution mechanisms, but we can make reasonable guesses. For example, Cr not associated with Al or P could substitute as Cr^{3+} dimers on octahedral sites, consistent with Gaister et al. (2003), and/or as Cr^{2+} , which is present in silicate liquids even at QFM (Roeder and Reynolds 1991; Berry and O'Neill 2004) and may therefore also be present in the olivine. $Al/Cr \approx 2$ (i.e., as indicated by the well-defined lines in Fig. 10a) would be consistent with an overall substitution reaction such as $^{iv}Si^{4+} + 5/2^{vi}M^{2+} = ^{iv}Al^{3+} + ^{vi}Cr^{3+} + ^{vi}Al^{3+} + 1/2^{vi}[]$. This reaction assumes that local charge balance of Al–Cr does not involve P, which must be the case for virtually all Al and associated Cr in the 94-1 komatiite olivine and much of it in other crystals. It is also important to emphasize that observed strong (roughly linear) correlations of Al and Cr with P could reflect indirect associations of these cations rather than a direct coupled substitution involving charge balancing. For example, distortions in the olivine structure associated with incorporation of P^{5+} might stabilize Al–Cr clusters, or perhaps solute trapping in rapidly grown olivine incorporates not only P but also Al $\pm$ Cr independently, leading to enhanced, correlated concentrations in the same regions of the crystals without necessarily influencing each other's local charge balance. It is, of course, also possible that some Al–Cr participates directly in a P substitution reaction such as $^{iv}Si^{4+} + 5^{vi}M^{2+} = ^{iv}P^{5+} + ^{vi}Cr^{3+} + 2^{vi}Al^{3+} + 2^{vi}[]$; and other components such as Fe^{3+} , H^{1+} , Na^{1+} , Li^{1+} , etc., may also influence the local charge

balance. Moreover, many substitution mechanisms may operate simultaneously, and indeed this seems likely based on the non-zero intercepts of lines in Figs. 9 and 10.

Regardless of specific substitution mechanisms, the presence of strong correlations among Al–Cr–P in experimental and natural olivine crystals with short residence times at high temperatures suggests that when the concentrations of these cations in the liquid phase are sufficient, interrelationships among their concentrations are likely to be robust initial features of rapidly grown igneous olivines. However, as described below (“[correlations between P, Al, and Cr—the possibility of constraining thermal histories](#)”), features in Al and Cr appear to be susceptible to diffusive relaxation if the olivines are not rapidly quenched; the data suggest that Al diffuses more rapidly than at least some of the Cr, leaving P and Cr zoning patterns highly correlated spatially but with essentially no zonation in Al (e.g., as observed in some Hawaiian phenocrysts and in ALHA 77005). Moreover, in many of these occurrences, although the Cr zonation does not appear to have been “smeared out” relative to the P zonation (i.e., delicate, sharp features are present in both the Cr and P X-ray maps), the intensity of the Cr enrichment in P-rich zones is much less than is characteristic of rapidly grown and quenched experimental and natural olivines. These observations may offer additional insights into substitution mechanisms; for example, if we assume that initial Al–Cr–P correlations reflect coupled substitutions, the fact that P and Cr zonation are retained despite nearly complete dissipation of Al zonation requires a change in substitution mechanism for Cr and probably P during Al diffusion; i.e., something else (e.g., Fe^{3+} , H^{+} , and/or vacancies) must diffuse into the Cr + P-rich zones to maintain the charge balance provided by Al^{3+} before it diffused away. Additionally, the preservation in phenocrysts of weak but “unsmeared” Cr zoning spatially correlated with much more intense P zonation (e.g., Fig. 3) may suggest at least two distinct charge balancing mechanisms for Cr: one with high diffusivity that is wiped out relatively early in the high-temperature history of a phenocryst (e.g., Cr^{2+} substituting for Fe^{2+} – Mg^{2+} , or Cr^{3+} bound to local octahedral vacancies); and a second that is highly resistant to diffusion (e.g., Cr^{3+} in strongly coupled substitutions with P^{5+}) and is thus responsible for retention of weak but sharp Cr zoning correlated with P zonation.

Correlations between P, Al, and Cr—the possibility of constraining thermal histories

The simplest interpretation of relationships among P, Al, and Cr zoning summarized above is that olivine initially crystallizes with complex, delicate, strongly correlated

zoning patterns superimposed on smooth, regular, normal zoning in Fe/Mg, but that diffusive relaxation leads first to homogenization of Fe/Mg zoning, followed by homogenization of Al, then Cr, and perhaps eventually P. The evolution in Al and Cr for a single spot in an igneous olivine is shown schematically by the heavy black curves in Fig. 10c (1 → 2 → 3): Al and Cr initially fall on linear trends with slope 0.5; these trends rotate counterclockwise towards vertical as Al homogenizes toward the average value for the grain; eventually, significant diffusion of Cr also occurs and the range in Cr concentrations in a crystal declines from a large value established during crystallization toward a narrow range near the average concentration for the crystal (perhaps also evolving due to interaction with melt), leading to clustering of Al and Cr around the average values for the grain. Data for olivines obtained in this study follow this simple schematic pattern: analyses from rapidly crystallized and cooled olivines array on a slope 0.5 trend in Fig. 10c; data for phenocrysts are either arrayed vertically (i.e., variable Cr with constant Al) or constant throughout the crystal (i.e., near the (1,1) point in Fig. 10c); and P zoning is equally intense and sharp regardless of the extent of retention of Al and Cr zoning. Additionally, although the Hawaiian microphenocrysts are zoned in all three elements, zoning patterns in Al and Cr can be more diffuse than in P (e.g., Fig. 4e–g), suggesting that thermal histories were long enough to produce the beginnings of detectable diffusive relaxation in Al and Cr.

Our interpretation of observed P zoning with no Cr or Al zoning and of Cr zonation with essentially no Al zonation in some phenocrysts (Fig. 10c) requires that $D(P) < D(Cr) < D(Al) < D(\text{divalent cations})$. This ordering applies only to the more slowly diffusing Cr component, which we infer may be strongly bonded to P; we also infer the existence of a more rapidly diffusing component of Cr to which this statement may not apply and which may diffuse at rates comparable to Al. This relative order of diffusivities makes qualitative sense: P^{5+} should be strongly bound in the tetrahedral site (“[substitution mechanisms](#)”; summary in Boesenberg et al. 2004), while Al^{3+} and Cr^{3+} are likely to be less strongly bound than P^{5+} , but more strongly bound than divalent cations (we assume P-associated Cr enrichments are mostly due to Cr^{3+} although significant amounts of Cr^{2+} may be present in basaltic liquids; Berry and O’Neill 2004). This sequence of bond strengths is expected to be mirrored in the diffusivities, $D(i)$, such that $D(P) \ll D(Cr^{3+}) \approx D(Al) < D(\text{divalent cations})$. Experimental determinations of diffusivities generally agree with our inferred order of $D(P) < D(Cr) < D(Al)$. Spandler et al.’s (2007) upper limit on $D(P)$ at 1300°C is ~ 1.5 log units lower than $D(Cr^{3+})$ of Ito and Ganguly (2006), which is lower than

$D(Al)$ of Jurewicz and Watson (1988) or $D(Al)$ inferred by Scowen et al. (1991) based on equilibration rates of chromite inclusions in olivine from a Kilauea lava lake. Spandler et al. (2007), however, report an upper limit on $D(Al)$ that is lower than previous determinations of $D(Al)$ or $D(Cr^{3+})$. The apparent inconsistency may reflect differences in diffusion tied to substitution mechanism and, in particular, whether or not P is involved. Despite these complications, it is plausible that phenocrysts experiencing prolonged exposure to high temperatures in the magma (or perhaps in a cumulate pile at the base of a magma chamber; Baker et al. 1996; Garcia 1996) retain their original zonation in P but that the original zonation in Fe/Mg was fully erased by diffusion while original zonation in Al and Cr was variably erased as described above. Similarly, observed oscillations in P near the edges of phenocrysts may reflect rapid crystal growth just prior to or during eruption, and one might therefore expect preservation of Al and Cr zoning in the rims even if the core is homogeneous (i.e., because they erupt soon after rim formation), as is indeed observed in crystals C1-a and C1-b (Fig. 1a[F]). The diffuse but still significant Cr and Al zonation of Hawaiian microphenocrysts is also consistent with their thermal histories, which are more extended than the instantaneous quenching of the experiments but significantly shorter than those experienced by the phenocrysts (months to years; Nicholls and Stout 1988; Mangan 1990).

Although the diffusivity of P^{5+} in olivine is currently unknown, it would have to be extremely low to preserve zoning on scales $\leq 5 \mu\text{m}$ such as those we have observed. If, for example, chemical diffusion of P in olivine were as slow as self-diffusion of Si along the *c*-axis (Dohmen et al. 2002), a $5 \mu\text{m}$ band with a $50 \mu\text{m}$ spacing between it and the adjacent band would homogenize in $\sim 10^6$ years at 1,200°C, which is longer than likely crustal storage times for basaltic magmas at Hawaii (e.g., $\sim 10^3$ years; Cooper et al. 2001) or in calc-alkaline provinces (e.g., 10^3 – 10^5 years; Hawkesworth et al. 2000; Reagan et al. 2003), and much longer than the years to decades pertinent to magma mixing and eruption events that resulted in the Fe/Mg zoning of olivine modeled by Costa and Chakraborty (2004). So, it may not be surprising that the P zoning patterns we observe are so common and resistant to diffusive relaxation. On the other hand, if we were to assume, for example, that the muted, patchy P zoning in the interior of olivine xenocryst Qcf4 (see Fig. 2b[D]) from Volcán San Pedro reflects partial diffusive homogenization of originally sharp P bands over $\sim 10^3$ to 10^5 years at 1,200°C (the time scale suggested for crustal residence of calc-alkaline magmas; Hawkesworth et al. 2000; Reagan et al. 2003), then chemical diffusion of P would have to be roughly 1–3 orders of magnitude slower than Spandler

et al.'s (2007) upper limit (i.e., roughly 0–3 orders of magnitude faster than self-diffusion of Si). Thus, while we have implicitly assumed P to be immobile in the above discussion, it is possible that there are in fact natural environments and time scales over which significant P diffusion in olivine can occur and, if so, it may be possible to use P in these occurrences to establish constraints on the thermal history once its diffusivity is determined experimentally.

Not all the olivines we studied follow precisely the patterns described above. For example, ALHA 77005 olivine shows strong spatial correlations between P and Cr zoning with no detectable features in Al, similar to the Hawaiian phenocrysts, but P contents extend to higher values and Al and Cr contents are significantly lower than those from Hawaii (Fig. 9). Some of these differences may simply reflect the differing compositions of terrestrial and martian magmas (e.g., the high P contents and low Al contents of martian olivine may relate to the bulk compositions of martian magmas; Gleason et al. 1997; Righter et al. 1998; Bridges and Warren 2006) and/or differences in their petrogenesis. However, the observed zoning patterns are also consistent with a thermal history sufficient to wipe out initial Al zoning while preserving Cr and P zonations and thus with these olivines being cumulus crystals (McSween et al. 1979; Bridges and Warren 2006). In support of this, although the Cr zoning in this sample is highly spatially correlated with P zoning, it is not very intense; thus, as described above for similar features in Hawaiian phenocrysts, its retention could reflect a component of Cr substitution that is very resistant to diffusive relaxation. Assuming Ito and Ganguly's (2006) values for $D(\text{Cr}^{3+})$ are applicable, such features would be expected to dissipate in years to decades at 1,100–1,200°C, which is likely inconsistent with an interpretation of the olivines in this meteorite as accumulated xenocrysts or phenocrysts (e.g., McSween et al. 1979; Edmunson et al. 2005). But as noted above, the diffusivity of Cr^{3+} in natural P–Al–Cr-enriched regions may differ from that of Cr^{3+} in the P-free olivines studied by Ito and Ganguly, and in particular, there may be a minor component of Cr associated with P that is highly resistant to diffusion. In any case, these calculations are meant to be representative rather than definitive; quantitative constraints on thermal histories will require careful experimentation to determine diffusion coefficients of Al and Cr in olivine similar in composition to P-rich natural crystals.

Summary

1. We observed P-zoning patterns in olivines from terrestrial basalts, andesites, dacites, and komatiites and from a martian meteorite. Zoning patterns include P-rich crystal cores with skeletal, hopper, or euhedral shapes; oscillatory zoning; structures suggesting replacement of P-rich zones by P-poor olivine; and sector zoning. Melt inclusions near P-rich zones typically contact low-P olivine that sometimes crosscut features in nearby P-rich olivine.
2. Dynamic crystallization experiments on basaltic compositions cooled at a constant rate produced olivines with P-zoning patterns similar to natural olivines, demonstrating that aspects of these patterns can form during simple cooling. P-enriched zones in experimentally produced and in natural olivine probably reflect incorporation of P during rapid olivine growth, and the complex zoning patterns primarily record variations in crystal growth rate. Most oscillatory zoning in P probably reflects internal factors whereby oscillating growth rates occur without external forcings, but some cases in natural olivines may reflect external forcings (e.g., magma mixing events, eruption) that result in variable crystal growth rates and/or P contents of the magma. The common occurrence of high-P phenocryst cores may reflect initial undercooling followed by nucleation and pulses of rapid crystal growth.
3. We suggest that P enrichment during rapid olivine growth reflects “solute trapping” and that P-enriched olivines are out of equilibrium with the melts from which they formed. In contact with melt, such P-rich olivine can dissolve, accompanied by subsequent slow precipitation of low-P olivine. This may explain the characteristic halos of low-P olivine around melt inclusions in natural olivines and the crosscutting by low-P olivine of features defined by high-P olivine. Similar features in our experiments suggest that this process can occur on time scales of hours.
4. P zoning is highly correlated with Al and Cr zoning in experimental olivines and in natural olivines with short high-temperature residence times. In contrast, Cr and Al zoning is weak to absent in natural phenocrysts with strong P zoning. Observed correlations of Al and Cr with P reflect coupled substitutions and/or kinetic controls on partitioning during rapid crystal growth. Crystal growth rate has little effect on the incorporation of common divalent cations into olivine, so complex zoning in P, Al, and Cr is independent of Fe/Mg zoning.
5. We suggest that igneous olivines grow with complex, correlated zoning in P–Al–Cr superimposed on smooth, normal Fe/Mg zoning. The Fe/Mg zoning is typically fully homogenized during magmatic residence of phenocrysts, while Al and Cr zoning is partially to fully homogenized, and P zoning left intact. The inferred

order of diffusivities within P-enriched regions of olivine (Fe, Mg >> Al > Cr >> P) suggests an approach to quantifying thermal histories of olivines once the relevant diffusivities are known, but applications may prove difficult because these diffusivities are likely to depend on small differences in olivine composition and variable substitution mechanisms.

6. P zoning is widespread in magmatic olivine, revealing details of crystal growth and intra-crystal stratigraphy in what otherwise appear to be relatively featureless crystals. Since it is preserved in early-formed olivines with prolonged residence times in magmas at high temperatures, it has promise as an archive of information on an otherwise largely inaccessible stage of a magma's history. Study of such features should be a valuable supplement to routine petrographic investigations of basic and ultrabasic rocks, especially because these features can be observed with standard electron microprobe techniques.

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Research paper

Experimental study of water diffusion in haplobasaltic and haploandesitic melts

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ABSTRACT

The diffusion of water in polymerized silicate melts has been studied extensively, but only limited data are available for water diffusion in depolymerized melts such as andesite and basalt. We report here results of eight experiments to determine the diffusivity of water ($D_{\text{H}_2\text{O}}$, defined to be the diffusivity of total H_2O ; i.e., regardless of speciation) in haplobasalt and haploandesite melts at 1300 °C and $P_{\text{H}_2\text{O}} = 0.3\text{--}100$ MPa using hydration and diffusion-couple methods. Water contents of the melts ranged from <0.1 to ~ 4 wt.%. Our results contribute to understanding the dependence of water diffusivity on melt composition, especially the concentration of water itself. Diffusion experiments were conducted for 420–1500 s using an internally heated pressure vessel. Water concentration vs. distance profiles in quenched glasses was determined using Fourier transform infrared (FTIR) spectroscopy. $D_{\text{H}_2\text{O}}$ values were determined by fitting these profiles using either Boltzmann–Matano methods, simple functional forms for the relationship between water content and $D_{\text{H}_2\text{O}}$, or the $D_{\text{H}_2\text{O}}$ vs. water content function implied by a simple water speciation model. For both of the compositions studied, $D_{\text{H}_2\text{O}}$ increases with increasing water content. The increase in $D_{\text{H}_2\text{O}}$ with water content can be modeled as exponential over the range investigated, and it is generally consistent with simple models of speciation in which dissolved molecular water is mobile and hydroxyl groups are immobile. The following equations can be used to calculate water diffusivity at various water contents in haplobasaltic and haploandesitic melts at 1300 °C:

$$D_{\text{H}_2\text{O}} = 1.27 \cdot \exp(0.538 \cdot C_{\text{H}_2\text{O}}) \cdot 10^{-10} \quad \text{haplobasalt}$$

$$D_{\text{H}_2\text{O}} = 4.90 \cdot \exp(0.493 \cdot C_{\text{H}_2\text{O}}) \cdot 10^{-11} \quad \text{haploandesite}$$

where $D_{\text{H}_2\text{O}}$ is in m^2/s and $C_{\text{H}_2\text{O}}$ is in weight percent.

Comparison of our results with those in the literature for other compositions suggest an overall correlation between water diffusivity and melt viscosity for $C_{\text{H}_2\text{O}} \leq 3$ wt.%. Given the availability of algorithms relating viscosity to melt composition, this correlation can be used to estimate $D_{\text{H}_2\text{O}}$ in melts for which it has not been experimentally determined and to model igneous processes for which $D_{\text{H}_2\text{O}}$ plays a role over a range of magma composition spanning rhyolite to basalt. The following equations can be used to calculate water diffusivity from the viscosity of depolymerized and polymerized melt compositions:

$$\log D_{\text{H}_2\text{O}} = -8.87 - 0.578 \cdot \log \eta \quad \text{depolymerized melt}$$

$$\log D_{\text{H}_2\text{O}} = -9.65 - 0.269 \cdot \log \eta \quad \text{polymerized melt}$$

where η is in Pa·s and $D_{\text{H}_2\text{O}}$ in m^2/s .

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1. Introduction

The diffusivity of water ($D_{\text{H}_2\text{O}}$, defined in this paper to be the diffusion coefficient of total water, regardless of the details of the speciation) in silicate melts is a useful parameter for understanding physical parameters such as electrical conductivity of magmas (Pommier et al., 2008) and igneous phenomena such as the degassing of magma and explosivity of volcanic eruptions. Over the past several

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decades, there have been many experimental and theoretical studies of the diffusion of water in silicate melts and glasses. Most of these have focused on relatively silica-rich, highly polymerized melts similar in composition to rhyolites and dacites (e.g., Shaw, 1974; Arzi, 1978; Jambon, 1979; Jambon et al., 1992; Delaney and Karsten, 1981; Karsten et al., 1982; Lapham et al., 1984; Persikov et al., 1990; Chekhmir and Epel'baum, 1991; Zhang et al., 1991; Behrens and Nowak, 1997; Nowak and Behrens, 1997; Doremus, 2000; Zhang and Behrens, 2000; Behrens et al., 2004; Liu et al., 2004; Acosta-Vigil et al., 2005; Behrens and Zhang, 2009; Wang et al., 2009). In contrast, only limited data are available on D_{H_2O} in less polymerized melts similar in composition to andesite (Behrens et al., 2004; Freda et al., 2003) and basalt (Zhang and Stolper, 1991). As a result, although much has been learned about the diffusion of water in silicate melts of geological interest (Watson, 1994), many aspects are incompletely understood (e.g., Behrens et al., 2004; Persikov et al., 2005; Newman et al., 2005; Baker et al., 2005); for example, although D_{H_2O} in highly polymerized silicate melts is known to vary strongly and non-linearly with the concentration of water, the concentration dependence of D_{H_2O} is not as well constrained for andesitic and basaltic melts, and little is known about the dependence of D_{H_2O} on the concentrations of the anhydrous components of silicate melts (Behrens et al., 2004; Zhang et al., 2007).

We report here results of an investigation of the diffusion of water in relatively depolymerized silicate melts. Our results constrain in such melts the dependence of D_{H_2O} on the concentration of water and the relationship of D_{H_2O} to melt structure and to the mechanisms of water diffusion. We focus particularly on D_{H_2O} in basic melt compositions to address the paucity of data for such liquids. We also examine the relationship between D_{H_2O} and melt viscosity, with the goal of finding correlations between these two transport properties that could be useful for estimating values of D_{H_2O} for melt compositions for which experiments are not available.

2. Experimental and analytical methods

2.1. Starting material and glass synthesis

Two starting compositions were used in this study (Table 1): They were mixtures of albite (Ab) from the Kolba massive (Kazakhstan; Persikov et al., 1990) and diopside (Di) and wollastonite (Wo) from the Ioko–Dovyren layered intrusion (Northern Baikal region, Russia; Kislov, 1998) in molar proportions of $Ab_{45}Di_{37}Wo_{18}$ (referred to as haplobasalt) or $Ab_{77}Di_{19.5}Wo_{3.5}$ (referred to as haploandesite). Although the SiO_2 content of the haplobasalt is closer to that of an andesite than a basalt, we refer to it as a haplobasalt based on its NBO/T parameter (67.7; Table 1; NBO/T is the ratio of non-bridging oxygens to those in tetrahedral sites), which is closer to that of a basalt than an andesite (average $100 \cdot NBO/T$ of 54 and 22, respectively, based on compositions given by LeMaitre, 1976; see details regarding NBO/T in

Mysen, 1988, and Persikov, 1991). Both “nominally dry”¹ and hydrous glasses were used in experiments.

Dry glasses for the two starting compositions were synthesized by melting 5 g of powdered mixtures of albite, diopside, and wollastonite (see Table 1) for 5 h at 1400 °C in air in covered platinum crucibles in a high-temperature furnace, followed by quenching in air. The glasses were removed from the platinum crucibles and ground in an agate mortar, and then approximately 200 mg of the glass powder was loaded into a platinum capsule open at one end (50 mm long, 3 mm OD, 0.1 mm wall thickness). The capsule was then heated with a natural gas torch to remove adsorbed components and immediately sealed by welding the open end with a tungsten-inert-gas (TIG) electrode. The sealed capsule was placed in the high-temperature furnace at 1 atm for 2 h at 1400 °C and quenched in air; the anhydrous glass cylinders formed during this step were used as starting materials for the diffusion experiments. These dry glasses were optically homogeneous and free of bubbles and crystallites; they contained 0.02–0.1 wt.% H_2O (determined by FTIR spectroscopy; see Section 2.3.2). Representative electron microprobe analyses of the starting glasses for the two compositions studied here are listed in Table 1.

Homogeneous hydrous glass starting materials with up to 4.5 wt.% H_2O were synthesized in an internally heated gas pressure vessel (IHPV) at the Institute of Experimental Mineralogy (IEM), Russian Academy of Sciences (described in Persikov et al., 1990; Persikov, 1991; Persikov and Bukhtiyarov, 2004) using the following procedures: Powders (~200 mg) of the two dry glass starting materials described above were loaded into Pt capsules open at one end (50 mm long, 3 mm in diameter, 0.1 mm wall thickness) along with 50–75 mg of doubly distilled H_2O (i.e., sufficient to fill the interstices of the powders). These open capsules were placed in the sample holder of the internal device in the constant temperature zone of the IHPV. The sample holder was then pressurized with doubly distilled water, and the two samples were held simultaneously at 1300 °C, 100 MPa P_{H_2O} for 5 h. At the beginning of each run, the temperature and water pressure were increased over ~1 h (approximately along the water isochore) up to the run temperature and 80 MPa water pressure and held there for 2 h. The water pressure was then increased to the target value of 100 MPa, and the final run conditions were maintained for 3 h, after which the samples were quenched isobarically by turning off the power to the heater. Measured initial cooling rates were ~300 °C/min down to 900 °C, followed by ~100 °C/min down to room temperature. After removal from the IHPV, the Pt capsules were peeled off, yielding cylinders of hydrous glass (8–12 mm long) that were used as starting materials for the diffusion-couple experiments. The ends were cut and polished to produce flat surfaces perpendicular to the axes of the cylinders for the diffusion-couple experiments. These glasses were optically homogeneous and free of bubbles and crystallites. The water contents of the quenched glasses and the homogeneity of the water distributions in the glass cylinders were determined by FTIR spectroscopy (see Section 2.3.2). Note that samples run in the IHPV were undeformed during these syntheses.

2.2. Diffusion experiments

Run conditions for the diffusion experiments are listed in Table 2. Two different types of experiments were done: hydration and diffusion-couple experiments. Hydration experiments were conducted by snipping off the welded tips of the Pt capsules used in the 1 atm syntheses of the dry glasses approximately 2 cm above the meniscus, leaving open capsules (30–35 mm long) that were exposed at one end to supercritical water vapor (or water-bearing fluid, in the case of run 1649; Table 2) and allowing water to diffuse into the silicate melt. For the diffusion-couple experiments, cylinders (2.8 mm

Table 1
Chemical composition¹ and structural chemical parameter ($100 \cdot NBO/T$) of starting materials.

	Albite, Kolba	Diopside, Ioko–Dovyren	Haploandesite ($Ab_{77}Di_{19.5}Wo_{3.5}$)	Haplobasalt ($Ab_{45}Di_{37}Wo_{18}$)
SiO_2	69.00 ± 0.46	55.99 ± 0.44	65.82 ± 0.59	62.2 ± 0.42
Al_2O_3	19.15 ± 0.26		15.1 ± 0.28	10.5 ± 0.22
Fe_2O_3	0.02 ± 0.03			
MgO		18.69 ± 0.26	3.17 ± 0.13	6.79 ± 0.24
CaO	0.02 ± 0.03	25.47 ± 0.26	7.00 ± 0.13	14.15 ± 0.22
Na_2O	11.77 ± 0.21		8.93 ± 0.24	6.34 ± 0.19
K_2O	0.03 ± 0.02			
Sum	99.99	100.15	100.02	99.98
$100 \cdot NBO/T$	0.3	197.00	28.7	67.7

Notes: ¹ analysis by electron microprobe.

¹ These glasses are referred to as “dry” from this point on, for convenience, despite the fact that they all contain small amounts of dissolved water.

Table 2
Experimental run conditions.

Sample	Temperature (°C)	P _{total} (MPa)	P _{H₂O} (MPa)	Pressurizing fluid	t _{dwell} (s)	t _{effective} (s)	Type of experiment	Composition
1641/2	1300	100	100	H ₂ O	420	480	Couple	Haplobasalt
1641/5	1300	100	100	H ₂ O	420	480	Hydration	Haploandesite
1649/1	1300	100	100	CO ₂ ^a	1200	1320	Couple	Haploandesite
1649/6 ^b	1300	100	3	CO ₂ ^a	1200	1320	Hydration	Haploandesite
1650/1	1300	100	100	H ₂ O	1500	1700	Couple	Haplobasalt
1650/3 ^b	1300	100	100	H ₂ O	1500	1700	Couple	Haploandesite
1650/5	1300	100	100	H ₂ O	1500	1700	Hydration	Haplobasalt
1650/6 ^b	1300	100	100	H ₂ O	1500	1700	Hydration	Haploandesite

^a For run 1649, the pressurizing fluid was CO₂ from a gas tank without any drying procedure. Therefore, the CO₂ contained a small amount of H₂O. Since sample 1649/1 was a couple experiment, sealed at both ends, the nature of the pressurizing fluid did not affect the composition of the volatiles within the capsule. However, the presence of a small amount of H₂O in the CO₂ fluid caused hydration in the dry starting material of experiment 1649/6, which was open at one end. The surface C_{H₂O} for this experiment, 0.29 wt.%, enabled us to estimate the C_{H₂O} of the experiment to be ~3 MPa.

^b These samples show evidence of diffusion of H₂O in from the sides of the run products.

diameter) of nominally dry and hydrous glasses synthesized as described above were cut to lengths of 5–6 mm, and both ends of each cylinder were polished. Two cylinders with the same base composition that had been sawed to produce flat surfaces perpendicular to the long axis – one dry and one hydrous – were placed together so that the polished surfaces were in contact. Each couple was then inserted into the same size Pt tube as the capsules used in the original synthesis. After crimping the Pt tube around the cylinders, the tube was sealed by welding a flat, circular cover to each end of the tube using a TIG electrode. During an experiment, water diffused across the interface between the two cylinders. Experiment durations were chosen so as to generate concentration profiles that could be measured by FTIR spectroscopy on the glasses after quenching. Chemical homogeneity (other than for water) was confirmed by microprobe analysis before and after diffusion experiments for several of each composition (see Fig. 1 for an example of each composition).

For each experiment, 2–4 Pt capsules were placed simultaneously in the sample holder (cross-hatched volume in Fig. 1 of Persikov et al., 1990), which was then filled with the desired pressurizing fluid and placed in the IHPV. For most experiments, two sealed capsules containing diffusion-couples (each with a different anhydrous base composition) and two capsules open at one end for hydration experiments (again, each with a different anhydrous base composition) were run simultaneously to ensure identical run times and conditions so that the results of the different types of experiments could be compared directly.

Most experiments were conducted at a total pressure and P_{H₂O} of 100 MPa for 420–1500 s at 1300 °C. The exception was one experiment pressurized to 100 MPa using nominally pure CO₂ (but with P_{H₂O} ~0.3 MPa, based on the measured water content for the sample) at 1300 °C for 1200 s (experiment 1649/6; see Tables 2 and 3). At the beginning of each experiment, the temperature and fluid pressure were raised over ~30 min to 800 °C and 100 MPa, approximately along an isochore. The temperature was then raised isobarically at ~120 °C/min to 1300 °C, after which the pressure and temperature were held at the final values to allow diffusion of water from the vapor into the melts across the interface at the open ends of the capsules in the hydration experiments or across the melt–melt interface in the diffusion-couple experiments. As for the runs synthesizing the hydrous starting glasses, samples were quenched isobarically. The time–temperature history of each experiment was recorded and the effective run duration at the dwell temperature was calculated (see Behrens et al., 2004; Zhang and Behrens, 2000, for details of these calculations). Typically, a correction amount of 60–200 s was added to the dwell time to account for heating, cooling, and overshooting (Table 2).

After quenching and removal from the Pt capsules, the glass run products were mounted in epoxy, sectioned along their cylindrical axes near the widest section of the cylinder, ground on both sides to a thickness of 50–300 μm, and then doubly polished for FTIR measurements. The final slices were optically homogeneous and free of bubbles and crystallites, with the exception of sample 1650/5, which contained quench crystals adjacent to the capsule walls.

Fig. 1. Examples of major element distribution along a water diffusion profile for each composition. The gray vertical line indicates the initial interface between the dry (water free) and wet (water-bearing) samples for haploandesite couple 1649/1, based on the lengths of the starting cylinders. Errors associated with major element compositions are ± 0.70 – 2.2% relative.

Fig. 2. Compositional dependence of molar absorption coefficients in silicate glasses for (a) hydroxyl groups (4500 cm^{-1} band) and (b) molecular water (5200 cm^{-1} band). Molar absorptivities for both bands correlate linearly with the NBO/T structural chemical parameter determined for the anhydrous composition. Best fit lines were calculated by least squares linear regression. Data from the literature included in the regression are shown as open symbols together with their reported uncertainties. The values calculated for the compositions studied here are indicated by solid symbols and given in Table 3. The errors given for these calculated values are the uncertainties for the best fit lines. Sources of data for regression:

1 – andesite (Mandeville et al., 2002); 2 – andesite (Ohlhorst et al., 2001); 3 – high-Al basalt (Yamashita et al., 1997); 4 – tholeiite (Yamashita et al., 1997); 5 – basalt (Dixon et al., 1995); 6 – basalt BI (Ohlhorst et al., 2001); 7 – $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ (Acocella et al., 1984; errors not indicated); 8 – NaKZnSiAl (Bartholomew et al., 1980; error for molar absorptivity for OH groups not indicated); 9 – CAS-7 (Silver et al., 1990); 10 – haploandesite (Vetere et al., 2006).

2.3. Analytical procedures

2.3.1. Electron microprobe analysis

The concentrations of major oxide components on traverses coinciding with the concentration profiles of water for selected hydration and diffusion-couple experiments were determined by electron microprobe using either a 10 μm wide and 100 μm long slit perpendicular to the cylindrical axis of the sample at IEM. Analyses were made using the digital electron microscope Vega TS 5130MM (CamScan MV2300) with energy dispersive X-ray spectrometry

(EDX) INCA Energy 200 (Table 1, Fig. 1). The standard INCA Energy 200 program (INCA Suite, Revision 4.04, program product of Oxford Instruments; Pouchou and Pichoir, 1991) and IEM RAS Data INCA program (A. Nekrasov, unpublished) were used for data reduction. Counting times were 100–140 s. Each profile was analyzed 3–5 times. Precisions were ± 0.70 –2.2% relative, as determined by averaging multiple analyses of the same location (Fig. 1).

2.3.2. FTIR spectroscopy

Total water contents ($\text{C}_{\text{H}_2\text{O}}$ = the sum of water dissolved as OH groups and H_2O molecules) along the diffusion profiles in the quenched experiments were determined for the samples by FTIR spectroscopy. IR spectra were collected using a Nicolet Magna-IR 860 FTIR spectrometer with a Nicolet Continuum IR microscope at Caltech. Concentration profiles generated in the diffusion experiments were analyzed along the cylindrical axis of the sample using a 20 μm wide and 120 μm long aperture oriented with its long axis perpendicular to the cylindrical axis. A computer-automated stage was used to move the sample parallel to the cylindrical axis in a controlled, reproducible fashion ($\pm 5 \mu\text{m}$) so as to generate concentration profiles. Spectra were recorded in the near infrared using a tungsten light source, a CaF_2 beamsplitter, and a narrow range MCT detector. Typically 512–1024 scans were accumulated for each spectrum with a spectral resolution of 8 cm^{-1} .

The absorption band at 3550 cm^{-1} was used to determine the total water content in the haploandesite 1649/6 experiment, in which the absorption was low enough (< 1.3 absorbance units) so as not to saturate the detector. The molar absorption coefficient used for this band in haploandesitic glass was $70 \pm 3.5 \text{ l/mol cm}$ (Mandeville et al., 2002).

For samples with maximum total water contents greater than $\sim 0.5 \text{ wt.}\%$, molecular H_2O and OH group concentrations (as H_2O) were calculated by summing the concentrations of OH groups and H_2O molecules determined from the peak heights of the absorption bands at 4500 cm^{-1} and 5230 cm^{-1} , respectively. Molar absorption coefficients for OH and H_2O bands in the infrared and near-infrared regions are known to vary with glass composition. Dixon et al. (1995) and Mandeville et al. (2002) showed that the molar absorption coefficients for the 5230 and 4500 cm^{-1} bands can be approximated as linear functions of the cation fraction of tetrahedral cations ($T = (\text{Si}^{4+} + \text{Al}^{3+})/(\text{total cations})$) over a significant compositional range. In this study, we have used the degree of polymerization (as measured by NBO/T) of the anhydrous melt as the independent variable. Fig. 2 shows the data available in the literature for the 5230 and 4500 cm^{-1} molar absorptivities vs. NBO/T. The molar absorption coefficients increase with increasing polymerization (i.e., to the left in this figure), in agreement with the parameterization of Dixon

Table 3

Water solubility in melts studied and densities and molar absorption coefficients of glasses.

Sample	Water pressure (MPa)	Temperature ($^{\circ}\text{C}$)	Water solubility (wt.%) $\pm 10\%$ relative	Type of experiment	^a Equations used to calculate density (g/l)	Molar absorptivities, ($\text{l mol}^{-1} \text{cm}^{-1}$)
Haplobasalt – $\text{Ab}_{45}\text{Di}_{37}\text{Wo}_{18}$					$\rho = -17.9 \cdot \text{C}_{\text{H}_2\text{O}} + 2580$	$\epsilon_{4500 \text{ cm}^{-1}} = 0.60 \pm 0.10$ $\epsilon_{5200 \text{ cm}^{-1}} = 0.77 \pm 0.09$
1641/2	100	1300	4.5 ± 0.45	Couple		
1650/1	100	1300	3.9 ± 0.38	Couple		
1650/5	100	1300	3.8 ± 0.38	Hydration		
Haploandesite – $\text{Ab}_{77}\text{Di}_{19.5}\text{Wo}_{3.5}$					$\rho = -11.9 \cdot \text{C}_{\text{H}_2\text{O}} + 2480$	$\epsilon_{4500 \text{ cm}^{-1}} = 0.86 \pm 0.10$ $\epsilon_{5200 \text{ cm}^{-1}} = 1.01 \pm 0.09$ ^b $\epsilon_{3500 \text{ cm}^{-1}} = 70 \pm 3.5$
1649/1	100	1300	3.8 ± 0.38	Couple		
1650/3	100	1300	4.2 ± 0.42	Couple		
1649/6	3	1300	0.39 ± 0.04	Hydration		
1650/6	100	1300	3.7 ± 0.37	Hydration		
1641/5	100	1300	4.2 ± 0.42	Hydration		

^a Based on unpublished experimental data by E. Persikov and P. Richet.

^b Andesitic glasses (Mandeville, 2002).

et al. (1995), which demonstrated that they increase with increasing $\text{Si}^{4+} + \text{Al}^{3+}$ (which, all other things being equal, corresponds to an increase in polymerization). The equations for the best-fit lines in Fig. 2 were used to calculate the molar absorption coefficients for the two compositions studied here (Table 3). The errors of these approximations are ± 0.10 and ± 0.09 l/mol cm for the molar absorption coefficients for the 4500 and 5230 cm^{-1} bands, respectively. These molar absorption coefficients are consistent, within the 10–15% relative errors of the molar absorptivity – NBO/T correlations in Fig. 2, with the values calculated using the $\text{Si}^{4+} + \text{Al}^{3+}$ correlation of Dixon et al. (1995) and Mandeville et al. (2002), within their 20% relative errors. The relative proportion of H_2O molecules to OH groups is known to change with temperature (e.g., Stolper, 1989; Zhang et al., 2000), and water speciation in the experiments in this study certainly re-equilibrated during quench, but provided the molar absorptivities are accurate, this should not affect the reported total water contents.

In addition to the molar absorption coefficients, conversion of absorption measurements into species concentration requires sample thickness and density. The thickness along the length of each sample was measured every millimeter with a digital micrometer (Mitutoyo; precision $\leq 2 \mu\text{m}$) and interpolated linearly between measurements. Glass density and water content were calculated iteratively, as described by Silver et al. (1990), except that the linear dependence of glass density on water content (Richet et al., 2000; Ohlhorst et al., 2001; Benne and Behrens, 2003) was determined experimentally for each of the compositions studied here (E. Persikov and P. Richet, unpublished data). The relationships used to calculate the densities of hydrous glasses along the diffusion profiles are given in Table 3.

3. Experimental results

The results of electron microprobe traverses of major anhydrous components along water diffusion profiles (for each base composition) indicate that our data can be treated as simple chemical diffusion of water because all oxides other than H_2O are essentially constant over the length of the concentration profiles of H_2O (e.g., Fig. 1); in particular, our data do not suggest that water diffusion involves significant interdiffusion of other components. This result is consistent with other work on water diffusion in silicate melts of geological interest (Shaw, 1974; Jambon, 1979; Jambon et al., 1992; Delaney and Karsten, 1981; Karsten et al., 1982; Lapham et al., 1984; Persikov et al., 1990; Chekhmir and Epel'baum, 1991; Zhang et al., 1991; Behrens and Nowak, 1997; Nowak and Behrens, 1997; Doremus, 2000; Zhang and Behrens, 2000; Behrens et al., 2004). Karsten (1982; 1983) noted mobility of Na and K during water diffusion in obsidian, but concluded that this was unique to hydration of glasses. Additionally, Acosta-Vigil et al. (2005) found variation of alkalis during hydration accompanied by melting close to the glass transition in a metaluminous haplo-granitic composition.

We note several complications in some experimental run products. Results from one hydration experiment are not included in this report because of an unusual decrease in $\text{C}_{\text{H}_2\text{O}}$ close to the surface; we attribute this to unknown experimental problems. A few samples, including both hydration and diffusion-couple runs (indicated in Table 2), show evidence of diffusion across the run product; i.e., into the sample, perpendicular to the expected one-dimensional diffusion. We infer that in these experiments, water either traveled along the interface between the melt and the Pt capsule. However, the increase in water content due to this was minor relative to the range of water content in each sample (typically 0.1–0.3 wt.%), and the diffusion coefficients are the same for experiments that experienced this problem and those that did not. As mentioned above, haploandesite 1650/5 contains quench crystals extending $\leq 500 \mu\text{m}$ in from the capsule walls, but they do not appear to have affected the diffusion profile along the axis of the capsule (Fig. 3c).

3.1. Water solubility

Although the emphasis of this study is the diffusion of water, our experiments also provide data on the solubility of water in basic silicate melts. First, since the hydrous glass starting materials were produced by quenching homogeneous, vapor-saturated melts, the water concentrations of the quenched glasses reflect water solubilities at the synthesis conditions. And second, the hydration experiments (except for 1649/6, for which $\text{P}_{\text{H}_2\text{O}} \ll \text{P}_{\text{total}}$) are saturated at the boundary with the essentially pure H_2O fluid, and thus the concentration of water at this boundary is the water solubility at the conditions of the experiment (although the concentration right at the boundary requires extrapolation of concentration measurements inward from the boundary; Fig. 3).

The solubilities of water as determined by these two approaches are presented in Table 3 and Fig. 3 for the two base compositions studied here. Although these represent the first measurements of water solubility in melts of these specific compositions, our values for haplobasalt and haploandesite are comparable to previous studies on similar compositions. For example, for temperatures in the range 1200 °C, Benne and Behrens (2002) present data for a similar haplobasaltic composition ($\text{Ab}_{54}\text{Di}_{46}$) that indicate 3.6 wt.% solubility at 100 MPa, compared with 3.8–4.5 wt.% for the haplobasaltic composition in this study. Hamilton et al. (1964) determined a water solubility of 4.5 wt.% at 103.4 MPa for andesite, compared with 3.7–4.2 wt.% for haploandesite at 100 MPa in this study. Note that the agreement between our data and data from the literature on water solubility obtained by different methods supports the molar absorption coefficients we have used (see Section 2.3.2).

3.2. Diffusively generated $\text{C}_{\text{H}_2\text{O}}$ profiles

As discussed in the Introduction, $\text{D}_{\text{H}_2\text{O}}$ in silicate melts is known to depend strongly on $\text{C}_{\text{H}_2\text{O}}$, and a key motivation for our investigation was to constrain the functional form of this dependence in basic melts. We determined $\text{D}_{\text{H}_2\text{O}}$ vs. $\text{C}_{\text{H}_2\text{O}}$ relationships for each concentration profile in several ways: (1) by direct calculation using Boltzmann–Matano methods (Crank, 1975; Sauer and Freise, 1962; den Broeder, 1969; Dayananda, 1983), which makes no assumptions about the functional form of the relationship; (2) by assuming simple functional forms for the relationship between $\text{D}_{\text{H}_2\text{O}}$ and $\text{C}_{\text{H}_2\text{O}}$ (e.g., $\text{D}_{\text{H}_2\text{O}}$ is a linear function of $\text{C}_{\text{H}_2\text{O}}$ (e.g., Shaw, 1974), or $\text{D}_{\text{H}_2\text{O}}$ is an exponential function of $\text{C}_{\text{H}_2\text{O}}$ (e.g., Delaney and Karsten, 1981)); or (3) by assuming a specific diffusion model based on the speciation of water dissolved in silicate melt (e.g., Stolper, 1982a,b; Zhang et al., 1991; Behrens and Nowak, 1997; Nowak and Behrens, 1997; Zhang, 1999; Doremus, 2000; Zhang and Behrens, 2000). By comparing the results of these various approaches to characterizing the $\text{D}_{\text{H}_2\text{O}}$ vs. $\text{C}_{\text{H}_2\text{O}}$ relationship, we can evaluate the confidence and detail with which this relationship can be determined from diffusion profiles of the sort we have obtained (i.e., that extend over a significant $\text{C}_{\text{H}_2\text{O}}$ range).

Measured concentration profiles for the eight experiments on the haplobasalt (2 diffusion-couple and 1 hydration experiments) and haploandesite (2 diffusion-couple and 3 hydration experiments) at 1300 °C are shown in Fig. 3. Note that only concentrations of total water are shown even though the concentrations of the individual dissolved species were generally determined, because, as mentioned above, the temperatures of all our experiments were sufficiently high for the quench rates of the experiments that OH group and H_2O molecule concentrations for the quenched glasses are not expected to reflect those for the melts at the temperatures of the experiments (Stolper, 1989; Zhang et al., 1991; Dingwell, 1995; Persikov, 1998; Nowak and Behrens, 1995, 1997; Shen and Keppler, 1995; Sowerby and Keppler, 1999; Behrens and Nowak, 2003).

In the following section, we describe and then compare the various approaches we used to extract $\text{D}_{\text{H}_2\text{O}}$ from these data.

Fig. 3. Water diffusion profiles determined by FTIR spectroscopy for all experiments. Also shown are calculated profiles assuming functional relationships between $D_{\text{H}_2\text{O}}$ and $C_{\text{H}_2\text{O}}$ ($D_{\text{H}_2\text{O}}$ constant, $D_{\text{H}_2\text{O}}$ proportional to $C_{\text{H}_2\text{O}}$, $D_{\text{H}_2\text{O}}$ exponential relative to $C_{\text{H}_2\text{O}}$, and the speciation model described in the text) and for the best-fit asymmetric sigmoidal function fits to the FTIR data. The table in each panel gives the correlation coefficients and the standard deviations of the model fits relative to the FTIR data, using the same colors as in the legend. The Boltzmann–Matano analysis was based on the asymmetric sigmoidal function fits, labeled B–M in the tables. The brown dots indicate the water solubilities, as discussed in the text and given in Table 3.

4. Data reduction to determine the dependence of water diffusivity on water content

4.1. Data reduction using Boltzmann–Matano methods

$D_{\text{H}_2\text{O}}$ was first determined along the length of each concentration profile using Boltzmann–Matano analysis for hydration experiments (e.g., Crank, 1975) and a modified Boltzmann–Matano analysis for diffusion-couple experiments (Sauer and Freise, 1962; den Broeder, 1969). This procedure is frequently used to calculate concentration dependent $D_{\text{H}_2\text{O}}$ values, and it is well described elsewhere (Nowak and Behrens, 1997; Behrens et al., 2004). A related method that fits diffusion profiles assuming constant, average diffusion coefficients

over user-defined regions of a profile was also applied to the diffusion couple experiments (“MultiDiFlux”; Dayananda, 1983; Dayananda and Sohn, 1999). Below, we will refer to all of these techniques as Boltzmann–Matano analysis. Here we analyze the application of Boltzmann–Matano methods to our results in some detail in order to understand uncertainties in the resulting $D_{\text{H}_2\text{O}}$ values. In all cases, $D_{\text{H}_2\text{O}}$ values were calculated from the Boltzmann–Matano methods at 10 μm increments along the profiles.

The Boltzmann–Matano technique requires a fit to the concentration profile in order to obtain the derivatives and integrals needed to determine the concentration-dependent diffusion coefficients. Since we were particularly concerned about the dependence of the data analysis on the details of the fit to the profiles, we fit each profile to

several different functions using least squares regression, applied the Boltzmann–Matano technique to each fit, and then compared the resultant D_{H_2O} vs. C_{H_2O} relationships (Fig. 4). Based on this comparison (including the results of application of the *MultiDiFlux* methodology), we evaluated the sensitivity of the results to this important step in application of Boltzmann–Matano analysis to this problem. The various fits were calculated using the CurveFit Tool of Matlab (The MathWorks, Natick, MA) and included polynomials of different orders (3–9), Gaussian curves, Fourier functions, the Boltzmann function, smoothing splines, and asymmetric sigmoidal functions (Spiess et al., 2008). Several of these functions (e.g., Gaussian curves, Fourier functions, polynomials) are not (or need not be) monotonic. For these, the fits were limited to the range of x -values with non-zero slopes between those where C_{H_2O} just reached the maximum and minimum plateaus for couple experiments and maximum absolute C_{H_2O} and minimum plateaus for hydration experiments. The *MultiDiFlux* methodology includes fits to user-defined segments of the concentration profile using Hermite interpolation to generate cubic polynomial fits (Fig. 4), built into the *MultiDiFlux* software (https://engineering.purdue.edu/MSE/Fac_Staff/Faculty/MultiDiFlux.zip); Dayananda, 1983; Dayananda and Sohn, 1999).

Fig. 4 shows that the D_{H_2O} – C_{H_2O} relationships derived from our data using Boltzmann–Matano techniques are sensitive to the details of the fits to the concentration profiles. Although Fig. 4 shows results from

our three experiments on haplobasalt, similar calculations were done for all of the experiments described in this paper. Fig. 4a, d, and g show that the various fits all do a reasonable (and for the most part a nearly indistinguishable) job of fitting the data. As a result, the D_{H_2O} – C_{H_2O} relationships determined from each fit are generally similar for each experiment, particularly near the middle of the C_{H_2O} range (see Fig. 4b, e, h). However, the D_{H_2O} – C_{H_2O} relationships based on the different fits to the same concentration profiles are not identical, and indeed they are highly variable, in some cases even divergent, at the extremes of the concentration ranges. Note that the results of the various fits are not systematic (i.e., no particular fit always results in the highest or lowest D_{H_2O} at a particular C_{H_2O}). At each C_{H_2O} we calculated the relative standard deviation of the D_{H_2O} values (% relative to the average D_{H_2O} at that C_{H_2O}) determined for the various concentration profile fits; these standard deviations are shown in Fig. 4c, f, i. Because of this variability at the extremes of C_{H_2O} and the known uncertainties with calculating diffusion coefficients at the extremes of the range of the concentration of the diffusing component (e.g., Crank, 1975), we have limited the concentration range for which we consider the D_{H_2O} values calculated by the Boltzmann–Matano methods to be meaningful. Based on results such as those shown in Fig. 4c, f, i, we arbitrarily chose to exclude from further consideration the D_{H_2O} values calculated for the low (0–10%) and high (80–100%) ends of the concentration ranges of each experiment; the shaded regions in Fig. 4 indicate the

Fig. 4. Results of Boltzmann–Matano analysis of the haplobasalt experiments using different fits to the FTIR data. For each experiment, the clear region, not shaded, indicates the C_{H_2O} between 10% and 80% of the entire range of each experiment. Vertical lines in the bottom two rows of plots indicate the extreme concentrations of each experiment.

a, d, g). FTIR data for each of the three experiments together with fits by different functions. Seventh order polynomials were used for the polynomial fits.

b, e, h). D_{H_2O} versus C_{H_2O} relationships calculated by Boltzmann–Matano analysis of the different fits.

c, f, i). Errors resulting from the use of different fits, presented as the percent standard deviation relative to the average D_{H_2O} at that C_{H_2O} .

excluded C_{H_2O} ranges. This is the same concentration range used by Behrens et al. (2004). The average value of the relative standard deviation for D_{H_2O} for the various fits in the 10–80% concentration range for the three haplobasalt experiments shown in Fig. 4 is 18%, with a range of 5–35%. For the five haploandesite experiments, the average standard deviation in the 10–80% C_{H_2O} range is 12%, with a range of 3–41%. There is no difference between the magnitude of the errors for couple and hydration experiments, as shown for the haplobasalt by comparing Fig. 4c and 4f (couple experiments) with Fig. 4i (hydration experiment).

Although several different fits were used in this exercise, for the data reported in the remainder of this paper we use the asymmetric sigmoidal function of Spiess and others (2008) for the Boltzmann–Matano calculations. We selected this function because, except for the smoothing splines, which can be made to fit profiles perfectly, the asymmetric sigmoidal function fit the FTIR profile data best (highest R^2 , lowest standard error) for the entire profile for five of the eight samples and second best for the other three samples. Moreover, the asymmetric sigmoidal function always resulted in monotonic, smoothly varying D_{H_2O} – C_{H_2O} relationships in the 10–80% concentration range, whereas the smoothing spline often resulted in irregular relationships (Fig. 4b, e, h).

In addition to evaluating the uncertainties in the Boltzmann–Matano-derived D_{H_2O} – C_{H_2O} relationships due to the function used to fit

the concentration profiles in our experiments, we evaluated the effects on the results of uncertainties in the FTIR data. We did this by starting with a fit to the concentration profile for each experiment using the asymmetric sigmoidal function, and then calculating “data points” for this fit at each of the actual distances along the profile of the FTIR data points. Each data point was then perturbed from the best fit value based on an assumed one sigma uncertainty in the C_{H_2O} determinations based on the FTIR data and assuming a Gaussian distribution of errors about the asymmetric sigmoidal fit (indicated for each experiment as B–M in the table of each panel in Fig. 3). Ten synthetic profiles were generated for each sample based on perturbing the best fit concentration profile in this way. Fig. 5 shows the results of this analysis for the same three haplobasalt experiments shown in Fig. 4; Fig. 5a, d, g show the actual FTIR data, the asymmetric sigmoidal fit to these data with the one-sigma uncertainties, and the synthetic data points from the ten synthetic profiles. Asymmetric sigmoidal fits to each of the ten synthetic profiles for each experiment using the Boltzmann–Matano analysis produced the family of D_{H_2O} – C_{H_2O} curves shown in Fig. 5b, e, h. The average relative standard deviations of the ten synthetic D_{H_2O} values at each C_{H_2O} along the Boltzmann–Matano calculation determined in this way are shown as functions of C_{H_2O} in Fig. 5c, f, i. It is interesting that, as for the results shown in Fig. 4 comparing the effects of different fits to the concentration profiles, the D_{H_2O} values are highly variable at the high and low extremes of the

Haplobasalt

Fig. 5. Effect of noise in the FTIR data on the Boltzmann–Matano calculation of the D_{H_2O} – C_{H_2O} relationship for the haplobasalt experiments. The clear region, not shaded, indicates the C_{H_2O} between 10% and 80% of the entire range of each experiment. Vertical lines in the bottom two rows of plots indicate the extreme concentrations of each experiment.

a, d, g). FTIR data together with the best-fit asymmetric sigmoidal function and synthetic data generated from the asymmetric best fit by adding random noise. To generate the synthetic data, we started with the root mean standard error of the best-fit asymmetric sigmoidal to the FTIR data and added random numbers with the same standard deviation. The random numbers were generated using the Random Number Generator of Microsoft Excel® to average zero.

b, e, h). D_{H_2O} versus C_{H_2O} relationships calculated by Boltzmann–Matano analysis of asymmetric sigmoidal fits to the synthetic and FTIR data sets.

c, f, i). Errors resulting from the use of fits to the different sets of noisy, synthetic data, presented as the percent standard deviation relative to the D_{H_2O} at that C_{H_2O} .

concentration profiles, emphasizing again the importance of excluding data at these ends of the concentration profiles. On the other hand, the values at the middle of the concentration range for each profile are robust for the asymmetric sigmoidal fit to the data (i.e., not significantly affected by the synthetic noise in the data). The average relative standard deviation in the range from 10 to 80% of C_{H_2O} for the three haplobasalts shown in Fig. 5 is 6%. For the haploandesite experiments, the average relative standard deviation over this range due to synthetic noise is 9%.

Based on our analyses of errors due to the fit and the noise in the FTIR data, we estimate that the typical uncertainty of D_{H_2O} from the direct calculation using Boltzmann–Matano techniques is ~20% for the range of 10–80% of C_{H_2O} , limited principally by the variability in the results depending on the choice of the functional form of the fit to the concentration profile used in the Boltzmann–Matano analysis.

4.2. Data reduction based on assumed functional forms for

$$D_{H_2O} = f(C_{H_2O})$$

In addition to the Boltzmann–Matano data analysis, which assumes no *a priori* functional form for the $D_{H_2O} = f(C_{H_2O})$ relationship, several previous studies of water diffusion in silicate melts have fit concentration profiles based on simple assumed functional forms for this relationship (e.g., Shaw, 1974; Delaney and Karsten, 1981; Zhang and Stolper, 1991; Chekhmir and Epel'baum, 1991; Behrens et al., 2004). We have done this as well, using Microsoft QuickBASIC programs written and provided by Youxue Zhang of the University of Michigan, and Fig. 3 superimposes best fits to the concentration profiles for several assumed functional forms for the D_{H_2O} vs. C_{H_2O} relationship on the data and on the asymmetric sigmoidal fit to the profiles used in the Boltzmann–Matano analysis described above: The best fit assuming D_{H_2O} is constant (i.e., independent of C_{H_2O} ; e.g., Behrens et al., 2004, for andesite) is shown in purple; the best fit assuming D_{H_2O} is proportional to C_{H_2O} (e.g., Shaw, 1974, for obsidian) is shown in green; and the best fit assuming D_{H_2O} is an exponential function of C_{H_2O} (e.g., Delaney and Karsten, 1981, and Karsten et al., 1982, for obsidian) is shown in blue. The best fit parameters for each of these fits (and the functional form) and each experiment are given in Table 4. Fig. 6 compares for each experiment the D_{H_2O} vs. C_{H_2O} relationships corresponding to these best fits to the concentration profiles and the relationship calculated from the Boltzmann–Matano

analysis based on an asymmetric sigmoidal fit. Note that D_{H_2O} goes to zero as C_{H_2O} goes to zero for the case of D_{H_2O} proportional to C_{H_2O} . However, in the case of an exponential relationship, D_{H_2O} approaches a constant (D_0) as C_{H_2O} approaches zero.

4.3. Data reduction based on the speciation/diffusion model of Zhang et al. (1991)

Zhang et al. (1991) developed a model for diffusion of water in silicate melts, referred to here as the speciation model, in which they assumed that water dissolves as both water molecules and hydroxyl groups in homogeneous equilibrium (Stolper, 1982a) but that while water molecules are mobile (with a constant diffusivity, $D_{H_2O\text{molecules}}$), hydroxyl groups are immobile. Since the proportion of the dissolved water present as water molecules increases with the total dissolved water content, D_{H_2O} also increases with C_{H_2O} , and approaches zero as C_{H_2O} approaches zero (as is the case for D_{H_2O} assumed to be proportional to C_{H_2O}). This model has been applied in several subsequent treatments of the diffusion of water in silicate melts (Behrens and Nowak, 1997; Zhang, 1999; Zhang and Behrens, 2000), and it has been extended to include the possibility that the diffusivity of water molecules is not constant but increases with total water content (Liu et al., 2004; Ni and Zhang, 2008). Best fits to the diffusion profiles assuming the speciation/diffusion model of Zhang et al. (1991) (i.e., an ideal solution model for the melt; an equilibrium constant, K , for the reaction $H_2O_{\text{molecular}} + O^{2-} = 2(OH^-)$; and a constant $D_{H_2O\text{molecules}}$) are shown as dashed red curves in Fig. 3, superimposed on the FTIR data for each experiment and compared with the Boltzmann–Matano fit (using an asymmetric sigmoidal fit to the data) and the fits based on various $D_{H_2O} = f(C_{H_2O})$ relationships described above. The free parameters in these fits are K , $D_{H_2O\text{molecules}}$, and the maximum and minimum water contents in each experiment. The value of K that best fits all but two of the experiments is between 0.9 and 1.0 (see Table 4). This value is consistent with the results of Zhang (1999) for rhyolite at 400–600 °C containing ≤2.4 wt.% water (although the composition and temperature of our results are admittedly quite different). The two experiments for which a different K fits the data best are haplobasalt couple 1650/1 and haploandesite hydration experiment 1649/6, and the best fit K is ~0 in both cases, although a K of 1 produces an almost equivalent fit for 1650/1 and only misfits the bottom 0.04 wt.% of the range for 1649/6. We also

Table 4
Fit parameters for functional models of D_{H_2O} (m^2/s).

Model	Constant D_{H_2O}	$D_{H_2O} = D_0 \cdot C_{H_2O}$	$D_{H_2O} = D_0 \cdot \exp(b \cdot C_{H_2O})$		Speciation model	
	D_{H_2O}	D_0^a	D_0^b	b	$D_{H_2O(\text{molecules})}$	K
<i>Haplobasalt</i>						
1641/2	$4.10 \cdot 10^{-10}$	$1.53 \cdot 10^{-10}$	$1.16 \cdot 10^{-10}$	0.462	$1.82 \cdot 10^{-10}$	1
min–max H_2O^c	0.55–4.50	0.55–4.40	0.55–4.44		0.66–4.44	
1650/1	$5.09 \cdot 10^{-10}$	$3.00 \cdot 10^{-10}$	$3.47 \cdot 10^{-10}$	0.203	$3.98 \cdot 10^{-10}$	0.16
min–max H_2O^c	0.50–4.09	0.50–3.98	0.50–3.87		0.50–3.87	
1650/5	$4.38 \cdot 10^{-10}$	$2.16 \cdot 10^{-10}$	$3.23 \cdot 10^{-11}$	1.108	$2.57 \cdot 10^{-10}$	1
min–max H_2O^c	0.55–4.64	0.55–4.22	0.53–3.80		0.56–4.00	
<i>Haploandesite</i>						
1649/1	$1.28 \cdot 10^{-10}$	$7.38 \cdot 10^{-11}$	$5.81 \cdot 10^{-11}$	0.415	$8.03 \cdot 10^{-11}$	0.94
min–max H_2O^c	0.10–3.85	0.10–3.85	0.10–3.85		0.12–3.87	
1650/3	$1.03 \cdot 10^{-10}$	$5.04 \cdot 10^{-11}$	$2.28 \cdot 10^{-11}$	0.704	$5.83 \cdot 10^{-11}$	1.0
min–max H_2O^c	0.67–4.18	0.67–4.18	0.67–4.18		0.68–4.17	
1649/6	$6.31 \cdot 10^{-11}$	$2.18 \cdot 10^{-10}$	$4.27 \cdot 10^{-11}$	0.740	$4.92 \cdot 10^{-11}$	0
min–max H_2O^c	0.026–0.395	0.026–0.380	0.026–0.395		0.031–0.380	
1650/6	$3.70 \cdot 10^{-10}$	$1.12 \cdot 10^{-10}$	$2.90 \cdot 10^{-11}$	0.822	$1.71 \cdot 10^{-10}$	1
min–max H_2O^c	0.10–5.00	0.10–4.00	0.10–4.00		0.095–4.35	
1641/5	$2.73 \cdot 10^{-10}$	$8.36 \cdot 10^{-11}$	$5.08 \cdot 10^{-11}$	0.542	$1.01 \cdot 10^{-10}$	1
min–max H_2O^c	0–5.00	0.02–4.20	0.02–4.10		0.022–4.18	

^a D_0 for the D_{H_2O} proportional to C_{H_2O} model is the diffusivity as C_{H_2O} goes to 1 wt.%.

^b D_0 for the D_{H_2O} exponential to C_{H_2O} model is the diffusivity as C_{H_2O} goes to 0 wt.%.

^c Indicates the minimum and maximum C_{H_2O} determined to best fit the individual models to the FTIR data.

Fig. 6. Diffusion coefficients as functions of total water content for all diffusion experiments, calculated for the various methods and models discussed in the text.

a–h) $D_{\text{H}_2\text{O}}$ versus $C_{\text{H}_2\text{O}}$ relationships for individual diffusion experiments. The clear regions, with no shading, indicate the range of $C_{\text{H}_2\text{O}}$ for which there are no artifacts due to the extremes of the profiles (Figs. 4 and 5), although the curves themselves are extrapolated to the concentration limits of the experiments. The “general exponential” curves are the best-fit curves calculated for all of the $D_{\text{H}_2\text{O}}-C_{\text{H}_2\text{O}}$ relationships for all experiments of the same composition at the same temperature, except for constant $D_{\text{H}_2\text{O}}$. This general exponential curve was calculated for the range of $C_{\text{H}_2\text{O}}$ for which there was data within the 10–80% concentration range for all samples of the same composition, i.e., the most restrictive range of $C_{\text{H}_2\text{O}}$ for each composition. Even though the $C_{\text{H}_2\text{O}}$ data for 1649/6 do not overlap those of the other haploandesitic samples, they were included in the best fit for haploandesite, in order to extend the range for which the calculated general exponential relationship for $D_{\text{H}_2\text{O}}-C_{\text{H}_2\text{O}}$ for this composition is applicable.

i) $D_{\text{H}_2\text{O}}$ versus $C_{\text{H}_2\text{O}}$ relationships for the average general exponential for each composition.

j) $D_{\text{H}_2\text{O}}$ versus $C_{\text{H}_2\text{O}}$ relationships for 1641/5 plotted on a log scale for $D_{\text{H}_2\text{O}}$ for comparison with panel h, which is plotted on a linear scale. This shows how different models, especially exponential and linear dependence of diffusivity on $C_{\text{H}_2\text{O}}$, can be distinguished from each other at varying $C_{\text{H}_2\text{O}}$.

note that these are the only experiments for which a constant $D_{\text{H}_2\text{O}}$ results in uncertainties of the fit within the range of the uncertainties for the other models (see tables in panels of Fig. 3), although for both of these samples, the Boltzmann–Matano, exponential, and speciation models are better fits than either the constant $D_{\text{H}_2\text{O}}$ or proportional models. The $D_{\text{H}_2\text{O}}$ vs. $C_{\text{H}_2\text{O}}$ relationships implied by the best fits for the speciation model are compared to the Boltzmann–Matano fits and the various best fits based on simple $D_{\text{H}_2\text{O}} = f(C_{\text{H}_2\text{O}})$ relationships in Fig. 6.

5. Discussion of the $D_{\text{H}_2\text{O}}$ vs. $C_{\text{H}_2\text{O}}$ relationship

The Boltzmann–Matano methods described in Section 4.1 generate, as they must, $D_{\text{H}_2\text{O}}$ vs. $C_{\text{H}_2\text{O}}$ relationships for each experiment that fit the measured concentration profiles, and they generate perfect fits to the asymmetric sigmoidal fits to these concentration profiles shown in black in Fig. 3. However, the assumed functional forms to the

$D_{\text{H}_2\text{O}}$ vs. $C_{\text{H}_2\text{O}}$ relationship described in Section 4.2 exhibit varying degrees of success in reproducing the FTIR data. A table comparing the R^2 and RMSE values (root-mean-squared error, i.e., the standard error of the regression) of the fits of the different models to the FTIR data is given for each profile in Fig. 3.

As found in nearly all previous studies of the diffusion of water in silicate melts and glasses (e.g., Shaw, 1974; Zhang et al., 1991; Zhang and Stolper, 1991; Zhang, 1999; Zhang and Behrens, 2000; Behrens et al., 2004; and references therein; the exception is the ambiguous results by Behrens et al., 2004, for an andesitic melt), the assumption of constant $D_{\text{H}_2\text{O}}$ (shown by the purple curves in Fig. 3) results in poor fits to the measured profiles (although, as mentioned above, in two cases [haplobasalt 1650/1 – couple, Fig. 3b; haploandesite 1649/6 – hydration, Fig. 3f], the data are also reasonably well fit [within the range of errors of the other models] by this assumption). Our data on basic silicate melts are thus consistent with previous results (mostly

obtained for higher silica, more polymerized melts) that D_{H_2O} in silicate melts cannot be treated as a constant over the significant concentration ranges generated in most diffusion experiments.

All of the other D_{H_2O} vs. C_{H_2O} functional forms (i.e., the speciation model; the exponential form [$D_{H_2O} = D_0 \cdot \exp(b \cdot C_{H_2O})$]; and the proportional form [$D_{H_2O} = D_0 \cdot C_{H_2O}$]) we have used to fit the data have D_{H_2O} increasing with C_{H_2O} , and all are successful at fitting the concentration profiles. However, overall, the exponential functional form provides the better fit to more of the concentration profiles, particularly for the hydration experiments (see Fig. 3). Nevertheless, our data cannot be used to distinguish among these (or other) functional forms, since the standard errors of the fits overlap each other. This limitation applies not only to our work, but to all previous efforts to parameterize the strong dependence of D_{H_2O} in silicate melts on C_{H_2O} (e.g., Shaw, 1974; Delaney and Karsten, 1981; Zhang et al., 1991; Behrens and Nowak, 1997; Nowak and Behrens, 1997; Zhang and Behrens, 2000; Behrens et al., 2004; Liu et al., 2004; Ni and Zhang, 2008): A key result of our study is that the success of fitting concentration profiles spanning large concentration ranges using particular functions does not strongly constrain the details of the shape of the D_{H_2O} vs. C_{H_2O} relationship.

This point is illustrated in Fig. 6, which compares the best-fit D_{H_2O} vs. C_{H_2O} relationships resulting from the Boltzmann–Matano analyses using the asymmetric sigmoidal fits to the data and to the various fits assuming a functional form for the relationship. All of the successful fits (i.e., all those except the best fit constant D_{H_2O} curves in purple) show strong increases in D_{H_2O} with C_{H_2O} . The important point, however, is that despite their differences (e.g., the various D_{H_2O} vs. C_{H_2O} relationships clearly have different shapes, and the total range of best fit D_{H_2O} values at a given C_{H_2O} in the 10–80% concentration range is up to a factor of 2.3; Fig. 6), inspection of Fig. 3 shows that in general all the fits provide good fits to the concentration profiles. For example, the concentration profiles of the haplobasalt couple 1641/2 (Fig. 3a) and haploandesite couple 1650/3 (Fig. 3e) are comparably fit by the asymmetric sigmoid, speciation, proportional, and exponential fits, but as shown in Fig. 6a and e, in detail the D_{H_2O} vs. C_{H_2O} relationships associated with these fits range from strongly concave up to concave down with values varying by a factor of up to 1.4 for 1641/2 and 1.6 for 1650/3 at a given C_{H_2O} , within 10–80% of C_{H_2O} . We return below to suggestions based on our work of how the precise functional form of the D_{H_2O} vs. C_{H_2O} relationship might be better constrained.

Even though we cannot establish the details of the functional form of the D_{H_2O} vs. C_{H_2O} relationships for the two compositions we have studied, it is nevertheless useful to provide a function consistent with our data that can be used to calculate D_{H_2O} over the concentration ranges we have studied. For each composition, we took all four of the non-constant D_{H_2O} fits to the D_{H_2O} vs. C_{H_2O} relationship for all the experiments (i.e., the Boltzmann–Matano, the proportional, the exponential, and the speciation model fits) and fit them to a single exponential function (Fig. 6i). These general exponential equations that can be used to calculate water diffusivity at various water contents in haplobasaltic and haploandesitic melts at 1300 °C are:

$$D_{H_2O} = 1.27 \cdot \exp(0.538 \cdot C_{H_2O}) \cdot 10^{-10} \quad \text{haplobasalt}$$

$$D_{H_2O} = 4.90 \cdot \exp(0.493 \cdot C_{H_2O}) \cdot 10^{-11} \quad \text{haploandesite}$$

where D_{H_2O} is in m^2/s and C_{H_2O} is in wt.%. The resultant D_{H_2O} vs. C_{H_2O} relationships are shown as the gray dashed curves in Fig. 6. Fig. 7 shows the fits to the concentration profiles using these average exponential functions; it is important to emphasize that all of the calculated profiles for a given composition were determined with the same exponential D_{H_2O} vs. C_{H_2O} function. It is clear from Fig. 7 that the average exponential function successfully fits all the concentration

profiles that we have obtained for each of the compositions. This emphasizes two points:

- For each composition, a single exponential function successfully fits both hydration and couple experiments, experiments of significantly different durations, and experiments spanning significantly different C_{H_2O} ranges (e.g., the hydration experiment done with H_2O – CO_2 fluid as the pressurizing medium [experiment 1649/6; see Fig. 7f], which has a much lower total water content at the high C_{H_2O} end of the profile than any other experiment [~ 0.4 wt.% vs ~ 4.5 wt.% for other experiments on the haploandesite composition] is fit to ± 0.008 wt.% by the same function as the other haploandesite experiments). The similarity between the hydration and couple experiments, which are susceptible to different potential experimental difficulties and the success of a single D_{H_2O} function for experiments of different duration support the robustness of our experiments and that the concentration profiles reflect simple diffusive processes.
- This comparison emphasizes the point made above that the concentration profiles can be well fit by a range of D_{H_2O} vs. C_{H_2O} relationships; i.e., as pointed out above, even though the various fits to each experiment differ, all can reproduce the concentration profiles, and here we see that even though each experiment has its own fits, and they are not identical, a single relationship for each composition can reproduce the data satisfactorily. Since it can be difficult to determine diffusion coefficients in silicate melts even when they are not dependent on the concentration of the diffusing species to better than a factor of 3 (e.g., for SiO_2 in melts with the same SiO_2 content; Watson and Baker, 1991), this agreement among several different approaches to extracting the D_{H_2O} vs. C_{H_2O} relationship is quite good. Indeed, the various functional fits for D_{H_2O} – C_{H_2O} for our individual experiments vary by factors of up to 2.3.

We conclude that the average exponential D_{H_2O} vs. C_{H_2O} functions for each composition given in Table 5 are accurate and precise, and can be used to model the dependence of the diffusion of water on water content in basic silicate melts over the concentration range for which they are constrained by our experiments. We emphasize, however, that given the significant latitude in the actual functional form of this relationship, these functions should not be used, even as rough estimates, outside the concentration ranges over which we have fit them.

As we have emphasized, data of the sort presented here and generally used by the petrological community to constrain the C_{H_2O} dependence of D_{H_2O} (i.e., using diffusively generated C_{H_2O} profiles spanning a significant C_{H_2O} range) do not permit firm conclusions to be reached about the precise functional form of D_{H_2O} vs. C_{H_2O} relationship. We conclude this section with a brief discussion of how one might, in principle, go about definitive determinations of the shape of the D_{H_2O} vs. C_{H_2O} relationship. Examination of Fig. 6 shows that although the various fits to the D_{H_2O} vs. C_{H_2O} relationship for a particular experiment can differ, and indeed tend to diverge at the high and low ends of the concentration ranges, for the diffusion experiments, the results near the center of the profiles vary on average by a factor of 1.1; indeed, even the assumption of constant (i.e., C_{H_2O} -independent) D_{H_2O} agrees within 67% relative with the C_{H_2O} -dependent models at the center of the profile. This is particularly true for the diffusion-couple experiments. Moreover, different functional fits tried for Boltzmann–Matano analysis (Fig. 4) also produce well-defined D_{H_2O} values at the center of the profile ($\pm 11\%$ relative at the center as opposed to $\pm 31\%$ relative averaged over the entire 10–80% range of C_{H_2O}). Thus, a potentially powerful approach that could circumvent the inherent uncertainties of fits to large concentration gradients would be to do a series of diffusion experiments in which the gradients in C_{H_2O} are small (~ 0.5 – 1.5 wt.%). Each such experiment would provide a well-constrained

Fig. 7. Comparison of the FTIR profiles with profiles calculated using the “general exponential” $D_{\text{H}_2\text{O}}\text{--}C_{\text{H}_2\text{O}}$ curves (see Fig. 6 and Table 5) for the conditions of the individual experiments. The dotted curves indicate the 95% confidence intervals for the calculated profiles, using the errors in coefficients of the fitted functions shown in Table 5.

value of $D_{\text{H}_2\text{O}}$ at its midpoint – independent of the methodology used to fit the concentration profile – and a series of such experiments, each of which provides information on a single $C_{\text{H}_2\text{O}}$ but that collectively span a significant range of $C_{\text{H}_2\text{O}}$, would allow a definitive determina-

tion of the $D_{\text{H}_2\text{O}} = f(C_{\text{H}_2\text{O}})$ function. Such experiments are underway (Newman et al., 2008).

It is noteworthy that the $D_{\text{H}_2\text{O}}$ vs. $C_{\text{H}_2\text{O}}$ relationships shown in Fig. 6 based on the various fits to the data are all concave up, except for those

Table 5
Results of water diffusion experiments.

Composition	T (°C)	$C_{\text{H}_2\text{O}}$ (wt.%) range for which $D_{\text{H}_2\text{O}}$ is valid	$D_{\text{H}_2\text{O}}$ (m^2/s) general exponential function of $C_{\text{H}_2\text{O}}$ for each temperature–composition combination
Haplobasalt $\text{Ab}_{45}\text{Di}_{37}\text{Wo}_{18}$	1300	1.0–3.0	$D_{\text{H}_2\text{O}} = 1.27 \left(\begin{smallmatrix} +0.13 \\ -0.12 \end{smallmatrix} \right) \exp [0.538(\pm 0.047)C_{\text{H}_2\text{O}}] \cdot 10^{-10}$
Haploandesite $\text{Ab}_{77}\text{Di}_{19.5}\text{Wo}_{3.5}$	1300	0.07–3.0	$D_{\text{H}_2\text{O}} = 4.90 \left(\begin{smallmatrix} +0.23 \\ -0.22 \end{smallmatrix} \right) \exp [0.493(\pm 0.024)C_{\text{H}_2\text{O}}] \cdot 10^{-11}$

based on the simple speciation model, which are all concave down. And thus it could be that by going to high enough values of C_{H_2O} , one might be able to distinguish between this functional form and the others. This concave downward shape reflects both the changing relative proportions of mobile molecular water and immobile hydroxyl groups with increasing C_{H_2O} in the simple speciation model we have used and the assumption that the diffusivity of molecular water is a constant (Zhang et al., 1991). However, the model can be modified simply to generate a concave-upward D_{H_2O} vs. C_{H_2O} relationship if the diffusivity of molecular water is assumed to increase with increasing water content (Lyakhovskiy et al., 1996; Zhang and Behrens, 2000), as has been done by Ni and Zhang (2008) and Wang et al. (2009). The speciation models could also be modified so as to relax the assumptions that water molecules are the only mobile species (i.e., perhaps hydroxyl groups are mobile, in addition to H_2O molecules).

We note one final approach to distinguishing the various D_{H_2O} vs. C_{H_2O} relationships proposed by us and others. Although it is not apparent in most of the panels of Fig. 6, which have linear scales, when these relationships are plotted as $\log(D_{H_2O})$ vs. C_{H_2O} (Fig. 6j), it is clear that the speciation model and the functional form in which D_{H_2O} is proportional to C_{H_2O} differ significantly from the exponential functional form as C_{H_2O} approaches zero; i.e., $D_{H_2O} \rightarrow 0$ as $C_{H_2O} \rightarrow 0$ in the two former cases whereas it approaches a finite constant value comparable to the values at ~ 0.5 – 1 wt.% for the exponential fit. (Indeed, for both of the two former cases, the D_{H_2O} – C_{H_2O} relationship is linear as C_{H_2O} approaches 0.) Thus, in principle, diffusion experiments focused on very low water content samples could distinguish between the exponential fit on the one hand and the proportional fit or speciation model on the other (provided that hydroxyl groups or other forms of dissolved water, even if not truly immobile, have diffusivities much lower than that of molecular water; Zhang et al., 1991; Behrens and Nowak, 1997).

6. Dependence of water diffusivity on anhydrous melt composition

Although our focus has been on characterizing the dependence of D_{H_2O} on C_{H_2O} , it would be useful if the growing data base on D_{H_2O} for a range of acidic to basic silicate liquid compositions could be systematized so as to make it possible to estimate D_{H_2O} as a function of C_{H_2O} for an arbitrary anhydrous base composition. That this is possible for transport properties of silicate melts is demonstrated by the considerable success that has been achieved with parameterizing the viscosity of molten silicate as a function of chemical composition (Bottinga and Weill, 1972; Shaw, 1972; Persikov, 1990, 1991, 1998, 2007; Persikov et al., 1990; Persikov and Bukhtiyarov, 2004; Dingwell and Mysen, 1985; Mysen, 1988; Baker, 1996; Hess and Dingwell, 1996; Richet et al., 1996; Giordano and Dingwell, 2003; Zhang et al., 2003; Whittington et al., 2004; Vetere et al., 2006; Hui and Zhang, 2007; Giordano et al., 2008). As a first approximation of the dependence of D_{H_2O} on anhydrous melt composition, Behrens et al. (2004) used SiO_2 content to represent compositional variation. Specifically, they suggested using the correlation between SiO_2 content and D_{H_2O} at 1 wt.% H_2O under isothermal conditions to predict D_{H_2O} in the compositional range of rhyolite through dacite. They explicitly recommended against applying the correlation to compositions with $SiO_2 < 65$ wt.%.

We explored another approach to systematizing the dependence of D_{H_2O} on melt composition: a comparison of D_{H_2O} with melt viscosity. It is well known, from the Stokes–Einstein and Eyring equations, that diffusivity is inversely proportional to the viscosity of a simple molecular liquid. Although the relationship between viscosity and diffusivities is more complex for silicate liquids, it is nevertheless clear that these transport properties are generally inversely correlated even in these materials (e.g., Shaw, 1974; Shimizu and Kushiro, 1984; Baker, 1991; Chekhmir and Epel'baum, 1991; Chekhmir et al., 1991; Persikov,

1990; Watson and Baker, 1991; Rubie et al., 1993; Behrens and Nowak, 1997; Ni and Zhang, 2008; Wang et al., 2009). Given the considerable success in parameterizing the viscosity of synthetic and natural silicate melts as a function of major element composition (see references in previous paragraph), if a relationship between viscosity and D_{H_2O} could be demonstrated, it would provide a straightforward approach for estimating D_{H_2O} in melt compositions and at conditions that have not been studied experimentally.

Fig. 8 shows that calculated viscosities for the full range of hydrous silicate melts from rhyolite to basalt (with water content 0.1–3 wt.%, spanning 54–78% SiO_2 ; 850–1500 °C; 10 MPa to 1.5 GPa) are correlated with measured D_{H_2O} from a large range of experimental studies over decades. For this comparison, viscosity was calculated as a function of pressure (both water pressure up to ~ 50 – 100 MPa depending on C_{H_2O} and total pressure up to 1.5 GPa), temperature, melt composition (including H_2O content up to 3 wt.%), and cation ratios $[Al^{3+}/(Al^{3+} + Si^{4+}); Fe^{2+}/(Fe^{2+} + Fe^{3+}); \text{and } Al^{3+}/(Na^+ + K^+ + Ca^{2+} + Mg^{2+} + Fe^{2+})]$ according to the structural-chemical model developed by Persikov (1984, 1991, 1998, 2007). Diffusion coefficients for total water content for the eight experiments discussed here are compared with data from the literature (Fig. 8), using values calculated for discrete water contents in 0.5 wt.% increments within the range of concentrations of the individual experiments, both those presented here and those from the literature. Fig. 8 shows that water diffusivity increases regularly from rhyolitic to basaltic melts, as the viscosity decreases. The inflection point in the $D_{H_2O} = f(\eta)$ relationship (at $\log \eta \approx 2.5$) has structural chemical significance in the context of the treatment of Persikov (1991, 1998, 2007); i.e., it divides the relationship into two compositional ranges: polymerized melts ($100 \cdot NBO/T < 20$) on the right-hand side of the diagram, and depolymerized melts ($100 \cdot NBO/T > 20$) on the left-hand side. Consequently, D_{H_2O} in the melt compositions plotted in Fig. 8, which span a significant range of temperature, pressure, and melt composition (including water content), may be estimated as a function of viscosity (therefore as a function of all of the parameters mentioned above for the viscosity calculations) using the following simple equations:

$$\log D_{H_2O} = -8.87(\pm 0.13) - 0.578(\pm 0.047) \cdot \log \eta - \text{depolymerized melts} \quad (4)$$

$$\log D_{H_2O} = -9.65(\pm 0.06) - 0.269(\pm 0.009) \cdot \log \eta - \text{polymerized melts} \quad (5)$$

where η is in Pa s, D_{H_2O} in m^2/s , and the logarithms are base 10. One sigma standard error for the calculated viscosity is 0.11 $\log \eta$ units, or $\pm 30\%$ relative; for the calculated D_{H_2O} , this value is 0.22 log units for depolymerized melts and 0.17 log units for polymerized melts. The standard deviation of the difference between measured D_{H_2O} and that calculated using these equations is 0.18 log units, or $\pm 43\%$ relative (inset to Fig. 8). Note in particular that this relationship (see Fig. 8) successfully accounts for the diffusion of water in basaltic and andesitic melts (from this study and Zhang and Stolper, 1991; Behrens et al., 2004), whereas the simple correlation with silica content under isothermal conditions and 1 wt.% H_2O suggested by Behrens et al. (2004; $T = 1300$ °C) and Zhang et al. (2007; $T = 1350$ °C) was not successful for basaltic melts, the latter only reproducing diffusivity for basaltic melts within a factor of 3 ± 1 , compared with a factor of 1.7 for our fit. The potential value of using this correlation to estimate D_{H_2O} for basaltic compositions is illustrated by comparing the diffusion coefficients for Fe-bearing basalt (Zhang and Stolper, 1991; open, dark blue diamonds) and Fe-free haplobasalt (this study; filled, light blue diamonds) in Fig. 8: results from the two sets of experiments overlap on this figure, despite different major element compositions and ranges in water content (≤ 0.4 wt.% and 0.5 – 4 wt.%, respectively), suggesting that viscosity (dependent on all compositional variables as well as T

Fig. 8. Relationship between water diffusivity and melt viscosity over the range of silicate melt compositions from rhyolite to basalt (see explanations in the text). The best-fit lines are shown for depolymerized (red) and polymerized (dark gray) compositions, together with the 2σ standard error bars of the regressions and $\log \eta$ values (the latter based on Persikov, 1998, 2007). The vertical line indicates the intersection of the two lines, at $\log \eta = 2.5$, within error of the transition between polymerized and depolymerized melts indicated by plotting activation energy of viscous flow versus NBO/T (Persikov, 1991, 1998) at $\log \eta = 2.4 \pm 0.1$. $D_{\text{H}_2\text{O}}$ values for the compositions studied here were calculated using the Boltzmann–Matano analyses presented in Fig. 3 and are plotted for 0.5 wt.% H_2O increments (increments of 0.05 wt.% H_2O for haploandesite 1649/6) for 10–80% of the range of water content for each experiment. Data from the literature are based on individual experiments presented by the authors, except for those for Shaw (1974), which were calculated using the linear relationship reported, since the individual data are not given. Where data needed to be calculated for experiments given fitting parameters (Nowak and Behrens (1997); Zhang and Behrens (2000); Freda et al. (2003); Behrens and Zhang, 2009; Wang et al., 2009), $D_{\text{H}_2\text{O, total}}$ was calculated for H_2O contents of 0.25, 0.5, 1, 1.5, 2, 2.5, and 3 wt.%, unless further restricted as indicated below. Viscosity values were calculated using the model developed by Persikov (1998, 2007). Conditions for the data plotted are as follows:

Haploandesite: 1300 °C, $P_{\text{total}} = 100$ MPa, $C_{\text{H}_2\text{O}} = 0.1\text{--}3$ wt.%, this study;
 Haplobasalt: 1300 °C, $P_{\text{total}} = 100$ MPa, $C_{\text{H}_2\text{O}} = 1.0\text{--}2.5$ wt.%, this study;
 Trachyte: 1061–1328 °C, $P_{\text{total}} = 1$ GPa, $C_{\text{H}_2\text{O}} = 0.25\text{--}2$ wt.% (Freda et al., 2003);
 Andesite: 1285–1575 °C, $P_{\text{total}} = 0.5\text{--}1.5$ GPa, $C_{\text{H}_2\text{O}} = 1$ wt.%, (Behrens et al., 2004);
 Dacite: 1185–1525 °C, $P_{\text{total}} = 0.5\text{--}1.5$ GPa, $C_{\text{H}_2\text{O}} = 1$ wt.%, (Behrens et al., 2004).
 MORB: 1300 °C, $P_{\text{total}} = 1$ GPa, $C_{\text{H}_2\text{O}} = 0.2\text{--}0.4$ wt.%, (Zhang and Stolper, 1991);
 Haplogranite: 800–1200 °C, $P_{\text{total}} 100$ and 500 MPa, $C_{\text{H}_2\text{O}} = 0.5\text{--}3$ wt.%, (Nowak and Behrens, 1997);
 Rhyolite: 853–1215 °C, $P_{\text{total}} 250$ and 500 MPa, $C_{\text{H}_2\text{O}} = 0.5\text{--}3$ wt.%, (Zhang and Behrens, 2000);
 Obsidian: 850 °C, P_{total} up to 200 MPa, $C_{\text{H}_2\text{O}} = 0.5\text{--}3$ wt.%, (Shaw, 1974);
 Obsidian: 850 °C, P_{total} up to 500 MPa, $C_{\text{H}_2\text{O}} = 0.8\text{--}3$ wt.%, (Lapham et al., 1984)
 Peraluminous rhyolite: 1024–1224 °C, $P_{\text{total}} 500$ MPa, $C_{\text{H}_2\text{O}} = 0.5\text{--}3$ wt.%, (Wang et al., 2009)
 Peraluminous rhyolite: 1000–1223 °C, $P_{\text{total}} 500$ MPa, $C_{\text{H}_2\text{O}} = 0.5\text{--}3$ wt.%, (Behrens and Zhang, 2009).

The inset compares $D_{\text{H}_2\text{O}}$ calculated using the best-fit lines with the original experimental data. The dashed lines indicate the standard deviation of $\pm 0.18 \log$ units for the residuals of the calculated $D_{\text{H}_2\text{O}}$ values relative to the experimental data.

and P) is a better predictor of $D_{\text{H}_2\text{O}}$ than any individual compositional variable.

While we emphasize that the relationships shown in Fig. 8 and the resulting equations for calculating $D_{\text{H}_2\text{O}}$ are unlikely to be universal, they do provide a useful means for estimating $D_{\text{H}_2\text{O}}$ for common, naturally occurring melt compositions. This should be useful both for guiding experiment design and for rough calculations needed to model magmatic processes when $D_{\text{H}_2\text{O}}$ is required but not yet known from experiment.

7. Conclusions

Measurements of $D_{\text{H}_2\text{O}}$ in haplobasaltic and haploandesitic melts containing up to ~4 wt.% H_2O show that it can be approximated by a simple exponential function in $C_{\text{H}_2\text{O}}$ for each composition at 1300 °C. These exponential functions (Table 5), using the intermediate 10–80% of the full range of water content (0.1–3 wt.% H_2O), produce profiles for the conditions of individual experiments that match the analytically determined profiles (Fig. 7). These functions are also broadly consistent with a simple speciation model in which water molecules are mobile (and have a constant diffusivity) and hydroxyl groups are immobile, although at lower water contents than we have studied, the two models deviate, and further work at low water contents could distinguish them. Fits to the data using a speciation model for water dissolved in silicate melts can be improved if the assumption of a constant diffusivity for water molecules is relaxed.

The extraction of concentration dependent diffusion coefficients for water from experiments of the sort we have conducted, which generate concentration profiles spanning a large concentration range over which the diffusion coefficient changes by a factor of 4 or more, is subject to considerable uncertainties. We conclude that no diffusion studies, including those reported here, have been designed in such a way as to provide definitive experimental determination of the functional relationship between $D_{\text{H}_2\text{O}}$ and $C_{\text{H}_2\text{O}}$ over the full range of water contents for each experiment that is independent of assumptions regarding such relationships and/or mechanisms of water diffusion in silicate melts. Based on our results, we conclude that one approach that would allow such a determination would be determination of $D_{\text{H}_2\text{O}}$ values using experiments that have only a small range in $C_{\text{H}_2\text{O}}$; determination of $D_{\text{H}_2\text{O}}$ for a series of small water gradient experiments that collectively span a wide range in $C_{\text{H}_2\text{O}}$ could yield a robust, model independent form of the variation of $D_{\text{H}_2\text{O}}$ as a function of $C_{\text{H}_2\text{O}}$.

Calculated viscosities of hydrous melts based on our data and data in the literature correlate reasonably well ($\pm 0.18 \log D_{\text{H}_2\text{O}}$ or ~40% relative 1σ) with $D_{\text{H}_2\text{O}}$ over a wide range of silicate melt composition (from rhyolite to basalt), temperature (850–1400 °C), pressure (10 MPa–1.5 GPa), and water content (0.1–3 wt.%), with a break in slope at $100 \cdot \text{NBO}/T = 20$ (i.e., between polymerized and depolymerized compositions at natural compositions corresponding to anhydrous andesitic melt). Given the wide availability of algorithms relating viscosity to melt composition, this correlation suggests an approach to estimating $D_{\text{H}_2\text{O}}$ in melts for which it has not been experimentally determined and thereby to model a wide range of igneous processes for which $D_{\text{H}_2\text{O}}$ plays a role.

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