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First measurements of OH-C exchange and temperature-dependent partitioning of OH and halogens in the system apatite–silicate melt

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ABSTRACT

We present the first integrated study of carbonate, hydroxyl, fluoride, and chloride ion partitioning in the apatite-melt system. We determined volatile partitioning behavior between apatite and silicate melt for both haplobasaltic andesite and trachyte bulk compositions at 0.5–1 GPa and 1250 °C using the piston-cylinder apparatus. All volatile species were analyzed directly in both apatite and glass using secondary ion mass spectrometry (SIMS) and electron probe microanalysis. Distribution coefficients for OH-halogen exchange are similar to those from previous studies, and together with literature data, reveal a significant log-linear relationship with temperature, while the effects of pressure and melt composition are minimal. Meanwhile, halogen-free experiments generate very high C contents (up to 5000 ppm) in apatite. Stoichiometry calculations and infrared spectra indicate that this C is mainly incorporated onto the channel volatile site together with hydroxyl. In halogen-bearing experiments, apatite crystals contain significantly lower C (≤500 ppm), which may be partly incorporated onto the phosphate site while the channel volatile site is filled by OH+F+Cl+C. Our experiments give the first constraints on H2O-CO2 exchange between apatite and silicate melt, with a Kp of 0.355 ± 0.05 for the trachyte and 0.629 ± 0.08 for the haplobasaltic andesite. The new constraints on the temperature-dependence of partitioning will enable quantitative modeling of apatite-volatile exchange in igneous systems, while this new partitioning data and method for direct, in situ analysis of C in apatite mark a significant advance that will permit future studies of magmatic C and other volatiles. This has a broad range of potential applications including magmatic differentiation, fractionation, and degassing; quantification of volatile budgets in extraterrestrial and deep earth environments; and mineralization processes.

Keywords: Apatite, volatiles, partitioning, carbon, halogens, water

INTRODUCTION

Volatile-bearing minerals such as apatite represent a useful source of information about the volatile compositions of the systems from which they crystallize. Apatite has a very flexible mineral structure, and igneous apatites can accommodate all the major volatile species of magmatic importance, i.e., H, C, F, Cl, and S, as well as other trace volatile species such as Br and I (e.g., Peng et al. 1997; Pan and Fleet 2002; Marks et al. 2012; Konecke et al. 2017). With some knowledge of the partitioning properties of these volatiles, apatite may be able to, therefore, provide quantitative information about multi-component degassing, and other processes, in terrestrial magmas. The apatite crystal formula is Ca10(PO4)6X, where X represents the channel volatile site that runs parallel to the crystallographic c-axis and is typically occupied by OH, F, and Cl. While there are several existing studies focusing on exchange between OH and halogens in the channel site (e.g., Mathez and Webster 2005; Webster et al. 2009, 2017; Doherty et al. 2014; Li and Hermann 2015, 2017; McCubbin et al. 2015; Potts et al. 2015), we are not aware of any previous work quantitatively examining the partitioning behavior of C between apatite and a silicate melt. Knowledge of the C partitioning behavior would be particularly valuable for studies of terrestrial volcanism because magmatic CO2 contents are difficult to infer using traditional methods such as melt inclusions. The solubility of CO2 in silicate melts is strongly dependent on pressure, which means that CO2 is typically degassed very early during magma ascent, and the highest (primary) CO2 contents are generally thought not to be trapped in melt inclusions, or are lost to shrinkage bubbles (e.g., Bureau et al. 1999; Wallace 2005; Blundy et al. 2010; Hartley et al. 2014; Moore et al. 2005; Wallace et al. 2015; Aster et al. 2016). Furthermore, it is commonly not clear as to the extent to which melt inclusions have been affected either by post-entrapment diffusive modification (e.g., Gaetani et al. 2012) or by fluxing of CO2-rich fluids through the magma reservoir during entrapment (e.g., Spilliaert et al. 2006; Collins et al. 2009; Blundy et al. 2010). The existing work on quantitative determination of carbonate contents of apatite is based on FTIR using doubly polished, oriented wafers. This level of sample preparation is almost prohibitively difficult for
magnatic apatites, which are typically small microphenocrysts or inclusions in other magnatic mineral phases. Here we successfully determine C in apatite using secondary ion mass spectrometry, and present data from a series of high-pressure and high-temperature experiments allowing us to constrain the combined partitioning behavior of H, C, F, and Cl between apatite and silicate melts.

**Experimental methods**

Our experimental approach was to examine volatile partitioning and exchange equilibria between apatite and silicate melts, with a particular focus on C and OH. We added halogens (F and Cl) in a subset of runs, to evaluate the extent to which this affects the partitioning of C and/or OH. The terminal run pressures (1.0 and 0.5 GPa) and temperatures (1250 °C) employed represent reasonable storage conditions for mid- to lower-crustal magma systems. Our chosen run conditions have the added advantages that (1) apatite + melt are commonly the only phases present, and (2) the glass fraction of run products is typically greater than 50% (e.g., Prowatke and Klemme 2006). These conditions simplify interpretation of the partitioning data and ensure that suitably sized areas of glass are available for ion microprobe analysis. Furthermore, it is helpful to avoid crystallization of other volatile-bearing phases (e.g., amphibole), which could complicate analysis of the partitioning behavior of volatiles between apatite and melt.

**Experimental starting materials**

We used two sets of synthetic starting materials (“BA” and “BM”; Table 1), allowing us to investigate the possible compositional effects on volatile partitioning. Both starting materials are based on compositions used in previous experimental studies and were chosen to take advantage of existing phase equilibrium constraints. Composition “BA” is a haplobasaltic andesite equivalent to composition SH3 of Prowatke and Klemme (2006). This composition produced large apatite crystals in trace-element partitioning experiments at similar temperatures and pressures (Prowatke and Klemme 2006) and enabled us to consider volatile partitioning in a simplified, Fe-free system in the first instance. Composition “BM” is a trachyte equivalent to the natural “ZAC” obsidian composition from Campi Flegrei, Naples, Italy (Falchieri and Carroll 2008). The nominal compositions of both starting materials are given in Table 1.

Starting materials were prepared as mechanical mixtures of reagent grade oxides (Al2O3, SiO2, MgO, MnO, FeO, Fe2O3, TiO2) and carbonates (Na2CO3, K2CO3, CaCO3), subsequently doped with varying amounts of phosphate [added as Ca3(PO4)2] and volatiles (added as described below). Prior to mixing, all components were dried overnight at 100 °C; the oxide powders SiO2, Al2O3, MgO, and TiO2 were additionally dried at 1000 °C to drive off residual moisture. Dried components were then mixed in the desired proportions, ground under ethanol to produce homogenous powders, and slowly decarbonated in a box furnace (600 to 1000 °C over 6 h). For starting material “BA,” four such powders were produced: a P-bearing split doped with ~25% Ca3(PO4)2; a P-free split equivalent to that reported in Table 1, but with added Ca3; and carbonated equivalents of both the P-free and P-bearing splits. Calcium was added to the P-free splits such that all splits had equal bulk CaO contents. In the case of C-bearing splits, the carbonate component was added following the decarbonation step. In this way, the bulk proportions of P and C in each run were varied by varying the proportions of the different splits added to each capsule. F and Cl were added directly to each capsule as CaF2, KF, or Na-fluorides and chlorides. Because the quantity of F and Cl added was small (typically <1 wt%), these additions did not significantly affect the proportions of the other components. Hydrogen, where present, was added as liquid water as described below.

Starting material “BM” was prepared as above, but with an additional glassing step following decarbonation: splits were heated to 1400 °C for 30 min in a gas mixing furnace, then ground dry to homogenize. The gas mixture was held near N2-O2 buffer conditions at the furnace temperature. This heating and grading process was repeated 1–3 times for each split. Fluorides and chlorides were added to prior to glassing, with carbonate added afterward as above, and splits were mixed to yield the desired bulk volatile proportions (excepting water) before being added to each capsule. These additional steps were employed to ensure the thorough homogenization of starting materials as needed to aid apatite growth and equilibration in a companion study at lower experimental temperatures and pressures. As we observe no systematic textural differences between the apatites produced by the BA and BM starting materials, we assume that the starting powders were sufficiently homogenized during equilibration at high temperatures to negate any potential differences owing to the different preparations of the two starting materials.

**Piston-cylinder experiments**

Starting powders were loaded into 3 mm diameter Pt capsules. In water-bearing experiments, distilled, deionized water was first added to the base of each capsule using a micro-syringe. Capsules were welded shut, then pressed into cylinders approximately 4 mm in length, and placed into 4 mm diameter outer Pt capsules containing identical proportions of starting powders ± H2O. The outer capsule was then welded shut and pressed into a cylindrical shape approximately 7–8 mm in length. Heating of inner and outer capsules helped to ensure an even distribution of surrounding materials in the nested assembly. The double-capsule technique employed is essential when using Pt capsules, to reduce gradients in the chemical potentials of H and C adjacent to the sample, and thus limit the rate of H2 and C exchange between the sample and the apparatus (Hall et al. 2004; Brooker et al. 1998). In lieu of a solid buffer, this method also helps to maintain a fixed fH2O (or fH2) in the inner capsule and helps to minimize volatile loss or gain during runs. After each welding step (inner and outer capsule), capsules were weighed to check for water loss, then heated and reweighed to ensure the integrity of the weld seal.

All experiments were run in end-loaded piston-cylinder apparatus (Boyd and England 1960) at the University of Bristol. A conventional ½ inch diameter vessel and piston was used for runs at 1 GPa. A ¼ inch diameter vessel was used for two runs at lower pressure (0.5 GPa). The complete sample assembly consisted of the 4 mm diameter outer Pt capsule surrounded by crushable MgO (⅛ inch diameter setup, for the geometry of this setup, see McDade et al. 2002, their Fig. 1d) or Al2O3 (⅜ inch diameter setup, for the geometry of this setup, see McDade et al. 2002, their Fig. 1e) spacers positioned to center the capsule in the hot spot of the graphite furnace. The furnace + capsule assembly was fitted within a Pyrex sheath and an outer NaCl (⅛ inch) or talc (⅛ inch) sleeve. Loaded assemblies were then heated and pressurized according to a “hot piston in” routine. After applying an initial pressure load, the assembly was allowed to settle for at least 20 min. Temperature and pressure were then increased simultaneously, with the final pressure applied upon reaching the run temperature. This routine is in keeping with that used to determine the talc- and salt-pyxrs friction correction for set pressures (~3%, McDade et al. 2002). Pressure was maintained by means of an automated pressure regulator to within ±1 psi of the target run pressure, yielding pressure variations of <1% relative. Run temperature was monitored using W-Re-W-Re2 (D-type) thermocouples, inserted along the assembly axis adjacent to the top of the charge. Temperature was maintained by automated adjustment of the operating power via a Eurotherm, with typical deviations from target of <1 °C. No attempt was made to correct temperatures for a pressure-dependence of e.m.f., although this effect is generally considered negligible for the type of thermocouple used here (Brooker and Kjaersgaard 2011).

To encourage growth of experimental apatites, runs were first heated to super-liquidus temperatures (1450–1500 °C), and then cooled at a constant rate to a terminal temperature of 1250 °C, following Prowatke and Klemme (2006). Super-liquidus heating reduces the availability of nuclei and/or secondary nucleation sites for crystalizing phases, fostering the growth of fewer, larger crystals. A slow cooling ramp results in lower degrees of undercooling and thus further favors crystal growth over nucleation (e.g., Swanson 1977). Typical cooling rates were 20 or 50 °C/h, depending on the bulk water content. Even lower cooling rates (<1 °C/h) were applied to some runs with lower bulk phosphate contents or nominally zero bulk OH contents (Table 2). Samples were then allowed to equilibrate at the final run temperature, during which time a small temperature cycle was applied (±10 °C at 1 °C/min) to enhance crystal growth (e.g., Mills and Glazner 2013). Total run times ranged from 20–24 h and were chosen to provide sufficient time for crystal-melt equilibration, as evidenced by experiments at similar conditions (Prowatke and Klemme 2006), while minimizing the time available for diffusive exchange at high temperatures. At the end of each run, charges were quenched isobarically by cutting the operating power while manually maintaining the terminal run pressure.

**Table 1. Target compositions for starting materials**

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>SiO2</td>
<td>53.50</td>
<td>62.20</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Al2O3</td>
<td>17.70</td>
<td>18.71</td>
</tr>
<tr>
<td>FeO</td>
<td>3.19</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>11.80</td>
<td>0.23</td>
</tr>
<tr>
<td>MnO</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>12.40</td>
<td>1.65</td>
</tr>
<tr>
<td>Na2O</td>
<td>2.80</td>
<td>6.16</td>
</tr>
<tr>
<td>K2O</td>
<td>1.80</td>
<td>7.14</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Following quench, capsules were removed from the assembly and sectioned using a micro-saw. To preserve the double capsule assembly, it was not possible to pierce inner capsules to test for the presence of a free fluid phase, and instead we take the absence of vesicles or gas pockets in most experiments as evidence of volatile undersaturation (two “BM” samples containing minor vesicles are indicated in Table 2). Sectioned capsules were ground using abrasive SiC papers (220 to 1200 grit) and progressively polished using diamond suspensions (6, 3, and 1 μm). Polished capsules were then mounted either in In metal or a thin layer of Epotek resin, with the aim of minimizing H backgrounds during subsequent ion microprobe analysis.

**ANALYTICAL METHODS**

**Electron probe microanalysis**

Apatite and glass major element compositions were determined by electron probe microanalysis using a Cameca SX100 5-spectrometer instrument at the University of Bristol. Glasses were analyzed using a 15 kV, 2 nA electron beam defocused to a 15 μm spot, with Na analyzed first to minimize alkali migration (Morgan and London 1996; Humphreys et al. 2006). Apatites were analyzed using a 15 kV, 10 nA beam defocused to 10 μm to minimize migration of halogens yet still enable accurate determination of minor elements (e.g., Goldoff et al. 2012; Stock et al. 2015; see Supplemental methods for details of analytical protocol). Calibration standards were albite for Na and Si; St. Johns olivine for Mg; sanidine for Al and K; Durango apatite for P; wollastonite or Durango apatite for Ca; ilmenite for Ti and Fe; Mn metal for Mn; MgF₂ for F; and NaCl for Cl. Count times were 30 s on peak for all elements except Fe and Mn (60 s on peak) and Cl and F (120 s on peak). Resulting detection limits for volatile elements in apatite were typically ~120 ppm for Cl and ~500 ppm for F; whereas in glass the detection limits were typically ~300 ppm for Cl and ~900 ppm for F (for full analytical conditions see Supplemental materials). Raw data were processed using a PAP matrix correction scheme. Accuracy and precision of the analytical setup were monitored by repeated analysis of well-characterized secondary standards (KN18, BCR2, and synthetic F-bearing haplobasalt for glasses; oriented Durango and Wilberforce apatite crystals for apatite).

**Secondary ion mass spectrometry**

Volatile compositions of apatite and coexisting glass were determined by secondary ion mass spectrometry using a Cameca ims-4f instrument at the NERC ion microprobe facility at the University of Edinburgh. The instrument is run utilizing Charles Evans and Associates PXT interface and software.

For apatite, a 5 nA ³⁰O primary beam with a net impact energy of 14.5 keV was accelerated onto the sample. An energy window of 75 ± 20 V was applied. The spot size was ~15–20 μm. A circular field aperture with an effective radius of 8 μm was used to lower H and C backgrounds coming from the edge of the sputtering pit. Backgrounds were monitored using either end-member (H-free) apatites from Schetttler et al. (2011) or a piece of quartz embedded within each sample mount.

In addition, a 4 min pre-sputter period at a raster size of 20 μm was employed to minimize contamination from the sample surface. The secondary ions ³¹H, ³¹C, ³²Mg, ³¹P, ³¹Na, ³¹Mg, ³²Si, ³¹P, ³¹Cl, ³¹K, and ³¹Ca were collected for 5, 10, 6, 10, 2, 5, 2, 10, 3, and 2 s, respectively, for each 6 cycles of the magnet. Only H₂O, CO₂, F, P₂O₅, and Cl were quantified. Other elements were used to monitor for contamination with the silicate glass. The OH and CO₂ contents of apatite were determined using daily working curves of ³¹H/³¹Ca vs. OH and ³¹C/³¹Ca vs. C acquired for a suite of natural apatite standards (Supplemental materials), after correction for isobaric interference by ³²Mg/³¹C (correction generally <5%, except in the...
most C-poor samples up to 15%). The same approach was taken for both F and Cl, with 95% prediction intervals calculated for every calibration line (Supplemental Table 1). For a small subset of apatite crystals (<15 μm in smallest dimension), the beam current was reduced to 2 nA resulting in a spot size of <10 μm. This process reduced the number of ions counted, but had no appreciable effect on the calibration curve slopes. Halogens were also quantified for halogen-free experiments as a check for contamination. No effect of apatite orientation (parallel vs. perpendicular to the c-axis) on working curves for H$_2$O, CO$_2$, F, and Cl was detected, consistent with the findings of Stock et al. (2015).

For the glass, a similar analytical setup and procedures were used as for apatite, apart from using a 50 ± 20 V energy window for C analysis (a 75 ± 20 V energy window was used for analysis of H and other elements). To ensure accurate determination of C contents in the Mg-rich glass, an initial set of analyses was collected at sufficient mass resolution to separate the C$^{12}$ and C$^{13}$ peaks, with secondary ions collected at 2Mg$^{2+}$, 3Si$^{4+}$, 3Mg$^{2+}$, 3Si$^{4+}$ and 3Si for 5, 10, 3, and 2 s, respectively, for each of 10 cycles of the magnet. In a second set of analyses on the same spot (with a 2 min pre-sputter period and 20 μm raster), the secondary ions H, B, F, Mg$^{2+}$, Si$^{4+}$, and Cl$^{−}$ were collected for 3, 3, 6, 2, 2, and 6 s, respectively (over 10 magnet cycles). As with apatite, H$_2$O and CO$_2$ contents of the glasses were determined using daily working curves of H$_2$O$^{−}$/H$_2$O$^{+}$ vs. H$_2$O$^{+}$ and CO$_2$O$^{−}$/CO$_2$O$^{+}$ vs. CO$_2$O$^{+}$, respectively, generated from standard glasses including basalts and phonolites. The calibration glasses included samples from Shishkina et al. (2010), Hauri et al. (2002), Mangan and Sisson (2000), and Brooker et al. (1999) (see Supplemental materials for details). A field aperture was used to reduce backgrounds for H and C, which were monitored using either a volatile-free glass from Shishkina et al. (2010) or a piece of quartz embedded within each sample mount. Halogens were calculated using Lipari glass (Hunt and Hill 1993) as the primary calibration standard for Cl, and NIST SRM610 glass as the primary calibration standard for F. Halogens were also quantified for halogen-free experiments as a check for possible contamination. Values were checked against internal secondary glass standards and synthetic halogen-rich glasses synthesized using the starting material SH3. SIMS glass halogen concentrations were also checked and compared against EPMA.

Secondary electron microscopy (SEM)

Backscattered SEM images of polished, mounted samples were collected using a Hitachi S-3500N scanning electron microscope at the University of Bristol, with a 15–20 kV accelerating voltage and 15 mm working distance. All samples were imaged prior to SIMS analysis to identify the phases present, produce image maps for sample navigation, and locate areas of apatite and glass suitable for ion microprobe work (sufficiently large and free from cracks and inclusions). To avoid contaminating the sample surface with C in advance of SIMS analysis, samples were not C coated prior to imaging in low vacuum mode. Run products were imaged again following ion microprobe work to confirm the location of sputter craters.

Apatite stoichiometry

We followed the calculation scheme of Ketcham (2015) for stoichiometric calculations, with formula proportions calculated on a 25-oxygen basis. We placed Mg, Mn, Fe, and Na on the Ca site, and Si onto the phosphate site. Any deficiency in P on the phosphate site was filled with carbonate where possible; any remaining carbonate was placed onto the channel volatile site together with F, Cl, and hydroxyl (Supplemental Table 1). Stoichiometric totals are generally good, with the Ca-site contents 9.967 ± 0.070, P-site contents 6.037 ± 0.030, and average X-site totals for the halogen-bearing experiments of 1.913 ± 0.087 (Supplemental Table 1), although halogen-free experiments have lower totals (see below). There is also a correlation between the measured OH and OH calculated by difference (see later discussion).

RESULTS

Experimental run products

Experimental run products for both starting materials typically comprise microcline-free glass + apatite, with a minority of samples also containing clinopyroxene ± fluid (see Table 2; Fig. 1). The experiments were designed to be volatile-undersaturated, because of the difficulty of constraining the composition of any fluid(s). The two experiments run at 0.5 GPa contain sparse vesicles, which may indicate that these samples had just reached volatile saturation. Apatites are large and euhedral (typically up to 100 μm perpendicular to c-axis and up to 1 mm parallel to the c-axis) and commonly contain melt inclusions that are visible in sections cut perpendicular to the c-axis (Fig. 1). Experiments run at lower pressures or higher cooling rates formed apatites with more skeletal or hopper textures.

Glasses. Experimental glasses from the “BA” experiments are Al-rich hlaplobasals with ~5 wt% total alkalis, 9–10 wt% MgO, 14–16 wt% Al$_2$O$_3$, and 18–30 wt% CaO on an anhydrous basis (Supplemental Table 2). SiO$_2$ contents are 44.4–49.6% SiO$_2$, normalized to 100% on an H- and C-free basis. The glasses have high volatile concentrations, as expected given the experimental run pressure of 1 GPa and nominal bulk volatile compositions (Table 2). Some CO$_2$ was found even in the nominally C-free runs, which we attribute to infiltration of C through the Pt capsule walls during the course of the experiment (Brooker et al. 1998) or possibly incomplete decarbonation of the starting material and/or atmospheric contamination. H$_2$O contents are in the range 0.7–7.1 wt%, and CO$_2$ concentrations range from 300 ppm to 1.3 wt% (Supplemental Table 2). Halogen concentrations in the glass are 0.8–1.6 wt% F and ~0.8 wt% Cl (Supplemental Table 2).

The “BM” experiments formed phonolitic glasses with 57.2–61.8 wt% SiO$_2$ and 12.6–16.3 wt% total alkalis (Supplemental Table 1). For the halogen-bearing “BM” experiments, halogens were added in the form of NaCl and NaF, so the melts for these experiments have correspondingly higher Na$_2$O contents (Supplemental Table 2). H$_2$O concentrations are in the range 1.3–7.1 wt% and CO$_2$ concentrations are 1600–7100 ppm, consistent with volatile concentrations in the BA experimental glasses. Fluorine contents are also similar to those in the BA glasses (0.85–1.0 wt% F) but Cl concentrations are higher (1.25 wt% Cl) for the same nominal bulk Cl added. Glasses are homogeneous throughout each sample, with typical relative standard deviations of approximately 1.2% for CO$_2$, H$_2$O, F, and Cl. This is smaller than the analytical uncertainty, and we therefore used the analytical uncertainty to estimate and propagate errors in the partitioning data.

Apatites. Experimental apatites from the halogen-free BA experiments are hydroxy-apatites with 0.7–1.7 wt% H$_2$O and a wide range of C contents up to 1.80 wt% (C expressed as CO$_2$) (Supplemental Table 1). Apatites from the halogen-bearing experiments are hydroxyl-bearing fluor-apatite, with ≥2 wt% F and com-

![Figure 1.](attachment:figure1.png)
positions systematically shifted to lower OH and C contents (≤0.8 wt% H$_2$O and ≤0.22 wt% CO$_2$, Supplemental Table 1). Apatites from these halogen-bearing experiments have volatile contents of F > Cl >> OH > C, even when these components were added in the same concentrations to the starting mixture (e.g., BA12, which had 1 wt% each of F, Cl, and OH in the starting material, Tables 2 and Supplemental Table 1). In the halogen-free experiments, the apatite H$_2$O and CO$_2$ contents increase with increasing dissolved H$_2$O and CO$_2$ in the coexisting glass, respectively, and the CO$_2$ content increases with increasing CO$_2$/H$_2$O+CO$_2$ in the glass (Fig. 2). The same pattern is observed in the halogen-bearing experiments, but with lower overall OH and C contents as described above. Similarly, experimental apatites from the BM experiments show high H$_2$O and CO$_2$ contents in the halogen-free runs, (0.7–1.2 wt% H$_2$O and up to 1.2 wt% CO$_2$) and significantly lower concentrations in the halogen-bearing experiments, which routinely produced fluor-apatite with >2.5 wt% F (Supplemental Table 1). Carbon contents increase with increasing concentration of the minor elements (Mg, Na, and Si; Fig. 3).

The stoichiometry calculations suggest that, for the halogen-free experiments, there is no space on the phosphate site for carbonate, such that all the carbonate and hydroxyl are accommodated on the channel site (Supplemental Table 1). In contrast, for some of the halogen-bearing experiments, there is sufficient space on the phosphate site to assign some of the carbonate, with the channel site occupied by the remaining carbonate, halogens, and hydroxyl.

Minor element concentrations in the apatites are clearly related to the host melt composition. Apatites from the BM experiments typically contain higher alkalis and lower Mg compared with those from the BA experiments (Supplemental Table 1).

**Partitioning data**

We used the experimental apatite and glass compositions to calculate the apparent Nernst partition coefficients, \( D_i = \left( \frac{C^+}{C^-} \right) \) where \( C \) is the concentration of element \( i \) in wt%. This representation allows the distribution of volatile species between apatite and melt to be directly compared with other literature data (in the case of H, F, and Cl), and to give the first experimentally determined partitioning data for C between apatite and silicate melts. Note that to maintain consistency with previous studies (e.g., McCubbin et al. 2015), we have calculated the partition coefficients between volatile abundances in apatite and melt as the same species, i.e., OH in apatite is calculated as the equivalent H$_2$O content, whereas CO$_2$ in apatite is calculated as the equivalent CO$_2$ content, on a concentration (wt%) basis. Our calculated \( D \) values show, as expected, that F is highly compatible in apatite, with \( D_F \) between 1.3 and 3.6 (average = 2.2). Chlorine is moderately compatible \( (D_{Cl} = 0.6 \text{ to } 2.3) \), and OH is generally incompatible \( (D_{OH} = 0.06 \text{ to } 0.97; \text{ average } = 0.27) \) (Supplemental Table 3), although its compatibility varies with a bulk mixed volatile content. \( D_{CO2} \) is variable, with values ranging from 0.05 to 2.1. Notably, CO$_3$$^{2-}$ was actually compatible in apatite in several of the halogen-free experiments. Both \( D_{CO2} \) and \( D_{OH} \) are significantly higher in the halogen-free runs.

Although Nernst partition coefficients \( (D) \) have been widely reported in studies of volatile partitioning in apatite, the more appropriate measure of partitioning for major chemical components competing for the same crystallographic site—such as F, Cl, and OH in apatite—is the exchange coefficient, \( K_o \) (e.g., Roeder and Emslie 1970), defined as the ratio of partition coefficients of two species, e.g.:

\[
K_{Ap-CI}^{CO2-Cl} = \left( \frac{OH_{ap}/OH_{CI}}{CI_{ap}/CI_{Cl}} \right) = \left( \frac{OH_{ap}/Cl_{ap}}{OH_{CI}/Cl_{Cl}} \right) 
\]  

(Fig. 3. Apatite carbonate concentrations increase systematically with Mg, Si, and Na contents in apatite. Minor element concentrations, overall, reflect the composition of the host melt. (a) “BA” haplobasaltic andesite experiments. (b) “BM” Breccia Museo (trachyte) experiments.)
According to the strict definition of these distribution coefficients, the volatile components should be calculated using activity (or mole fraction if assuming ideal behavior). However, it is not obvious that this approach brings greater clarity to the results of these experiments. In particular, the high pressures and range of melt compositions used means that there is some considerable uncertainty concerning the validity of models describing the distribution of dissolved water and C species in the melt (e.g., Brooker et al. 1999; Sowerby and Keppler 1999; Morizet et al. 2002; Hui et al. 2008), even if the apatite behavior is ideal at high pressure and temperature (see Li and Hermann 2017 for a discussion). For completeness, we give apatite-melt $K_{\text{D}}^{\text{Cl-F}}$, $K_{\text{D}}^{\text{OH-Cl}}$, and $K_{\text{D}}^{\text{OH-F}}$ in mole fraction form (Supplemental Table 1) using the same water speciation model as Li and Hermann (2017) for consistency with their approach, though this may not be the most appropriate for the range of melt compositions included. These $K_{\text{D}}$ values are calculated by normalizing the volatile site contents such that $X_{\text{OH}^{-}} + X_{\text{F}^{-}} + X_{\text{Cl}^{-}} = 1$, excluding carbonate (Supplemental materials). For OH-carbonate exchange, however, we present only $K_{\text{D}}$ values calculated on a concentration basis to avoid introducing errors as a result of the poorly understood variation in C speciation in silicate melts (e.g., Morizet et al. 2002).

From our experiments, the resulting distribution coefficients (calculated following McCubbin et al. 2015 as the ratio of partition coefficients) are $K_{\text{D}}^{\text{OH-Cl}} = 0.023 \pm 0.009$, $K_{\text{D}}^{\text{OH-Cl}} = 0.07 \pm 0.11$, and $K_{\text{D}}^{\text{OH-F}} = 0.27 \pm 0.98$ (Supplemental Table 1). Apatite-melt distribution coefficients for $\text{H}_{2}\text{O}$-$\text{CO}_2$ exchange are defined more rigorously in Figure 4 through $\log K_{\text{D}}^{\text{CO}_2-\text{Cl}} = \log D_{\text{CO}_2} - \log D_{\text{H}_2\text{O}}$, where $\log K_{\text{D}}$ is the intercept. This gives $K_{\text{D}}^{\text{CO}_2-\text{Cl}} = 0.355 \pm 0.05$ for the “BM” experiments and $0.629 \pm 0.08$ for the “BA” experiments (uncertainties represent a 95% prediction interval). This suggests a dependence on the melt major element composition, with systematically higher $K_{\text{D}}$ values (as calculated for individual experiments) in the BM system (Fig. 4). The gradient in Figure 4 is approximately 0.65 for both the BM and BA experiments, whereas for an ideal system it should be equal to 1.0. This suggests that C-H partitioning may be non-ideal for high-temperature igneous apatites, which would be consistent with the development of significant vacancy concentrations in the more carbonate-rich apatites (see below).

**DISCUSSION**

**CO$_2^+$ in apatite**

Our primary focus was to define the carbonate partitioning behavior between hydroxyl-bearing apatite and hydrous silicate melt. The apatites themselves contain quite high carbonate concentrations, typically several hundred to a few thousand parts per million, even in the halogen-bearing experiments. This is in contrast with natural silicate melts, which commonly record magmatic volatile concentrations only after significant degassing of CO$_2$, either into a fluid phase or during post-entrapment modification and formation of a shrinkage bubble, resulting in lower CO$_2$ contents of typically a few hundred parts per million (Wallace 2005; Blundy et al. 2010; Hudgins et al. 2015; Tuohy et al. 2016; Macleman 2017). The $K_{\text{D}}$ values for OH-carbonate exchange ($K_{\text{D}}^{\text{H}_2\text{O-\text{CO}_2}}$) appear to be dependent on the melt major element composition, with higher values in the BM experiments than in the BA experiments (see Fig. 4; Supplemental Table 3).

In contrast, the apparent carbonate-halogen exchange coefficients are very low, with $K_{\text{D}}^{\text{CO}_2-\text{Cl}} < 0.17$ and $K_{\text{D}}^{\text{CO}_2-\text{F}} < 0.11$ (Supplemental Table 3). To the best of our knowledge, these are the first experimental constraints on carbonate partitioning in igneous apatite, so we are unable to compare our data with those of other studies. The advantage of SIMS analysis is that the total C concentration is technically easy to measure in situ on unoriented grains, although it cannot provide structural information related to site occupancy, which requires techniques such as FTIR, XRD, or NMR (e.g., Fleet 2017).

**Incorporation of CO$_2^+$ in experimental igneous apatites**

Previous work has identified that carbonate can be accommodated in apatite via two key substitution mechanisms. In “Type A” apatite, carbonate is incorporated by exchange of a hydroxyl ion...
for a carbonate anion within the c-axis channel site, plus an OH vacancy for charge compensation (e.g., LeGeros et al. 1969; Bonel 1972; Young et al. 1981):

$$\text{CO}_3^{2-} + \square = 2(\text{OH}^-, \text{F}^-, \text{Cl}^-).$$  \hspace{1cm} (2)

In “Type B” carbonate, the CO$_3^{2-}$ ion is substituted for PO$_4^{3-}$, as demonstrated by substantially lower P concentrations in carbonated apatite. This substitution may be charge-balanced according to the mechanism

$$\text{PO}_4^{3-} = \text{CO}_3^{2-} + \text{F}^-$$  \hspace{1cm} (3)

(e.g., Binder and Troll 1989), although NMR work shows that the charge-balancing F$^-$ is not directly interacting with carbonate as a tetrahedral complex (Mason et al. 2009). Various other substitution mechanisms are also possible (e.g., Pan and Fleet 2002):

$$\text{Ca}^{2+} + 2\text{PO}_4^{3-} = \square^{4+} + 2\text{CO}_3^{2-}$$  \hspace{1cm} (4)

$$\text{Ca}^{2+} + \text{PO}_4^{3-} = \text{Na}^+ + \text{CO}_3^{2-}$$  \hspace{1cm} (5)

$$\text{Ca}^{2+} + \text{F}^- = \text{REE}^{3+} + \text{CO}_3^{2-}.$$  \hspace{1cm} (6)

Apatite data from our halogen-free experiments indicate that the Type A substitution mechanism is the dominant one for the carbonate anion. Both the carbonate and OH contents of apatite vary systematically with increasing CO$_2$/(H$_2$O+CO$_2$) in the host melt (see Fig. 2). This indicates that the apatite carbonate concentrations are directly linked to the volatile composition of the melt. Since OH is well known to occupy the channel site, this indicates that carbonate is also incorporated into the channel site. The stoichiometry calculations also indicate that there is insufficient space on the phosphate site to accommodate any significant Type B carbonate, and therefore the carbonate should sit on the X-site (Type A; see Supplemental Table 1). This has been confirmed using FTIR (see Supplemental Fig. 1) where the positions of the carbonate ν$_1$, vibrational peaks are consistent with dominantly A-site occupation (e.g., Fleet et al. 2004; Fleet 2017). However, while OH calculated by charge balance in the channel site is equivalent to measured OH in the most OH-rich samples, for samples with higher carbonate contents the measured OH is significantly lower than OH calculated by charge balance (Fig. 5). This suggests that the incorporation of carbonate into igneous apatite at high temperatures may involve the creation of vacancies, significantly greater than the number of OH$^-$ vacancies predicted to charge balance CO$_3^{2-}$ via Equation 2. The presence of structural H$_2$O in the channel site (e.g., Mason et al. 2009; Yoder et al. 2012) seems unlikely given the high run temperatures of the experiments.

In fact, the under-occupancy of the X-site suggests the formation of a significant “oxyapatite” component, with O$^2-$ (and a vacancy) substituting for 2OH$^-$ within the channel site (Trombe and Montel 1978; Young et al. 1981; Schettler et al. 2011). First-principles calculations support the idea that significant defects on the channel site can be formed at high temperatures (>1000 K), including the formation of oxyapatite coupled to OH$^-$ vacancies, resulting in significant non-stoichiometry at high temperatures (Matsunaga and Kuwabara 2007; Kubota et al. 2014). This deviation from stoichiometric mineral formulas is consistent with our interpretation that C-H exchange is non-ideal.

Our observations are also consistent with experiments that resulted in the formation of Type A carbonate apatite by the reaction of hydroxyapatite with dry CO$_2$ (Bonel 1972); and with first-principles calculations that indicate a greater stability of the Type A substitution at high temperatures (Kubota et al. 2014). The lack of negative correlation between CO$_3^{2-}$ and Ca or P also argues against a significant B-type substitution (De Maeyer et al. 1993). However, the highest total carbonate contents are also associated with high minor element concentrations (e.g., Mg, Na), which suggests a subsidiary Type B substitution similar to Equation 5 or 6. Peroos et al. (2006) showed that although the Type A substitution was energetically favorable, a Type B substitution, charge balanced by Na$^+$, was also favorable when Type-A carbonate was already present.

In contrast, the stoichiometry of apatites from our halogen-bearing experiments suggests the additional formation of some B-type carbonate apatite. In some of these apatites, the phosphate site has enough space to accommodate some carbonate, and the channel site incorporates the remainder plus halogens and OH (Supplemental Table 1). In contrast with apatites from the halogen-free experiments, there is good agreement between OH contents calculated by difference and measured OH for the halogen-bearing experiments (Fig. 5). This suggests that these calculated site assignments are reasonable, and consistent with calculations showing that at high temperatures the Type A carbonate substitution should be more stable than Type B (e.g., Kubota et al. 2014). However, we suggest that in the presence of abundant halogens, the formation of F-Cl-OH apatite is the most energetically favorable, and that carbonate can be shifted onto the phosphate site.

**OH-Cl-F distribution between apatite and silicate melt**

The OH-F-Cl apatite-melt exchange coefficients calculated from our experimental data are consistent with those of other studies, but with some significant differences. There are only two other experimental Cl-OH-F apatite-melt partitioning studies...
The data set also includes a mixture of volatile-saturated and volatile-undersaturated experiments (see Table 3), and at least necessary. These “by difference” calculations are subject to a significant uncertainty (e.g., Devine et al. 1995; Humphreys et al. 2006), and the direct analysis of all volatile components in both melt and apatite is strongly encouraged for future work. The data set also includes a mixture of volatile-saturated and volatile-undersaturated experiments (see Table 3), and at least with direct measurements of all channel site components. The extended abstract by Potts et al. (2015) reported experiments conducted at 1 GPa and 1350–1450 °C with a composition similar to the mesostasis of lunar basalts, while McCubbin et al. (2015) performed apatite-melt experiments at 1–1.2 GPa and 950–1000 °C using an Fe-rich basalt.

Our calculated nominal $D_{\text{H}_2\text{O}}$, $D_{\text{Cl}}$, and $D_{\text{OH}}$ are within the range reported by these and other previous studies (Fig. 6; Table 3). This includes experiments without direct measurement of OH, for which we calculated nominal $D_{\text{OH}}$ “by difference” (see Table 3; Doherty et al. 2014, rhyodacite at 50 MPa, 850–950 °C; Webster et al. 2009, rhyodacite at 200 MPa, −900 °C; Mathez and Webster 2005, basalt, 1050–1150 °C; Webster et al. 2017, “pelite” experiments; black squares = “BM” experiments).

Table 3: Summary of experimental conditions for studies included in multiple regression analysis

<table>
<thead>
<tr>
<th>Reference</th>
<th>Bulk composition</th>
<th>T°C</th>
<th>P(MPa)</th>
<th>Apatite measured</th>
<th>Melt measured</th>
<th>Fluid measured</th>
<th>Volatile state</th>
<th>Method measured</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Haplo-basaltic andesite</td>
<td>15.7–19.0</td>
<td>1250</td>
<td>OH, F, Cl, C (SIMS); H₂O (mass balance)</td>
<td>n/a</td>
<td>n/a</td>
<td>Volatile-undersaturated</td>
<td>Cl (chloridometer)</td>
<td>mostly volatile-saturated.</td>
</tr>
<tr>
<td>This study</td>
<td>Trachyte</td>
<td>2.4–3.3</td>
<td>1250</td>
<td>OH, F, Cl, C (SIMS); H₂O (mass balance)</td>
<td>n/a</td>
<td>n/a</td>
<td>Volatile-undersaturated</td>
<td>Cl (chloridometer)</td>
<td>mostly volatile-saturated.</td>
</tr>
<tr>
<td>Doherty et al. (2014)</td>
<td>Rhyodacite</td>
<td>0.4–3.1</td>
<td>800–900</td>
<td>OH, F, Cl, C (SIMS); H₂O (mass balance)</td>
<td>Cl (mass balance)</td>
<td>Cl (mass balance)</td>
<td>Mostly volatile-saturated</td>
<td>OH, F, Cl, C (SIMS); H₂O (mass balance)</td>
<td>mostly volatile-saturated.</td>
</tr>
<tr>
<td>Li and Hermann (2015)</td>
<td>Pelite</td>
<td>2.3–2.5</td>
<td>600–900</td>
<td>OH, F, Cl, C (SIMS); H₂O (FTIR); F, Cl (EPMA)</td>
<td>F, Cl (EPMA); n/a</td>
<td>Volatile-undersaturated</td>
<td>Mostly volatile-saturated</td>
<td>F, Cl (EPMA); n/a</td>
<td>mostly volatile-saturated.</td>
</tr>
<tr>
<td>Mathez and Webster (2005)</td>
<td>Basalt</td>
<td>5.3–16.9</td>
<td>1066–1150</td>
<td>OH, F, Cl, C (SIMS); F, Cl (EPMA)</td>
<td>F, Cl (EPMA); Cl (mass balance)</td>
<td>Cl (chloridometer)</td>
<td>Mostly volatile-saturated</td>
<td>F, Cl (EPMA); Cl (mass balance)</td>
<td>mostly volatile-saturated.</td>
</tr>
<tr>
<td>McCubbin et al. (2014)</td>
<td>Fe-rich basalt</td>
<td>3.8–9.0</td>
<td>950–1000</td>
<td>OH, F, Cl (SIMS); H₂O, F, Cl (SIMS)</td>
<td>n/a</td>
<td>n/a</td>
<td>Mostly volatile-saturated</td>
<td>OH, F, Cl (SIMS); H₂O, F, Cl (SIMS)</td>
<td>mostly volatile-saturated.</td>
</tr>
<tr>
<td>Potts et al. (2015)</td>
<td>Lunar basalt mesostasis</td>
<td>8.0–9.0</td>
<td>1350–1450</td>
<td>OH, F, Cl (SIMS); H₂O, F, Cl (SIMS)</td>
<td>n/a</td>
<td>n/a</td>
<td>Volatile-undersaturated</td>
<td>OH, F, Cl (SIMS); H₂O, F, Cl (SIMS)</td>
<td>mostly volatile-saturated.</td>
</tr>
<tr>
<td>Webster et al. (2009)</td>
<td>Rhyodacite to rhyolite</td>
<td>0.5–2.4</td>
<td>900–923</td>
<td>OH, F, Cl (SIMS); H₂O, F, Cl (SIMS)</td>
<td>n/a</td>
<td>n/a</td>
<td>Volatile-undersaturated</td>
<td>OH, F, Cl (SIMS); H₂O, F, Cl (SIMS)</td>
<td>mostly volatile-saturated.</td>
</tr>
<tr>
<td>Webster et al. (2017)</td>
<td>High-Si rhyolite</td>
<td>0.1–2.1</td>
<td>722–1000</td>
<td>OH, F, Cl (SIMS); H₂O (FTIR); F, Cl (EPMA)</td>
<td>F, Cl (EPMA); n/a</td>
<td>Volatile-undersaturated</td>
<td>Mostly volatile-saturated</td>
<td>OH, F, Cl (SIMS); H₂O (FTIR); F, Cl (EPMA)</td>
<td>mostly volatile-saturated.</td>
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</table>

These runs typically contained <25 ppm CO₂ as contaminant (not studied).

For the compiled literature data set, $D_{\text{H}_2\text{O}}$ and $D_{\text{Cl}}$, and, to a lesser extent, $D_{\text{Cl}}$, with increasing temperature and increasing melt CaO content in the compiled literature data set. Increasing experimental pressure causes only a minimal decrease in $D_{\text{Cl}}$.

As with Figure 4, the distribution coefficients for OH-halogen exchange are equivalent to the intercept in Figure 6. Thus, our calculated $K^{\text{H}_2\text{O}}_{\text{Cl}}$ are slightly lower than those of Potts et al. (2015)
but higher than those of McCubbin et al. (2015). Each study was conducted at the same pressure (1 GPa), so we interpret these differences in $K_D$ as predominantly a result of differences in temperature (in the range 950 to 1450 °C). This is borne out by the results of a multiple regression analysis of the full literature data set, including our new experiments (Fig. 8), to an equation of the form

$$\log K_D = a + b/T + c(P - 1)/T$$

following the approach of Piccoli and Candela (1994). This shows a clear log-linear increase in $K_D^{\text{OH-halogen}}$ with increasing temperature, which indicates a preference for the OH end-member at higher temperatures for a given melt composition. Despite the inclusion of both volatile-saturated and volatile-undersaturated experiments from rhyolite to basalt, the relative consistency of the published $K_D$ values, as a function of temperature, is striking, and confirms that temperature is the dominant overall control on apatite-melt volatile partitioning. The CaO content in the melt was not a significant variable, presumably due to covariation with temperature. The pressure term was of subsidiary significance and we obtained similar confidence on the parameter values when excluding the third term in Equation 2 (Table 4). For OH-Cl exchange, the results gave $a = 1.0729 \pm 0.2353$ and $b = -2938.4 \pm 282.3$, whereas for OH-F exchange, $a = 1.2590 \pm 0.2942$ and $b = -3853.6 \pm 367.8$ (Fig. 8, Table 4).

We compared these results with earlier thermodynamic expressions derived by Piccoli and Candela (1994) for the system apatite-fluid. Their $K_D^{\text{apo-fl}}$ were calculated using the thermodynamic data of Zhu and Sverjensky (1991) to give the fugacity ratio for the coexisting aqueous fluid, with aqueous species data derived from Robie et al. (1978) and Stull and Prophet (1971). High-temperature values for $K_D^{\text{apo-cl}}$ are up to an order of magnitude lower for the apatite-fluid than for the apatite-melt $K_D$ exchange data, but there is better agreement between the two systems at low temperatures (Fig. 8). There is also agreement on the direction of change of $K_D$ with temperature (cf. Li and Hermann 2015). In contrast, the values for $K_D^{\text{apo-fl}}$ are 2–3 orders of magnitude lower for apatite-fluid exchange.

**Figure 7.** Experimentally derived distribution coefficients for OH-halogen exchange between apatite and silicate melt (calculated on a wt% basis), in comparison with $K_D$ values from the literature. Symbols are the same as for Figure 6.

**Figure 8.** Regression analyses of experimentally determined halogen-OH distribution coefficients for apatite-melt (wt% basis), with dependence on both $P$ and $T$ [$\log K_D = a + b/T + c(P - 1)/T$] or temperature only [$\log K_D = a + b/T$]. Regression coefficients for $T$-only analysis are given. Data symbols are the same as for Figure 6. Dark gray lines = predicted variations at 1 GPa (solid) and 50 MPa (dashed). Light gray lines = predicted variations for the system apatite-fluid from Piccoli and Candela (1994) at 1 GPa (dashed) and 50 MPa (dotted). Black dotted line shows the $T$-only regression. Gray fields show the experimental range of Li and Hermann (2017; 2.5 GPa). Dashed light gray outlines show the experimental range of Li and Hermann (2015; 2.5–4.5 GPa).

**Table 4.** Summary of multiple regression results for literature data set of OH-halogen $K_D$ values ($T$ in K, $P$ in bar)

<table>
<thead>
<tr>
<th></th>
<th>OH-Cl</th>
<th>OH-F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>1.33</td>
<td>1.259</td>
</tr>
<tr>
<td>$b$</td>
<td>-3864</td>
<td>-3853.6</td>
</tr>
<tr>
<td>$c$</td>
<td>0.3907</td>
<td>0.2942</td>
</tr>
</tbody>
</table>

Equation 1: $\log K_D = a + b/T + c(P - 1)/T$

Equation 2: $\log K_D = a + b/T$
(Piccoli and Candela 1994) than for apatite-melt (literature data compilation, Fig. 8). The cause of this mismatch for $K_{\text{F}}^{\text{apatite}}$ is unclear, particularly given that there is relatively good agreement for $K_{\text{Cl}}^{\text{apatite}}$ at low temperatures (where one or more fluid phases are most likely to be present). Calculating $K_{\text{F}}$ values using OH and halogen mole fractions instead of $H_2O$ results in higher values in Figure 8. The experiments do not contain any other phases that could incorporate significant F. Our calculations (together with those of the other studies in the literature) were done using melt F concentrations instead of activities, and fluoride activity varies with both melt composition (e.g., Scaillet and Macdonald 2004) and temperature (e.g., Webster 1990). Piccoli and Candela (1994) attempted to apply their method to the Bishop Tuff and found similar problems, with good agreement between predicted (from apatite) and measured (from melt inclusions) Cl concentrations, but a much wider discrepancy for F, which they interpreted as a problem with the assumption that F is present only as HF in the fluid. We therefore suggest that improved fluoride activity and speciation models for silicate melts and fluids may help to resolve this problem.

**Implications**

Recent experimental studies of apatite–melt partitioning have greatly enhanced the potential of apatite as a tool for interpreting magmatic volatile contents, in both terrestrial and planetary settings (Piccoli and Candela 1994; Boyce and Hervig 2008; McCubbin et al. 2015). The results presented here extend this work to the important magmatic volatile C, which records key information regarding deep magma storage and early degassing processes. Our new partitioning experiments on hylabasaltic anesite and trachyte melts provide the first constraints on partitioning mechanisms and exchange coefficients for C in high-temperature igneous apatite. Stoichiometry calculations and preliminary FTIR-ATR analysis indicates that carbonate is accommodated primarily in the e-axis channel in our experiments. OH calculated by difference agrees relatively well with measured OH for the halogen-bearing experiments but is systematically low for the halogen-free experiments. This suggests the presence of a significant oxypatite component at high temperatures, and emphasizes that calculations of OH by difference should be treated with care. Analysis of C in apatite represents a potential new route to better understanding the original $CO_2$ contents of melts, particularly in arc systems, where melt inclusion $CO_2$ concentrations likely represent a significant underestimate of $CO_2$ in the un-degassed melt. The ease of SIMS analysis, as demonstrated here, should facilitate this goal, particularly for small natural crystals and inclusions within phenocrysts. We encourage future work comparing $CO_2$ in arc melt inclusions with $CO_2$ inferred from coexisting apatite inclusions, and suggest that this may help to improve our understanding of volatile fluxes at subduction zones.

Regression of our new partitioning data, alongside previously published experimental data in the system apatite–silicate melt, shows that while measurements of Cl–OH exchange are in good agreement with existing estimates for the system apatite–fluid (Piccoli and Candela 1994), there is a large discrepancy for F–OH exchange, which may be due to relatively poor understanding of the fluoride activity and speciation in silicate melts and fluids. This highlights the need for further experimental work focused on clarifying the mobility and compatibility of halogens between solids, melt, and fluids close to the magmatic-hydrothermal transition. Nonetheless, the current study marks a significant advance in the understanding of volatile partitioning in high-temperature igneous apatites and opens up the potential for quantitative analysis and modeling of magmatic volatile systematics in both terrestrial and extraterrestrial environments. Apatite can accommodate the full range of volatile elements and, in our view, future work should focus on the quantitative modeling of variations in apatite composition during common igneous processes such as cooling, ascent, and degassing of fluid(s), with the aim of fully developing apatite as a tool for investigating magmatic storage and degassing processes.

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**References Cited**


