1 Revision 2

Experimental investigation of F, Cl, and OH partitioning between apatite and Fe-rich basaltic melt at 1.0-1.2 GPa and 950-1000 °C

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Abstract

Apatite-melt partitioning experiments were conducted in a piston cylinder press at 1.0-1.2 GPa and 950-1000 °C using an Fe-rich basaltic starting composition and an oxygen fugacity within the range of ΔIW-1 to ΔIW+2. Each experiment had a unique F:Cl:OH ratio to assess the partitioning as a function of the volatile content of apatite and melt. The quenched melt and apatite were analyzed by electron probe microanalysis and secondary ion mass spectrometry techniques. The mineral-melt partition coefficients (D values) determined in this study are as follows: $D_F^{Ap-Melt} = 4.4 - 19$, $D_{Cl}^{Ap-Melt} = 1.1 - 5$, $D_{OH}^{Ap-Melt} = 0.07 - 0.24$. This large range in values indicates that a linear relationship does not exist between the concentrations of F, Cl, or OH in apatite and F, Cl, or OH in melt, respectively. This non-Nernstian behavior is a direct consequence of F, Cl, and OH being essential structural constituents in apatite and minor to trace components in the melt. Therefore mineral-melt D values for F, Cl, and OH in apatite should not be used to directly determine the volatile abundances of coexisting silicate melts. However, the

32   apatite-melt D values for F, Cl, and OH are necessarily interdependent given that F, Cl, and OH

33   all mix on the same crystallographic site in apatite. Consequently, we examined the ratio of D

34   values (exchange coefficients) for each volatile pair (OH-F, Cl-F, and OH-Cl) and observed that

35   they display much less variability: $K_{d_{Cl-F}}^{Ap-Melt} = 0.21 \pm 0.03$, $K_{d_{OH-F}}^{Ap-Melt} = 0.014 \pm 0.002$,

36   and $K_{d_{OH-Cl}}^{Ap-Melt} = 0.06 \pm 0.02$. However, variations with apatite composition, specifically when

37   mole fractions of F in the apatite X-site were low ($X_F < 0.18$), were observed and warrant

38   additional study. To implement the exchange coefficient to determine the H_2O content of a

39   silicate melt at the time of apatite crystallization (apatite-based melt hygrometry), the H_2O

40   abundance of the apatite, an apatite-melt exchange K_d that includes OH (either OH-F or OH-Cl),

41   and the abundance of F or Cl in the apatite and F or Cl in the melt at the time of apatite

42   crystallization are needed (F if using the OH-F K_d and Cl if using the OH-Cl K_d). To determine

43   the H_2O content of the parental melt, the F or Cl abundance of the parental melt is needed in

44   place of the F or Cl abundance of the melt at the time of apatite crystallization. Importantly,

45   however, exchange coefficients may vary as a function of temperature, pressure, melt

46   composition, apatite composition, and/or oxygen fugacity, so the combined effects of these

47   parameters must be investigated further before exchange coefficients are applied broadly to

48   determine volatile abundances of coexisting melt from apatite volatile abundances.

49

50   **Keywords:** lunar water, water on Mars, QUE 94201, phosphates, piston cylinder

51

52   **Introduction**

53   The mineral apatite $Ca_5(PO_4)_3(F,Cl,OH)$ is the primary reservoir for phosphorus in the

54   Earth's crust and mantle, and is one of several hosts for phosphorus in extraterrestrial rocks

55   (Hughes and Rakovan, 2002; Jones et al., 2014; Pan and Fleet, 2002; Patiño Douce and Roden,

56   2006; Patiño Douce et al., 2011). Apatite forms in igneous, metamorphic, and sedimentary

57   environments, and it is also produced through biomineralization processes (Elliott, 2002; Hughes

58   and Rakovan, 2002; Knudsen and Gunter, 2002; Mason et al., 2009; Piccoli and Candela, 2002;

59   Spear and Pyle, 2002). Although apatite is ubiquitous among a wide range of rock types, it

60   typically occurs in only trace abundances, with modal abundances commonly less than 1 vol%

61   (Patiño Douce and Roden, 2006; Piccoli and Candela, 2002; Spear and Pyle, 2002).

62   The ubiquity of apatite in rocks from the Earth and beyond have motivated studies aimed at

63   using apatite as a geologic tool to record petrogenetic histories of the rocks within which they are

64   hosted. Specifically, the presence of volatiles within its crystal structure have facilitated many

65   studies to use apatite to constrain the volatile contents of magmas and magmatic source regions

66   (Barnes et al., 2013; 2014; Boyce and Hervig, 2008; 2009; Boyce et al., 2010; Filiberto and

67   Treiman, 2009; Greenwood et al., 2011; Gross et al., 2013; McCubbin and Nekvasil, 2008;

68   McCubbin et al., 2010a; 2010b; 2011; 2012; 2013; 2015; Patiño Douce and Roden, 2006; Patiño

69   Douce et al., 2011; Tartèse et al., 2013; 2014; Treiman et al., 2014). In order to use the volatile

70   contents of apatite to precisely determine the abundances of volatiles in coexisting silicate melt

71   or fluids, thermodynamic models for the apatite solid solution and for the apatite components in

72   multi-component silicate melts and fluids are required. Although some thermodynamic models

73   involving apatite have been developed (i.e., Candela, 1986; Hovis and Harlov, 2010; Hovis et al.,

74   2014; Patiño Douce and Roden, 2006; Tacker and Stormer, 1989; 1993; Zhu and Sverjensky,

75   1991), they are incomplete. Furthermore, no independent predictive mixing model is available

76   for all of the apatite components in silicate melts or fluids, especially for the F and Cl

77   components. Several experimental studies have investigated the apatite-melt and apatite-fluid

78   partitioning behavior of F and Cl in terrestrial systems (i.e., Brenan, 1993; Mathez and Webster,

79   2005; Webster et al., 2009; Zhu and Sverjensky, 1991). However, the partitioning behavior

80   between apatite and melts is not straightforward and appears to vary as a function of melt

81   composition (i.e., Mathez and Webster, 2005; Webster et al., 2009). Most of these studies, that

82   used apatite to constrain the magmatic abundances of volatiles, are focused on Fe-rich basalts

83   from extraterrestrial bodies (i.e., Moon and Mars). No previous experimental studies on apatite-

84   melt partitioning of volatiles have utilized melt compositions relevant to Fe-rich basalts.

85   Previous studies investigating apatite-melt partitioning of F and Cl have attempted to

86   describe this partitioning using a Nernst-like partition coefficient:

87    $$D_X^{Ap-Melt} = \frac{X_{Ap}}{X_{Melt}}$$ (1)

88   where $D_X^{Ap-Melt}$ is the apatite-melt partition coefficient for component X, X_{Ap} is the

89   concentration of X in apatite, and X_{Melt} is the concentration of X in the coexisting melt. The

90   application of equation (1) to apatite-melt systems assumes that, at fixed temperature and

91   pressure, the value of the partition coefficient is a constant, independent of the concentration of

92   X in the system. However, previous studies have reported large variations in values for $D_X^{Ap-Melt}$

93   as a function of changing volatile ratios in the melt (Doherty et al., 2014; Mathez and Webster,

94   2005; Webster et al., 2009). This observation indicates that a singular canonical D value cannot

95   be used to adequately describe the partitioning behavior of F, Cl, or OH between apatite and

96   silicate melts or fluids. This result is not surprising because F, Cl, and OH are essential structural

97   constituents (ESC's) in the mineral apatite. Specifically, the variable $D_X^{Ap-Melt}$ values arise

98   because the combined concentrations of F, Cl, and OH in apatite are fixed (based on apatite

99   stoichiometry) and the concentrations of F, Cl, and OH in vapor-undersaturated silicate melts are

100   unconstrained. However, $D_X^{Ap-Melt}$ values for F, Cl, and OH may exhibit predictable

101   interdependence despite the large reported range in D values. This interdependence can be

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102   identified by examining exchange coefficients (i.e., ratios of mineral-melt D values) instead of

103   Nernst-like partition coefficients (Eq. 1). One commonly implemented example of this approach

104   is the Fe-Mg exchange equilibrium between melt and olivine (Filiberto and Dasgupta, 2011;

105   Roeder and Emslie, 1970; Toplis, 2005). This exchange equilibrium is analogous to F-Cl-OH

106   partitioning between apatite and melt given that Fe and Mg are ESC's in olivine that mix on the

107   same crystallographic site, and F, Cl, and OH are ESC's in apatite that mix on the same

108   crystallographic site (X-site; Hughes and Rakovan, 2002; Pan and Fleet, 2002).

109   In the present study, the partitioning behavior of F, Cl, and OH between apatite and

110   silicate melt will be examined based on exchange equilibria between each of the three Cl-F, OH-

111   F, and OH-Cl apatite-melt equilibrium pairs, which can be described in a general form by the

112   reaction:

113    $$X_{Apatite} + Y_{Melt} \Leftrightarrow Y_{Apatite} + X_{Melt} \qquad (2)$$

114   Here, $X_{Apatite}$ and $Y_{Apatite}$ represent the two endmember apatite components involved in the

115   exchange reaction (i.e., Cl-F, OH-F, or OH-Cl), and Y_{Melt} and X_{Melt} represent those same

116   components in the silicate melt. At equilibrium, the equilibrium constant ($K^{Y-X}_{Ap-Melt}$) for this

117   reaction can be expressed as:

118    $$K^{Y-X}_{Ap-Melt} = \frac{a^X_{melt} \times a^Y_{Apatite}}{a^Y_{melt} \times a^X_{Apatite}} \qquad (3)$$

119   where $a^X_{Apatite}$ and $a^Y_{Apatite}$ represent the activities of component X and Y, respectively, in

120   apatite, and a^X_{melt} and a^Y_{melt} represent the activities of components X and Y, respectively, in the

121   melt. This equilibrium constant can then be related to the partition coefficient (Eq. 1) as an

122   exchange coefficient (K_d) (i.e., ratio of partition coefficients) for each apatite-melt pair according

123   to the equation:

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124
$$K_{d_{Y-X}}^{Ap-Melt} = \frac{X_{Melt} \times Y_{Ap}}{Y_{Melt} \times X_{Ap}} \qquad (4)$$

125   Here, $K_{d_{Y-X}}^{Ap-Melt}$ is the apatite-melt exchange coefficient for components X and Y, X_{Melt} and

126   Y_{Melt} are the concentrations of X and Y in the melt, respectively, and X_{Ap} and Y_{Ap} are the

127   concentrations of X and Y in the apatite, respectively. As written (i.e., without activity

128   coefficients), equation (4) includes an implicit assumption of ideality, which may not be valid.

129   This approach to examining apatite-melt partitioning was recently described in Boyce et al.,

130   (2014).

131   This partitioning model was evaluated using new apatite-melt partitioning experiments

132   carried out in a piston cylinder press at 1.0-1.2 GPa and 950-1000 °C on a synthetic Fe-rich

133   (Martian) basalt composition equivalent to the basaltic shergottite Queen Alexandria Range

134   (QUE) 94201. These experiments were conducted to assess the effects of apatite X-site

135   chemistry (i.e., the monovalent anion site in apatite) on the partitioning behavior of F, Cl, and

136   OH (reported as the H_2O component) between apatite and a Fe-rich basaltic melt. These

137   experiments will test the potential utility of the exchange equilibrium model for describing

138   volatile partitioning between apatite and silicate melts. Although temperature, pressure, melt

139   composition, cation composition of apatite, and oxygen fugacity may also affect apatite-melt

140   exchange coefficients, these effects will not be investigated in the present study.

Experimental and Analytical Methods

142   **Starting compositions**

143   One of the primary goals of the present study is to assess apatite-melt partitioning as a

144   function of apatite X-site occupancy. This requires the starting material having flexibility in the

145   F:Cl:OH ratio. To accomplish this goal, three powdered mixtures were synthesized using a single

146   base composition modeled after the Fe-rich basaltic shergottite QUE 94201 (from Kring et al.,

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147   2003) with approximately 5 wt% additional P_2O_5 component to induce early phosphate

148   saturation. Each of the three mixtures was either a F, Cl, or H_2O endmember with approximately

149   1 wt.% of either F, Cl, or H_2O (Table 1), although H_2O contents were typically higher in the melt

150   after the experiments (2.3-3.6 wt%) due to the use of talc cells and/or inner parts and starting

151   materials that were not pre-dried in an oven. The mixtures were generated by accurately

152   weighing silicates, oxides, $Ca_2P_2O_7$, $Ca(OH)_2$, CaF_2, and $MgCl_2$ powders in the proportions

153   needed for obtaining the desired starting compositions. Next, the powders were mechanically

154   mixed sequentially by volume in an automatic agate mortar/pestle grinder for a total of 3.5 hours

155   under ethanol. Both hematite and synthetic fayalite were used as an Fe source in our starting

156   compositions. The $Fe^{3+}/\sum Fe$ value in each mixture was set to 0.10 based on the fayalite:hematite

157   ratio used. Details on the synthesis conditions of the fayalite are provided in Vander Kaaden et

158   al., (2015). $MgCl_2$ is soluble in ethanol, so the Cl-bearing mixture was ground dry.

159   **Piston cylinder experiments**

160   All experiments were conducted in a 13 mm non end-loaded piston cylinder apparatus

161   (Quickpress from Depths of the Earth) using assemblies consisting of crushable MgO, a graphite

162   furnace, and either talc-pyrex or salt-pyrex sleeves as a pressure medium (Table 2). Each

163   experiment reported in the present study was conducted under "wet" conditions (nondried

164   starting materials and inner parts). Each experiment was contained in a graphite or Mo^0 capsule

165   within which a powdered mixture, consisting of one, two, or three of the starting mixes (each

166   experiment had a different F:Cl:OH ratio), was packed inside (Table 2). The capsules were then

167   loaded into either a talc-pyrex cell or a salt-pyrex cell. We used the same cell assembly and parts

168   reported by Elardo et al., (2011) for the talc-pyrex cell and we conducted a pressure calibration

169   for the talc-pyrex cell that is described in Appendix A (Figures A1-A2). For the salt-pyrex cells,

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170   we used the same cell assembly, parts, and calibration reported by Vander Kaaden et al., (2015).

171   The assembled cell was placed within the 1.27 cm (diameter) bore of the pressure vessel and

172   taken up to the desired pressure before heating. Next, the temperature was raised to a super-

173   liquidus melting temperature of 1200 °C and allowed to homogenize for 20 minutes. The

174   pressure was manually adjusted during heating so that the target pressure was maintained. The

175   temperature was subsequently dropped to the desired crystallization temperature (950-1000 °C)

176   at a rate of 500 °C/min and allowed to crystallize for 2.75-26.5 hours (Table 2). The first few

177   experiments conducted in this manner resulted in the crystallization of many small apatite

178   crystals (too small to be analyzed by the Cameca 6f secondary ion mass spectrometer), so we

179   carried out three experiments for which a much slower cooling rate (0.18-0.27 °C/min) was used

180   from 1050 °C to the target temperature with the intention of growing larger apatites (Table 2).

181   The slower cooling rate did not result in larger apatite crystals, so this technique was abandoned

182   for all subsequent experiments. To compensate for the small size of the apatite crystals, we

183   decided to use a NanoSIMS ion probe for the analysis of apatite crystals. The temperature of

184   each experiment was controlled by a W_5Re_{95}-$W_{26}Re_{74}$ (Type C) thermocouple. At the end of

185   each experiment, the run was rapidly quenched by shutting off power to the system. The

186   temperature typically reached <200 °C within 5-10 seconds. Temperature uncertainties for our

187   runs are approximately 12 °C, and our pressure uncertainty is approximately 0.1 GPa (Vander

188   Kaaden et al., 2015). Experimental charges were removed from the assembly and pressed into

189   indium metal contained within 1" aluminum metal discs. The charges were then polished using

190   alumina powder down to a 0.3 μm finish for subsequent analysis by secondary ion mass

191   spectrometry (SIMS) (Cameca 6f ion probe and NanoSIMS) and electron probe microanalysis

192   (EPMA).

193   Although there is no direct test for determining whether or not our experiments were at

194   equilibrium, steady state apatite-melt partitioning of F, Cl, and OH can be assessed by

195   monitoring the apatite-melt exchange-equilibria as a function of time. Given that the duration of

196   the apatite-bearing runs ranged from 2.75-18.5 hours, it provided a built-in check of steady-state

197   conditions. Figure 1 demonstrates that the exchange-equilibria are consistent, within uncertainty,

198   over the entire run duration range utilized in the present study with the exception of one outlier

199   in the values reported for $K_{d_{OH-Cl}}^{Ap-Melt}$, which is discussed later. Steady-state conditions were

200   anticipated for our experiments because we grew the apatites directly from the melt at the P and

201   T (within 50 °C of target T) of interest instead of trying to equilibrate apatite seeds via diffusion.

202   Although the volatile components in apatite have been reported to diffusively equilibrate at rapid

203   timescales with coexisting melt or fluid at high pressure (Brenan, 1993, 1994), our temperatures

204   and run durations correspond to F, Cl, and OH equilibration on the length scales of

205   approximately 8-17 μm in the [001] direction. Notably, the diffusion rates of F, Cl, and OH in

206   apatite are reported to be anisotropic, and fastest along the c-axis "channels" (i.e., [001]

207   direction) that host F, Cl, and OH (Brenan, 1994; White et al., 2005). Finally, if our experiments

208   were not at equilibrium, this would have manifested itself in a range of apatite compositions

209   across a single experiment, which we did not see. We determined the standard deviation of the

210   mean composition (for apatite and melt) from each experiment and propagated this uncertainty

211   when computing the D values and exchange K_d.

212   Although oxygen fugacity (f_{O2}) was not buffered in our experiments, the capsule

213   materials (C and Mo[0]) affected the f_{O2} in each experiment. The experiments conducted in

214   graphite capsules were at or below the graphite-CO fluid (GCO) buffer curve, which is

215   approximately 2 log units above the iron-wüstite (IW) buffer at 1.0-1.2 GPa and 1000 °C

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216   (ΔIW+2) (O'Neill and Pownceby, 1993; Ulmer and Luth, 1991). The experiments run in Mo

217   metal capsules were at or below the Mo-MoO$_2$ (MMO) buffer curve, which is approximately

218   equal to the IW buffer at 1.0-1.2 GPa and 1000 °C (ΔIW+0) (Burkemper et al., 2012; O'Neill and

219   Pownceby, 1993; O'Neill, 1986). The minimum oxygen fugacities for each experiment cannot be

220   directly determined. However, the experiments are all likely to be above ΔIW-1 given the

221   elevated abundances of FeO in the melt (13.8-18.14 wt.% FeO) and the absence of Fe metal,

222   both as a separate phase or as a measurable component in the Mo metal (as determined by energy

223   dispersive spectroscopy).

224   **Electron probe microanalysis**

225   Apatites and quenched glasses in the experimental run products were analyzed using a

226   JEOL JXA 8200 electron microprobe in the Institute of Meteoritics at the University of New

227   Mexico. An accelerating voltage of 15 kV and a nominal beam current of 25 nA were used

228   during each analysis, following the procedure of McCubbin et al. (2011). We analyzed the

229   elements Si, Ti, Al, Cr, Mg, Fe, Mn, Ca, Na, P, F, and Cl in apatite and quenched glasses.

230   Fluorine was analyzed using a light-element LDE1 detector crystal, and Cl was analyzed using a

231   PET detector crystal. The standards were as follows: Ca and P were standardized with a natural

232   fluorapatite from India (Ap020 from McCubbin et al., 2012). F was standardized with synthetic

233   SrF$_2$, and Ap020 was used as a secondary check for F. Cl was standardized with sodalite from

234   Sharp et al. (1989), and scapolite from the Smithsonian was used as a secondary standard

235   (Jarosewich et al., 1980); Mn was standardized using Taylor spessartine garnet (Taylor standard

236   block, information from Taylor multi element standard documentation, by C.M. Taylor, C.M.

237   Taylor Company). Magnesium was standardized using Taylor enstatite. Sodium and Al were

238   standardized using Taylor albite. Silicon and Fe were standardized on an almandine garnet from

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239   Austinburg, Ohio. Chromium was standardized on Taylor chromite. Titanium was standardized

240   using Taylor sphene. In order to reduce or eliminate electron beam damage, we used a 10 μm

241   defocused beam for standardization and 1 to 10 μm diameter beam for analysis of apatite grains.

242   A 10 μm defocused beam was used for analysis of quenched glass in all samples. Electron beam

243   tests using the Durango apatite show that count rates for F are consistent for spot sizes down to

244   about 2 μm (McCubbin et al., 2010a).

245   Stormer et al. (1993) documented that F and Cl X-ray count rates change with time

246   during electron microprobe analysis of apatite as a function of crystallographic orientation.

247   Goldoff et al. (2012) presented a method to minimize changes in count rate for F and Cl,

248   however the apatites analyzed in the present study were too small (1-10 μm in the shortest

249   dimension) to apply this technique. Accordingly, we monitored the apatite analyses for time-

250   dependent count rates in real time with the chart recorder function in the JEOL software.

251   However, we could not use this information to construct count rate vs. time plots, which are

252   required for correcting the F X-ray count-rate variation. Therefore, any analyses that displayed

253   highly variable F X-ray count rates from our samples were rejected from further consideration.

254   Hydroxyl cannot be measured directly by the EPMA technique. However, a missing

255   component in the X-site of apatite can be calculated on the basis of stoichiometry. If both F and

256   Cl are analyzed with sufficient accuracy, this missing component can be attributed to some

257   combination of the anions OH^-, O^{2-}, CO_3^{2-}, S^{2-}, Br^-, and I^- and/or structural vacancies (Pan and

258   Fleet, 2002) and/or structural H_2O (Mason et al., 2009). The most likely constituent for this

259   missing component in terrestrial, lunar, vestan, and martian igneous systems is OH^- (Boyce et al.,

260   2010; Greenwood et al., 2008; Gross et al., 2013; Leshin, 2000; McCubbin et al., 2010b; 2012;

261   Piccoli and Candela, 2002; Sarafian et al., 2013; 2014).

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262   **Secondary ion mass spectrometry**

263   The measurements of F, H_2O (as OH^-), Cl, and S in the basaltic glass portion of several

264   experiments was performed on a Cameca 6f ion microprobe at the Department of Terrestrial

265   Magnetism, Washington, DC using the procedure of Hauri et al. (2002). The focused (5-10 nA)

266   10kV Cs^+ primary ion beam was rastered on the indium-mounted sample to a 25 μm x 25 μm

267   area. The secondary ion beam was extracted at -5 kV from an 8 micron diameter portion of the

268   rastered area with a field aperture. An electron flood gun (-5 kV) was used to compensate for

269   charge build up in the analysis area. A mass resolution of 6000 was tuned to eliminate all of the

270   mass interferences relevant to our analytical routine. Standardization on multiple basaltic glass

271   compositions with a wide range of volatile contents was performed at the beginning of the

272   session. Information concerning the compositions of the standards used (1833-1, 1846-12, 1833-

273   11, WOK28-3, 519-4-1, 1654-3, B330, B333, B366) has been published previously (Deloule et

274   al., 1995; Hauri et al., 2002; Hauri et al., 2006). An amphibole crystal from Spitsbergen,

275   Svalbard of known composition was also used as a secondary check on H_2O and F abundances.

276   The composition of the amphibole is provided in Table S1. Each analysis lasted about 15

277   minutes. The most F-rich standard used in the present study had 446 ppm F, which was not

278   appropriate for the F-rich compositions of our glasses, so the F data from the Cameca 6f ion

279   microprobe is not reported.

280   The abundances of F, Cl, and OH in apatite and the quenched glasses were measured in

281   several experiments using the Cameca NanoSIMS 50L at the Open University. Before each

282   analysis, a large Cs^+ primary beam of ~3 nA current with an accelerating voltage of 16 kV was

283   rastered on the sample surface over a 12 μm × 12 μm area during a 1 min pre-sputter to eliminate

284   any surface contamination. Secondary species of $^{16}O^1H$, ^{18}O, ^{28}Si, $^{19}F^{16}O$, ^{37}Cl and $^{40}Ca^{16}O$ were

285   then collected simultaneously on electron multipliers for ~3 min from a rastered central area of

286   ~4 μm × 4 μm, using 25% electronic gating and primary beam currents of 200 to 500 pA,

287   depending on the analytical session. An electron gun was used for charge compensation. The

288   mass resolving power was set to ~6000, sufficient to readily resolve isobaric interferences such

289   as $^{16}O^1H$ from ^{17}O and $^{19}F^{16}O$ from ^{35}Cl. The OH, F and Cl contents of the apatites were

290   calibrated using the measured $^{16}O^1H/^{18}O$, $^{19}F^{16}O/^{18}O$, and $^{37}Cl/^{18}O$ ratios and calibrations derived

291   using reference apatites with known OH, F, and Cl abundances (McCubbin et al., 2012). For

292   glass analyses, calibrations were derived from the $^{16}O^1H/^{18}O$, $^{19}F^{16}O/^{18}O$, and $^{37}Cl/^{18}O$ ratios

293   measured on experimentally synthesized glasses using each of the three powdered starting

294   materials (Q1.001, Q1.003 and Q1.019, see Table 1). The F and Cl abundances of the glasses

295   were determined by EPMA. Their OH contents were determined with the Cameca 6f ion

296   microprobe at the Department of Terrestrial Magnetism, Washington, DC using the procedure

297   described above. The amphibole crystal from Spitsbergen, Svalbard, also described above (see

298   Table S1), the NIST 612 glass standard (Jochum et al., 2011), and a natural obsidian from

299   Tulancingo, Mexico (0.21 wt% F; 0.19 wt% Cl; RLS 132 in MacDonald et al., 1992) were also

300   used as standards. The range of the OH, F and Cl contents covered by these standards are 0.02-

301   2.80 wt% H_2O, 0.01-0.99 wt% F and 0.01-1.25 wt% Cl.

302   **Results**

303   Each experiment resulted in a series of phases represented by some combination of

304   pyroxene, silica, ilmenite, apatite, plagioclase, merrillite, and melt. The assemblage present from

305   each experiment is listed in Table 2. The apatites are distributed throughout the charges and

306   occur as small, highly acicular, prismatic crystals that ranged in width (short dimension) from

307   about 1 to 10 μm with aspect ratios of about 1:10 to 1:60 (Figure 2). The largest apatites that

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308   grew from the silicate melt were approximately 10 μm in the shortest dimension and

309   approximately 300 μm in the longest dimension (Figure 2), which was too small for

310   measurement using the 6f ion microprobe. Consequently, apatites were analyzed by NanoSIMS

311   and EPMA. Where possible, the quenched glasses were analyzed using the 6f ion microprobe,

312   NanoSIMS, and EPMA for F, Cl, and H_2O abundances.

313   **Cation composition of apatite and melt from each experiment**

314   The average compositions of apatite and melt from each experiment, as determined by

315   EPMA, are provided in Table S2. The apatite compositions have elevated abundances of Fe and

316   Mg compared to endmember Ca-apatite with FeO abundances ranging from 2.38 to 4.12 wt.%

317   and MgO abundances ranging from 0.72 to 1.08 wt.%. The apatites also had trace to minor

318   abundances of SiO_2, MnO, and Na_2O, with 0.33 to 0.89 wt.% SiO_2, 0.22 to 0.41 wt.% MnO, and

319   0.07 to 0.32 wt.% Na_2O. These apatite compositions are similar to the ranges observed in many

320   natural apatites from terrestrial worlds across the Solar system, including, Earth, Moon, Mars,

321   Vesta, and ordinary chondrite parent bodies (e.g., Harlov et al., 2006; Jones et al., 2014;

322   McCubbin et al., 2013; McCubbin et al., 2011; Sarafian et al., 2013).

323   The silicate melt compositions, from which the apatite crystallized, ranged from basalt to

324   basaltic andesite (Lebas et al., 1986) with SiO_2 abundances ranging from 47.49 to 55.72 wt.%,

325   using volatile-free melt compositions after normalization to 100% totals (VFNT). The FeO

326   abundances were also consistently high and ranged from 13.80 to 18.14 wt.% FeO, VFNT,

327   which is consistent with these liquids being ferrobasalts (>14 wt.% FeO). The Mg#'s of these

328   compositions were fairly low and ranged from 18.7 to 26.7. All of the melt compositions were

329   peraluminous with an alkalinity index ranging from 0.16 to 0.23. The ratio of non-bridging

330   oxygens to tetrahedrally coordinated cations (Mysen, 1987) was difficult to compute for these

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331   compositions given the elevated abundances of P. Assuming P^{5+} is not tetrahedral coordinated,

332   we calculated a range of 0.29 to 0.60. Assuming P^{5+} is only tetrahedrally coordinated, we

333   calculated a range of 0.18 to 0.38.

334   **F, Cl, and H$_2$O abundances of apatite and melt from each experiment**

335   The F, Cl, and H$_2$O contents of glass and coexisting apatites are presented in Table 3 for

336   all experiments based on an average of approximately 5-12 analyses. Complete average bulk

337   compositions of the apatites and quenched melts for all of the experiments are provided in Table

338   S2. A F-Cl-OH ternary plot of all apatites from the present study is provided in Figure 3. The

339   melt compositions from each experiment were also projected into the F-Cl-OH ternary space.

340   The analyses presented in Table 3 represent the values from several different analytical

341   techniques. Fluorine and Cl analyses of all glasses are from EPMA unless noted in Table 3, in

342   which case they are from NanoSIMS. All H$_2$O abundances are from NanoSIMS unless noted in

343   Table 3. Fluorine values for NanoSIMS and EPMA in apatite were very similar and typically

344   within 1σ standard deviation, so the F value reported in Table 3 is an average value from both the

345   EPMA and NanoSIMS techniques with the exception of experiment Q1.010 for which only

346   NanoSIMS data was collected. Chlorine data for apatite are from EPMA unless noted in Table 3,

347   in which case they are from NanoSIMS. All of the experiments contained relatively high H$_2$O

348   contents, which was expected from the use of talc-pyrex cells, undried starting materials, and

349   unsealed capsules.

350   Two of the experimental charges exhibited spatial heterogeneity in F, Cl, and OH

351   abundances (Q1.057 and Q1.062). This resulted in average concentrations for melt and apatite to

352   have large computed standard deviations. To better assess the results from these two

353   experiments, we conducted analyses of apatite-melt pairs, which we define here as an analysis of

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354   apatite and an analysis of melt within 10-20 μm of the apatite. This procedure was developed to

355   assess local chemical consistency in apatite-melt partitioning throughout the charges. Apatite-

356   melt partition coefficients were calculated for each individual apatite-melt pair and subsequently

357   averaged instead of using an average melt composition and an average apatite composition for

358   the entire experimental charge (c.f. Table 3). This procedure resulted in much lower standard

359   deviations for the apatite-melt partition coefficients and apatite-melt exchange coefficients for

360   Q1.057 and Q1.062 (c.f. Table 4). The data for each of the mineral-melt pairs are presented in

361   Table S3 for Q1.057 and Table S4 for Q1.062. The homogeneity of the other experimental

362   charges resulted in the same D and exchange K_d values whether or not sample averages or

363   apatite-melt pairs were used.

364   **Apatite-melt partitioning of F, Cl, and OH**

365   From the data in Table 3, one can calculate a range of apatite-melt partition coefficients

366   (using Eq. 1) for F (4.4-19), Cl (1.1-5), and OH (0.07-0.24) (Figure 4). These are the first apatite-

367   melt partitioning data reported for OH that have been derived from the direct analysis of OH in

368   both melt and apatite. Importantly, the wide range in partition coefficients calculated using Eq.

369   (1) from our data demonstrates the importance of not using a single D value to determine volatile

370   abundances in silicate melts from apatite. Unlike the partition coefficients, the apatite-melt

371   exchange K_d values for OH-F, Cl-F, and OH-Cl do not vary substantially and demonstrate the

372   importance of using exchange-equilibria to describe the partitioning relationship of volatiles

373   between apatite and silicate melts. The exchange K_d (from Eq. 4) values are provided in Table 4,

374   and summarized here: $K_{d_{Cl-F}}^{Ap-Melt} = 0.21 \pm 0.03$, $K_{d_{OH-F}}^{Ap-Melt} = 0.014 \pm 0.002$, and $K_{d_{OH-Cl}}^{Ap-Melt} =$

375   0.06 ± 0.02. Importantly, these exchange coefficients are only valid at 1.0-1.2 GPa and 950-

376   1000 °C in Fe-rich basalts to Fe-rich basaltic andesites at an oxygen fugacity of ΔIW-1 to

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377   ΔIW+2. Exchange coefficients can vary as a function of temperature, pressure, melt

378   composition, apatite composition, and/or oxygen fugacity, so the combined effects of these

379   parameters must be investigated before these exchange coefficients can be used to determine

380   volatile abundances of coexisting melt from apatite volatile abundances.

381   **Discussion**

382   The apatite-melt partitioning data from this study illustrate the importance of using

383   exchange coefficients to describe the partitioning of F, Cl, and OH between apatite and silicate

384   melt. Furthermore, the experiments demonstrate a clear preference of F over Cl and Cl over OH

385   in the apatite structure, which has been noted in many previous studies (e.g., Hughes et al., 1989;

386   Hughes et al., 1990; Stormer and Carmichael, 1971; Zhu and Sverjensky, 1991). This relative

387   partitioning preference has several important consequences for the behavior of volatiles in

388   natural systems. First, this behavior will result in extreme fractionation of F from Cl and OH

389   during fractional crystallization when apatite is part of the fractionating assemblage (e.g., Boyce

390   et al., 2014; Meurer and Boudreau, 1996). Additionally, this process results in F being a

391   compatible element in apatite during magmatic crystallization, whereas Cl and H_2O are more

392   likely to remain in the melt to higher degrees of crystallization, making Cl and H_2O more likely

393   to be lost by late-stage degassing. Importantly, this assertion only applies to systems that have

394   sufficient P to accommodate the F in apatite (i.e., typical basaltic systems but not all rhyolitic

395   systems where P_2O_5 abundances at apatite saturation are quite low; Green and Watson, 1982;

396   Harrison and Watson, 1984; Watson, 1979). The compatibility of F during magmatic

397   differentiation of volcanic rocks has been observed previously, and this observation was

398   interpreted to indicate that F is less susceptible to degassing than Cl and H_2O (Aiuppa et al.,

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399   2009). We show here that apatite, as a major sink for F, is likely to be at least partially

400   responsible for this observation.

The effect of apatite anion chemistry (X-site) on apatite-melt partitioning of F, Cl, and OH

402   The experiments from this study present a wide range of apatite X-site compositions and

403   F:Cl:OH ratios in the melt, as illustrated by the F-Cl-OH ternary in Figure 3 and values in Table

404   3, but it is not exhaustive. Additionally, this range of apatite compositions was generated from a

405   fairly limited range of melt H_2O abundances (2.6-3.56 wt.% H_2O; Table 3), so caution should be

406   taken before extrapolating these results to much lower or higher melt H_2O abundances. We

407   examined the exchange K_d values as a function of F and Cl abundances in both silicate melt and

408   apatite to assess the assumption of ideality in Eq. 4. Our results indicate that the OH-F and Cl-F

409   data do not deviate from a constant value within the uncertainties of the exchange K_d for large

410   ranges in F and Cl abundances in apatites and melts (Figure 5). However, the OH-Cl exchange

411   K_d is non-linear near the OH-Cl binary and becomes constant for apatite with $\geq$ 0.7 wt.% F (i.e.,

412   F mole fraction of $\geq$ 0.18 in the X-site; Figure 5C). Given that F, Cl, and OH are fairly minor

413   components of the silicate liquid and are essential components of apatite, we anticipate that the

414   non-linearity of the OH-Cl exchange K_d at low F abundances is likely attributable to the mixing

415   properties of F, Cl, and OH in apatite rather than in the silicate melt. This is further supported by

416   Figure 5B, which displays an irregular correlation of the OH-Cl exchange K_d as a function of Cl

417   abundance in the melt. We conclude that the apatite X-site composition does not have a large

418   effect on the apatite-melt exchange K_d's over much of the limited ternary space investigated here

419   (Figure 5), indicating that the implicit assumption of ideality in Eq. 4 was valid for this limited

420   compositional space. However, the presence or absence of F does appear to have a strong effect

421   on apatite-melt exchange K_d's, so further investigations within the remaining apatite ternary

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422 space are needed to precisely determine the portion of the ternary that does not lend itself to this

423 assumption.

424 **Inferences from existing thermodynamic data on apatite.** Although the mixing

425 properties of F, Cl, and OH in ternary apatites is poorly constrained (as discussed by Tacker and

426 Stormer, 1989), our results are consistent with thermodynamic studies of the mixing properties

427 of F and OH in apatite along the OH-F apatite binary join, which is ideal for F-rich apatite (up to

428 60 mol% F in the X-site; Hovis et al., 2014). However, OH-rich apatites along the OH-F apatite

429 join exhibit negative enthalpies of OH-F mixing (Hovis et al., 2014). Hence apatites with more

430 than 40% of the X-site occupied with OH may not have exchange K_d values consistent with

431 those reported in the present study.

432 Thermodynamic data along the Cl-F apatite binary indicate substantial deviations from

433 ideality with enthalpies of mixing as high as 8.3 kJ/mol (Hovis and Harlov, 2010). In fact, it has

434 been demonstrated experimentally that low-OH Cl-F apatite must create a special F position to

435 accommodate long-term Cl-F mixing in the apatite channels along the c-axis (Hughes et al.,

436 2014). However, it has also been demonstrated that at mole fractions of OH as low as 0.12 in the

437 apatite X-site, the need for that special F position to accommodate long-term Cl-F neighboring is

438 eliminated (McCubbin et al., 2008). Using this structural information as a proxy for the

439 thermodynamic mixing behavior of F and Cl in apatite, we conclude that OH abundances in the

440 Cl-F apatite from the present study were sufficiently high (e.g., Exp. # Q1.057 had Cl-F apatite

441 with lowest OH, $F_{0.42} Cl_{0.44} OH_{0.14}$; Table 3) so that we did not reach the non-ideal portion of the

442 ternary inferred from the results of Hovis and Harlov (2010) along the Cl-F binary. However, we

443 anticipate exchange K_d's to deviate from those reported in the present study as the Cl-F binary

444 join is approached at some OH value below the 0.12 mole fraction on the X-site.

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445   The thermodynamics of Cl and OH mixing along the OH-Cl binary have not been

446   investigated in sufficient detail, but available data indicate they likely mix ideally at magmatic

447   temperatures (Tacker and Stormer, 1989), though still this remains an additional unknown. Only

448   one of our experiments was along the OH-Cl join and it had an anomalously low OH-Cl

449   exchange K_d compared to all of the other experiments. Substantial weight should not be placed

450   on the result of a single experiment, but it would be consistent with the presence or absence of F

451   having an effect on apatite-melt exchange K_d's, which is also evident when exchange K_d's are

452   plotted as a function of F abundance in apatite (Figure 5). Therefore, the exchange K_d's reported

453   in the present study should not be applied for compositions along the OH-Cl join or in the

454   ternary system when apatite has < 0.18 mole fraction F on the X-site (Figure 5).

455   The comparison of our results with existing thermodynamic data along the binary Cl-F,

456   OH-Cl, and OH-F joins further supports the idea that additional efforts are needed to truly

457   determine the effects of apatite anion chemistry on the partitioning behavior of F, Cl, and OH

458   between apatite and silicate melts. Based on the preliminary findings here and the existing excess

459   enthalpy data on binary apatite crystalline solutions, we have conservatively estimated a field

460   within the F-Cl-OH apatite ternary where we anticipate ideal F-Cl-OH mixing in apatite, as

461   projected from the fluorapatite apex (white shaded region of Figure 6). Furthermore, we infer

462   that the apatite-melt partitioning behavior of apatites in the ideal-mixing field of Figure 6 can be

463   described using the exchange K_d values reported herein within the confines of the P-T-X_{Melt}-f_{O2}

464   conditions of our experiments. Furthermore, we anticipate apatites that plot within the ideal-

465   mixing field in Figure 6 to exhibit the same apatite-melt exchange K_d's for a given set of P-T-

466   X_{Melt}-f_{O2} conditions that are outside of those investigated here (even though the actual exchange

467   K_d's themselves may change as a function of P-T-X_{Melt}-f_{O2} conditions). Importantly, the

20

468   estimated field of ideal F-Cl-OH mixing could be wider than the white region depicted in Figure

469   6, but additional experimental results are needed to assess the true boundaries of this field.

470   Additionally, there may be more than one discrete field of ideal F-Cl-OH mixing within the

471   apatite F-Cl-OH ternary space, but we anticipate each discrete field will have its own set of

472   consistent apatite-melt exchange K_d values that should be investigated experimentally.

473   **Variability of apatite-melt exchange coefficients as a function of *P, T, X*, and f_{O2}**

474   Previous experimental studies have investigated apatite-melt partitioning. However they

475   focused only upon the partitioning behavior of F and Cl, even though H_2O was present in the

476   coexisting melt and fluid in those experiments (Doherty et al., 2014; Mathez and Webster, 2005;

477   Webster et al., 2009). The work of Mathez and Webster (2005) and Webster et al., (2009)

478   represents some of the first experimental data on apatite-melt partitioning for F and Cl. These

479   studies reported apatite-melt partition coefficients (D_X from Eq. 1) for F (3.4-40) and Cl (0.8-4.5)

480   that display an even wider range than those reported here (Figure 4), although the previous

481   studies were conducted at 0.2 GPa over a wider range of temperatures (900-1150 °C) and melt

482   compositions (basalt-rhyodacite). Our experiments were carried out over a small range in

483   pressure (1.0-1.2 GPa), temperature (950-1000 °C), and melt composition (ferrobasalt to

484   ferrobasaltic andesite). Consequently, direct comparisons of the previously published data with

485   our own can only demonstrate whether or not exchange K_d's are likely to vary as a function of

486   temperature, pressure, and/or melt composition. Based on the previous apatite-melt partitioning

487   studies, the Cl-F exchange coefficient (K_d from Eq. 4) ranges from 0.06 to 0.59 (K_d's computed

488   from experimental data in Mathez and Webster, 2005; Webster et al., 2009), compared to the

489   value from our study of 0.21 ± 0.03. These previously published results illustrate that apatite-

490   melt exchange coefficients are not constant over a wide range of parameter space and highlight

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491 the importance of investigating how these values may change as a function of temperature,

492 pressure, melt composition, apatite composition, and/or oxygen fugacity.

493 **Does OH always behave incompatibly in apatite-melt systems?**

494 The range in D values for OH in the present study is 0.07-0.24, indicating OH behaves

495 incompatibly with respect to apatite. However, these results do not reflect the entire range in

496 apatite-melt D values for OH that can arise as a consequence of the apatite-melt exchange

497 equilibrium model. Although the abundances of F, Cl, and OH in apatite are fixed based on the

498 stoichiometry of the X site in apatite, which typically sums to one structural formula unit, the F,

499 Cl, and OH abundances in the silicate melt can vary from zero to their respective levels of

500 saturation. As a result, the lower the concentration of F, Cl, and OH in the melt, the higher the

501 apatite-melt D that is required to maintain a full X-site in apatite and a constant ratio of D values

502 for F, Cl, and OH. Figure 7 illustrates the possible range of apatite-melt D values for OH as a

503 function of melt F and H_2O abundance in a Cl-free system. This plot indicates that apatite-melt D

504 values for OH could be much greater than one, and that OH may behave compatibly in apatite

505 under certain conditions. Additional experiments, that address the minimum abundance of

506 volatiles in the melt to stabilize apatite, are required to assess the true upper limits on the apatite-

507 melt D values for F, Cl, and OH.

508 Many studies have attempted to estimate a conservatively high apatite-melt D value for

509 OH and use this value to estimate "minimum H_2O abundances" in the melt from which the

510 apatites crystallized (e.g., Barnes et al., 2014; Boyce et al., 2010; Hu et al., 2014; McCubbin et

511 al., 2010b; 2012; Robinson and Taylor, 2014; Tartèse et al., 2013; 2014). The D value that was

512 typically used for this purpose is 0.25, which was calculated by McCubbin et al., (2010b) from

513 data in Mathez and Webster (2005). Based on the apatite-melt partitioning results of the present

22

study, and assuming it is appropriate to apply those results, the conservative estimate of 0.25 for

an apatite-melt D_{OH} is only a valid assumption if the abundance of F in the melt is ≥ 2000 ppm at

the time of apatite crystallization (Figure 7). Lower abundances of F in the melt at the time of

apatite saturation would require higher apatite-melt D values for OH.

The entire compositional range illustrated in Figure 7 does not necessarily reflect reality

because at some point the abundances of volatiles in the melt will be insufficient to stabilize

apatite at phosphate saturation and merrillite ($Ca_{18}Na_2Mg_2(PO_4)_{14}$) will form instead (e.g., Exp#

Q1.022 from this study). Although merrillite is uncommon in terrestrial systems and exists only

as a component in terrestrial whitlockite ($Ca_9(Mg,Fe^{2+})(PO_4)_6[PO_3(OH)]$), it is commonly found

in extraterrestrial rocks (Hughes et al., 2006; 2008; Jolliff et al., 1993; 2006). The stability of

merrillite relative to apatite is primarily governed by the halogen fugacity and the ratio of P to

the halogens (Patiño Douce and Roden, 2006; Patiño Douce et al., 2011). However, the effect of

H_2O on merrillite stability in silicate melts remains unclear (e.g., McCubbin et al., 2014).

Additional experimental work to determine the phase boundary between merrillite and apatite

stability (with respect to halogen and H_2O fugacities) in silicate melts is required to place upper

limits on apatite-melt D values for F, Cl, and OH.

Consequences of apatite-melt partitioning on apatite-based melt hygrometry

Apatite-based melt hygrometry is the practice of using the H_2O abundances of apatite to

determine the abundance of H_2O in the melt from which it formed. The ultimate goal of this task

is to determine an estimate of the H_2O abundance in the parental melt or the magmatic source

region from which the parental melt was derived. In this section, we first present the methods

that were employed prior to this study to conduct apatite-based melt hygrometry, and we follow

it up with modifications to these methods, resulting from this work.

23

Implementation of apatite-based melt hygrometry using "D values". As a cautionary note, the implementation of apatite-based melt hygrometry using "D values" is a practice that should end immediately because there is no single apatite-melt D value for H_2O that can be used to implement equations 5 and 6 below. However we describe the process involved in such calculations and the rationale behind them to support the discussion in the next section where exchange K_d values are used in place of D values. Quantitative estimates of H_2O abundances in parental melts (X) or magmatic source regions (Y) from apatite have recently been determined from the general batch melting equation with slight modifications involving Eq. (1) to solve for the abundance of H_2O in the melt:

$$X_{H_2O}^{PM} = \frac{\left(1 - F_P^{Saturation}\right) \times X_{H_2O}^{Ap}}{D_{H_2O}^{Ap-Melt}} \tag{5}$$

$$Y_{H_2O}^{MS} = \frac{\left(1 - F_P^{Saturation}\right) \times F_{Source}^{Partial\ Melting} \times X_{H_2O}^{Ap}}{D_{H_2O}^{Ap-Melt}} \tag{6}$$

Here, $X_{H_2O}^{PM}$ is the H_2O content (wt%) of the parental melt, $Y_{H_2O}^{MS}$ is the H_2O content (wt%) of the mantle source, $F_P^{Saturation}$ is the degree of crystallization before apatite saturation, $X_{H_2O}^{Ap}$ is the amount of H_2O in apatite (wt%), $D_{H_2O}^{Ap-Melt}$ is the apatite-melt partition coefficient for H_2O, and $F_{Source}^{Partial\ Melting}$ is the degree of partial melting that occurred to produce the parental melt.

The degree of crystallization, before phosphate saturation in a silicate melt, is determined by using the bulk rock P_2O_5 abundance, which assumes that the bulk rock composition represents that of the parental melt composition (as opposed to a differentiated product, a cumulate, or a partial cumulate). It is then assumed that P behaves as an incompatible element until the melt reaches apatite saturation, which can be predicted from existing models of apatite saturation in

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558   silicate melts (Green and Watson, 1982; Harrison and Watson, 1984; Watson, 1979). Phosphate

559   saturation is very sensitive to temperature and melt SiO_2, but based on the existing models,

560   basaltic liquids can be expected to reach apatite saturation at approximately 2 wt.% P_2O_5

561   between about 950 and 1050 °C. It should be pointed out, however, that these models cannot

562   reproduce the P_2O_5 contents of the silicate melts at apatite saturation from the present study

563   (3.16-4.69 wt.% P_2O_5; Table S2), suggesting there are additional controls on apatite saturation in

564   silicate liquids that require further investigation. From this information, $F_P^{Saturation}$ can be

565   calculated based on the following equation:

$$F_P^{Saturation} = 1 - \frac{X_{P_2O_5}^{Bulk}}{X_{P_2O_5}^{Saturation}} \tag{7}$$

567   where $F_P^{Saturation}$ is the degree of crystallization before apatite saturation, $X_{P_2O_5}^{Bulk}$ is the bulk rock

568   P_2O_5 content (wt.%), and $X_{P_2O_5}^{Saturation}$ is the P_2O_5 content of the silicate melt at apatite saturation.

569   Equations 5-7 rely on determining the H_2O content of the melt at the time of apatite

570   crystallization and using a proxy for the degree of crystallization to back-calculate the H_2O

571   abundance of the parental melt or source region. As shown above, the proxy of choice (apatite

572   saturation in the silicate melt), is poorly constrained. It has resulted in a very large degree of

573   uncertainty for all estimates of parental melt and source region H_2O abundances from apatite. It

574   demonstrates that even "conservative" estimates of apatite-melt D values for H_2O are invalid

575   when using equations 5 and 6, which is the primary reason why equations 5-7 should no longer

576   be used to conduct apatite-based melt hygrometry.

577   **Implementation of apatite-based melt hygrometry using "exchange K_d values".** Based

578   on the results from the present study, the use of apatite-melt D values is prohibited, so these

579   equations require modification to accommodate the K_d (exchange coefficients). Equations 5 and

580   6 must be modified to account for the use of exchange K_d's, which incorporate Eq. (2) to solve

581   for the abundance of H_2O in the melt as opposed to Eq. (1):

582
$$X_{H_2O}^{PM} = \frac{X_{H_2O}^{Ap} \times X_Z^{Parent\ Melt}}{K_{d_{OH-Z}}^{Ap-Melt} \times X_Z^{Ap}}$$
(8)

583

584
$$Y_{H_2O}^{MS} = \frac{F_{Source}^{Partial\ Melting} \times X_{H_2O}^{Ap} \times X_Z^{Parent\ Melt}}{K_{d_{OH-Z}}^{Ap-Melt} \times X_Z^{Ap}}$$
(9)

585   where Z is either F or Cl, $K_{d_{OH-Z}}^{Ap-Melt}$ (c.f. Eq. 2) that includes OH-F or OH-Cl, and $X_Z^{Parent\ Melt}$ is

586   the F or Cl content of the parent melt. When using equations (5) and (6), only the H_2O content of

587   the apatite and the D value for OH were needed to determine the abundance of H_2O in the melt at

588   the time of apatite crystallization. To use equations (8) and (9), the H_2O content of the apatite, an

589   apatite-melt exchange K_d that includes OH, the abundance of F or Cl in the apatite, and the

590   abundance of F or Cl in the parent melt are needed. Using the parental melt F or Cl abundance,

591   in place of the F or Cl abundance in melt that is in equilibrium with the apatite, serves as a built-

592   in proxy for relating the apatite composition to the H_2O content of the parent melt, and it takes

593   the place of using the bulk rock P_2O_5 abundance as a proxy for the degree of crystallization prior

594   to apatite saturation. It does assume that F behaved as an incompatible element up to the point of

595   apatite crystallization and that the F:H_2O ratio of the melt was not modified up to the point of

596   apatite crystallization, the latter of which may be difficult to prove. The implementation of

597   equations 8 and 9 requires that the F or Cl content of the parent melt can be estimated. This

598   would typically require knowing the bulk rock F or Cl abundance of the sample containing the

599   apatites and knowledge of whether or not that sample represents the bulk composition of the

600   parent melt. Given the potential susceptibility to degassing of Cl and the more compatible nature

601   of F in apatite as described above, apatite-based melt hygrometry would be best implemented

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602   using OH-F exchange K_d's as opposed to OH-Cl exchange K_d's. The level of uncertainty

603   inherent in the implementation of equations 5 and 6 is substantially reduced using the version

604   that implements Eqs. 8 and 9 because it does not include the uncertainty regarding the controls

605   on apatite saturation in silicate liquids. Before its implementation, however, further experimental

606   work is needed to constrain the combined effects of melt composition, pressure, temperature,

607   apatite composition, and oxygen fugacity on the apatite-melt exchange coefficients.

608   Importantly, all of these apatite-based melt hygrometry equations (5-9) assume equilibrium

609   crystallization at the time of apatite saturation (and during apatite crystallization), which may not

610   be a valid assumption in many cases (Boyce et al., 2014). If a system is undergoing fractional

611   crystallization and apatite is part of the fractionating assemblage, the F:Cl:OH ratio in the melt

612   changes during apatite crystallization, rendering any estimates of melt OH abundances

613   impossible from apatite (Boyce et al., 2014). Consequently, one should proceed with caution

614   when using apatite to determine the H_2O abundances of the coexisting or parental melt. Much

615   like any technique to determine volatile abundances in melt (e.g., melt inclusions; Bucholz et al.,

616   2013; Gaetani et al., 2012), many assumptions and caveats apply. However, with additional

617   constraints, apatite has the potential of becoming a powerful and useful tool in determining the

618   volatile abundances of magmatic systems on Earth and beyond.

619   **Implications**

620   A substantial investment has been made in apatite for determining the abundances of H_2O

621   in planetary bodies due to its ubiquitous presence in various planetary materials and the paucity

622   of other volatile-bearing phases. Although we outline much caution in using apatite for this task,

623   the results presented here are an important step forward to reaching the goal of apatite becoming

624   a calibrated melt hygrometer. Furthermore, these results have some important implications for

625 the type of information that will be required in order to complete such a task. Previous estimates

626 of H_2O in silicate melts using apatite-melt D values required knowing only the OH content of

627 apatite, and as a result, many analyses in the literature have been published without F and Cl

628 abundances. We demonstrate here the importance of reporting all three anion X-site constituents,

629 and this should become standard practice for apatite analyses going forward. In addition, we

630 demonstrate the importance of knowing the bulk rock F contents of the apatite-hosting rocks

631 under investigation, which are required for determining bulk rock F/H_2O ratios from the apatite-

632 melt exchange K_d. Currently, there is very little high-precision data for bulk rock F abundances

633 in planetary materials and this represents an important area of potential growth for any future

634 implementations of apatite-based melt hygrometry. In conclusion, while additional experimental

635 work is needed to calibrate apatite as a melt hygrometer, additional steps are also required in the

636 analysis of planetary samples to be able to use a more accurately calibrated apatite-based melt

637 hygrometer.

638 **Acknowledgements**

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Appendix A

921 **Piston Cylinder Pressure Calibration**

922   Pressure calibration of the talc-pyrex cell assembly was conducted using the melting

923 point of natural NaCl (Clark, 1959; Pistorius, 1966). The NaCl was ground to a fine grained

924 powder and kept in a vacuum oven at 100 °C until the time of each experiment. Before each

925 calibration experiment, all inner parts of the talc cell assembly were dried at 800 °C for 20

926 minutes and then kept in a vacuum oven at 100 °C. The melting T of NaCl was bracketed using a

927 variation of the falling sphere method. A thin layer of natural NaCl ($\rho \approx 2.16$ g/cm^3) powder was

928 loaded into a molybdenum capsule, followed by 2-3 Fo$_{90}$ ($\rho \approx 3.31$ g/cm^3) or Fo$_{83}$ ($\rho \approx 3.44$ g/cm^3)

929 spheres. The remainder of the capsule was then filled with ground NaCl powder. The assembly is

930 inverted during the experimental run, so the bottom of the capsule with olivine spheres is now at

931 the top of the assembly during the experiment. An experimental assembly identical to those

932 described in the "Piston Cylinder Experiments" section of this manuscript was employed unless

933 otherwise noted. Exceptions to the procedure include using run durations of 10-20 minutes and

934 using a Type B (Pt$_{30}$Rh$_{70}$/ Pt$_6$Rh$_{94}$) thermocouple and Eurotherm (2416) controller to control and

935 monitor temperature throughout the duration of the run. For each experiment, the temperature

936 was initially raised to 800 °C at 200 °C/min, then to 20 °C below the target temperature at 125

937 °C/min, and finally to the target temperature at 50 °C/min. The temperature of our thermocouple

938 was calibrated against the melting points of NaCl (801 °C), MgCl$_2$ (714 °C), and Na$_2$CO$_3$ (851

939 °C) (Vander Kaaden et al., 2015) at 1 bar. The estimated thermal gradient over our capsule is

940 $\leq$12 °C, which results in an uncertainty of 0.1 GPa when this T uncertainty is propagated as a

941 function of pressure. Experiments were quenched at ~90 °C/s. Cross sections of the quenched

942 capsules were polished dry using boron nitride powder as a lubricant. If the spheres were still at

943 the top of the cell assembly after quench, the NaCl was assumed not to have melted. If the

944   spheres were at the bottom of the assembly at the end of the experiment, the NaCl was assumed

945   to have melted. The experimental results used to bracket the melting point of NaCl are shown in

946   Figure A1A and converted to kbar using the melting point of natural NaCl as a function of

947   pressure in Figure A1B.

948   We also provide an update to the pressure calibration of our salt-pyrex cell that was

949   initially described by Vander Kaaden et al., (2015). The pressure calibration for this cell was

950   inconsistent with the melting temperature of diopside at 1 bar (1392 °C), and based on all of the

951   diopside melting data, additional checks were needed for the portion of the curve at 100 bars of

952   oil pressure. Consequently, we conducted NaCl melting experiments at 100 bars of oil pressure,

953   identical to those described above for calibration of the talc-pyrex cell. We determined that a

954   pressure adjustment to the calibration was needed, and we provide the adjusted pressure

955   calibration in Figure A2. The NaCl melting calibration experiments are consistent with the

956   diopside melting experiments conducted at 75 and 50 bars of oil pressure by Vander Kaaden et

957   al., (2015) as well as the 1 bar melting point of diopside.

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967 **Figure Captions**

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969 **Figure 1.** Plot of computed exchange K_d's displayed as a function of run duration, where run

970 duration is defined by the number of hours spent at the crystallization temperature. The average

971 value for each exchange K_d (Cl-F, OH-F, and OH-Cl) is plotted as a horizontal line. Error bars

972 for the exchange K_d were derived from propagating the standard deviation of the mean from each

973 average analysis through the K_d value.

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975 **Figure 2.** Backscattered electron images of experimental run products from experiments Q1.010,

976 Q1.012, Q1.017, and Q1.024. Scale bars for each image are provided, and all phases present are

977 labeled as follows: M – melt, Ap – apatite, Px – pyroxene, Si – silica, Ilm – ilmenite.

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979 **Figure 3.** Ternary plot of apatite X-site occupancy (mol%) from the apatite-melt partitioning

980 experiments. Apatites are plotted in green (along with their respective experiment number), and

981 silicate melts were projected into the ternary space and are plotted in purple. The region of the

982 ternary containing the silicate melt points was enlarged and shown as an inset so that the

983 experiment number of each melt datum could be identified. When SIMS data was not available,

984 an OH component was calculated by stoichiometry from EPMA data assuming $1 - Cl - F = OH$

985 (structural formula units).

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987 **Figure 4.** Plot displaying the observed ranges in apatite-melt partition coefficients for F, Cl, and

988 OH from the present study. Error bars on the partition coefficient (D value) were derived from

989 propagating the standard deviation from each average value used to compute the D value.

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Figure 5. Plots of exchange K_d values versus F or Cl abundances in apatite or silicate melt. Error

bars on the exchange K_d were derived from propagating the standard deviation of the mean from

each average analysis through the K_d value. A) F in silicate melt, B) Cl in silicate melt, C) F in

apatite, D) Cl in apatite.

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Figure 6. Ternary plot of F-Cl-OH components in apatite with regions shaded in white to

indicate apatite compositions that are likely to have constant apatite-melt exchange K_d's (OH-F,

OH-Cl, and Cl-F) equal to those determined from the present study. Regions of the ternary

shaded in grey indicate apatite compositions that may deviate from apatite-melt exchange K_d's

(OH-F, OH-Cl, and Cl-F) determined in this study. Apatite compositions from each of the

apatite-bearing experiments are plotted in green, and the experiment numbers for each apatite

composition are given in Figure 3. Area of shaded regions were determined from the apatite-melt

partitioning results obtained experimentally in this study and were inferred from previously

published thermodynamic data (excess enthalpies of mixing) for the OH-F and Cl-F apatite

binary joins from Hovis et al., (2014) and Hovis and Harlov, (2010), respectively. For the

portions of the ternary constrained only by excess enthalpy of mixing data for apatite binaries,

we have used a dashed line to indicate a higher degree of uncertainty in these regions. The

exchange K_d values themselves can vary as a function of P and T, so the specific P-T conditions

to which the exchange K_d values are applicable are shown.

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Figure 7. Model illustrating how the D value for OH can vary greatly as a function of F and H_2O

abundance in the melt. This model was constructed for a Cl-free melt using the OH-F exchange

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1013 K_d value and the following two assumptions: 1) the apatite that forms from the melt is

1014 stoichiometric with no X-site vacancies, and 2) apatite is the stable phosphate mineral that would

1015 form from the melt. The commonly used apatite-melt D value of 0.25 for OH is plotted for

1016 reference. Additional information is required on the stability of merrillite relative to apatite to

1017 constrain a realistic limit on the apatite melt D value for H_2O.

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1019 **Figure A1. A)** Results from NaCl melting experiments in talc-pyrex cells. The black line shows

1020 the best fit through this data. Downward facing triangles indicate that the NaCl melted and

1021 upwards facing triangles indicate that the NaCl did not melt. The best fit line is anchored at the

1022 1-bar melting T of NaCl (800.5 °C). **B)** Conversion of pressure in oil bars to pressure in kilobars

1023 for the talc-pyrex cell. The black line shows the best fit through this data ($y = 0.1017x - 0.1509$,

1024 $R^2 = 0.9974$). This calibration line is used to determine the kbar equivalent of the applied oil

1025 pressure (in bars) using the talc-pyrex cell assembly.

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1027 **Figure A2. A)** Results from NaCl melting experiments in a salt-pyrex cell. The black line shows

1028 the best fit through this data. Downward facing triangles indicate that the NaCl melted and

1029 upwards facing triangles indicate that the NaCl did not melt. The best fit line is anchored at the

1030 1-bar melting T of NaCl (800.5 °C). **B)** Conversion of pressure in oil bars to pressure in kilobars

1031 for the salt-pyrex cell. Data points from 50 and 75 oil bars are from Vander Kaaden et al., (2015)

1032 using the melting point of diopside from Williams and Kennedy (1969). The black line shows the

1033 best fit through this data ($y = 0.1173x - 0.1457$, $R^2 = 0.9934$). This calibration line is used to

1034 determine the kbar equivalent of the applied oil pressure (in bars) using the salt-pyrex cell

1035 assembly.

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Tables

Table 1: QUE 94201 meteorite composition (from Kring et al., 2003) as well as F, Cl, and OH endmember mixtures of QUE 94201 composition with added phosphorus. Values represent EPMA and SIMS analysis of quenched glass from a super liquidus experiment (1200 °C at 1.0 GPa) of each respective mixture composition.

Oxide (wt.%)	QUE 94201[b]	QUE 94201 F Mixture	QUE 94201 Cl Mixture	QUE 94201 OH Mixture
SiO_2	47.03	44.5 (3)	44.6 (3)	44.7 (3)
TiO_2	1.84	1.4 (2)	1.5 (2)	1.6 (1)
Al_2O_3	11.1	10.88 (6)	11.11 (9)	11.11 (4)
Cr_2O_3	0.14	0.14 (1)	0.14 (1)	0.18 (1)
FeO^T	18.5	16.8 (1)	16.5 (2)	16.9 (1)
MnO	0.45	0.40 (2)	0.32 (2)	0.45 (2)
MgO	6.1	5.5 (1)	4.83 (6)	5.2 (1)
CaO	11.1	8.65 (7)	8.40 (9)	8.46 (9)
Na_2O	1.64	1.34 (3)	0.98 (3)	1.53 (2)
K_2O	0.05	-	-	-
P_2O_5	2.05	7.7 (1)	7.7 (1)	7.23 (7)
H_2O^b	-	2.21 (7)	2.93 (7)	2.66 (6)
F	-	0.99 (2)	0.02 (1)	0.04 (2)
Cl	-	0.010 (4)	1.25 (2)	0.015 (4)
-O = F+ Cl	-	0.42	0.29	0.02
Total[d]	100.00	100.00	100.00	100.00
mg#[c]	0.37	0.39	0.37	0.38
Exp#	-	Q1.001	Q1.019	Q1.003

Each composition represents the average of 10 EPMA analyses
All parenthetical values represent 1σ standard deviation of the mean (1σ SDOM) and are always larger than the 2σ analytical uncertainty (2σ AU).
[a] Determined using the 6f SIMS at DTM
[b]QUE 94201 composition from Kring et al. (2003)
[c] mg# = Molar Mg/(Mg + Fe^{2+}) assuming an $Fe^{2+}/\sum Fe = 0.9$.
[T]All Fe measured as FeO
[d]Analytical totals normalized to 100% for easy direct comparison between mixtures

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Table 2: Experiments and experimental run conditions from the present study

Exp. #	Capsule[a]	Cell[b]	T (°C)	P (GPa)	Duration (hours)	Cooling rate[e] (°C/min)	Mixture type[c]	Phases[d]
Q1.001	G	T-P	1200	1.0	0.33	-	F	M
Q1.003	G	T-P	1200	1.0	0.33	-	OH	M
Q1.007	G	T-P	1000	1.0	8.5	500	F, Cl, OH	M, A, P, S, I
Q1.010	G	T-P	1000	1.0	2.75	500	F, Cl, OH	M, A, P, S, I
Q1.012	G	T-P	1000	1.0	3	500	F, Cl, OH	M, A, P, S, I
Q1.013	G	T-P	1000	1.0	3.25	500	F, Cl, OH	M, A, P, S, I
Q1.016	G	T-P	990	1.0	5.5	0.18	F, Cl, OH	M, A, P
Q1.017	G	T-P	990	1.0	7	0.27	F, Cl, OH	M, A, P, S
Q1.018	G	T-P	990	1.0	6.5	0.24	F, Cl, OH	M, A, P, I
Q1.019	G	T-P	1200	1.0	0.33	-	Cl	M
Q1.020	G	T-P	995	1.0	18.5	500	Cl	M, A, P, S, I
Q1.022	G	T-P	995	1.0	26.5	500	OH	M, Me, P, S, Pl, I
Q1.024	G	T-P	985	1.0	12.5	500	F	M, A, P, S, I
Q1.057	Mo	S-P	1000	1.2	8	500	F, Cl	M, A, P, S, I
Q1.061	Mo	S-P	1000	1.2	7	500	F, Cl	M, A, P, S, I
Q1.062	Mo	S-P	950	1.2	8.5	500	F, Cl	M, A, P, S, I

[a] G – graphite, Mo – molybdenum metal
[b] T-P – talc-pyrex cell, S-P – salt-pyrex cell
[c] F – QUE 94201 F mixture, Cl – QUE 94201 Cl mixture, OH – QUE 94201 OH mixture (Table 1)
[d] M – melt, A – apatite, P – pyroxene, S – silica, Me – merrillite, I – ilmenite, Pl – plagioclase
[e] Represents cooling rate from 1050 °C to target temperature. Cooling rate from 1200 °C super liquidus melting step to 1050 °C = 500 °C/min for all experiments.

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Table 3: Volatile abundances of apatite and co-existing melt from experiments in weight percent.

Exp. #	H_2O_{melt}	H_2O_{Ap}	F_{melt}	F_{Ap}	Cl_{melt}	Cl_{Ap}	X_F	X_{Cl}	X_{OH}	$\sum X$
Q1.007	2.6^a (1)	0.6^b (2)	0.08 (3)	1.5 (3)	0.3 (1)	1.7 (2)	0.41	0.24	0.35	1.00
Q1.010	3.56 (7)	0.44 (2)	0.15^c (2)	1.6 (2)	1.18^c (3)	2.7^c (2)	0.42	0.39	0.24	1.05
Q1.012	2.72 (4)	0.34 (3)	0.38 (2)	3.0 (3)	0.5 (1)	0.6 (2)	0.80	0.09	0.19	1.08
Q1.013	2.86 (2)	0.32 (1)	0.44 (3)	3.1 (2)	0.36 (4)	0.5 (1)	0.85	0.08	0.18	1.11
Q1.016	2.92 (3)	0.56 (2)	0.17 (2)	2.2 (4)	0.47 (4)	1.3 (2)	0.59	0.19	0.32	1.10
Q1.017	3.05 (4)	0.51 (2)	0.18 (2)	1.8 (2)	0.93 (2)	1.9 (2)	0.50	0.27	0.28	1.05
Q1.018	2.81 (5)	0.49 (4)	0.22 (2)	2.7 (5)	0.32 (2)	0.7 (2)	0.74	0.10	0.27	1.11
Q1.020	3.3 (2)	0.24 (5)	$<0.005^c$	0.010^c (2)	1.37 (3)	5.6 (2)	0.0	0.82	0.14	0.96
Q1.024	3.1 (2)	$<0.08^b$	0.81 (8)	3.6 (2)	0.015 (3)	0.016 (3)	0.98	0.0	0.02	1.00
Q1.057	3.01 (8)	0.26^b (6)	0.30 (9)	1.6 (6)	2.1 (5)	3.0 (9)	0.42	0.44	0.14	1.00
Q1.061	3.4 (2)	0.26 (5)	0.02^c (1)	0.2 (2)	2.43 (4)	4.5 (1)	0.06	0.67	0.15	0.88
Q1.062	3.34 (5)	0.30^b (8)	0.12 (8)	0.7 (5)	3.23 (2)	4.3 (8)	0.17	0.66	0.17	1.00

Unless otherwise noted, H_2O_{melt} and H_2O_{Ap} from NanoSIMS; F_{melt}, Cl_{melt}, and Cl_{Ap} from EPMA; F_{Ap} is an average of EPMA and NanoSIMS data.
Parenthetical values represent 1σ SDOM and are always larger than the 2σ AU.
[a]Value represents 6f SIMS data
[b]H_2O abundance estimated by stoichiometry assuming OH = 1 – F – Cl.
[c]Value represents only NanoSIMS data.

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Table 4: Apatite-melt partition coefficients and exchange coefficients.

Exp. #	D_F	D_{Cl}	D_{OH}	Kd_{Cl-F}	Kd_{OH-F}	Kd_{OH-Cl}
Q1.007	19 (8)	5 (2)	0.24 (7)	0.3 (2)	0.013 (7)	0.05 (2)
Q1.010	10 (2)	2.3 (2)	0.124 (6)	0.22 (5)	0.012 (2)	0.054 (5)
Q1.012	7.8 (8)	1.4 (6)	0.13 (1)	0.18 (8)	0.016 (2)	0.09 (4)
Q1.013	7.1 (7)	1.5 (3)	0.112 (4)	0.21 (5)	0.016 (2)	0.08 (2)
Q1.016	13 (3)	2.7 (5)	0.192 (7)	0.21 (6)	0.015 (3)	0.07 (1)
Q1.017	10 (2)	2.0 (2)	0.167 (7)	0.20 (4)	0.016 (2)	0.082 (8)
Q1.018	12 (2)	2.1 (6)	0.17 (1)	0.17 (6)	0.014 (3)	0.08 (2)
Q1.020	-	4.1 (1)	0.07 (2)	-	-	0.018 (4)
Q1.024	4.4 (5)	1.1 (3)	-	0.24 (7)	-	-
Q1.057[a]	5.5 (6)	1.3 (2)	0.09 (2)	0.25 (4)	0.016 (4)	0.06 (2)
Q1.061	-	1.86 (7)	0.08 (2)	-	-	0.041 (8)
Q1.062[a]	7 (1)	1.3 (2)	0.09 (2)	0.19 (4)	0.014 (3)	0.07 (2)
Averages	10 (4)	2 (1)	0.13 (5)	0.21 (3)	0.014 (2)	0.06 (2)
Hi	19	5	0.24	0.3	0.016	0.09
Lo	4.4	1.1	0.07	0.17	0.012	0.018

Values from Table 3 used to calculate all partition coefficients and exchange coefficients unless otherwise noted.

Parenthetical values represent 1σ SDOM and are always larger than the 2σ AU.

[a]Sample displayed spatial heterogeneity, so D values were computed for individual mineral-melt pairs and subsequently averaged for computation of the exchange Kd's

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