Effect of Fluorine on Near-Liquidus Phase Equilibria of an Fe-Mg Rich Basalt

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Abstract

Volatile species (H_2O, CO_2, F, Cl, etc) have important effects on the formation and crystallization history of basaltic magmas. Here, we have experimentally investigated the effects of F on phase equilibria of Fe-Mg-rich basalt. Our results show that fluorine has large effects on the liquidus temperature and the chemistry of crystallizing minerals. Compared to the F-free system, addition of ~2 wt.% F moves the olivine-pigeonite liquidus point down ~2 kbar and 95 °C (from 12 kbar, 1375 °C to 10 kbar, 1280 °C). With increasing fluorine concentrations, $Kd^{Fe-Mg}_{Mineral-Melt}$ dramatically increases for both pyroxene and olivine, suggesting that fluorine in basaltic magmas complexes primarily with MgO. Complexing with MgO in the melt decreases its MgO activity, and forces the

23   crystallizing minerals to greater Fe/Mg, and so increases $Kd^{Fe-Mg}_{Mineral-Melt}$. Models of basalt

24   generation, where the magma is fluorine-rich, need to include the effect of not only water

25   but fluorine on liquidus depression and minerals crystallizing/melting. Our results

26   suggest that fluorine may significantly aid in the petrogenesis of silica-poor, alkali-rich

27   magmas in the Earth and Mars.

28

29   Keywords: halogens, martian meteorites, alkali basalts, basalt crystallization, phase

30   equilibria, fluorine

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1. **Introduction**

Volatile species (H_2O, CO_2, F, Cl, etc) are important in basalt genesis and mantle melting in arc, plume, ridge, and other planetary tectono-magmatic settings. Previous experimental work has mainly focused on the effects of water and carbon dioxide on liquidus temperature, phase relations, and compositions of basalts produced in these systems (e.g., Danyushevsky, 2001; Dasgupta et al., 2007; Feig et al., 2010; Feig et al., 2006; Gaetani and Grove, 1998; Gerbode and Dasgupta, 2010; Green, 1970; Grove et al., 2002; Grove et al., 2006; Médard and Grove, 2008; Mysen, 1975; Nekvasil et al., 2004). The effects of halogens in general, and those of fluorine in particular, have received far less attention (e.g., Brey et al., 2009; Filiberto and Treiman, 2009a; Filiberto and Treiman, 2009b; Foley et al., 1986). However, melts in planetary interiors can have non-negligible halogen concentrations, and the importance of chlorine and fluorine in basalt petrogenesis has been emphasized in recent literature both for Earth (Aoki et al., 1981; Brey et al., 2009) and Mars (Filiberto and Treiman, 2009a,b). Here, we explore the effects of fluorine on near-liquidus phase equilibria of a basalt.

Fluorine concentrations in terrestrial magmas: Evolved magmas (rhyolites and phonolites) can contain more than 5 wt% F (e.g., Carroll and Webster, 1994; Giordano et al., 2004; Harms and Schmincke, 2000; Webster et al., 1997); basaltic magmas typically contain less F than their evolved counter parts as summarized by Aoki et al. (1981) and Stecher (1998) for continental and oceanic basaltic rocks. They found that the abundance of F typically correlates with that of K_2O for most basaltic magmas, although this correlation breaks down at high K_2O concentrations. In tholeiites, F concentrations range from 30 to 1000 ppm (Aoki et al., 1981; Stecher, 1998; Yoshida et al., 1971); higher

55 primitive fluorine concentrations are seen in alkali rich rocks: nephelinites and

56 kimberlites have concentrations up to 2000 ppm; and some lamproites contain up to

57 20,000 ppm (2 wt%) F (Aoki et al., 1981). This suggests that fluorine may be especially

58 important for alkali-rich basaltic magmas. For example, primitive mantle of the Earth is

59 estimated to have 25 ppm F (McDonough and Sun, 1995), thus with bulk partition

60 coefficient of ~0.08 during mantle melting (Dalou et al., 2012), 0.1 to 2 wt.% partial

61 melts will have F concentration of ~300 ppm (**Figure 1**).

62   *Fluorine concentrations in martian magmas:* Less is known about the fluorine

63 concentrations of martian magmas. Bulk fluorine contents of the martian basalts

64 (meteorites) are similar to those of terrestrial tholeiites (29-41 ppm, Dreibus and Wänke,

65 1985). But based on the F to Ti ratio, martian basalts and the bulk martian mantle are

66 thought to be 2-3 times richer in F (and other halogens) than terrestrial basalts and mantle

67 (Dreibus and Wänke, 1987; Treiman et al., 1986). If the F content of the martian mantle

68 were three times greater than that of the Earth, similar low degree partial melting (as in

69 the example above, 0.1-2 wt. %) should yield magmas with 950 to 750 ppm F (**Figure 1**).

70 Further, alkalic basalts (typically rich in fluorine on Earth) have been suggested to occur,

71 and maybe significant, on Mars (Dunn et al., 2007; McSween et al., 2006; Nekvasil et al.,

72 2007). All of this, and the chemistry of volatile-bearing minerals in martian meteorites

73 (amphiboles and apatite) suggests that fluorine, like chlorine (Filiberto and Treiman,

74 2009a; Filiberto and Treiman, 2009b; Patiño Douce and Roden, 2006; Patiño Douce et

75 al., 2011), may be an important factor controlling basalt genesis in Mars (possibly to the

76 extent of replacing water as the dominant volatile species).

77   *Previous work on fluorine in igneous systems:* Previous studies on fluorine in

78   magmatic systems have mainly focused on the solubility mechanisms of F in

79   aluminosilicate (+/-Na) melt and its effect on melt viscosity (Liu and Nekvasil, 2002; Liu

80   and Tossell, 2003; Mysen et al., 2004; Schaller et al., 1992; Zeng et al., 1999). Nuclear

81   magnetic resonance (NMR) studies of aluminosilicate glasses have shown that fluorine

82   preferentially complexes with Al and possibly Si (Liu and Nekvasil, 2002; Liu and

83   Tossell, 2003; Schaller et al., 1992; Zeng et al., 1999). For Na-aluminosilicate glasses

84   four predominant complexes have been identified: Na-F, Na-Al-F (with Al in 4-fold

85   coordination), Na-Al-F (with Al in 6-fold coordination), and Al-F (with Al in 6-fold

86   coordination) (Mysen et al., 2004; Zeng and Stebbins, 2000). By complexing

87   predominantly with Al in silica-rich magmas, F decreases their viscosity by

88   depolymerizing the melt (Dingwell, 1989; Dingwell and Hess, 1998; Dingwell et al.,

89   1985; Giordano et al., 2004; Zimova and Webb, 2007). This is a similar effect on melt

90   structure and viscosity as dissolved water (e.g., Giordano et al., 2004).

91   Similar to NMR studies, most experiments on phase equilibria in F-bearing

92   magmas have been on granitic or simplified systems (e.g, Dolejs and Baker, 2007a;

93   Dolejs and Baker, 2007b; Foley et al., 1986; Lukkari and Holtz, 2007; Manning, 1981;

94   Scaillet and MacDonald, 2001; Scaillet and MacDonald, 2003; Scaillet and Macdonald,

95   2006; Weidner and Martin, 1987; Xiao-lin et al., 1999; Xiong et al., 2002). Fluorine has

96   dramatic effects on crystallizing phases (e.g, Dolejs and Baker, 2007a; Dolejs and Baker,

97   2007b; Foley et al., 1986; Manning, 1981). At 1 bar, in the Qz-Ab-Or-H_2O system,

98   addition of fluorine shifts the boundary of the quartz-alkali feldspar liquidus field away

99   from the quartz apex; addition of 4 %wt F shifts the minimum melting compositions from

100    $Qz_{37}Ab_{34}Or_{29}$ to $Qz_{15}Ab_{58}Or_{27}$ (Manning, 1981). In the $NaAlSiO_4$-$CaMgSi_2O_6$-SiO_2

101   system, also at 1 bar, fluorine reduces the liquidus temperature and changes the

102   compositions of the liquids produced (Luth, 1988a). For example, the liquid in

103   equilibrium with diopside at 1250° C in the F-bearing experiments is $Di_{56}Ab_{44}$ compared

104   with $Di_{33}Ab_{67}$ in the F-free experiments. The results suggests that F is complexing with

105   Ca and Mg in the liquid in a $NaAlSiO_4$-$CaMgSi_2O_6$-SiO_2 simplified system (Luth,

106   1988a). At higher pressure (28 kbar) in the $KAlSiO_4$-Mg_2SiO_4-SiO_2 system, fluorine

107   expands the field of enstatite stability with respect to that of forsterite by complexing

108   with Mg, K, and Al in the melt (Foley et al., 1986).

109   However, the solution mechanism for F in natural basaltic melts maybe more

110   complicated than in the simple systems. Recent NMR work has shown that a significant

111   proportion (>30%) of dissolved fluorine complexes with Mg (Kiczenski et al., 2004);

112   while experimental results combined with NMR and Raman spectroscopy studies have

113   suggested that F may complex with Ca (Luth, 1988b; Zeng and Stebbins, 2000). Fluorine

114   complexation with cations other than Al will not only lower the liquidus and affect the

115   viscosity, but also change the phase relations of crystallizing magmas. However, these

116   complexations are presumably bulk composition dependent.

117   In order to understand how fluorine behaves in a Si-poor, Mg, Fe-rich basaltic

118   system we have experimentally determined near liquidus phase relations of a synthetic

119   basalt doped with F. The results of these experiments can be directly compared with our

120   previous work on the same synthetic basalt conducted nominally volatile-free (Filiberto

121   et al., 2008) and doped with chlorine (Filiberto and Treiman, 2009a).

122   **2. Methods**

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123   *2.2 Experimental approach*

124   *2.2.1 Starting composition*

125   We have conducted nominally anhydrous piston cylinder experiments on an Fe-

126   rich model basalt composition synthetic starting material (**Table 1**). The choice of the

127   basalt composition was motivated by the fact that the same composition had previously

128   been used to study the effect of chlorine on near-liquidus phase equilibria (Filiberto and

129   Treiman, 2009a). The synthetic starting material was made from reagent grade oxides and

130   carbonates ground together under acetone in an automatic mortar and pestle for 15

131   minutes to ensure homogeneity (Filiberto et al., 2008). This powdered mix was melted in

132   an iron-saturated Pt crucible in a muffle furnace at 1500°C under air, quenched to a glass,

133   and reground for 15 minutes. The same powder and experimental techniques from our

134   previous work was used for this study thus allowing comparisons between current and

135   past studies (Filiberto and Treiman, 2009a; Filiberto et al., 2008); however, 2.1 wt%

136   fluorine was added to the starting mix as AgF_2.

137   *2.2.2 Experimental Technique*

138   High pressure experiments were conducted in a non-end-loaded QuickPress[©]

139   piston-cylinder apparatus at Johnson Space Center High Pressure Laboratory. Standard

140   methods were employed. Starting materials were held in graphite sample capsules, which

141   were installed in straight graphite furnaces, insulated with $BaCO_3$ sleeves and crushable

142   MgO spacers (Filiberto et al., 2008). Before each run, the synthetic powder plus AgF_2

143   was loaded into a graphite capsule and stored for at least 12 hours in an oven at 150 °C in

144   order to drive off absorbed H_2O. Temperature was measured using a W5%Re/W25%Re

145   thermocouple placed in an indentation in the graphite sample capsule and range from

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146 above the liquidus to just below the liquidus. Pressure in the experiments was measured

147 on a Heise gauge and corrected for friction by -0.3 kbar based on the location of the

148 diopside melting curve (Filiberto et al., 2008). Pressures in these experiments ranged

149 from 5.7 kbar to 14.7 kbar and friction corrected pressures are reported (**Table 2**). The

150 oxygen fugacity, $f\mathrm{O}_2$, of our experiments has not been directly measured. However, the

151 graphite capsules constrain the $f\mathrm{O}_2$ of the assemblage, at elevated pressures, to ~1-2 log

152 units below the FMQ oxygen buffer (Frost and Wood, 1995; Médard et al., 2008).

153   Experiments were conducted using a piston-out procedure – the experiment was

154 pressurized cold to 2 kbar above the experimental pressure, brought to the desired

155 temperature, and then brought down to the final pressure. Samples were kept for 30

156 minutes above the liquidus temperature, rapidly cooled to the final crystallization

157 temperature where they remained for at least one hour, and finally quenched at pressure.

158 This technique was employed in order to mimic natural magmatic conditions where

159 crystals form directly from a molten liquid, rather than synthesis techniques of going

160 directly to the crystallization temperature where crystals form from the powder.

161   In order to determine mineral abundances and verify that the experiments were

162 chemically closed systems, mass balance calculations were conducted using the average

163 starting bulk composition (**Table 1**) and the compositions of the crystallized phases and

164 residual glass (**Table 3**), using the least square computations of the IgPet software

165 package (Carr, 2000).

166

167 *2.3 Chemical Analyses*

168 *2.3.1 Major Element Analyses*

169   Experimental run products, glasses and crystalline phases, were analyzed for

170   major and minor element abundances using the Cameca SX-100 electron microprobe at

171   the NASA Johnson Space Center. Analytical conditions were 15 kV accelerating

172   potential and focused electron beam of 20 nA current for minerals, and 15 kV electron

173   accelerating potential and a defocused 5 µm electron beam of 10 nA current for quenched

174   glasses. Analytical standards were synthetic oxides and minerals for minerals and natural

175   and synthetic glasses for glasses.

176   *2.3.2 F analysis*

177   Glass in experimental run products was analyzed for dissolved F using a Cameca

178   IMS 1280 ion probe at the Woods Hole Oceanographic Institution. Analytical standards

179   were well characterized basaltic glasses. Experimental and standard samples were

180   mounted in indium and gold-coated for analysis. The $^{19}F/^{30}Si$ ratio was measured by the

181   ion probe, and F abundances were calculated using Si abundances measured by EMP

182   (Helo et al., 2011). Replicate analyses were done on each sample to gauge precision, and

183   an analytical uncertainty of ~10% of the measured abundance of F reflects uncertainties

184   from counting statistics, and standard compositions (Table 2). Because the basaltic

185   standards had lower F concentrations than our experimental sample glasses, a linear

186   extrapolation of the calibration curve was adopted (e.g., Helo et al., 2011).

187   *2.3.3 H_2O and CO_2 analyses*

188   Because small amounts of dissolved water can have large effects on basalt

189   liquidus temperatures (e.g., Almeev et al., 2007; Danyushevsky, 2001; Médard and

190   Grove, 2008) and because performing completely dry but other volatile-bearing

191   experiments is practically impossible, micro-FTIR analyses were conducted to determine

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192   the water contamination of the experimental glasses. Samples were analyzed using a

193   Nicolet Contiuum FTIR in the geochemistry laboratory at Rice University. Total

194   dissolved water contents were determined on doubly polished glass wafers from the

195   intensity of the broad band at 3570 cm^{-1}. Each doubly polished wafer was measured for

196   thickness using a Mitutoyo electronic indicator with a 0.015″ carbine needlepoint tip. For

197   each sample 512 scans were used to acquire each IR spectrum. Density of the glass was

198   calculated from the bulk composition using the procedure of Dixon et al. (1995). A molar

199   absorptivity value of 65 (L/mol-cm) was applied (King et al., 2004). Total water

200   concentrations are reported in **Table 3**. They were calculated using the total H_2O

201   vibration band at 3550 cm^{-1} and the procedures of Dixon et al. (1995) and King et al.

202   (2004).

203   Because the starting material for our experiments was not reduced prior to the

204   high-pressure experiments, our experimental glasses were expected to suffer

205   contamination by small amount of CO_2, owing to reduction of Fe^{3+} to Fe^{2+} by reaction

206   with graphite. Micro-FTIR analysis was used to determine the dissolved CO_3^{2-} contents

207   of our experimental glasses. For each sample 512 scans were used to acquire each IR

208   spectrum. Density was of the glass was calculated from the bulk composition using the

209   procedure of Dixon et al. (1995). Total CO_3^{2-} concentrations were calculated using molar

210   absorptivity values of 284 and 281 (L/mol-cm) for the carbonate ion vibration band at

211   1515 and 1430 cm^{-1} respectively (King et al., 2004) and the procedures of Dixon et al.

212   (1995) and King et al. (2004).

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214

215   **3. Results**

216   The FTIR spectra, for representative sample Hf18, shows peaks for both dissolved

217   H_2O and CO_3^{2-} (**Figure 2**) representing volatile contamination in our experiments. The

218   fluorine-bearing experiments contain an average of 0.34 ± 0.07 wt. % H_2O. Selected

219   samples analyzed for dissolved carbon show that the CO_2 contaminations are more

220   scattered and give approximate average dissolved CO_2 contents of 0.53 ± 0.28 wt. %

221   (**Table 3**).

222   **Figure 3** shows the near-liquidus phase diagram for the F-bearing basaltic

223   composition in *P-T* space. Above 12 kbar, pigeonite is the liquidus phase; below 10 kbar,

224   olivine is on the liquidus. At approximately 10 kbar and 1265 °C, the bulk composition

225   with ~2 wt.% fluorine is multiply saturated with both olivine (Fo_{67}) and pigeonite

226   ($En_{64}Wo_7Fs_{29}$). In the *P-T* range of our experiments, the olivine composition spans the

227   range from Fo_{67} near the liquidus to Fo_{58} at lower temperatures. The pyroxenes are all

228   pigeonite, and range from $En_{67}Wo_7Fs_{26}$ near the liquidus through $En_{57}Wo_{12}Fs_{30}$ at lower

229   temperatures.

230

231   **4. Discussion**

232   *4.1 Liquidus depression effect of Fluorine*

233   Liquidus temperatures (at a given pressure) determined in this study for the F-

234   bearing composition, are systematically lower than those of the F-free composition

235   investigated earlier (Filiberto et al., 2008). However, quantification of the basalt liquidus

236   depression effect of fluorine requires comparing all the data at the same background

237   volatile content level. The fluorine-bearing experiments in our study contain more water

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238 contamination (~0.34 wt% H_2O; **Table 3**) than the previous fluorine free experiments

239 (~0.1 wt% H_2O; Filiberto et al. 2008) and water is known to depress the liquidus

240 temperature (e.g., Médard and Grove, 2008); therefore, in order to make a direct

241 comparison, temperatures of all experiments need to be corrected to a water-free system,

242 i.e.,

243 $$\Delta T \, (\,°C)^F = \Delta T \, (\,°C)^{Total} - \Delta T \, (\,°C)^{H_2O} \qquad (1)$$

244 where $\Delta T \, (\,°C)^F$ is the liquidus temperature depression caused by fluorine only, ΔT

245 $(°C)^{H_2O}$ is the liquidus temperature depression caused by water only and $\Delta T \, (\,°C)^{Total}$ is

246 the total liquidus temperature depression observed in our experiments. In equation (1), we

247 assume that the liquidus depression effects of water and fluorine are additive. To

248 calculate $\Delta T \, (\,°C)^{H_2O}$ we use the liquidus depression equation from Médard and Grove

249 (2008)

250 $$\Delta T \, (\,°C)^{H_2O} = 40.4 \, (C_{melt}^{H2O}) - 2.97 \, (C_{melt}^{H2O})^2 + 0.0761 \, (C_{melt}^{H2O})^3] \qquad (2)$$

251 and add the calculated $\Delta T \, (\,°C)^{H_2O}$ to all of our experimental temperatures. Uncorrected

252 and corrected temperatures (T^*) are reported in **Tables 2** but all temperatures used in

253 **Figures 4-7** are corrected for dissolved water and hence reflect the estimated

254 temperatures of the experimental assemblages if no water was present in the experiments.

255   No correction has been applied to account for the small amount of dissolved CO_2

256 because it likely has no discernable effect on the liquidus temperature of our experiments.

257 Brey and Green (1977; 1976) estimated the effect of dissolved CO_2 on the high pressure

258 liquidus temperature of olivine melilitite. Their study indicates that ~0.5 wt% dissolved

259 CO_2 (as carbonate) at 3 GPa lowers the liquidus of olivine melilitite, an extremely silica-

260 undersaturated magma, by less than 10-15 °C. The effect of CO_2 at lower pressures (this

261 study) and for more silica-rich basalt compositions will be even less pronounced (<< 10

262 °C).

263   We assume that the effects of different volatiles, i.e., H_2O and halogens on

264 liquidus depression are additive (equation 1). In order to test this assumption, we

265 calculated the expected liquidus depression for basalt from the study of McCubbin et al.

266 (2008). The basalt composition from the study of McCubbin et al. (2008) is similar to the

267 bulk composition from our experiments (this work, Filiberto and Treiman, 2009a;

268 Filiberto et al., 2008) but with two important differences – (1) their experiments were

269 doped with H_2O, Cl, and F and (2) their bulk composition contained Cr, therefore, had

270 chromite as the liquidus phases. Because our experiments were conducted Cr-free, we

271 ignored possible effect of chromite and considered the Ol-Pyx liquidus only. In their

272 study, experiments were conducted at 9.3 kbar with two different bulk compositions – (1)

273 0.07 wt% H_2O, 0.56 wt% F, and 0.15 wt% Cl and (2) 1.67 wt% H_2O, 0.55 wt% F, and

274 0.21 wt% Cl, respectively (McCubbin et al., 2008). For the effect of H_2O on the liquidus

275 depression we use equation 2 from Médard and Grove (2008), for the effect of F and Cl

276 on liquidus depression we use the results from our experiments (equation 3 below). For

277 bulk composition 1, starting from the volatile-free solidus of Filiberto et al. (2008), we

278 calculate an ol-opx liquidus temperature of 1300 °C at 9.3 kbar whereas the actual

279 experimental results have an ol-opx liquidus temperature of 1260 +/-10 °C at 9.3 kbar

280 (McCubbin et al., 2008). Similarly, for bulk composition 2, the actual experimental

281 results have an ol-opx liquidus temperature of 1225 +/- 25 °C (McCubbin et al., 2008)

282 whereas we estimated a temperature of 1240 °C. This shows the validity of the

283 assumption that basalt liquidus depression caused by a mixed halogen-water can be

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284   within error approximated by the addition of the effect of individual species. The good

285   reproduction of the McCubbin et al. (2008) liquidus suggests that at least for similar bulk

286   and volatile composition this approach may be reasonable.

287   **Figure 4** compares the pressure-temperature phase relations for the F-bearing

288   experiments and the F-free experiments (Filiberto et al. 2008) after their nominal

289   temperatures have been corrected for dissolved water. It is apparent from **Figure 4** that

290   fluorine has a significant and large effect on the liquidus position and phase boundaries in

291   basaltic system. Addition of ~2 wt.% F moves the olivine-pigeonite liquidus point down

292   ~2 kbar and 95 °C (from 12 kbar and 1375 °C to 10 kbar and 1280 °C) by expanding the

293   stability field of pigeonite to lower pressure compared to the F-free experiments. We note

294   that although we feel confident about correcting for the variable amount of water for the

295   basalt liquidus when olivine is the sole liquidus phase, such correction for higher pressure

296   experiments, i.e., with pigeonite as the liquidus phase, is less certain. This is because the

297   liquidus depression effect of water on the liquidus of pigeonite is not constrained for

298   composition similar to that explored in our study.

299

300   *4.2 Fluorine Complexation in the Melt and Compositions of Crystallizing Phases*

301   In order to constrain how fluorine is complexing in the melt, we can investigate

302   the effect of dissolved fluorine on Fe-Mg partitioning between minerals and melt

303   ($Kd_{Mineral-Melt}^{Fe-Mg}$ = [$X_{FeO}^{(ol, pig)}X_{MgO}^{L}$]/[$X_{MgO}^{(ol,pig)}X_{FeO}^{L}$]). **Figure 5** shows $Kd_{Mineral-Melt}^{Fe-Mg}$ for

304   both olivine and pyroxene compared with the wt.% fluorine in the melt as analyzed by

305   SIMS. With increasing fluorine concentrations, $Kd_{Mineral-Melt}^{Fe-Mg}$ dramatically increases for

306   both pyroxene and olivine, suggesting that fluorine in the basaltic magma is complexing

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307   with MgO over FeO in the melt. Complexing with MgO in the melt will decrease the

308   MgO activity in the melt and force the minerals crystallizing to be more ferroan (higher

309   Fe/Mg) than they would be without fluorine in the melt. Our results are thus consistent

310   with NMR studies, which suggest the presence of Mg-F complexes in fluorine bearing

311   aluminosilicate glasses (Kiczenski et al., 2004). However, the nature of the F-cation

312   complexes is likely highly compositionally dependent (Liu and Nekvasil, 2002; Liu and

313   Tossell, 2003; Luth, 1988b; Schaller et al., 1992; Zeng et al., 1999; Zeng and Stebbins,

314   2000). Therefore, the effect of fluorine on liquidus depression and mineral crystallization

315   will depend on the melt composition and we caution the readers against applying our

316   liquidus depression parameterization to other melt compositions.

317   *4.3 Fluorine Solubility*

318   The results here can also help to constrain our understanding of fluorine solubility

319   in basaltic magmas. There is limited experimental data for fluorine solubility in magmas

320   (for a review see Carroll and Webster, 1994). What experimental data there is for Si-rich

321   magmas is mainly at low pressure and low temperature (Dolejs and Baker, 2007a; Dolejs

322   and Baker, 2007b; Mysen et al., 2004; Scaillet and Macdonald, 2004; Webster, 1990).

323   For example, $NaAlSi_3O_8$ magma compositions can contain up to ~20 wt% F at 15 Kbar,

324   Ca-poor peralkaline rhyolitic melts can contain up to 4.28 wt% at 1 bar, and rhyolitic

325   magma at pressures from 0.5-5 kbar can contain up to 8.5 wt% F (for a review see,

326   Carroll and Webster, 1994; Scaillet and Macdonald, 2004; Webster, 1990). In natural

327   carbonatitic melts, F content of up to 16 wt. % have been reported and in carbonated

328   silicate melts of kimberlitic/melilititc affinity, F content of as much as 13 wt.% have been

329   measured (Brey et al., 2009). Therefore, F solubility is likely compositionally dependent

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330 and there is currently no experimental solubility data on natural basaltic magmas at

331 pressure. The results here present constraints on the lower solubility limit of F in Fe-Mg-

332 rich basaltic magmas at 5.7-11.7 kbar pressure. Because the magmas are not in

333 equilibrium with fluorite, these results are only a minimum for the solubility. The glass in

334 these experiments contain up to 2.89 wt. % suggesting that the F solubility in basaltic

335 magmas are higher than this value.

336 *4.4 Comparison to the effects of chlorine*

337   Experiments have been previously conducted on the same bulk composition used

338 in this study to investigate the effect of chlorine on near-liquidus equilibria (Filiberto and

339 Treiman, 2009a). Therefore, we can directly compare the effect of fluorine and chlorine

340 on liquidus depression and $Kd^{Fe-Mg}_{Mineral-Melt}$ on the same bulk composition. **Figure 6** shows

341 the effect of dissolved volatile contents (Cl and F) on liquidus depression (a) and

342 $Kd^{Fe-Mg}_{Mineral-Melt}$ (b). These results show that for the pressures, temperatures, and

343 compositions studied, fluorine and chlorine have similar effects on liquidus depression

344 and a single power curve can be fit through the data to explain both data sets (equation 3).

345

346        $\Delta T \,(°C) = 46.737(C_{melt}^{\text{F or Cl}} \text{ in wt\%})^{0.6263}$ (3)

347

348 However, fluorine and chlorine have opposite effects on $Kd^{Fe-Mg}_{Mineral-Melt}$. Fluorine increases

349 $Kd^{Fe-Mg}_{Mineral-Melt}$ because it complexes mainly with Mg whereas chlorine decreases

350 $Kd^{Fe-Mg}_{Mineral-Melt}$ because it complexes mainly with Fe (Filiberto and Treiman, 2009a).

351 Because F and Cl likely form different ion-complexes in the melt, a single power curve

352 fitting for both data sets in Figure 6a is surprising and likely coincidental.

353

354 *4.5 Comparison to the effects of water*

355   In order to compare these results to the effect of water, we rely on experiments

356 and models of the effect of water on liquidus depression conducted on varying basaltic

357 bulk compositions over a range of pressures (0.1-10 kbar), temperatures (1350-1130 °C),

358 water contents (0-11.5 wt.%), and approaches (Almeev et al., 2007; Ghiorso et al., 2002;

359 Katz et al., 2003; Médard and Grove, 2008). **Figure 6** shows the effect of volatile

360 contents (H_2O, Cl, and F) on ΔT (°C), the depression of the liquidus temperature. It

361 appears that the effect of increasing H_2O, Cl and F on basalt liquidus depression can be

362 parameterized with similar function when compared on a weight percent basis. While

363 analyzing and reporting Cl, F, and H_2O in weight percent basis are the routine

364 geochemical practice, to compare the freezing point depression effect of F, Cl and H_2O

365 on a more thermodynamically rigorous basis, it is more desirable to compare liquidus

366 depression based on the atomic fraction of F, Cl and H. On an atomic fraction basis, F

367 and Cl are actually 2-3 times more efficient at liquidus depression than H (**Figure 7**).

368   The effects of dissolved Cl, F, and H_2O on $Kd_{Mineral-Melt}^{Fe-Mg}$ are rather dissimilar which

369 suggests that these species have different solution mechanisms, i.e. are sited differently in

370 silicate magmas. Dissolved F increases $Kd_{Mineral-Melt}^{Fe-Mg}$, dissolved Cl decreases $Kd_{Mineral-Melt}^{Fe-Mg}$,

371 and dissolved H_2O has no discernible effect on $Kd_{Mineral-Melt}^{Fe-Mg}$ (Figure 6, Filiberto and

372 Treiman, 2009a; Gaetani and Grove, 1998; Médard and Grove, 2008; Whitaker et al.,

373 2008). This is consistent with complexation of F and Cl with divalent 'network-

17

374 modifying' cations while H_2O does not complex with 'network-modifying' cations at all

375 but bonds dominantly with Al (e.g., Burnham and Davis, 1974; Giordano et al., 2004).

376

5. Implications

378   Fluorine has a large effect on liquidus depression of basalts and the chemistry of

379 crystallizing minerals; these effects will be especially important for low-degree partial

380 melts, which may start with relatively high abundances of fluorine. If we extrapolate

381 these experimental results to alkalic magma compositions (terrestrial or martian) with up

382 to 5000 ppm F (likely derived from a F-rich source and/or as a result of very low-extent

383 of melting; **Figure 1**), liquidus temperature can be depressed by an extra ~30°C which is

384 not accounted for by dissolved water alone. If this can be further extrapolated to mantle

385 temperatures, a ~30 °C shift in temperature, with a shift in ol:pyx stability field as well,

386 enables alkalic melts to be produced at lower temperatures. This suggests that fluorine

387 may significantly aid in the petrogenesis of silica-poor, alkali-rich magmas in the Earth

388 and Mars. Because martian magmas can be more F-rich, it is perhaps more appropriate to

389 further comment on the effect of fluorine on the multiple saturation point of olivine-opx-

390 melt in martian igneous system. With average F content of ~5000 ppm, our present study

391 suggests that the mantle potential temperatures relevant for Mars can be as low as 1335-

392 1495 °C, distinctly lower than a recent estimate based on olivine-melt Mg-exchange

393 thermometry (Filiberto and Dasgupta, 2011).

399

Figure Captions:

Figure 1. Plausible concentration of fluorine in near-solidus partial melts of garnet peridotite as a function of melting degree for Earth (bulk F concentration from McDonough and Sun, 1995) and Mars (assuming that martian mantle contains three times F than that in the Earth's mantle). Bulk partition coefficient, D_F (peridotite-basalt), of 0.0785 is used based on olivine-melt D_F of 0.1164, opx-melt D_F of 0.0158, cpx-melt D_F of 0.0428, and garnet-melt D_F of 0.0123 from the study of Dalou et al. (2012). Garnet-melt, opx-melt, and cpx-melt D_F values are taken from the experiment C4p#25kb and that of olivine-melt D_F from the experiment CC01#8kb4 of Dalou et al. (2012). Peridotite mineral modes used for the calculations are 60% olivine, 20% opx, and 10% each of cpx and garnet. Because of the uncertainties in D_F (mineral-melt) for Martian mantle phase compositions, melt compositional trends for $D_F = 0$ are also shown for reference.

Figure 2. Representative FTIR spectrum of sample Hf18 showing distinct peaks for total H_2O and CO_3^{2-} peaks.

Figure 3. Experimentally determined near-liquidus phase relations for synthetic basaltic composition with 2.17 wt% F.

Figure 4. Experimentally determined near-liquidus phase relations for synthetic basaltic composition with 2.17 wt% F (black symbols) compared with nominally volatile-free (gray symbols) experiments (Filiberto et al., 2008). Both data sets are corrected for dissolved water in experimental glasses.

Figure 5. $Kd_{Mineral-Melt}^{Fe-Mg}$ as a function of F (wt%) for olivine-bearing (black circles) and pigenoite-bearing (open circles) experimental charges. Black lines represent linear

422   regressions through the data with $R^2 = 0.8890$ for olivine and 0.9076 for pyroxene bearing

423   experiments.

424   **Figure 6. (a)** Calculated liquidus depression ($\Delta T°$ in C) as a function of volatile element

425   (F or Cl) content in the melt (wt%) for fluorine-bearing experiments (this study; circles)

426   and chlorine-bearing experiments (squares) (Filiberto and Treiman, 2009a), compared

427   with the calculated olivine-liquidus depression from previous studies (Almeev et al.,

428   2007; Ghiorso et al., 2002; Katz et al., 2003; Médard and Grove, 2008). Experiments

429   containing only liquid are shown by open symbols and those containing crystals (either

430   olivine or pyroxene or both) are shown by closed symbols. All curves are fit through the

431   origin. One sigma uncertainties in volatile concentrations are shown with error bars.

432   Where error bars are not shown for chlorine concentrations, the 1σ uncertainty is smaller

433   than the size of the symbol. **(b)** $Kd^{Fe-Mg}_{Mineral-Melt}$ as a function of volatile content (F, Cl, or

434   H_2O) in the melt. Closed symbols represent olivine-liquidus experiments and open

435   symbols represent pyroxene-liquidus experiments. Data for water-bearing experiments

436   (diamonds) from: Gaetani and Grove (1998, gray); Médard and Grove (2008, black);

437   Whitaker et al. (2008, white), regression shown for all data (black solid line).

438   **Figure 7.** Calculated liquidus depression (ΔT in °C) as a function of the atomic fraction

439   of volatile species (F, Cl, H) in the melt for containing fluorine-bearing experiments (this

440   study; circles) compared with previous chlorine-bearing experiments (squares) (Filiberto

441   and Treiman, 2009a) and H-bearing olivine-liquidus experiments (triangles; Almeev et al.

442   2007) and (diamonds; Médard and Grove 2008). Experiments containing only liquid are

443   shown by open symbols and those containing crystals (either olivine or pyroxene or both)

444   are shown by closed symbols. All curves are fit through the origin.

445

446   **References**

447   Almeev, R.R., Holtz, F., Koepke, J., Parat, F., Botcharnikov, R.E., 2007. The effect of
448   H_2O on olivine crystallization in MORB: Experimental calibration at 200 MPa.
449   American Mineralogist, 92: 670-674.

450   Aoki, K., Ishiwaka, K., Kanisawa, S., 1981. Fluorine geochemistry of basaltic rocks from
451   continental and oceanic regions and petrogenetic application. Contributions to
452   Mineralogy and Petrology, 76(1): 53-59.

453   Brey, G., Green, D.H., 1977. Systematic study of liquidas phase relations in olivine
454   melilitite +H2O +CO2 at high pressures and petrogenesis of an olivine melilitite
455   magma. Contributions to Mineralogy and Petrology, 61(2): 141-162.

456   Brey, G.P., Bulatov, V.K., Girnis, A.V., 2009. Influence of water and fluorine on melting
457   of carbonated peridotite at 6 and 10 GPa. Lithos, 112(Supplement 1): 249-259.

458   Brey, G.P., Green, D.H., 1976. Solubility of CO2 in olivine melilitite at high pressures
459   and role of CO2 in the earth's upper mantle. Contributions to Mineralogy and
460   Petrology, 55(2): 217-230.

461   Burnham, C.W., Davis, F.A., 1974. The role of H_2O in silicate melts II: Thermodynamic
462   and phase relations in the system $NaAlSi_3O_8$-H_2O to 10 kilobars, 700° to 1000^oC.
463   American Journal of Science, 274: 902-940.

464   Carr, M.J., 2000. Igpet for Windows. Terra Softa Inc., Somerset, N.J.

465   Carroll, M.R., Webster, J.D., 1994. Solubilities of sulfur, noble gases, nitrogen, chlorine,
466   and fluorine in magmas. In: Carroll, M.R., Webster, J.D. (Eds.), Volatiles in
467   Magmas. Reviews in Mineralogy. Mineralogical Society of America,
468   Washington, D.C., pp. 231-279.

469   Dalou, C., Koga, K., Shimizu, N., Boulon, J., Devidal, J.-L., 2012. Experimental
470   determination of F and Cl partitioning between lherzolite and basaltic melt.
471   Contributions to Mineralogy and Petrology: 10.1007/s00410-011-0688-2.

472   Danyushevsky, L.V., 2001. The effect of small amounts of H_2O on crystallisation of mid-
473   ocean ridge and backarc basin magmas. Journal of Volcanology and Geothermal
474   Research, 110(3): 265-280.

475   Dasgupta, R., Hirschmann, M., Smith, N., 2007. Partial melting experiments of peridotite
476   + CO2 at 3 GPa and genesis of alkalic ocean island basalts. Journal of Petrology,
477   48(11): 2093-2124.

478   Dingwell, D.B., 1989. Effect of fluorine on the viscosity of diopside liquid. American
479   Mineralogist, 74(3-4): 333-338.

480   Dingwell, D.B., Hess, K.U., 1998. Melt viscosities in the system Na-Fe-Si-OF-Cl;
481   contrasting effects of F and Cl in alkaline melts. American Mineralogist, 83(9-
482   10): 1016-1021.

483   Dingwell, D.B., Scarfe, C.M., Cronin, D.J., 1985. The effect of fluorine on viscosities in
484   the system $Na_2O-Al_2O_3 SiO_2$; implications for phonolites, trachytes and rhyolites.
485   American Mineralogist, 70(1-2): 80-87.

486   Dixon, J.E., Stolper, E.M., Holloway, J.R., 1995. An Experimental Study of Water and
487   Carbon Dioxide Solubilities in Mid-Ocean Ridge Basaltic Liquids. Journal of
488   Petrology, 36(6): 1607-1631.

489   Dolejs, D., Baker, D.R., 2007a. Liquidus Equilibria in the System $K_2O-Na_2O-Al_2O_3$-
490         $SiO_2-F_2O^{-1}-H_2O$ to 100 MPa: I. Silicate-Fluoride Liquid Immiscibility in
491   Anhydrous Systems. Journal of Petrology, 48(4): 785-806.

492   Dolejs, D., Baker, D.R., 2007b. Liquidus Equilibria in the System $K_2O-Na_2O-Al_2O_3$-
493         $SiO_2-F_2O^{-1}-H_2O$ to 100 MPa: II. Differentiation Paths of Fluorosilicic Magmas in
494   Hydrous Systems. Journal of Petrology, 48(4): 807-828.

495   Dreibus, G., Wänke, H., 1985. Mars, a Volatile-Rich Planet. Meteoritics, 20(2): 367-381.

496   Dreibus, G., Wänke, H., 1987. Volatiles on Earth and Mars - a Comparison. Icarus,
497   71(2): 225-240.

498   Dunn, T.L., McSween, H.Y., Jr., Christensen, P.R., 2007. Thermal emission spectra of
499   terrestrial alkaline volcanic rocks: Applications to Martian remote sensing. J.
500   Geophys. Res., 112(E05001): doi:10.1029/2006JE002766.

501   Feig, S., Koepke, J., Snow, J., 2010. Effect of oxygen fugacity and water on phase
502   equilibria of a hydrous tholeiitic basalt. Contributions to Mineralogy and
503   Petrology, 160(4): 551-568.

504   Feig, S.T., Koepke, J., Snow, J.E., 2006. Effect of water on tholeiitic basalt phase
505   equilibria: an experimental study under oxidizing conditions. Contributions to
506   Mineralogy and Petrology, 152(5): 611-638.

507   Filiberto, J., Dasgupta, R., 2011. Fe^{2+}-Mg partitioning between olivine and basaltic melts:
508   Applications to genesis of olivine-phyric shergottites and conditions of melting in
509   the Martian interior. Earth and Planetary Science Letters, 304(3-4): 527-537.

510   Filiberto, J., Treiman, A.H., 2009a. The effect of chlorine on the liquidus of basalt: First
511   results and implications for basalt genesis on Mars and Earth. Chemical Geology,
512   263(1-4): 60-68.

513   Filiberto, J., Treiman, A.H., 2009b. Martian magmas contained abundant chlorine, but
514   little water. Geology, 37(12): 1087-1090.

Filiberto, J., Treiman, A.H., Le, L., 2008. Crystallization experiments on a Gusev Adirondack basalt composition. Meteoritics & Planetary Science, 43(7): 1137-1146.

Foley, S.F., Taylor, W.R., Green, D.H., 1986. The effect of fluorine on phase relationships in the system KAlSiO4-Mg2SiO4-SiO2 at 28 kbar and the solution mechanism of fluorine in silicate melts. Contributions to Mineralogy and Petrology, 93(1): 46-55.

Frost, D., Wood, B., 1995. Experimental measurements of the graphite C−O equilibrium and CO_2 fugacities at high temperature and pressure. Contributions to Mineralogy and Petrology, 121(3): 303-308.

Gaetani, G.A., Grove, T.L., 1998. The influence of water on melting of mantle peridotite. Contributions to Mineralogy and Petrology, 131(4): 323-346.

Gerbode, C., Dasgupta, R., 2010. Carbonate-fluxed Melting of MORB-like Pyroxenite at 2·9 GPa and Genesis 51(10): 2067-2088.

Ghiorso, M.S., Hirschmann, M.M., Reiners, P.W., Kress, V.C., 2002. The pMELTS: A revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. Geochemistry Geophysics Geosystems, 3: 1030, doi:10.1029/2001GC000217

Giordano, D., Romano, C., Dingwell, D.B., Poe, B., Behrens, H., 2004. The combined effects of water and fluorine on the viscosity of silicic magmas. Geochimica et Cosmochimica Acta, 68(24): 5159-5168.

Green, D.H., 1970. A review of experimental evidence on the origin of basaltic and nephelinitic magmas. Physics of The Earth and Planetary Interiors, 3: 221-235.

Grove, T., Parman, S., Bowring, S., Price, R., Baker, M., 2002. The role of an H_2O-rich fluid component in the generation of primitive basaltic andesites and andesites from the Mt. Shasta region, N California. Contributions to Mineralogy and Petrology, 142(4): 375-396.

Grove, T.L., Chatterjee, N., Parman, S.W., Médard, E., 2006. The influence of H2O on mantle wedge melting. Earth and Planetary Science Letters, 249(1-2): 74-89.

Harms, E., Schmincke, H.U., 2000. Volatile composition of the phonolitic Laacher See magma (12900 yr BP): implications for syn-eruptive degassing of S, F, Cl, and H2O. Contributions to Mineralogy and Petrology, 138: 84-98.

Helo, C., Longpre, M.-A., Shimizu, N., Clague, D.A., Stix, J., 2011. Explosive eruptions at mid-ocean ridges driven by CO2-rich magmas. Nature Geosci, 4(4): 260-263.

550 Katz, R.F., Spiegelman, M., Langmuir, C.H., 2003. A new parameterization of hydrous
551   mantle melting Geochemistry Geophysics Geosystems, 4(9): 1073; DOI
552   10.1029/2002GC000433

553 Kiczenski, T.J., Du, L.-S., Stebbins, J.F., 2004. F-19 NMR study of the ordering of high
554   field strength cations at fluoride sites in silicate and aluminosilicate glasses.
555   Journal of Non-Crystalline Solids, 337(2): 142-149.

556 King, P.L., McMillian, P.F., Moore, G.M., 2004. INFRARED SPECTROSCOPY OF
557   SILICATE GLASSES WITH APPLICATION TO NATURAL SYSTEMS. In:
558   King, P.L., Ramsey, M.S., Swayze, G.A. (Eds.), Infrared Spectroscopy in
559   Geochemistry, Exploration Geochemistry and Remote Sensing. Mineralogical
560   Association of Canada, Short Course Series, pp. 93-133.

561 Liu, Y., Nekvasil, H., 2002. Si-F bonding in aluminosilicate glasses: Inferences from ab
562   initio NMR calculations. American Mineralogist, 87(2-3): 339-346.

563 Liu, Y., Tossell, J., 2003. Possible Al−F Bonding Environment in Fluorine-Bearing
564   Sodium Aluminosilicate Glasses: From Calculatio
565   Journal of Physical Chemistry B, 107(41): 11280-11289.

566 Lukkari, S., Holtz, F., 2007. Phase relations of a F-enriched peraluminous granite: an
567   experimental study of the Kymi topaz granite stock, southern Finland.
568   Contributions to Mineralogy and Petrology, 153(3): 273-288.

569 Luth, R.W., 1988a. Effects of F on phase equilibria and liquid structure in the system
570      $NaAlSiO_4$-$CaMgSi_2O_6$-SiO_2. American Mineralogist, 73(3-4): 306-312.

571 Luth, R.W., 1988b. Raman spectroscopic study of the solubility mechanisms of F in
572   glasses in the system CaO-CaF-SiO. American Mineralogist, 73: 297-305.

573 Mandeville, C.W. et al., 2002. Determination of molar absorptivities in infrared
574   absorption bands of H_2O in andesitic glasses. Am. Mineralogist, 87: 813-821.

575 Manning, D.A.C., 1981. The effect of fluorine on liquidus phase relationships in the
576   system Qz-Ab-Or with excess water at 1 kb. Contributions to Mineralogy and
577   Petrology, 76(2): 206-215.

578 McCubbin, F.M., Nekvasil, H., Harrington, A.D., Elardo, S.M., Lindsley, D.H., 2008.
579   Compositional diversity and stratification of the Martian crust: Inferences from
580   crystallization experiments on the picrobasalt Humphrey from Gusev Crater,
581   Mars,. Journal of Geophysical Research, 113(E11013):
582   doi:10.1029/2008JE003165.

583 McDonough, W.F., Sun, S.s., 1995. The composition of the Earth. Chemical Geology,
584   120(3-4): 223-253.

585 McSween, H.Y. et al., 2006. Alkaline volcanic rocks from the Columbia Hills, Gusev
586   crater, Mars. J. Geophys. Res., 111(E9): E09S91.

587 Médard, E., Grove, T., 2008. The effect of H_2O on the olivine liquidus of basaltic melts:
588   experiments and thermodynamic models. Contributions to Mineralogy and
589   Petrology, 155(4): 417-432.

590 Médard, E., McCammon, C.A., Barr, J.A., Grove, T.L., 2008. Oxygen fugacity,
591   temperature reproducibility, and H_2O contents of nominally anhydrous piston-
592   cylinder experiments using graphite capsules. American Mineralogist, 93: 1838-
593   1844.

594 Monders, A.G., Médard, E., Grove, T.L., 2007. Phase equilibrium investigations of the
595   Adirondack class basalts from the Gusev plains, Gusev crater, Mars. Meteoritics
596   & Planetary Science, 42(1): 131-148.

597 Mysen, B., 1975. Melting of hydrous mantle: I. Phase relations of natural peridotite at
598   high pressures and temperatures with controlled activities of water, carbon
599   dioxide and hydrogen. Journal of Petrology, 16(3): 520-548.

600 Mysen, B.O., Cody, G.D., Smith, A., 2004. Solubility mechanisms of fluorine in
601   peralkaline and meta-aluminous silicate glasses and in melts to magmatic
602   temperatures. Geochimica et Cosmochimica Acta, 68(12): 2745-2769.

603 Nekvasil, H. et al., 2004. The origin and evolution of silica-saturated alkalic suites: an
604   experimental study. Journal of Petrology, 45(4): 693-721.

605 Nekvasil, H., Filiberto, J., McCubbin, F.M., Lindsley, D.H., 2007. Alkalic parental
606   magmas for the chassignites? Meteoritics & Planetary Science, 42(6): 979-992.

607 Patiño Douce, A.E., Roden, M., 2006. Apatite as a probe of halogen and water fugacities
608   in the terrestrial planets. Geochimica et Cosmochimica Acta, 70(12): 3173-3196.

609 Patiño Douce, A.E., Roden, M.F., Chaumba, J., Fleisher, C., Yogodzinski, G., 2011.
610   Compositional variability of terrestrial mantle apatites, thermodynamic modeling
611   of apatite volatile contents, and the halogen and water budgets of planetary
612   mantles. Chemical Geology, 288(1-2): 14-31.

613 Scaillet, B., MacDonald, R., 2001. Phase Relations of Peralkaline Silicic Magmas and
614   Petrogenetic Implications. Journal of Petrology, 42(4): 825-845.

615 Scaillet, B., MacDonald, R., 2003. Experimental Constraints on the Relationships
616   between Peralkaline Rhyolites of the Kenya Rift Valley. Journal of Petrology,
617   44(10): 1867-1894.

618 Scaillet, B., Macdonald, R., 2004. Fluorite stability in silicic magmas. Contributions to
619   Mineralogy and Petrology, 147(3): 319-329.

620 Scaillet, B., Macdonald, R., 2006. Experimental constraints on pre-eruption conditions of
621   pantelleritic magmas: Evidence from the Eburru complex, Kenya Rift. Lithos,
622   91(1-4): 95-108.

623 Schaller, T. et al., 1992. Fluorine in silicate glasses: A multinuclear nuclear magnetic
624   resonance study. Geochimica et Cosmochimica Acta, 56(2): 701-707.

625 Stecher, O., 1998. Fluorine geochemistry in volcanic rock series: examples from Iceland
626   and Jan Mayen. Geochimica et Cosmochimica Acta, 62(18): 3117-3130.

627 Treiman, A.H., Drake, M.J., Janssens, M.-J., Wolf, R., Ebihara, M., 1986. Core formation
628   in the Earth and Shergottite Parent Body (SPB): Chemical evidence from basalts.
629   Geochimica et Cosmochimica Acta, 50(6): 1071-1091.

630 Webster, J.D., 1990. Partitioning of F between H_2O and CO_2 fluids and topaz rhyolite
631   melt. Contributions to Mineralogy and Petrology, 104(4): 424-438.

632 Webster, J.D., Thomas, R., Rhede, D., Förster, H.-J., Seltmann, R., 1997. Melt inclusions
633   in quartz from an evolved peraluminous pegmatite: Geochemical evidence for
634   strong tin enrichment in fluorine-rich and phosphorus-rich residual liquids.
635   Geochimica et Cosmochimica Acta, 61(13): 2589-2604.

636 Weidner, J.R., Martin, R.F., 1987. Phase equilibria of a fluorine-rich leucogranite from
637   the St. Austell pluton, Cornwall. Geochimica et Cosmochimica Acta, 51(6): 1591-
638   1597.

639 Whitaker, M., Nekvasil, H., Lindsley, D., McCurry, M., 2008. Can crystallization of
640   olivine tholeiite give rise to potassic rhyolites?—an experimental investigation.
641   Bulletin of Volcanology, 70(3): 417-434.

642 Xiao-lin, X., Zhenhua, Z., Jinchu, Z., Bing, R., 1999. Phase relations in albite granite-
643   H_2O-HF system and their petrogenetic applications. Geochemical Journal, 33(3):
644   199-214.

645 Xiong, X.-L., Rao, B., Chen, F.-R., Zhu, J.-C., Zhao, Z.-H., 2002. Crystallization and
646   melting experiments of a fluorine-rich leucogranite from the Xianghualing Pluton,
647   South China, at 150 MPa and H_2O-saturated conditions. Journal of Asian Earth
648   Sciences, 21(2): 175-188.

649 Yoshida, M., Takahashi, K., Yonehara, N., Ozawa, T., Iwasaki, I., 1971. FLUORINE,
650   CHLORINE, BROMINE, AND IODINE CONTENTS OF VOLCANIC ROCKS
651   IN JAPAN. Bulletin of the Chemical Society of Japan, 44(7): 1844-1850.

652 Zeng, Q., Nekvasil, H., Grey, C.P., 1999. Proton environments in hydrous aluminosilicate
653   glasses: A H-1 MAS, H-1/Al-27, and H-1/Na-23 TRAPDOR NMR study. Journal
654   of Physical Chemistry B, 103(35): 7406-7415.

655 Zeng, Q., Stebbins, J.F., 2000. Fluoride sites in aluminosilicate glasses; high-resolution
656   19 F NMR results. American Mineralogist, 85(5-6): 863-867.

657 Zimova, M., Webb, S.L., 2007. The combined effects of chlorine and fluorine on the
658   viscosity of aluminosilicate melts. Geochimica et Cosmochimica Acta, 71(6):
659   1553-1562.
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661

black lines - terrestrial mantle (25 ppm bulk F)
grey lines - Martian mantle (75 ppm bulk F)

$D = 0$

$D = 0.0785$

$D = 0$

$D = 0.0785$

Fluorine in basaltic magma (wt.%)

Extent of partial melting (wt.%)