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3 # On the origin of fluorine-poor apatite in chondrite parent bodies

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19 **Abstract**

20 We conducted a petrologic study of apatite within one LL chondrite, six R chondrites, and six

21 CK chondrites. These data were combined with previously published apatite data from a broader

22 range of chondritic meteorites to determine that chondrites host either chlorapatite or

23 hydroxylapatite with $\leq$ 33 mol% F in the apatite X-site (unless affected by partial melting by

24 impacts, which can cause F-enrichment of residual apatite). These data indicate that either

25 fluorapatite was not a primary condensate from the solar nebula or it did not survive lower

26 temperature nebular processes and/or parent body processes. Bulk rock Cl and F data from

27 chondrites were used to determine that the solar system has a Cl/F ratio of 10.5 ± 1.0 (3σ). The

28 Cl/F ratios of apatite from chondrites are broadly reflective of the solar system Cl/F value,

29 indicating that apatite in chondrites are fluorine poor because the solar system has about an order

30 of magnitude more Cl than F. The Cl/F ratio of the solar system was combined with known

31 apatite-melt partitioning relationships for F and Cl to predict the range of apatite compositions

32 that would form from a melt with a chondritic Cl/F ratio. This range of apatite compositions

33   allowed for the development of a crude model to use apatite X-site compositions from

34   achondrites (and chondrite melt rocks) to determine whether they derive from a volatile-depleted

35   and/or differentiated source, albeit with important caveats that are detailed in the manuscript.

36   This study further highlights the utility of apatite as a mineralogical tool to understand the origin

37   of volatiles (including H_2O) and the diversity of their associated geological processes throughout

38   the history of our solar system, including at its nascent stage.

39   **Introduction**

40   The mineral apatite $[Ca_5(PO_4)_3(F,Cl,OH)]$ is one of the primary mineralogical reservoirs

41   for phosphorus on Earth (Piccoli and Candela, 2002), and it is a common phosphate mineral

42   within a broad range of extraterrestrial samples (e.g., McCubbin and Jones, 2015). Naturally

43   occurring apatite hosts F, Cl, and OH as essential structural constituents (ESC), and all three

44   make up the apatite endmembers fluorapatite, chlorapatite, and hydroxylapatite, respectively

45   (Hughes et al., 1989; Hughes et al., 1990). In addition to full ternary solution in the F-Cl-OH

46   apatite system, natural apatite can host a wide range of anions and/or molecules in this anion site

47   (henceforth referred to as the X-site) including Br^-, I^-, S^{2-}, O^{2-}, CO_3^{2-}, and H_2O among others

48   (Brounce et al., 2019; Fleet et al., 2004; Hughes and Rakovan, 2015; Mason et al., 2009; Pan and

49   Fleet, 2002; Schettler et al., 2011), potentially making it a broadly applicable mineralogical tool

50   to understand volatile abundances and processes in Earth and planetary systems. In fact, apatite

51   has gained prestige over the last two decades as one of the only volatile-bearing minerals that

52   occurs within a broad array of astromaterials (e.g., McCubbin and Jones, 2015). However, as its

53   name implies (i.e., the name apatite is derived from the Greek verb "to deceive"; Patrick and

54   Martine, 2015), apatite has also gained notoriety as being a particularly difficult phase to analyze

55   and interpret (e.g., Boyce et al., 2014; Černok et al., 2019; Goldoff et al., 2012; McCubbin et al.,

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56   2010; Stock et al., 2015; Stormer et al., 1993; Webster and Piccoli, 2015). Nonetheless,

57   substantial progress has been achieved in developing apatite as a quantitative tool to understand

58   the origin, abundances, and isotopic compositions of volatiles in Earth and planetary systems.

59   Apatite has been used to determine the abundances of F, Cl, and H_2O in magmas and

60   magmatic source regions on Earth, Moon, Mars, and the asteroid 4 Vesta (e.g., Filiberto et al.,

61   2016b; Gross et al., 2013a; Kendall-Langley et al., 2021; McCubbin and Barnes, 2019;

62   McCubbin et al., 2016; McCubbin et al., 2015a; McCubbin et al., 2021; Patiño Douce and

63   Roden, 2006; Patiño Douce et al., 2011; Sarafian et al., 2017b; Tartèse et al., 2013), and it has

64   also been used to characterize the H- and Cl-isotopic compositions of numerous parent bodies

65   (e.g., Barnes et al., 2019; Barnes et al., 2020; Barrett et al., 2019; Barrett et al., 2016; Boyce et

66   al., 2015; Davidson et al., 2020; Greenwood et al., 2011; Hallis, 2017; Hu et al., 2019;

67   McCubbin and Barnes, 2020; Sarafian et al., 2017b; Sarafian et al., 2014; Smith et al., 2020;

68   Stephant et al., 2021; Tartèse et al., 2013; Tartèse et al., 2019; Williams et al., 2016). With the

69   exception of ordinary chondrites, much of the effort to determine and characterize apatite volatile

70   abundances in astromaterials have focused on planetary basalts; however, apatite also occurs in

71   primitive meteorites not formed by melting, including chondrites and primitive achondrites.

72   The presence of apatite in primitive parent bodies indicates that apatite may hold a record

73   of volatiles and their associated processes during the nascent stages of planetesimal formation

74   and evolution. In particular, apatite in primitive solar system materials may hold a volatile record

75   of ancient parent bodies that formed within the timespan of about 1–4 Ma after solar system

76   formation (as defined by the formation of calcium-aluminum-rich inclusions at 4567.30 ± 0.16

77   Ma; Connelly et al., 2012). Apatite is commonly cited as a primary condensate from nebular gas

78   at 710–734 K (fluorapatite) to define the 50% condensation temperature of fluorine (e.g., Fegley

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79 and Schaefer, 2010; Lodders, 2003) and at 470–472 K (chlorapatite) to define the 38^i–50%

80 condensation temperature for Cl (Fegley and Schaefer, 2010; Wood et al., 2019). At 850–1285

81 K, the physicochemical conditions within the nebula favor the formation of phosphides and

82 phosphorus components in Fe-rich metal (Fegley and Schaefer, 2010; Hazen and Morrison,

83 2021; Jones et al., 2014; Pasek, 2019; Zanda et al., 1994). Nebular phosphides begin to oxidize

84 to form phosphates at about 850 K (Pasek, 2019). However, not all (possibly very few) apatite

85 within chondrites are preserved condensates from the nebula. In fact, apatite in ordinary

86 chondrites are reported to form through metasomatic parent body processes involving the

87 oxidation of phosphorus in metals to form merrillite followed by metasomatism of merrillite by

88 H_2O-poor, Cl-rich fluids to form apatite (Jones et al., 2014; Jones et al., 2016; Lewis and Jones,

89 2016; McCubbin and Jones, 2015; Walton et al., 2021). Notably, reaction of whitlockite with

90 gaseous nebular HCl is thought to be the process by which chlorapatite formed in the nebula at

91 470 K (Fegley and Schaefer, 2010). Nonetheless, the primary hosts for F and Cl in the most

92 primitive solar system materials remains uncertain (Brearley and Jones, 2018). However, the

93 presence of apatite in primitive materials offers a window into volatile processing within parent

94 bodies that represent possible building blocks of the terrestrial planets, and in turn may provide

95 clues as to the processes that redistribute volatiles during accretion and differentiation.

96   Apatite in planetary basalts have ternary compositions that span nearly the full range of

97 F-Cl-OH space, but the predominant apatite in planetary basalts from most (exclusive of Mars)

98 differentiated parent bodies is fluorapatite (McCubbin et al., 2022; McCubbin and Jones, 2015;

99 Meurer and Natland, 2001; Piccoli and Candela, 2002; Sarafian et al., 2013). In contrast, apatite

100 in primitive meteorites are often reported as chlorapatite, although many studies have not

101 reported quantitative abundances of F and Cl in apatite (e.g., Fuchs, 1969; Rubin, 1997).

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102   Detailed studies of apatite from ordinary chondrites indicate they are predominantly chlorine-

103   rich (Jones et al., 2014; Jones et al., 2016; Lewis and Jones, 2016; Li and Hsu, 2018; Ward et al.,

104   2017; Wu and Hsu, 2019), but the limited data on apatite compositions in other chondrites

105   indicate variations from Cl-rich to OH-rich apatite (McCanta et al., 2008; Piralla et al., 2021;

106   Ward et al., 2017; Zhang et al., 2016; Zhang and Yurimoto, 2013).

107   The purportedly Cl- and/or OH-rich nature of apatite from chondrites contrasts with the

108   fluorine-rich nature of apatite in many planetary basalts, and this difference could have important

109   implications for the evolution of volatiles during planetary differentiation processes. However,

110   given the limited amount of apatite data from chondrites (exclusive of ordinary chondrites), it is

111   not clear as to what extent this apparent dichotomy is simply a function of a paucity of analyses

112   of chondritic apatite. In the present study we characterize the apatite compositions from ordinary

113   chondrites, carbonaceous Karoonda-type (CK) chondrites, and Rumuruti-type (R) chondrites.

114   We use these data, along with chondritic apatite data from the literature, to characterize the

115   population of apatite compositions from chondrite parent bodies. These results are interpreted

116   through the use of published experimental data on the partitioning behavior of F, Cl, and OH

117   between apatite and silicate melt to model apatite compositional evolution during melting of

118   chondritic sources. The overall aims of this study are to (1) understand the nature of apatite in

119   chondrites and (2) to develop a model for apatite crystallization from chondritic melts to

120   establish apatite volatile compositions that would be expected from melting of undifferentiated

121   and undegassed (i.e., chondritic) sources and differentiated and/or degassed sources.

122   **Methods**

123   Apatite compositions from six R chondrites, one ordinary chondrite, and six CK

124   chondrites were determined by electron probe microanalysis (EPMA). These data were

125   combined with literature data on 20 additional ordinary chondrites and four other carbonaceous

126   chondrites, and a complete list of all the meteorites considered in this study, as well as their

127   petrologic types, is provided in Tables 1–2. Samples analyzed in this study were loaned from the

128   following: the meteorite collection in the Institute of Meteoritics (IOM) at the University of New

129   Mexico (UNM) (Parnallee, Karoonda, Northwest Africa (NWA) 8186); the United States

130   Antarctic Meteorite Collection at NASA Johnson Space Center (JSC)/Smithsonian Institution

131   (David Glacier (DAV) 92300, Elephant Moraine (EET) 87507, Larkman Nunatak (LAR) 06872,

132   Allan Hills (ALH) 85151, Pecora Escarpment (PCA) 91002, Mount Prestrud (PRE) 95410,

133   LaPaz Icefield (LAP) 04840, LAP 03639, and Miller Range (MIL) 11207); and the personal

134   collection of Dr. Lindsay Keller (Maralinga).

Electron probe microanalysis (EPMA)

136   Major and minor element compositions of apatite were acquired by electron probe

137   microanalysis at multiple electron microprobe labs. This study utilized CAMECA SX-100

138   electron microprobes from the American Museum of Natural History (MIL 11207) and NASA

139   Johnson Space Center (LAP 04840). Additionally, a JEOL 8530 field emission electron

140   microprobe from NASA Johnson Space Center (DAV 92300, EET 87507, LAR 06872, ALH

141   85151, PCA 91002, PRE 95410, Maralinga, Karoonda) and a JEOL JXA 8200 electron

142   microprobe at the University of New Mexico (Parnallee and NWA 8186) were used during this

143   study. In addition to collecting major and minor element compositions of apatite, these

144   instruments were used to attain back-scattered electron (BSE) images of apatite in select

145   samples. All analyses include the elements P, Fe, Mg, Ca, Na, F, and Cl; however, the minor

146   elements Si, Ce, Y, Mn, and S were also included for some analyses. The beam conditions and

147   details on the analytical methods used for each apatite dataset is provided in the online

148   supplementary files.

149   The apatite X-site hosts F, Cl, and OH as ESCs; however, we did not measure OH in this

150   study. A missing component in the X-site of apatite can be calculated on the basis of

151   stoichiometry if both F and Cl are analyzed with sufficient accuracy. Estimating a missing

152   component with accuracy is often challenging because fluorine and chlorine X-ray count rates

153   can vary over the course of an electron microprobe analysis of apatite (Stormer et al., 1993),

154   although this problem seems to affect F substantially more than Cl (McCubbin et al., 2010). If a

155   missing component is detected, it can be attributed to some combination of the anions OH^-, O^{2-},

156   CO_3^{2-}, S^{2-}, Br^-, and I^- and/or structural vacancies (Pan and Fleet, 2002) and/or structural H_2O

157   (Mason et al., 2009). Although OH is the most likely constituent for this missing component in

158   apatite from many planetary basalts (e.g., McCubbin et al., 2016; Sarafian et al., 2013; Tartèse et

159   al., 2013), both natural and synthetic Cl-rich apatite often exhibit F-Cl-OH X-site sums that are

160   sub-stoichiometric (Jones et al., 2014; McCubbin and Ustunisik, 2018; Schettler et al., 2011).

161   This deficiency has been attributed to some combination of O^{2-} and structural vacancies in the

162   apatite X-site (Hovis and Harlov, 2010; Schettler et al., 2011), but additional work is needed to

163   fully characterize the nature and cause of the observed X-site deficiencies in Cl-rich apatite.

164   The quality of apatite analyses was assessed based on stoichiometric constraints and

165   electron microprobe totals. If analytical totals were outside of the range 96.0–102.0 wt.%, the

166   analysis was discarded. The leniency on analytical total deficiency was due to the possibility of

167   up to 1.79 wt.% H_2O (as OH^- groups) in apatite, which cannot be detected by the electron

168   microprobe. Furthermore, if the stoichiometry of cation sites deviated by more than ±2% (i.e.,

169   0.16 structural formula units (sfu) on a 13-anion basis for the ideal cation total of 8.0 sfu), the

170   analysis was discarded.

171   **Results**

172   **Apatite in ordinary chondrites**

173   Detailed textural studies of apatite in ordinary chondrites have been reported in previous

174   studies for all samples listed in Table 1 with the exception of the LL3.6 chondrite Parnallee. The

175   apatite in Parnallee will be described here for the first time. Apatite in ordinary chondrites

176   exhibit a wide range of grain sizes with shortest dimensions ranging from <10 μm to >200 μm

177   (Jones et al., 2014; Jones et al., 2016; Lewis and Jones, 2016; Li and Hsu, 2018; Wu and Hsu,

178   2019). Both apatite and merrillite are present in all ordinary chondrites, and merrillite is typically

179   more abundant than apatite (Jones et al., 2014; Jones et al., 2016; Lewis and Jones, 2016; Li and

180   Hsu, 2018; Wu and Hsu, 2019). Apatite occurs in ordinary chondrites as (1) discrete grains with

181   subhedral-anhedral habit, (2) grains associated with vein-filling material or impact melt pockets,

182   (3) intergrowths with merrillite where apatite seems to have replaced merrillite, or (4) anhedral

183   to euhedral grains that are intergrown with irregular Fe-Ni metal and sulfide (Jones et al., 2014;

184   Jones et al., 2016; Lewis and Jones, 2016; Li and Hsu, 2018; Wu and Hsu, 2019). In Parnallee,

185   apatite exhibits a similar range of grain sizes and textures as those in the other ordinary

186   chondrites with at least one large >100 μm anhedral grain that hosts inclusions of plagioclase and

187   olivine (Figure 1a), similar to some apatite grains described by Jones et al., (2014) in Bjurböle

188   and by Walton et al., (2021) in Chelyabinsk.

189   Apatite in non-brecciated ordinary chondrites have X-site populations that cluster in the

190   chlorapatite portion of the apatite F-Cl-OH ternary, with slight variations in average apatite

191   composition between each of the H, L, and LL ordinary chondrite types (Lewis and Jones, 2016;

192   Figure 2). Direct measurement of OH by secondary ion mass spectrometry (SIMS) of apatite in

193   ordinary chondrites have demonstrated that the missing X-site component cannot be accounted

194   for solely by OH (Jones et al., 2014; Jones et al., 2016), which is why the "OH" apex of the

195   apatite F-Cl-OH ternary in Figure 2 is labelled as a "missing component". The apatite X-site data

196   for Parnallee are similar to apatite compositions exhibited by other LL ordinary chondrites,

197   perhaps with slightly higher Cl abundances, with chlorine abundances ranging from 72 to 77

198   mol% of the X-site, fluorine abundances ranging from 12 to 20 mol% of the X-site, and missing

199   component abundances ranging from 6 to 13 mol% of the X-site (Table S1; Figure 2). All apatite

200   X-site data from the ordinary chondrites considered in this study are provided in Table S1

201   (Parnallee) and Table S15 (previously published data), and the average major and minor element

202   composition of apatite in Parnallee is provided in Table 3.

203   The brecciated ordinary chondrites and an L-melt rock host apatite that exhibit more

204   variability in X-site composition that range from the apatite compositions in non-brecciated

205   ordinary chondrites to F-rich compositions (Jones et al., 2016; Lewis and Jones, 2016; Li and

206   Hsu, 2018; Wu and Hsu, 2019; Table 1, S15). However, the F-rich apatite compositions in

207   ordinary chondrites are limited to (1) an H6 clast in Zag (termed H6-1 by Jones et al., 2016), (2)

208   the L4 breccia matrix in the L chondrite Kendleton (Lewis and Jones, 2016), (3) impact melt

209   veins in L4 melt breccia NWA 7251 (Wu and Hsu, 2018), and (4) the L-melt rock NWA 11042

210   (Li and Hsu, 2019). All four of these lithologies exhibit evidence of partial (or complete) melting

211   due to impact processes (Jones et al., 2016; Lewis and Jones, 2016; Li and Hsu, 2018; Wu and

212   Hsu, 2019). The F-rich apatite in all four lithologies are plotted as a separate group in Figure 2,

213   and their apatite X-site compositions are provided in Table S15.

214   **Apatite in Rumuruti-like (R) chondrites**

215   Apatite has been reported in all R chondrites, but it makes up a small fraction of the

216   modal mineralogy with total phosphate abundances reported to be <1.0 vol% (Bischoff et al.,

217   1994; Bischoff et al., 2011; McCanta et al., 2008; Rubin and Kallemeyn, 1994; Schulze et al.,

218   1994; Weisberg et al., 1991). In addition to apatite, some R chondrites also host

219   merrillite/whitlockite, although the OH abundance, which is the primary distinguishing feature

220   between merrillite versus whitlockite, has not been determined. Apatite exhibits a wide range of

221   grain sizes with shortest dimensions ranging from <10 μm to >180 μm (Bischoff et al., 1994;

222   McCanta et al., 2008; Figure 1). Apatite exhibits a variety of textures in R chondrites, including

223   as (1) discrete grains with subhedral-anhedral habit (Figure 1b-c), (2) anhedral-subhedral

224   intergrowths with silicate phases like olivine (Bischoff et al., 1994), and (3) as anhedral-

225   subhedral grains in close association with Fe-Ni sulfides. In the R chondrites investigated in the

226   present study, apatite occurs as discrete grains with subhedral to euhedral habit and grain sizes

227   ranging from ~5 μm to ~100 μm in their shortest dimension. Many of the apatite in R chondrites

228   host smaller oxide and/or sulfide phases (e.g., Figure 1b).

229   Apatite in R chondrites have been reported as chlorapatite or hydroxylapatite (Bischoff et

230   al., 1994; Bischoff et al., 2011; Gross et al., 2023; Gross et al., 2013b; McCanta et al., 2008;

231   Rubin and Kallemeyn, 1994; Schulze et al., 1994; Weisberg et al., 1991); however, very few

232   studies of R chondrites have reported quantitative analyses of apatite (i.e., Gross et al., 2013b;

233   McCanta et al., 2008), and none have reported quantitative analyses of chlorapatite. The samples

234   reported to have hydroxylapatite come from a subgroup of amphibole- and biotite-bearing R

235   chondrites (Gross et al., 2023; Gross et al., 2013b; McCanta et al., 2008), whereas chlorapatite

236   has been reported in typical R chondrites that do not have amphibole or biotite (Bischoff et al.,

237   1994; Bischoff et al., 2011; Rubin and Kallemeyn, 1994; Schulze et al., 1994; Weisberg et al.,

238   1991). We analyzed apatite from two amphibole- and biotite-bearing R chondrites (i.e., LAP

239   04840 and MIL 11207) and four typical R chondrites (i.e., ALH 85151, PCA 91002, LAP 03639,

240   and PRE 95410). The two amphibole- and biotite-bearing R chondrites host apatite with X-site

241   populations that cluster in the hydroxylapatite portion of the apatite F-Cl-OH ternary (Figure 2;

242   Table 1). The apatite X-site data for LAP 04840 and MIL 11207 indicate chlorine abundances

243   ranging from 27 to 32 mol% of the X-site, fluorine abundances ranging from 0 to 15 mol% of the

244   X-site, and OH abundances ranging from 55 to 73 mol% of the X-site (Table S2–S3; Figure 2).

245   The four R chondrites without amphibole or biotite host apatite with X-site populations that span

246   a range of compositions within the Cl-OH portion of the apatite ternary (Figure 2; Table 1). The

247   apatite X-site data for ALH 85151, PCA 91002, LAP 03639, and PRE 95410 indicate chlorine

248   abundances ranging from 38 to 88 mol% of the X-site, fluorine abundances ranging from 2 to 25

249   mol% of the X-site, and missing components attributed to OH ranging from 5 to 50 mol% of the

250   X-site (Table S4–S7; Figure 2). All apatite X-site data from R chondrites considered in this study

251   are provided in Tables S2–S7 and Table S15, and the average major and minor element

252   compositions of apatite in LAP 04840, MIL 11207, ALH 85151, PCA 91002, LAP 03639, and

253   PRE 95410 are provided in Table 3. Attribution of the missing component in the X-site of R

254   chondrite apatite to OH is presumed and will need to be verified in subsequent studies of these

255   samples.

256   **Apatite in Karoonda-like (CK) carbonaceous chondrites**

257   Apatite has been reported as a minor phase in many CK chondrites, and it occurs in a

258   range of textural occurrences, including (1) within magnetite-sulfide chondrules, (2) as discrete

259   grains within CK matrix, and (3) within anorthite-olivine-spinel-magnetite CAIs in the

260   anomalous CK4 Maralinga (Keller et al., 1992; Kurat et al., 2002; Rubin, 1993; Ward et al.,

261   2017; Figure 1d-f). Apatite typically coexists with merrillite, and both minerals make up the

262   dominant phosphate mineralogy in CK chondrites. All of the CK chondrite samples investigated

263   in the present study host apatite that exhibit one or more of the three apatite textural occurrences

264   described above from previous studies (Figure 1d-f) with the exception of NWA 8186. In NWA

265   8186 (CK7), apatite occurs as anhedral-subhedral oikocrysts that fill the interstitial space

266   between olivine grains. This textural distinction may be related to the high petrologic type of

267   NWA 8186 (Srinivasan et al., 2017) in comparison to other CK chondrites. Apatite in CK

268   chondrites exhibit a wide range of grain sizes with shortest dimensions ranging from ~1 μm to

269   ~100 μm, and many of the apatite in CK chondrites host smaller oxide phases (e.g., Figure 1d-f).

270   Notably, apatite within anorthite-olivine-spinel-magnetite CAIs in the anomalous CK4

271   Maralinga have apatite grains that span hundreds of microns in their longest dimension (Figure

272   1f).

273   Apatite in CK chondrites have been reported as chlorapatite (Keller et al., 1992; Kurat et

274   al., 2002; Rubin, 1993; Ward et al., 2017); however, very few studies have reported quantitative

275   analyses of both F and Cl in apatite from CK chondrites (e.g., Ward et al., 2017). The apatite X-

276   site data for CK chondrites analyzed in this study, exclusive of the apatite associated with CAIs

277   in Maralinga, indicate chlorine abundances ranging from 35 to 100 mol% of the X-site, fluorine

278   abundances ranging from 0 to 28 mol% of the X-site, and OH abundances ranging from 0 to 54

279   mol% of the X-site (Table S8–S13; Figure 2). The X-site data for the apatite associated with

280   CAIs in Maralinga indicate chlorine abundances ranging from 39 to 100 mol% of the X-site,

281   fluorine abundances ranging from 0 to 10 mol% of the X-site, and missing components attributed

282   to OH ranging from 0 to 52 mol% of the X-site (Table S14; Figure 2). All apatite X-site data

283   from CK chondrites considered in this study are provided in Tables S8–S15, and the average

284   composition of apatite in Karoonda, DAV 92300, Maralinga, Maralinga CAIs, EET 87507, LAR

285   06872, and NWA 8186 are provided in Table 4. Attribution of the missing component in the X-

286   site of CK chondrite apatite to OH is presumed and will need to be verified in subsequent studies

287   of these samples.

Apatite in other carbonaceous chondrites

289   Apatite has been reported as a minor to trace phase in other carbonaceous chondrites,

290   including Allende, Dar al Gani (DaG) 978, Boriskino, and Bench Crater, which is a

291   carbonaceous chondrite found in an Apollo 12 soil on the surface of the Moon (Dyl et al., 2015;

292   Joy et al., 2020; Piralla et al., 2021; Zhang et al., 2016; Zhang and Yurimoto, 2013). The apatite

293   in DaG 978 (C3 chondrite) occurs as discrete grains ranging in size from ~10 to 100 μm. The

294   apatite exhibit numerous textural occurrences including (1) grains that are closely associated

295   with CAIs, (2) grains at the margins of FeNi metal grains, (3) grains that form a "chain of beads"

296   in the matrix, and (4) as large grains with clinopyroxene inclusions (Zhang et al., 2016). The

297   apatite in Allende (CV3 chondrite), Boriskino (CM2 chondrite), and Bench Crater (C1 chondrite)

298   occur as grains ranging in size from ~3 to 20 μm, and the apatite occurs as subhedral to euhedral

299   grains or grain clusters in all three samples (Dyl et al., 2015; Piralla et al., 2021). The apatite

300   exhibit two main textural occurrences including (1) within fine-grained matrix in Bench Crater

301   and Boriskino and (2) within aqueously altered chondrules in Bench Crater and Allende (Dyl et

302   al., 2015; Piralla et al., 2021). Apatite in Boriskino also occurs as anhedral fluffy fine-grained

303   material (Piralla et al., 2021).

304   Apatite in DaG 978 are chlorapatite and plot in the portion of the apatite F-Cl-OH ternary

305   that is shared with many CK and R chondrite apatite (Zhang et al., 2016; Zhang and Yurimoto,

306   2013; Figure 2). The apatite X-site data for DaG 978 indicate chlorine abundances ranging from

307   64 to 87 mol% of the X-site, fluorine abundances ranging from 1 to 12 mol% of the X-site, and

308   OH abundances ranging from 3 to 24 mol% of the X-site (Table S15; Figure 2). The apatite in

309   Allende, Boriskino, and Bench Crater are hydroxylapatite and represent the most halogen-poor

310   apatite reported from chondrites (Dyl et al., 2015; Piralla et al., 2021; Figure 2). The apatite X-

311   site data for Allende, Boriskino, and Bench Crater indicate chlorine abundances ranging from 0

312   to 20 mol% of the X-site, fluorine abundances ranging from 5 to 33 mol% of the X-site, and OH

313   abundances ranging from 58 to 95 mol% of the X-site (Table S15; Figure 2). Attribution of the

314   missing component in the X-site of apatite to OH in Allende, Boriskino, and Bench Crater has

315   been confirmed by SIMS (Dyl et al., 2015; Piralla et al., 2021), but further work is needed to

316   confirm OH in DaG 978.

317   **Abundance of F and Cl in chondrites and the solar system**

318   To determine the behavior of F and Cl during melting and partial melting of chondritic

319   sources, we need to know the bulk F and Cl abundances of chondrites. Numerous studies have

320   reported bulk F and/or Cl values of individual meteorites (see Brearley and Jones, 2018) from

321   which averages can be determined. However, the reported values vary widely within studies and

322   between studies owing to differences between analytical techniques, various sources of analytical

323   error, terrestrial contamination, and sample heterogeneity (see detailed discussion in Brearley

324   and Jones, 2018). These considerations have been evaluated by several studies aiming to compile

325   the bulk compositions of chondrites.

326   CI chondrites have the most rigorously vetted compilations (typically using Orgueil) that

327   list values of F and Cl of 54–66 ppm and 600–704 ppm, respectively, with Cl/F ratios between

328   10.6 and 12.6 (Anders and Ebihara, 1982; Anders and Grevesse, 1989; Lodders, 2003; Lodders

329   and Fegley, 1998; Lodders et al., 2009; McDonough and Sun, 1995; Palme and Beer, 1993;

330   Palme and Jones, 2003; Palme et al., 2014; Palme et al., 1981; Palme and Zipfel, 2021; Wasson

331   and Kallemeyn, 1988). The most recent compilation is by Palme et al. (2014) for F and Palme

332   and Zipfel (2021) for Cl with Cl = 600 ppm, F = 58 ppm, and Cl/F = 10.34, which is similar to

333   previous compilation values by Anders and Ebihara (1982), Palme and Beer (1993), Palme and

334   Jones (2003), and Lodders et al. (2009). Palme and Zipfel (2021) and Palme et al. (2014) reports

335   a precision of 11% and 15% for the Cl and F values, respectively, which is greater than the range

336   of values provided by all CI compilations cited above.

337   For CM, CO, and CV carbonaceous chondrites, only two compilations exist: Wasson and

338   Kallemeyn (1988) and Lodders and Fegley (1998). The F values for these two compilations are

339   identical for all three groups, 38 ppm, 24 ppm, and 30 ppm for CM, CO, and CV, respectively,

340   and they are sourced from a single study (Dreibus et al., 1979) that measured Murchison and

341   Murray. The values for Cl in CM chondrites are significantly lower for Wasson and Kallemeyn

342   (1988) than Lodders and Fegley (1998) (i.e., 160 ppm and 430 ppm, respectively). Lodders and

343   Fegley (1998) use the average of three measurements from Mighei (Goles et al., 1967; Reed and

344   Allen, 1966). Wasson and Kallemeyn (1988) appear to have focused on the lower values in

345   Murchison and Murray (i.e., Dreibus et al., 1979), which have considerable variation. CV and

346   CO chondrites are more consistent between the two compilations, and we use the values from

347   Lodders and Fegley (1998) for all three groups.

348   The CK chondrites are only complied by Lodders and Fegley (1998) with F and Cl

349   abundances of 20 ppm and 260 ppm, respectively. The CK chondrites have a Cl/F ratio of 13.0.

350   These values come from analyses of Karoonda where Cl was averaged from two measurements

351   (Dreibus et al., 1979; Greenland and Lovering, 1965), and F abundances are based on one

352   measurement reported in Dreibus et al. (1979). The study by Greenland and Lovering (1965) was

353   omitted because it reports uniformly high values of F (190 ppm for Karoonda) for all meteorites

354   (see discussion in Brearley and Jones, 2018). Reliable bulk rock abundances of F and Cl values

355 are not available for CR chondrites, and they have not been reported for CH chondrites. For CR

356 chondrites, analyses of Cl have only been reported on Antarctic samples (e.g., Clay et al., 2017),

357 which are known to have anomalous halogen abundances (Brearley and Jones, 2018; Kato et al.,

358 2000; Langenauer and Krähenbühl, 1993).

359   Bulk compositions of ordinary chondrites are only compiled by Wasson and Kallemeyn

360 (1988) and Lodders and Fegley (1998). For F and Cl, these compilations are neither consistent

361 with each other nor with estimates from secondary minerals (Lewis and Jones, 2016). For F,

362 there is a reliance on studies such as Greenland and Lovering (1965) in which the values are

363 known to be too high (Brearley and Jones, 2018). Apatite is the only known carrier of F and Cl

364 in the equilibrated ordinary chondrites, and apatite compositions and modal abundances in

365 ordinary chondrites have been reported by several studies (Jones et al., 2014; Jones et al., 2016;

366 Lewis and Jones, 2016). These studies report group average Cl/F ratios of 13.2, 10.3, and 6.9 for

367 non-brecciated H, L, and LL falls, respectively. Dreibus et al. (1979) is the only study that

368 reports ordinary chondrite F and Cl values in the same range and with similar ratios. We will

369 adopt F and Cl averages for non-brecciated H and L chondrite falls from this study. Dreibus et al.

370 (1979) did not measure any LL chondrites, so we will use the analysis of the L/LL chondrite

371 Tuxtuac.

372   Enstatite chondrites suffer from many of the same issues as the ordinary chondrites,

373 particularly an overreliance on poor F data. There is only one analysis of F (64 ppm) from

374 Dreibus et al. (1979) from the EH4 chondrite Abee. Fluorine has only been measured in EL

375 chondrites by Greenland and Lovering (1965). The Cl values compiled by Wasson and

376 Kallemeyn (1988) appear to be more consistent with the reported data, and we will use these

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377   values for the EH and EL chondrites (660 ppm and 210 ppm, respectively). However, without

378   reliable F abundances, we do not use EH chondrites to estimate the solar system Cl/F ratio.

379   On the basis of all the chondrite groups for which reliable bulk rock F and Cl data is

380   available, we estimate that the solar system has a Cl/F ratio of 10.5 ± 1.0 (3σ). This value was

381   determined based on the slope of a linear regression through the F and Cl data for the

382   carbonaceous, ordinary, and EH chondrites (Figure 3). From this slope and the Cl abundance we

383   are using for EL chondrites (210 ppm Cl), we estimate that the bulk rock abundance of F in EL

384   chondrites is 20 ppm F (white circle in Figure 3).

Discussion

386   Both fluorapatite and chlorapatite are reported to form during nebular condensation

387   (Fegley and Schaefer, 2010; Lodders, 2003; Pasek, 2019). Fluorapatite is thought to have

388   condensed out of nebular gas at 710–734 K, prior to the formation of chlorapatite at about 470 K

389   (e.g., Fegley and Schaefer, 2010; Lodders, 2003). However, the results of this study show that

390   apatite from a broad range of chondrite meteorites are predominantly chlorapatite or

391   hydroxylapatite (Figure 2, 4a). Consequently, if fluorapatite did condense from nebular gas, it

392   did not survive subsequent nebular and/or parent body processing. It is unclear whether (1)

393   apatite compositions evolved towards Cl- and/or OH-rich compositions with decreasing

394   temperature through reactions with nebular gas prior to incorporation into chondrite parent

395   bodies and/or (2) the X-site compositions of apatite observed in chondrites are the result of

396   parent body processes (i.e., parent-body alteration of apatite that condensed from nebular gas or

397   formation of apatite within the parent body as a result of endogenous parent-body processes).

398   Neither scenario can be ruled out, and they are not mutually exclusive.

399   **Origin of fluorine-poor apatite in chondrites**

400   The Cl/F compositions of apatite in chondrites are broadly similar to the Cl/F ratio in

401   chondrite parent bodies/the solar system (Figure 4a). Despite the broad similarities with the solar

402   system Cl/F ratio and the near constant Cl/F ratio among chondrite groups, our apatite data

403   exhibit substantial inter- and intra-sample variations indicating that parent body processes play

404   an important role on the composition of any particular apatite in a chondrite. Here we explore

405   some of those parent body processes to better understand variations in apatite compositions in

406   chondrite samples.

407   Apatite from chondrite parent bodies are either chlorapatite or hydroxylapatite and

408   typically have less than 33 mol% of the apatite X-site occupied by F (Figure 2, 4b, 4d).

409   However, fluorapatite is reported in portions of four brecciated ordinary chondrite samples (Zag

410   H6-1 clast, Kendleton L4 matrix, impact melt veins in NWA 7251, and L melt rock NWA

411   11042) that were likely affected by impact melting (Jones et al., 2016; Lewis and Jones, 2016; Li

412   and Hsu, 2018; Wu and Hsu, 2019; Figure 2). To better understand why there would be more F-

413   rich apatite in these samples, we consider the effects of impact melting on apatite halogen

414   abundances using experimental data on the apatite-melt partitioning behavior of F and Cl (e.g.,

415   Boyce et al., 2014; Candela, 1986; Doherty et al., 2014; Li and Hermann, 2015; Li and Hermann,

416   2017; Li and Costa, 2020; Mathez and Webster, 2005; McCubbin and Ustunisik, 2018;

417   McCubbin et al., 2015b; Riker et al., 2018; Webster et al., 2017; Webster et al., 2009). Fluorine

418   is much more compatible in apatite compared to OH and Cl, particularly for OH-poor apatite

419   (McCubbin and Ustunisik, 2018) like those in ordinary chondrites (Jones et al., 2014; Jones et

420   al., 2016). Consequently, as an apatite-bearing rock undergoes partial melting by impacts, the

421   residual apatite would evolve to more F-rich compositions given the stronger affinity for Cl and

422   H in the melt and F in apatite. From this assessment, we infer that the more F-rich compositions

18

423   in Zag, Kendleton, NWA 7251, and NWA 11042 (Table 1) may have been caused by impact-

424   induced partial melting. Furthermore, we infer that endogenous parent body processes and/or

425   nebular processes have limited apatite compositions in chondrites to be dominantly Cl-OH

426   apatite with less than 33 mol% F in the apatite X-site for a broad range of chondrite parent

427   bodies from both the inner and outer solar system geochemical reservoirs (Figure 4d).

428   Most of the apatite reported in this study come from the H, L, LL, R, and CK chondrites,

429   all samples that experienced varying degrees of thermal metamorphism on their parent body.

430   Although a clear petrogenetic sequence has been developed for P-bearing Fe-rich metal,

431   merrillite, and chlorapatite in ordinary chondrites (Jones et al., 2014; Jones et al., 2016; Lewis

432   and Jones, 2016; McCubbin and Jones, 2015), the origin of apatite in other chondrite groups is

433   less clear, particularly for more oxidized thermally metamorphosed chondrites like R and CK

434   chondrites (Righter and Neff, 2007) where their precursor materials may have been sufficiently

435   oxidized to incorporate nebular apatite. Regardless of their origin, thermally metamorphosed

436   chondrites from both reduced (e.g., H, L, and LL) and oxidized (e.g., CK and R) parent bodies

437   host apatite with Cl/F ratios that largely straddle the Cl/F ratio of the solar system (Figure 4a).

438   The intrasample variation exhibited by apatite X-site compositions in most samples is on the

439   order of the variation exhibited between samples of the same group (Tables S1-S15). The large

440   intrasample variation in apatite X-site compositions in CK, R, and Maralinga CAIs may indicate

441   that (1) apatite with a range of X-site compositions were incorporated into the parent body and/or

442   (2) parent body metasomatic processes occurred under low fluid-rock ratios, preventing

443   homogenization during thermal metamorphism.

444   There are two notable exceptions to the large intrasample variation in apatite X-site

445   compositions. The amphibole- and biotite-bearing R chondrites LAP 04840 and MIL 11207 both

446   have apatite X-site compositions that cluster tightly compared to the other R chondrites (Figure

447   2; Tables S2-S7). These samples have apatite that are more OH-rich than the other R chondrites,

448   which exhibit a wide range of Cl-OH compositions similar to the CK chondrites and apatite in

449   Maralinga CAIs (Figure 2; Tables S4-S14). The amphibole and biotite in LAP 04840 were used

450   to estimate total P_{H_2O} between 250 and 500 bars (McCanta et al., 2008), indicating a high

451   fluid:rock ratio for that sample and by inference MIL 11207. The high P_{H_2O} likely resulted in less

452   apatite X-site variation in the amphibole- and biotite-bearing R chondrites. Notably, apatite in

453   the amphibole- and biotite-bearing R chondrites also straddle the solar system Cl/F ratio but at

454   higher OH than the other R chondrite apatite.

455   Far fewer of the apatite reported and discussed in this study come from samples that

456   experienced varying degrees of low-temperature (–20 °C to ~300 °C; e.g., Krot et al., 2021;

457   Velbel and Zolensky, 2021) aqueous alteration on their parent body (i.e., CM and CV

458   chondrites). All of the apatite from samples that experienced aqueous alteration plot at lower

459   Cl/F ratios than the solar system value, but they still exhibit apatite X-site compositions with ≤

460   33 mol% F (Figure 2, 4a), making them all hydroxylapatite (Dyl et al., 2015; Piralla et al., 2021;

461   Table S15). Unlike apatite from the thermally metamorphosed samples, many of the apatite in

462   the aqueously altered samples exhibit Cl/F < 1 (Table S15). Allende, which experienced both

463   aqueous alteration and subsequent thermal metamorphism (Krot et al., 2021), hosts apatite that

464   exhibit a considerable range in Cl/F ratios (Dyl et al., 2015; Table S15). Although CV and CM

465   chondrite parent bodies have similar Cl/F ratios compared to H, L, LL, and CK chondrites

466   (Figure 3), their apatite are depleted in Cl relative to the apatite from H, L, LL, and CK

467   chondrites. Consequently, apatite is not the primary Cl host in CV and CM chondrites. In fact,

468   other Cl-bearing phases, including the Cl-rich mineral sodalite, have been reported in CV and

469   CM meteorites (Brearley and Jones, 2018; Krot et al., 1998; Lee et al., 2019). The origin of Cl

470   depletion in apatite from CM and CV apatite likely results from their lower temperature of

471   formation in aqueous/hydrothermal fluids, which strongly favors incorporation of F in apatite

472   over Cl (Zhu and Sverjensky, 1991). In fact, the larger range in Cl/F ratio exhibited by Allende is

473   likely a reflection of that sample having experienced both aqueous alteration at 200–250 °C and

474   subsequent thermal metamorphism at ~500 °C (Krot et al., 2021), the latter of which would

475   facilitate more Cl incorporation into apatite compared to lower temperatures (Li and Hermann,

476   2015; Li and Hermann, 2017; Zhu and Sverjensky, 1991).

477   **Igneous apatite compositions from magmatic source regions with chondritic Cl/F ratios**

478   Numerous studies have reported the partitioning behavior of F, Cl, and OH between

479   apatite and silicate melt as well as apatite and fluid over a wide range of pressures, temperatures,

480   and (apatite/melt/fluid) compositions (e.g., Boyce et al., 2014; Candela, 1986; Doherty et al.,

481   2014; Li and Hermann, 2015; Li and Hermann, 2017; Li and Costa, 2020; Mathez and Webster,

482   2005; McCubbin and Ustunisik, 2018; McCubbin et al., 2015b; Riker et al., 2018; Webster et al.,

483   2017; Webster and Piccoli, 2015; Webster et al., 2009; Zhu and Sverjensky, 1991). These studies

484   have demonstrated that apatite-melt partition coefficients for individual X-site anions are highly

485   variable, but the exchange equilibria among the anions between apatite and melt vary

486   systematically as a function of P, T, X_{melt}, $X_{Apatite}$, and fO_2 (e.g., Boyce et al., 2014; Li and

487   Hermann, 2017; McCubbin and Ustunisik, 2018; McCubbin et al., 2015b), similar to the

488   behavior of Fe-Mg exchange equilibrium between olivine and melt (e.g., Filiberto and Dasgupta,

489   2011; Roeder and Emslie, 1970; Toplis, 2005). This systematic variation in apatite-melt

490   exchange equilibria for F, Cl, and OH enables the estimation of magmatic volatile abundances of

491   magmas and magmatic source regions from apatite, and it allows for the prediction of initial

492   apatite compositions that would crystallize from melts with known volatile abundance ratios.

493   Despite apatite being a late-forming phase in many extraterrestrial igneous systems, it is

494   often the only mineral phase with F and Cl as ESCs (McCubbin and Jones, 2015). The Cl/F

495   ratios of parental melts are likely to remain unchanged until the appearance of apatite because

496   the closed-system crystallization of nominally volatile-free minerals will not greatly affect the

497   Cl/F ratio prior to apatite saturation (Aiuppa et al., 2009; McCubbin et al., 2015b). As a result,

498   the halogen compositions of the first formed apatite in an igneous system can be predicted on the

499   basis of source Cl/F ratios. Using the estimated Cl/F mass ratio of chondrite parent bodies of

500   10.5 ± 1.0 (3σ), we compute a range of initial apatite compositions that would crystallize from a

501   melt with a chondritic Cl/F ratio using the Cl-F apatite-melt exchange K_d of 0.21 ± 0.03 reported

502   by McCubbin et al. (2015b) for basaltic liquids at 950–1000 °C, 1.0–1.2 GPa, and oxygen

503   fugacity within about a log unit of the iron–wüstite buffer. This range of apatite compositions is

504   shown in Figure 4a and is projected from the OH/missing component apex of the ternary. The

505   Cl/F mass ratio of apatite that would form from melts with a chondritic Cl/F ratio range from

506   1.64–2.79, which corresponds to apatite F-Cl X-site compositions of $Cl_{60}F_{40}$–$Cl_{47}F_{53}$ (teal region

507   in Figure 4a). The initial apatite composition that would form from melts with chondritic Cl/F

508   may shift as a function of P, T, X, and fO_2, but experimental data over a wide range of conditions

509   indicate that X and T likely play the largest role in affecting the apatite-melt partitioning behavior

510   of F, Cl, and OH. In particular, higher temperatures (i.e., above 1000 °C) would favor a higher

511   proportion of Cl in apatite and hence a higher Cl-F apatite-melt exchange K_d (Candela, 1986;

512   Doherty et al., 2014; Li and Hermann, 2015; Li and Hermann, 2017; Li and Costa, 2020; Mathez

513   and Webster, 2005; Riker et al., 2018; Webster et al., 2017; Webster et al., 2009). In contrast,

514   lower temperatures (i.e., below 950 °C) and/or H_2O-poor conditions (particularly at high Cl/F

515   ratios in the melt) would favor a lower proportion of Cl in apatite and hence a lower Cl-F apatite-

516   melt exchange K_d (Candela, 1986; Doherty et al., 2014; Li and Hermann, 2015; Li and Hermann,

517   2017; Li and Costa, 2020; Mathez and Webster, 2005; McCubbin and Ustunisik, 2018; Riker et

518   al., 2018; Webster et al., 2017; Webster et al., 2009; Zhu and Sverjensky, 1991).

519   The chondritic apatite crystallization field in Figure 4a only represents initial apatite

520   compositions that would crystallize from a silicate melt with a chondritic Cl/F ratio because

521   continued equilibrium crystallization and/or fractional crystallization would drive apatite to more

522   Cl-rich compositions (Boyce et al., 2014; McCubbin et al., 2016). In fact, any apatite forming

523   from a melt with an initially chondritic Cl/F ratio should only produce apatite that plot within or

524   above the field defined by the initial chondritic apatite compositions (Figure 4c) unless they

525   experience open-system processes like degassing or fluid loss. Degassing or fluid loss would

526   preferentially remove Cl from the melt relative to F (Aiuppa et al., 2009; Ustunisik et al., 2011;

527   Ustunisik et al., 2015; Webster, 1997; Webster, 2004; Webster and De Vivo, 2002; Webster et

528   al., 1999; Webster and Rebbert, 1998), driving the evolution of apatite compositions towards the

529   fluorine apex of the apatite F-Cl-OH ternary (McCubbin et al., 2016; Ustunisik et al., 2015).

530   Although this apatite crystallization model (Figure 4c) is intended to be applied to

531   achondrites, it could also be applied to apatite that crystallizes from impact melts in chondrite

532   samples (e.g., impact melt veins or melt rocks). In particular, this model could be used to assess

533   whether an impact melt of a chondrite experienced degassing prior to apatite saturation, as

534   apatite compositions from degassed impact melt could fall below the chondritic range (i.e., teal

535   wedge in Figure 4c). Knowing whether impact melt has degassed prior to apatite saturation could

536   be important for interpreting isotopic compositions recorded in apatite that may be attributed to

537   degassing processes. The range in composition of apatite in chondrite melt rocks or impact melts

538   could also be used to assess for other processes such as fractional vs equilibrium crystallization

539   of an impact melt, as demonstrated by Wu and Hsu, (2019) in the NWA 11042 L melt rock.

540   Detailed petrographic studies of apatite in impact melted chondrites will be crucial to making

541   accurate interpretations because F-rich apatite can form in chondrite samples either through

542   crystallization from a degassed impact melt or by having survived partial melting during impact

543   processes. Other geochemical indicators like REE abundances in apatite may be important for

544   distinguishing between residual apatite and apatite that crystallized from an impact melt (e.g.,

545   Wu and Hsu, 2019).

546   **Apatite as a potential indicator of planetary differentiation**

547   Planetary differentiation, defined here as primary metal-silicate separation and the

548   development of primary geochemical reservoirs in the silicate portion of a planetary body, is a

549   fundamental process that has affected many, if not most, planetary bodies (e.g., Elkins-Tanton,

550   2012; Elkins-Tanton et al., 2011; Greenwood et al., 2005; Righter and Drake, 1996; Rubie et al.,

551   2011; Weiss et al., 2008). In particular, melting, either partially or through planet-scale magma

552   oceans, is the most common process by which the terrestrial planets and large asteroids (like 4-

553   Vesta) are believed to have differentiated (e.g., Bouvier et al., 2018; Brown and Elkins-Tanton,

554   2009; Elardo et al., 2011; Elkins-Tanton, 2012; Elkins-Tanton et al., 2005; Elkins-Tanton et al.,

555   2003; Elkins-Tanton et al., 2011; Greenwood et al., 2005; McCubbin et al., 2021; Righter and

556   Drake, 1997; Riner et al., 2009; Stolper, 1977; Taylor et al., 1993; Wood et al., 2006).

557   In the context of preserving initial bulk silicate Cl/F ratios in differentiated mantle

558   sources, the style and degree of melting will have important implications for the abundance,

559   distribution, and possible fractionation of Cl from F in a mantle source. Chlorine is more

560   incompatible than F in the nominally volatile-free minerals that typically comprise cumulate

561   mantle sources that form from magma ocean crystallization (Baker et al., 2022; Beyer et al.,

562   2012; Hauri et al., 2006; O'Leary et al., 2010; Potts et al., 2021) or are left behind as

563   restites/residues from partial melting. The consequence of this partitioning relationship is that the

564   primary crustal reservoir (i.e., first generation of melt) of a parent body will exhibit a more

565   accurate reflection of the initial bulk silicate Cl/F ratio of a differentiated parent body than its

566   corresponding mantle source, particularly if the halogen abundances of that mantle source are

567   controlled by the partitioning behavior of Cl and F between nominally volatile-free minerals and

568   melt (as opposed to being controlled by trapped and/or residual melt or apatite).

569   On the Moon, it has been demonstrated that the mantle and primary crustal reservoirs

570   (i.e., KREEP) have distinct Cl/F with a mantle that is highly depleted in Cl relative to its primary

571   crust because the hybridized cumulate lunar mantle did not retain sufficient trapped melt to have

572   a Cl/F ratio reflective of its bulk silicate composition (Boyce et al., 2018; McCubbin et al.,

573   2015a; Potts et al., 2021). If the lunar mantle is a reasonable analogy to other large, differentiated

574   parent bodies, it indicates that mantle sources that have undergone multiple episodes of melting

575   will have lower Cl/F ratios than their initial (un-melted) starting compositions unless they were

576   able to retain considerably more trapped melt than mantle sources on the Moon. Consequently,

577   the initial apatite that crystallizes from melts or partial melts of previously melted sources (i.e.,

578   mantles that have volatile abundances that reflect the partitioning behavior of F and Cl between

579   nominally volatile-free minerals and melt) will plot below the chondritic apatite crystallization

580   field (teal wedge in Figure 4a, 4c), even if the parent body has a chondritic Cl/F ratio.

581   Equilibrium crystallization of that apatite would keep it below the chondritic apatite

582   crystallization field, but fractional crystallization (where apatite is part of the fractionating

583   assemblage) could drive subsequent apatite compositions into and beyond that field (Boyce et

584   al., 2014; McCubbin et al., 2016).

585   **Apatite as a potential indicator of volatile depletion**

586   Moderately volatile elements are those that, at nebular pressures of 10^{-4} bars, have 50%

587   condensation temperatures between 1290 K and 664 K, and volatile elements are those with 50%

588   condensation temperatures below 664 K (Lodders, 2003). Many achondrite parent bodies and all

589   of the terrestrial planets are depleted in moderately volatile and volatile elements relative to

590   chondrites to varying degrees (Davis, 2006; McCubbin et al., 2012). The depletions in volatile

591   elements could have been inherited by the primary building blocks of differentiated parent

592   bodies, resulted from primary accretion processes, and/or occurred through later parent body

593   processes (e.g., Albarede, 2009; Boyce et al., 2015; Davis, 2006; Hirschmann et al., 2021;

594   Jackson et al., 2018; Lichtenberg and Krijt, 2021; Sharp and Draper, 2013). Volatile depletion

595   can have a substantial impact on the Cl/F ratios of differentiated planetary bodies because F is a

596   moderately volatile element (50% T_C = 710–734 K; Fegley and Schaefer, 2010; Lodders, 2003)

597   and Cl is a volatile element (50% T_C = 420 K; Fegley and Schaefer, 2010), so volatile depletion

598   processes tend to result in sub-chondritic Cl/F ratios (e.g., Boyce et al., 2018; Dreibus et al.,

599   1977; McCubbin et al., 2022; McCubbin et al., 2021; McDonough and Sun, 1995).

600   Apatite from parent bodies that have sub-chondritic Cl/F ratios would plot below the

601   chondritic apatite crystallization field (Figure 4a, 4c), even if the sample containing apatite

602   represents a primary melt of that differentiated body (e.g., eucrites on the differentiated asteroid

603   4 Vesta; McCubbin et al., 2021). Consequently, both volatile depletion and differentiation would

604   drive the formation of apatite on differentiated bodies to be more F-rich than apatite that would

605   form from a melt with chondritic Cl/F ratios. Given that volatile-element depletion is typically

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606   more pronounced on differentiated parent bodies than undifferentiated parent bodies (Davis,

607   2006), these two processes (i.e., planetary differentiation and volatile-depletion) should work in

608   tandem to cause a prevalence of F-rich apatite in planetary basalts, which matches published

609   apatite compositions from numerous differentiated parent bodies, with the exception of Mars

610   (Filiberto et al., 2016a; McCubbin and Jones, 2015).

Implications

612   In this contribution, we report the first comprehensive dataset on the compositions of

613   apatite from R and CK chondrites. In contrast to apatite in Ordinary chondrites, our data indicate

614   a substantial missing component in the X-site of CK and R chondrite apatite that could be

615   attributed to OH. One of the most fundamental questions in planetary science is the origin and

616   abundance of H_2O and how it was distributed within the circumstellar disk within the first 4 Ma

617   of the birth of our solar system. To answer this question, we need to investigate the earliest-

618   formed samples of our solar system, which includes a variety of chondrites and achondrites

619   (Alexander, 2017; Alexander et al., 2012; Deligny et al., 2021; Marrocchi et al., 2018;

620   McCubbin and Barnes, 2019; Piani and Marrocchi, 2018; Piani et al., 2020; Piani et al., 2015;

621   Piani et al., 2018; Sarafian et al., 2017a; Sarafian et al., 2014; Vacher et al., 2020). Given the

622   likely record of H_2O in apatite from R and CK chondrites, these samples have untapped potential

623   to provide important constraints on the origin of H_2O within the inner (R chondrite) and outer

624   (CK chondrite) solar system reservoirs through H-isotopic analyses.

625   Although encouraging, the missing components in CK and R chondrite apatite has not

626   been measured and is only presumed to be OH. Such caution is particularly warranted because

627   the missing component detected in the X-site of apatite from ordinary chondrites was much

628   larger than the measured abundances of OH (Jones et al., 2014; Jones et al., 2016). Nonetheless,

629   there is reason to be cautiously optimistic about the attribution of the missing X-site components

27

630   of CK and R chondrite apatite to OH. In particular, the H_2O-rich nature of fluids on the R

631   chondrite parent body is supported by the presence of H_2O-rich amphibole and biotite within a

632   subgroup of R chondrites (Gross et al., 2023; Gross et al., 2013b; McCanta et al., 2008).

633   Moreover, both CK and R chondrites are more oxidized than ordinary chondrites. The R

634   chondrites exhibit fO_2 values as high as the fayalite-magnetite-quartz (FMQ) buffer, and the CK

635   chondrites exhibit fO_2 values up to FMQ +4.5 (Righter and Neff, 2007). These fO_2 values would

636   correspond to high fH_2O/fH_2 ratios of any parent body fluids (e.g., Sharp et al., 2013), making

637   oxidized hydrogen available for incorporation into minerals during thermal metamorphism. In

638   contrast, the metal-rich ordinary chondrites likely had parent body fluids with low fH_2O/fH_2

639   ratios (Alexander, 2017; McCubbin and Barnes, 2019; Sutton et al., 2017), which would limit

640   OH incorporation into minerals during thermal metamorphism. In summary, the apatite in CK

641   and R chondrites are prime targets for gaining additional information about the origin of H_2O in

642   our solar system.

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1135

Figure Captions

1136 **Figure 1.** High-resolution back-scattered electron images of apatite from chondrites a) Parnallee
1137 (LL3.6) b) LAP 04840 (R5) c) PCA 91002 (R3.8-6) d) Karoonda (CK4) e) DAV 92300 (CK4) f)
1138 Maralinga (CK4). All phases present are identified, and the phase abbreviations are indicated as
1139 follows: Amp = amphibole, An = anorthite, Ap = apatite, Bt = biotite, Chr = chromite, Cpx =
1140 clinopyroxene, Fas = fassaite, Mag = magnetite, Opx = orthopyroxene, Ol = olivine, Pl =
1141 plagioclase, Pn = pentlandite, Po = pyrrhotite, Spl = spinel.

1142

1143 **Figure 2.** Ternary plot of apatite X-site components (mol%) from all chondrites analyzed in the
1144 present study (data points in color) as well as from the literature (data points in gray and/or
1145 black; Dyl et al., 2015; Jones et al., 2014; Jones et al., 2016; Lewis and Jones, 2016; Li and Hsu,
1146 2018; McCanta et al., 2008; Piralla et al., 2021; Ward et al., 2017; Wu and Hsu, 2019; Zhang et
1147 al., 2016; Zhang and Yurimoto, 2013). The missing component was calculated based on 1 – F –
1148 Cl = missing component. All new data plotted in the ternary are tabulated in Tables S1–S14, and
1149 all published data, along with their corresponding sources, are listed in Table S15. IM – impact
1150 melt.

1151

1152 **Figure 3.** Bulk rock F and Cl mass abundances for various chondrite meteorite groups based on
1153 literature data compilations (Dreibus et al., 1979; Lodders and Fegley, 1998; Palme et al., 2014;
1154 Palme and Zipfel, 2021; Wasson and Kallemeyn, 1988). Abundance of F in EL (white symbol)
1155 was estimated by the slope of a linear regression through the F and Cl data for the other
1156 chondrites in the plot.

1157

1158 **Figure 4.** Ternary plots of apatite X-site components (mol%), a) Plot showing the Cl/F ratio of
1159 the solar system (orange wedge) and Cl/F ratio of initial apatite that would crystallize from a
1160 silicate melt with a chondritic Cl/F ratio (turquoise wedge) superimposed on the apatite X-site
1161 compositions from chondrites (gray symbols with chondrite types indicated by legend) from
1162 Figure 2, exclusive of apatite from chondrite samples known to be affected by impact melting.
1163 The dotted line represents an empirically determined limit on F occupancy in chondrite apatite
1164 exclusive of samples known to be affected by impact melting. b) Plot showing the Cl/F ratio of
1165 the solar system (orange wedge) superimposed on the apatite X-site compositions from
1166 chondrites (gray symbols with chondrite types indicated by legend in panel a) from Figure 2,
1167 inclusive of samples known to be affected by impact melting (yellow symbols). The dotted line
1168 near ~30% F is the same one that appears in panel a and represents an empirically determined
1169 limit on F occupancy in chondrite apatite exclusive of samples known to be affected by impact
1170 melting. A second dotted line represents an empirically determined limit on F occupancy in
1171 chondrite apatite inclusive of samples known to be affected by impact melting. c) Model for
1172 using apatite to understand volatile depletion or differentiation of samples from achondrite[‡]
1173 parent bodies on the basis of their apatite X-site compositions. The turquoise wedge is the same
1174 wedge from panel a and represents the Cl/F ratio of initial apatite that would crystallize from a
1175 silicate melt with a chondritic Cl/F ratio. Apatite that plots below that wedge (dark green region)
1176 indicates apatite that formed through equilibrium or fractional crystallization[*] from a melt or
1177 partial melt derived from a volatile depleted source or a differentiated source with volatile
1178 abundances controlled by the F and Cl partitioning relationships between nominally volatile-free
1179 minerals (NVFM) and silicate melt. Apatite that plots above the turquoise wedge (dark blue

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1180   region) indicates equilibrium or fractional crystallization from a melt or partial melt derived from
1181   a chondritic source (i.e., not volatile depleted) that has not undergone prior melting. *Fractional
1182   crystallization can cause apatite to evolve into and beyond the chondritic apatite wedge even if
1183   the initial apatite compositions would plot below the wedge (Boyce et al., 2014; McCubbin et al.,
1184   2016), so caution must be used for samples with petrogenetic histories that may have included
1185   fractional crystallization where apatite was part of the fractionating assemblage. ‡Achondrite
1186   parent bodies, exclusive of primitive achondrites. d) Plot showing the empirically determined
1187   boundaries for apatite compositions in chondrite meteorites. The Cl/F ratio of the solar system
1188   (orange wedge) is superimposed on the empirically determined field of apatite compositions that
1189   arise from either nebular condensation or endogenous parent body processes exclusive of melting
1190   (purple field). The field between the two dotted lines is the empirically determined range of
1191   apatite compositions that have arisen through partial melting by impacts (light blue field). The
1192   white field represents the portion of apatite X-site ternary space where apatite compositions have
1193   not been reported. The two dotted lines are the same ones that appear in panel b and define the
1194   empirically-determined boundaries discussed in this panel.

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[i] Fegley and Schafer (2010) report a 50% condensation temperature of 420 K for Cl because only ~38% of Cl is
condensed at 470 K as chlorapatite, and 50% condensation is reached at 420 K during the formation of halite.

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Table 1. List of inner solar system chondrite samples in which apatite was analyzed during this study, including apatite data published in previous studies (Jones et al., 2014; Jones et al., 2016; Lewis and Jones, 2016; Li and Hsu, 2018; McCanta et al., 2008; Ward et al., 2017; Wu and Hsu, 2019). The class, group, and petrologic type of each sample along with average structural occupancies of fluorine, chlorine, and hydroxyl in the apatite X-site from each sample are provided. All data are provided in Tables S1–S7 and Table S15.

Name	Class	Group & Type	Avg. F[a] in X-site	Avg. Cl in X-site	Avg. missing in X-site[b]
Devgaon		H3.8	0.14 (2)	0.81 (3)	0.05 (4)
Ybbsitz		H4	0.15 (6)	0.73 (3)	0.12 (4)
Avanhandava		H4	0.16 (2)	0.80 (2)	0.04 (2)
Zag		H4 Matrix	0.05 (2)	0.87 (3)	0.09 (2)
Richardton		H5	0.09 (3)	0.90 (3)	0.01 (2)
Oro Grande		H5	0.21 (3)	0.73 (3)	0.05 (2)
Estacado		H6	0.11 (3)	0.81 (3)	0.08 (4)
Portales Valley		H6	0.08 (3)	0.81 (2)	0.11 (1)
Zag		H6-1 Clast	0.39 (9)	0.54 (8)	0.07 (2)
Zag		H6-2 Clast	0.07 (5)	0.84 (6)	0.09 (2)
Kendleton		L3 Clast	0.14 (3)	0.73 (6)	0.13 (3)
Santa Barbara		L4	0.12 (2)	0.78 (3)	0.10 (4)
Kendleton	Ordinary	L4 Matrix	0.31 (4)	0.57 (3)	0.12 (5)
NWA 7251	Chondrites	L4 Host	0.19 (5)	0.70 (5)	0.11 (5)
Elenovka		L5	0.14 (4)	0.78 (3)	0.08 (2)
Kendleton		L5 Clast	0.16 (3)	0.74 (3)	0.10 (3)
Bruderheim		L6	0.15 (4)	0.76 (4)	0.09 (3)
Villalbeto de la Peña		L6	0.21 (4)	0.75 (5)	0.05 (6)
NWA 7251		L Melt Clasts	0.3 (2)	0.6 (2)	0.1 (1)
NWA 11042		L Melt Rock	0.2 (2)	0.7 (2)	0.1 (1)
Parnallee		LL3.6	0.16 (2)	0.75 (1)	0.10 (2)
Bo Xian		LL3.9	0.19 (2)	0.68 (5)	0.13 (5)
Bjurböle		L/LL4	0.14 (4)	0.71 (6)	0.16 (5)
Tuxtuac		LL5	0.22 (4)	0.60 (3)	0.19 (3)
St. Séverin		LL6	0.19 (6)	0.62 (7)	0.19 (3)
Adzhi-Bogdo		LL3-6	0.05 (1)	0.88 (4)	0.08 (4)
PRE 95410		R3	0.12 (3)	0.7 (1)	0.2 (1)
ALH 85151		R3.6	0.09 (4)	0.7 (1)	0.2 (1)
PCA 91002	Rumuruti	R3.8-6	0.11 (5)	0.7 (1)	0.2 (1)
LAP 03639	Chondrites	R4	0.18 (3)	0.67 (8)	0.15 (9)
LAP 04840		R5	0.00 (1)	0.29 (1)	0.70 (1)
MIL 11207		R6	0.06 (4)	0.29 (1)	0.65 (5)

All parenthetical values represent 1-sigma standard deviation of the mean (1σSDOM)
[a]If X-site sum exceeds 1 sfu, F was computed assuming $X_F = 1 - X_{Cl}$
[b]Missing component computed based on stoichiometry assuming $X_{Missing} = 1 - (X_F + X_{Cl})$ unless otherwise noted

Table 2. List of outer solar system chondrite samples from which apatite was analyzed during this study, including apatite data published in previous studies (Dyl et al., 2015; Piralla et al., 2021; Zhang et al., 2016; Zhang and Yurimoto, 2013). The class, group, and petrologic type of each sample along with average structural occupancies of fluorine, chlorine, and hydroxyl in the apatite X-site from each sample are provided. All data are provided in Tables S8–S15.

Name	Class	Group & Type	Avg. F[a] in X-site	Avg. Cl in X-site	Avg. missing in X-site[b]
Karoonda		CK4	0.09 (5)	0.7 (1)	0.23 (9)
DAV 92300		CK4	0.13 (3)	0.6 (1)	0.3 (1)
Maralinga	CK Chondrites	CK4 Anomalous	0.06 (4)	0.6 (2)	0.4 (1)
Maralinga CAI		CK4 Anomalous	0.04 (3)	0.7 (2)	0.2 (1)
EET 87507		CK5	0.14 (3)	0.6 (1)	0.3 (1)
LAR 06872		CK6	0.13 (4)	0.6 (1)	0.3 (1)
NWA 8186		CK7	0.08 (4)	0.73 (6)	0.19 (5)
Boriskino		CM2	0.07 (2)	0.003 (2)	0.93 (2)
Allende	Other Carbonaceous Chondrites	CV3	0.22 (5)	0.07 (6)	0.71 (6)
DaG 978		C3	0.05 (4)	0.78 (7)	0.17 (6)
Bench Crater		C1	0.23 (5)	0.006 (2)	0.76 (5)

All parenthetical values represent 1-sigma standard deviation of the mean (1σSDOM)

[a]If X-site sum exceeds 1 sfu, F was computed assuming $X_F = 1 - X_{Cl}$

[b]Missing component computed based on stoichiometry assuming $X_{Missing} = 1 - (X_F + X_{Cl})$ unless otherwise noted

Table 3. Average electron microprobe analyses of apatite analyzed in inner solar system chondrites. All individual analyses from which the mean apatite composition was computed for each sample are reported in Tables S1–S7.

Oxide	*LL Chondrites* Parnallee	*R Chondrites* LAP 04840	MIL 11207	ALH 85151	PCA 91002	PRE 95410	LAP 03639
P_2O_5	41.0 (3)	42.1 (4)	41.6 (8)	41.7 (5)	41.6 (5)	41.8 (6)	40.7 (5)
SiO_2	n.d.	0.1 (2)	0.04 (4)	0.1 (2)	0.1 (1)	0.07 (8)	0.1 (3)
Ce_2O_3	0.02 (2)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Y_2O_3	0.01 (1)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	0.5 (3)	0.7 (5)	0.5 (2)	0.5 (4)	0.6 (3)	1.0 (6)	1.1 (3)
MnO	n.d.	0.06 (1)	0.04 (2)	0.02 (1)	0.02 (2)	0.02 (1)	0.03 (1)
MgO	0.07 (5)	0.13 (4)	0.16 (2)	0.04 (5)	0.11 (8)	0.03 (4)	0.09 (9)
CaO	52.5 (7)	52.9 (9)	55.7 (9)	53.0 (6)	53.1 (6)	52.9 (8)	52 (1)
Na_2O	0.47 (3)	0.14 (8)	0.14 (5)	0.43 (7)	0.42 (5)	0.44 (2)	0.45 (3)
F	0.57 (7)	0.02 (3)	0.2 (2)	0.3 (1)	0.4 (2)	0.4 (1)	0.6 (1)
Cl	5.1 (1)	2.02 (8)	2.07 (7)	4.9 (8)	5.0 (9)	4.8 (9)	4.6 (5)
S	n.d.	0.01 (1)	0.01 (1)	0.03 (4)	0.06 (5)	0.06 (8)	0.10 (7)
$-O \equiv F + Cl + S$	1.39	0.47	0.56	1.26	1.33	1.30	1.34
Total	**98.85**	**97.71**	**99.90**	**99.76**	**100.08**	**100.22**	**98.43**
N	18	42	30	26	25	19	19
Structural formulae based on 13 anions							
P	3.01	3.03	2.94	3.02	3.01	3.02	2.99
Si	-	0.01	0.00	0.01	0.01	0.01	0.01
Ce	0.00	-	-	-	-	-	-
Y	0.00	-	-	-	-	-	-
Fe	0.04	0.05	0.03	0.04	0.05	0.07	0.08
Mn	-	0.01	0.00	0.00	0.00	0.00	0.00
Mg	0.01	0.02	0.02	0.01	0.02	0.00	0.01
Ca	4.87	4.82	5.07	4.85	4.85	4.84	4.88
Na	0.08	0.02	0.02	0.07	0.07	0.07	0.08
∑ Cations	*8.01*	*7.96*	*8.08*	*8.00*	*8.01*	*8.01*	*8.05*
F^a	0.16	0.00	0.06	0.09	0.11	0.12	0.18
Cl	0.75	0.29	0.29	0.71	0.72	0.69	0.67
S	-	0.00	0.00	0.01	0.01	0.01	0.02
OH^b	0.09	0.70	0.65	0.2	0.16	0.18	0.14
∑ Anions	*1.00*	*0.99*	*1.00*	*1.01*	*1.00*	*1.00*	*1.01*

N – number of analyses
- signifies that a value was not computed
n.d. – abundance was not determined
All parenthetical values represent 1-sigma standard deviation of the mean (1σSDOM)
[a]If sum of X_F and X_{Cl} exceeds 1 sfu, F was computed assuming $X_F = 1 – X_{Cl}$.
[b]Calculated assuming that $X_F + X_{Cl} + X_{OH} = 1$ sfu

Table 4. Average electron microprobe analyses of apatite analyzed in outer solar system chondrites. All individual analyses from

which the mean apatite composition was computed for each sample are reported in Tables S8–S14.

Oxide	CK Chondrites						CAI in Maralinga
	Karoonda	NWA 8186	DAV 92300	EET 87507	LAR 06872	Maralinga	
P_2O_5	41.4 (6)	41.5 (5)	42.0 (4)	41.3 (8)	41.4 (6)	41.5 (5)	41.3 (4)
SiO_2	0.1 (2)	0.3 (1)	0.1 (2)	0.5 (5)	0.4 (4)	0.1 (2)	0.1 (2)
Ce_2O_3	0.02 (1)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Y_2O_3	0.00 (0)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	0.9 (6)	0.3 (2)	0.4 (3)	1.1 (2)	1.4 (2)	1.1 (4)	0.5 (3)
MnO	0.05 (2)	n.d.	0.02 (1)	0.02 (1)	0.01 (1)	0.02 (1)	0.02 (3)
MgO	0.09 (9)	0.02 (7)	0.02 (7)	0.2 (2)	0.2 (2)	0.0 (1)	0.03 (7)
CaO	53.2 (6)	53.4 (8)	53.6 (3)	53.0 (9)	53.3 (7)	52.8 (6)	52.6 (6)
Na_2O	0.16 (2)	0.52 (7)	0.31 (2)	0.32 (3)	0.36 (4)	0.33 (2)	0.34 (2)
F	0.3 (2)	0.3 (2)	0.5 (1)	0.5 (1)	0.5 (2)	0.2 (1)	0.1 (1)
Cl	4.7 (8)	5.0 (4)	4.1 (8)	3.9 (8)	4 (1)	4 (1)	5 (1)
S	0.06 (6)	n.d.	0.02 (2)	0.07 (5)	0.1 (2)	0.02 (2)	0.01 (1)
$-O \equiv F + Cl + S$	1.20	1.26	1.13	1.12	1.13	1.00	1.18
Total	99.78	100.08	99.94	99.79	100.54	99.07	98.82
N	21	46	45	23	18	35	93
Structural formulae based on 13 anions							
P	3.00	3.00	3.02	2.98	2.97	3.01	3.02
Si	0.01	0.02	0.01	0.04	0.04	0.01	0.01
Ce	0.00	-	-	-	-	-	-
Y	0.00	-	-	-	-	-	-
Fe	0.06	0.03	0.03	0.08	0.10	0.08	0.04
Mn	0.00	-	0.00	0.00	0.00	0.00	0.00
Mg	0.01	0.00	0.00	0.03	0.03	0.01	0.00
Ca	4.89	4.88	4.88	4.84	4.84	4.85	4.86
Na	0.03	0.09	0.05	0.05	0.06	0.06	0.06
$\sum$ *Cations*	*8.00*	*8.02*	*7.99*	*8.02*	*8.04*	*8.02*	*7.99*
F^a	0.09	0.08	0.13	0.14	0.13	0.06	0.04
Cl	0.68	0.73	0.59	0.56	0.56	0.58	0.72
S	0.01	-	0.00	0.01	0.02	0.00	0.00
OH^b	0.22	0.19	0.29	0.29	0.30	0.36	0.24
$\sum$ *Anions*	*1.00*	*1.00*	*1.01*	*1.00*	*1.01*	*1.00*	*1.00*

N – number of analyses

- signifies that a value was not computed

n.d. – abundance was not determined

All parenthetical values represent 1-sigma standard deviation of the mean (1σSDOM)

[a]If sum of X_F and X_{Cl} exceeds 1 sfu, F was computed assuming $X_F = 1 – X_{Cl}$.

[b]Calculated assuming that $X_F + X_{Cl} + X_{OH} = 1$ sfu

$y = 10.447x$
$r^2 = 0.9955$