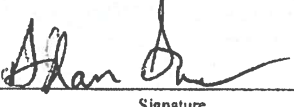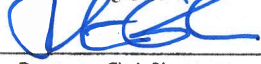**Justin G. Casaus**

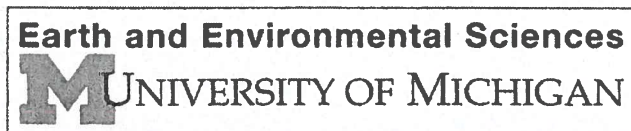**An Experimental Study of The Incorporation of Sulfur In Fluorapatite During Metasomatism**

submitted in partial fulfillment of the requirements for the degree of
Master of Science in Earth and Environmental Sciences
Department of Earth and Environmental Sciences
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Accepted by:

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5

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16

17   **Abstract**

18   The mineral apatite [$Ca_{10}(PO_4)_6(F,Cl,OH)_2$] is ubiquitous in terrestrial geologic systems. The

19   apatite supergroup is capable of incorporating a significant portion of the periodic table of

20   elements. As such, apatite is commonly used as a tool for, *inter alia*, U-Pb and fission track

21   dating of processes in igneous and metamorphic systems, determining the water content of

22   silicate melts at the time of apatite crystallization, and using Sr-Nd isotope systematics

23   fingerprinting the source of magmas and possible assimilation of crustal rocks. Despite apatite

24   being ubiquitous in igneous and magmatic-hydrothermal systems, there is a dearth of data that

25   constrain the partitioning of trace elements between apatite and aqueous hydrothermal fluids.

26   Here, we report results from hydrothermal alteration and crystallization experiments at 800 °C

27   and 1 GPa that constrain the partitioning of sulfur, iron, strontium, and the rare earth element

28   (REE) cerium between fluorapatite and fluids of variable compositions. The data demonstrate

29   that sulfur is incorporated in apatite through a balanced coupled substitution with Na and Si. The

30   data also demonstrate that the presence of Sr in the aqueous fluid promotes the incorporation of

31   Na and S in apatite. Our data reveal a previously unknown intrinsic relationship among Fe, Ce,

32   and S in metasomatized fluorapatite that is explained by coupled substitutions between Fe^{3+} and

33   Ce^{3+} with S^{4+}. The concentrations of Cl, OH, and S in run-produce apatite are positively

34   correlated with each other, which indicates that the halogen chemistry of apatite plays a

35   determinative role in the incorporation of S in apatite. Overall, the data demonstrate that

36   incorporation of sulfate and sulfite into apatite during metasomatism depends on the abundance

37   of charge-balancing cations in the hydrothermal fluid.

38

40

41   **INTRODUCTION**

42   Apatite is a common accessory mineral in sedimentary, igneous, and metamorphic rocks. The

43   apatite supergroup crystal chemical formula is $^{IX}M1_4{}^{VII}M2_6({}^{IV}TO_4)_6X_2$ (Z = 1),where the M sites

44   are most commonly occupied by Ca, the T site by P, and the X site by F, Cl or OH. The Roman

45   numeral superscripts indicate the ideal coordination numbers. Apatite can structurally

46   incorporate dozens of elements including Pb^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Na^+, Ce^{3+}, La^{3+}, Y^{3+} and Bi^{3+} on

the M-sites, and As^{5+}, V^{5+}, Si^{4+}, S^{6+} and B^{3+} on the T-site (Pasero et al., 2010; Pan and Fleet, 2002). Apatite can also incorporate multiple oxidation states of sulfur, with S^{6+} and S^{4+} on the T-site and S^{2-} on the X-site (Kim et al., 2017, 2022). The incorporation of non-essential structural constituents into the M, T and X sites is dictated by pressure, temperature, redox conditions, and for igneous and hydrothermal apatite the composition of the fluid medium from which apatite grows or, in the case of metamorphic apatite, the prograde and retrograde P-T paths. A plethora of studies have documented that the abundances of elements and their isotopes in apatite that crystallized from silicate melt can provide insight into the evolution of the magmatic system provided that metasomatism and/or dissolution-reprecipitation did not occur after crystallization (Watson and Green, 1981; Zhu and Sverjensky, 1991; Pan and Fleet, 2002). For example, the concentrations of rare earth elements (REE) in apatite can be used to infer melt source, the U-Pb and Lu-Hf concentrations in apatite can be used to quantify the timing of apatite crystallization (Spear and Pyle, 2002; Chew and Spikings, 2015), and the temperature controlled F-OH partitioning between apatite and biotite is used as a geothermometer (Sallet, 2000). Several studies have reported that the concentrations of the trace elements Sr, Mn and Y, chondrite-normalized REE patterns and Eu anomaly severity, and halogen fractionation (Br/Cl and I/Cl) in apatite are unique to specific rock types and have implications for mineral exploration (Andersson et al., 2019; Belousova et al., 2002; Mao et al., 2016; Zhou et al., 2022). Lastly, the measured abundances of S^{6+}, S^{4+} and S^{2-}, reported as the ratio of $S^{6+}/\Sigma S$, in magmatic apatite can be used to quantify oxygen fugacity (fO_2) at the time of apatite crystallization (Konecke et al., 2019). The compositions and textures of magmatic apatite have also been used to understand how fluid-induced metasomatism affects primary apatite. For example, Harlov et al. (2002b) reported that hydrothermal alteration of primary fluorapatite in samples from the Kiirunavaara

70   magnetite-apatite deposit in northern Sweden resulted in decreased concentrations of Na, S, Fe,

71   Sr, and Ce concentrations in regions of individual grains that were metasomatized by a Cl-OH-

72   fluid. Contrarily, Palma et al. (2019) reported that hydrothermal alteration of fluorapatite in

73   samples from the Mina Carmen iron oxide-apatite (IOA) deposit of northern Chile resulted in an

74   increase in the concentrations of Na, S, Fe, and Sr in regions of apatite grains that were

75   metasomatized by a Cl-OH-S-fluid. Konecke et al. (2017) reported that the same metasomatized

76   fluorapatite grains studied by Palma et al. (2019) contain S^{6+}, S^{4+}, and S^{2-}, in the metasomatized

77   regions of individual grains.

78

79   A limited number of experimental studies have been conducted in order to better understand how

80   the composition of apatite is affected by hydrothermal (metasomatic) alteration. Harlov et al.

81   (2002a) experimentally reacted unaltered Ødegårdens Verk chlorapatite grains with pure H_2O, a

82   50/50 molar mix of H_2O and CaF_2, and CO_2 with 1-2 wt.% H_2O at 300 – 900 °C and 0.5 – 1

83   GPa. They report that hydrothermal alteration of the chlorapatite grains with pure H_2O resulted

84   in a depletion of Na, Si, and (Y + REE) in apatite and concomitant growth of monazite and

85   xenotime inclusions. Those authors also reported that hydrothermal alteration of chlorapatite

86   grains with a F-bearing fluid resulted in the enrichment of F and Si in apatite and sparse growth

87   of monazite. Those authors reported that reaction of chlorapatite with a CO_2-bearing fluid

88   resulted in no measurable changes to the starting apatite. Harlov and Förster (2003)

89   experimentally reacted natural light REE (LREE) enriched Durango fluorapatite grains with pure

90   H_2O, brines bearing Na, Ca, or K, and CO_2 bearing fluids at 300 – 900 °C and 0.5 – 1 GPa.

91   Those authors reported increased fluorapatite reactivity with increased temperature and the

92   leaching of the LREEs, Na, and Si from metasomatized regions of the run-product fluorapatite

93 grains. They also reported that the increased activity of Na and Ca in the fluids stabilized the

94 LREEs in the Durango fluorapatite grains and prevented the formation of accessory monazite.

95 Harlov et al. (2005) experimentally reacted natural LREE enriched Durango fluorapatite grains

96 with 1 and 2 N HCl and H_2SO_4 solutions at 300 – 900 °C and 0.5 – 1 GPa and reported the

97 depletion of the REEs, Na, Si, S, and Cl in the metasomatized regions and the formation of

98 accessory monazite, consistent with Harlov and Förster (2003). The aforementioned experiments

99 elucidated the formation of REE-bearing monazite commonly observed in magmatic and

100 hydrothermal systems.

101

102 There is a dearth of published experimental data that elucidate the formation of Na-, S-, Fe- and

103 Sr-bearing apatite in hydrothermal systems (Konecke et al., 2017; Palma et al., 2019). Existing

104 experimental data demonstrate a relationship among Na, Si, and S in magmatic apatite that is

105 explained by coupled substitution of Na and/or Si ions with S^{6+} according to the following

106 charge balanced coupled substitutions (Rouse and Dunn, 1982; Liu and Comodi, 1993; Tepper

107 and Kuehner, 1999; Parat et al., 2011):

108 $$S^{6+} + Na^+ = P^{5+} + Ca^{2+} \tag{1}$$

109 $$S^{6+} + Si^{4+} = 2P^{5+} \tag{2}$$
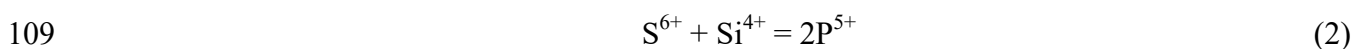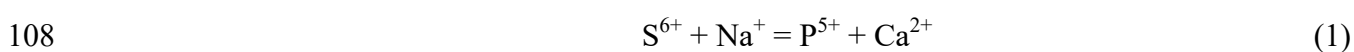
110 Palma et al. (2019) also reported that the concentrations of S, Fe, and Sr in fluorapatite from the

111 magmatic-hydrothermal Mina Carmen iron oxide-apatite deposit were positively correlated with

112 each other and that fluorapatite grains contained secondary inclusions of monazite. That the

113 monazite is secondary is evinced by the consistent presence of hydrothermal magnetite veinlets

114 that crosscut primary fluorapatite. Those authors did not propose an explanation for the elevated

115 Sr concentrations in metasomatized fluorapatite from Mina Carmen, but Hughes et al. (1991) and

116 Rakovan and Hughes (2000) reported that Sr^{2+} prefers to substitute for Ca^{2+} on the M2 site in

117 apatite while Na^+ and REE^{3+} alternate occupying the M1 site. In this instance, the Na charge

118 balances the REE via the following coupled substitution for Ca (Pan and Fleet, 2002):

119 $$Na^+ + REE^{3+} = 2Ca^{2+} \tag{3}$$
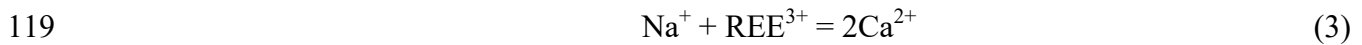
120 Palma et al. (2019) reported an overall decrease of REE concentrations in the metasomatized

121 fluorapatite grains, which suggests an influence of Sr on the coupled substitution of Na and S

122 described in Equation 1 rather than Equation 3. Apatite in natural magmatic and magmatic-

123 hydrothermal systems is commonly zoned with respect to F, Cl, and OH, and there is often a

124 positive correlation among the concentrations of Cl, OH, and S contents in the metasomatized

125 fluorapatite grains from Mina Carmen (Palma et al., 2019).

126

127 To our knowledge, there are no published experimental studies that constrain the partitioning of

128 S and REEs between apatite and a hydrothermal fluid. Here, we report the results of a series of

129 experiments wherein synthetic fluorapatite grains were reacted with a series of hydrothermal

130 fluids with different compositions to assess the effects of coupled dissolution-reprecipitation and

131 hydrothermal crystallization on the incorporation of S in metasomatized apatite. Experiments

132 were conducted at 800 °C and 1 GPa wherein synthetic S-free fluorapatite grains were reacted

133 with a variety of aqueous solutions containing dissolved S, Si, Fe, Ce, Sr, Na, Cl, F, and OH in

134 varying amounts (Table 1). The new data reported here provide insight into the incorporation of

135 S into fluorapatite that precipitates from, or re-equilibrates with, a S-bearing hydrothermal fluid.

136

137 **METHODS**

138 **Experimental Methods**

139 Endmember fluorapatite (APS-102) grains used in the experiments were synthesized using the

140 molten flux method outlined by Schettler et al. (2011) (see also Cherniak, 2000). Starting

141 synthetic fluorapatite grains were euhedral, elongate, and homogenous in back scattered electron

142 (BSE) image grayscale (Fig. 1). Experimental charges for metasomatism experiments consisted

143 of 20 mg of starting synthetic fluorapatite grains (APS-102), 5 mg of H_2O, 5 mg of a powdered

144 S-bearing compound or a S-bearing solution source, and compounds possessing the necessary

145 elements to effect charge balance for the coupled substitutions defined by Equations 1 and 2

146 (Table 1). Experimental charges for the hydrothermal crystal growth experiments consisted of

147 H_2O, synthetic fluorapatite (APS-102) seed crystals, powdered β-$Ca_3(PO_4)_2$ (Fluka, LOT

148 4558807/1-223043209) as a Ca and P source, and powdered NaF as a Na and F source. Here,

149 Na_2SO_4 served as the S source as well as providing the charge balancing cation Na^+ (Eqn. 1),

150 whereas SiO_2 served as the source of the charge balancing cation Si^{4+} (cf. Eqn. 2) (Table 1).

151

152 Charges were loaded either into 3 mm wide, 1 cm long Pt capsules for oxidized S sources or into

153 3 mm wide, 1 cm long Au capsules for reduced S sources, and then micro arc-welded shut.

154 Capsules were checked for leaks by first weighing, then placed in a drying oven at 110 °C for a

155 minimum of 8 hours and then weighing again. Platinum capsules have been known to react with

156 S to form sulfide complexes, resulting in embrittlement and/or corrosion of capsules, which can

157 potentially result in capsule failure (Webster and Botcharnikov, 2011). In our experiments, Pt

158 capsules containing sulfate-bearing reagents maintained capsule integrity over a 5-day duration

159 of the experimental run.

160

161   Experiments at 800 °C and 1 GPa for 5 days were conducted for 4 Au or 4 Pt capsules at the

162   same time using a 'Johannes Type' non-end load piston cylinder apparatus (Johannes et al.,

163   1971; Johannes, 1973), a solid CaF_2 assembly as the pressure medium, and a cylindrical graphite

164   oven (Angiboust and Harlov, 2017; see their Fig.3 for assembly cross section). The capsules

165   were gently flattened and loaded vertically into an approximately 5 x 5 x 12 mm pocket in the

166   CaF_2 assembly. The capsules were separated by biotite sheets to prevent them from welding

167   together and packed with powdered CaF_2. A Ni-Cr thermocouple was inserted into the CaF_2

168   assembly with the tip halfway up along the side of the experimental charges. A thermal gradient

169   along the length of the 1 cm experiment capsule meant that either end of the capsule was

170   approximately 20 °C lower than the temperature measured at the center. Once the CaF_2 assembly

171   was loaded into the apparatus, the pressure was increased to approximately 15% below the final

172   pressure. The temperature was increased to the final 800 °C, such that thermal expansion

173   increased the pressure to near the desired 1 GPa. Minor adjustments were then made to achieve

174   the final pressure, which was maintained automatically within a preset range of ± 0.015 GPa for

175   the duration of the experiments. Experiments were quenched non-isobarically by turning off the

176   heating current and automatic pressure control, which allowed the water cooling jackets and

177   mass of the apparatus to cool the experiments to below 100 °C in approximately 30 seconds. The

178   capsules were then extracted from the CaF_2 assembly, cleaned, and weighed to determine

179   whether capsule integrity was maintained. Cleaned capsules that did not maintain their starting

180   mass were discarded.

181

182   All experiment capsules were punctured, placed in a drying oven at 110 °C for 24 hrs., and

183   weighed again to determine the amount of fluid present. The dried run products were removed

184   from the experiment capsules and rinsed three times in DI H_2O to remove any solutes. A random

185   sampling of run product grains (i.e. a literal scoop) for each experiment were then dried,

186   mounted in epoxy, and polished for scanning electron microscopy (SEM), BSE imaging, and

187   quantitative EPMA.

188

189   **Analytical Methods**

190   **Scanning electron microscopy (SEM) and Electron probe micro-analysis (EPMA).**

191   Carbon-coated epoxy grain mounts were first analyzed on a JEOL JSM-7800FLV SEM using an

192   accelerating voltage of 20 kV at the Robert B. Mitchell Electron Microbeam Analysis Lab

193   (EMAL), University of Michigan, Ann Arbor, Michigan, USA. High-contrast BSE imagery was

194   utilized to record mineral textures of the experiment run-product fluorapatite. EPMA quantitative

195   analyses of run-product fluorapatite compositions were conducted on a Cameca SX-100 electron

196   microprobe (EMP) at EMAL, using a 15 keV electron beam and a beam current of 20 nA.

197   Counting times were 10 seconds on-peak and 5 seconds off-peak for all elements measured using

198   the mean atomic number (MAN) continuum X-ray correction method outlined in Donovan and

199   Tingle (1996). Because of the F and Cl X-ray count rate variation in response to electron beam

200   exposure (Goldoff et al., 2012), F and Cl were measured first as well as using Time-Dependent

201   Intensity (TDI) corrections incorporated into ProbeForWindows software (Donovan et al., 2007).

202   Quantitative analyses were conducted prior to the collection of representative BSE images.

203   Multiple points on multiple grains from each experiment were selected so as to obtain a random

204   dataset large enough for statistical consideration. Concentrations were obtained from raw counts

205   using a ZAF intensity correction. EPMA data and standards used for peak positions are listed in

206   the Supplementary Table 1. Wavelength dispersive spectroscopy (WDS) maps and

207   cathodoluminescence (CL) monochromatic grayscale images were collected post-quantitative

208   analyses on the Cameca SX-100 EMP using a 15 keV electron beam, a beam current of 40 nA, a

209   0.5 μm step size, and a 60 ms dwell time.

210

211   **Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).** The

212   concentrations of Sc, Mn, Fe, Y, Ba and REEs in the starting synthetic fluorapatite grains (APS-

213   102) were measured by LA-ICP-MS using an ESI NWR193 laser ablation system attached to an

214   Agilent Technologies 7900s quadrupole ICP-MS, housed at the Holder Laser Ablation ICP-MS

215   Laboratory, University of Michigan, Ann Arbor, Michigan, USA (Supplementary Table 2).

216   Analyses were conducted by using a 70 μm spot size, a fluence of 1.4 J/cm^2, at 6 Hz repetition,

217   30 sec of ablation, and a 20 sec baseline. The analyte in a He carrier gas was transported from

218   the LA system to a glass mixing bulb where the sample aerosol was mixed with Ar gas prior to

219   the ICP-MS. Trace element concentrations and detection limits were calculated using the method

220   outlined by Longerich et al. (1996), with the Ca concentration from EPMA analyses (Table 2) as

221   an internal standard, and using NIST610 glass as a secondary standard. The glass standards

222   NIST610 and NIST612 were analyzed throughout the session to correct for instrument drift.

223

224   **RESULTS**

225   Major and trace element concentrations of the starting synthetic fluorapatite grains measured by

226   EPMA are reported in Table 2. The chemical formula for run product apatite grains was

227   calculated using 5 cations and 26 oxygens (Ketcham, 2015); with the halogen site (X) occupied

228   by F, Cl, OH, and sulfur as S^{6+} and S^{4+} in the tetrahedral site (T). It is understood and

229   acknowledged by the geochemical community that nano scale inclusions below a polished grain

230   surface may be present in the electron beam excitation volume. In order to address this potential

231   issue, points selected for EPMA avoided cracks, intact and compromised fluid inclusions, and

232   avoided regions with pervasive accessory phases (i.e. Monazite). EPMA points which yielded

233   non-stoichiometric apatite chemical formula, insufficient sums, or indicated a secondary phase

234   were discarded and not used in this study. Pearson correlation coefficients (ρ) were calculated

235   from EPMA point analyses for ion pairs of interest (Pearson, 1895). A correlation coefficient

236   speaks to the linearity of data such that a coefficient of unity would plot on a straight line.

237   However, a correlation coefficient does not inform on the slope of the data trend (e.g. ratios in

238   ionic substitutions) or the extent of the data trend (e.g. minimum and maximum concentrations).

239   We define a strong correlation as $\rho > 0.75$, a moderate correlation as $0.5 < \rho < 0.75$, and a weak

240   correlation as $0.25 < \rho < 0.5$.

241

242   **Results from sulfate reagent experiments**

243   **Experiments at 800°C and 1 GPa involving H_2O + S ± Na ± Si.** Run product

244   fluorapatite grains from experiment FS2 (Table 1; 800 °C, 1GPa; FlAp + Na_2SO_4 + H_2O) are

245   dominantly anhedral, occasionally fractured, present with little evidence for dissolution, and are

246   homogenous in high-contrast BSE images (Supp. Fig. 1b). Run product fluorapatite grains from

247   experiment FS3 (Table 1; 800 °C, 1GPa; FlAp + 1M H_2SO_4 + SiO_2 + H_2O) are homogenous in

248   high-contrast BSE images, show minor evidence of dissolution with slightly rounded grains that

249   are subhedral to anhedral and are occasionally mantled by a silicate glass that was not analyzed

250   for its chemical composition (Supp. Fig. 1c). The compositions of run product fluorapatite grains

251   from FS2 and FS3 are equivalent to the starting synthetic fluorapatite grains (Table 2); notably

252   the S concentration is below the EPMA detection limit. Run product fluorapatite grains from

253 experiment FS12 (Table 1; 800 °C, 1 GPa; FlAp + Na_2SO_4 + $Na_2Si_2O_5$ + H_2O) are slightly

254 rounded, subhedral to anhedral, exhibit a subtle greyscale zonation in the high-contrast BSE

255 image, and a diffused zonation in the CL image (Fig. 2b) where darker regions are spatially

256 correlated with increased Na, Si, and S in the WDS maps (Figs. 2c,d,e). Run product fluorapatite

257 grains from experiment FS12 exhibit a 0.32 wt.% decrease in P to 18.22 wt.%, measurable S at

258 347 µg/g, an increase of Na to 0.03 wt.%, and an increase of Si to 228 µg/g (Table 2). For

259 experiment FS12 there exists a strong positive correlation between S with Na (ρ = +0.95), and S

260 with Si (ρ = +0.98) for the calculated atomic proportions (Fig. 2g). The data points for Na vs. S

261 are above and nearly straddle the stoichiometric 1:1 line whereas the Si vs. S data points with

262 elevated S concentrations are below and subparallel to the 1:1 line (Fig. 2g). Data clusters that

263 plot above the stoichiometric 1:1 line indicate an excess of the charge balancing cation and data

264 clusters that plot below the 1:1 line indicate an excess of S with respect to the charge balancing

265 cation. Run product fluorapatite grains from experiment FS15 (800 °C, 1GPa; FlAp + Na_2SO_4 +

266 SiO_2 + β-$Ca_3(PO_4)_2$ + NaF + H_2O) are euhedral to anhedral, and tens to hundreds of micrometers

267 in diameter. Aggregates of small euhedral fluorapatite grains coalesce into larger subhedral

268 grains, where the larger grains present with subtle zonation in the high-contrast BSE and CL

269 images (Supp. Figs. 2a,b) that is spatially correlated with elevated Na and S in the WDS maps

270 (Supp. Figs. 2c,e). In the WDS maps of Na and S, the zonation is more apparent and exhibits a

271 sharp reaction front separating a distinct core from the rim (Supp. Figs. 2c,e). The core appears

272 elongate, ca. 30 µm in diameter, subhedral with distinct parallel facets, and presents topotaxial to

273 the crystal habit of the rim. The Na and S poor core is the remnant parent crystal that has been

274 overgrown by a new Na and S bearing daughter material that precipitates from the fluid. Run

275 product fluorapatite grains from experiment FS15 exhibit measurable S with an average of 436

276　μg/g, an increase of Na to ca. 0.07 wt.%, and an increase of Si to ca. 55 μg/g (Table 2). There are

277　two distinct populations for Na, Si, and S concentrations in the run-product fluorapatite; a S

278　below detection limit group that plots on or near the Y-axis from measurements of grain cores

279　and a group where S concentrations range from ca. 0.011 to 0.027 a.p.f.u. for rim measurements

280　(Supp. Figs. 2g). There is a strong positive correlation between Na and S (ρ = +0.98) and no

281　correlation between Si and S (ρ = +0.04) (Fig. 4g). The Na vs. S trend plots above and

282　subparallel to the 1:1 atomic ratio line (Supp. Figs. 2g).

283

284　**Experiments at 800 °C and 1 GPa involving H_2O + S ± Na ± Si ± Cl ± F ± OH.** Run

285　product fluorapatite grains from experiment FS7 (Table 1; 800 °C, 1 GPa; FlAp + Na_2SO_4 +

286　$CaCl_2$ + H_2O) are subhedral to anhedral and homogenous in high-contrast BSE imagery (Supp.

287　Fig. 1e). Run product fluorapatite grains from experiment FS16 (800 °C, 1 GPa; FlAp + Na_2SO_4

288　+ $Ca(OH)_2$ + H_2O) are subhedral to anhedral, homogenous in high-contrast BSE imagery, with

289　partially healed fractures and clusters of small (≤ 15μm) fluorapatite grains found on rims of

290　larger grains (Supp. Fig. 1f). Run product fluorapatite grains from experiment FS20 (Table 1;

291　800 °C, 1 GPa; FlAp + Na_2SO_4 + SiO_2 + $CaCl_2$ + H_2O) are subhedral to anhedral, with shallow

292　etch pits, and occasional subtle rounding of corners (Supp. Fig. 1g). Large (> 300 μm) elongate

293　aggregate masses of small (≤ 50 μm) euhedral to subhedral secondary quartz grains are present

294　but were not analyzed for their chemical composition. The compositions of the run product

295　fluorapatite grains from FS7, FS16, and FS20 are comparable to the starting synthetic

296　fluorapatite grains (Table 2); notably, S is below the EPMA detection limit.

297

298   Run product fluorapatite grains from experiment FS8 (Table 1; 800 °C, 1 GPa; FlAp + 1M

299   H_2SO_4 + SiO_2 + $CaCl_2$ + H_2O) are subhedral to anhedral with rounded margins, are homogenous

300   in the high-contrast BSE and CL images (Supp. Figs. 3a,b) with spatially correlated elevated S

301   and Cl in the WDS maps (Supp. Figs. 3d,f). Experiment FS8 run product fluorapatite grains

302   exhibit a 0.25 wt.% decrease in P to 18.29 wt.%, measurable S at 105 µg/g, and an increase in Na

303   and Si to 0.03 wt.% and 43 µg/g, respectively (Table 2). The run product halogen chemistry of

304   experiment FS8 exhibit a 0.30 wt.% decrease of F to 3.40 wt.%, an increase of Cl to 0.44 wt.%,

305   and an estimated OH concentration of 0.21 wt.% (Table 2). There is a weak negative statistical

306   correlation between measured S and Si concentrations (ρ = -0.38) and a weak positive

307   correlation between S and Na (ρ = +0.36). When the below detection limit data points are

308   removed from consideration, the Na-S correlation coefficient increases to ρ = +0.42 and the Si-S

309   correlation coefficient increases to ρ = -0.34. There is a strong positive correlation between S

310   and Cl (ρ = +0.91) concentrations and a weak negative correlation with the estimated OH content

311   (ρ = -0.31). Run product fluorapatite grains from experiment FS11 (Table 1; 800 °C, 1 GPa;

312   FlAp + Na_2SO_4 + NaF + H_2O) are subhedral to anhedral, slightly rounded with partially healed

313   fractures, homogenous in the high-contrast BSE images (Fig. 3a), and a subtle zonation in the CL

314   image where brighter areas are spatially correlated with elevated Na and S in the WDS maps

315   (Figs. 3b,c,e). Run product fluorapatite grains from experiment FS11 exhibit a 0.30 wt.%

316   decrease in the P concentration to 18.24 wt.%, measurable S at 452 µg/g, a 0.05 wt.% increase of

317   Na to 0.07 wt.%, and a 30 µg/g increase of Si to 68 µg/g (Table 2). Experiment FS11 run product

318   halogen chemistry exhibits a 0.07 wt.% decrease of F to 3.63 wt.% and an estimated OH

319   concentration of 0.23 wt.% (Table 2). There is a strong positive correlation for Na and S

320   concentrations (ρ = +0.98) that plot above and subparallel to the 1:1 line and a weak inverse

321   correlation for Si and S (ρ = -0.31) that plot on or near the X-axis (Fig. 3g). There is no statistical

322   correlation for S concentrations with those of F (ρ = -0.22), Cl (ρ = -0.23), or OH (ρ = +0.22).

323   Run product fluorapatite grains from experiment FS13 (Table 1; 800 °C, 1 GPA; FlAp + Na_2SO_4

324   + $Na_2Si_2O_5$ + $CaCl_2$ + H_2O) are subhedral to anhedral, homogenous in high-contrast BSE image

325   grayscale (Supp. Fig. 4a) with occasional aggregates of smaller ($\leq$ 15μm) grains coalescing to

326   form larger anhedral grains. Elongate grains of accessory wollastonite ($Ca_3(Si_3O_9)$) and

327   spheroids of sodium silicate glass are present (Supp. Fig. 4a) but were not analyzed for their

328   chemical compositions. Distinct zonation in the high-contrast CL image is visible with a spatial

329   correlation between brighter CL areas and elevated Na, Si, and S in the WDS maps (Supp. Figs.

330   4b,c,d,e). Run product fluorapatite grains from FS13 exhibit a 0.33 wt.% decrease of P to 18.21

331   wt.%, measurable S at 416 μg/g, Ca and Na average concentrations are unchanged with an

332   increase of Si to 440 μg/g (Table 2). Experiment FS13 run product fluorapatite grain halogen

333   chemistry exhibits a 0.36 wt.% decrease of F to 3.34 wt.%, Cl is unchanged at 0.01 wt.%., and an

334   estimated OH concentration of 0.46 wt.% (Table 2). There exists a strong positive correlation

335   between S with Na (ρ = +0.96) and Si (ρ = +0.99) concentrations (Supp. Fig. 4g), and a

336   moderate positive correlation with Cl (ρ = +0.70) and estimated OH (ρ = +0.55). The Si vs. S

337   a.p.f.u. concentrations plot on the atomic ratio 1:1 line while the Na vs. S a.p.f.u. concentrations

338   plot below and subparallel (Supp. Fig. 4g). Run product fluorapatite grains from experiment

339   FS17 (Table 1; 800 °C, 1 GPa; FlAp + Na_2SO_4 + $CaCl_2$ + $Ca(OH)_2$ + H_2O) are dominantly

340   subhedral to anhedral with partially healed fractures. Larger grains (> 100 μm) are occasionally

341   an aggregate of smaller ($\leq$ 15μm) euhedral to subhedral grains (Fig. 8a). Experiment FS17 run

342   products exhibit grain to grain variation in the high-contrast BSE image grayscale (Supp. Fig. 5a)

343   that does not display a clear and consistent correlation with zonation in the CL image or zonation

344 in the WDS maps (Supp. Figs. 5b-f). There is a distinct zonation in the run-product WDS map of

345 F that exhibits an inverse relationship with Cl (Supp. Figs. 5e,f) and a Na and S spatial

346 correlation of elevated concentrations along fractures and grain margins (Supp. Figs. 5c,d). Run

347 product fluorapatite grains from experiment FS17 exhibit a 0.32 wt.% decrease of P to 18.22

348 wt.%, measurable S at 156 µg/g, an increase of Na to 0.03 wt.%, and Si remains unchanged

349 (Table 2). The Na and S concentrations plot below and appear subparallel to the 1:1 atomic ratio

350 line while Si data points plot near the X-axis (Supp. Fig. 5g). Halogen concentrations of run

351 products from experiment FS17 exhibit a 0.49 wt.% decrease of F to 3.21 wt.%, an increase of Cl

352 to 0.03 wt.%, and an estimated OH concentration of 0.56 wt.% (Table 2). There is a moderate

353 positive correlation between S and Cl ($\rho = +0.58$) and between S and the estimated OH content

354 ($\rho = +0.55$).

355

356 **Experiments at 800 °C and 1 GPa involving $H_2O + S + Cl \pm Na \pm Fe \pm Sr \pm Ce$.** Run

357 product fluorapatite grains from experiment FS1 (Table 1; 800 °C, 1 GPa; FlAp + 1M H_2SO_4 +

358 $FeCl_3$ + H_2O) are subhedral to anhedral, with few rounded grain margins (Supp. Fig. 1a). Run

359 product fluorapatite grains from experiment FS4 (Table 1; 800 °C, 1 GPa; FlAp + 1M H_2SO_4 +

360 $CeCl_3$ + H_2O) are subhedral to anhedral, slightly rounded from dissolution, with sub-micrometer

361 monazite grains found in partially healed fractures and mantling the fluorapatite grains (Supp.

362 Fig. 1d). Run product fluorapatite grains from experiment FS21 (Table 1; 800 °C, 1 GPa; FlAp +

363 Na_2SO_4 + $CeCl_3$ + $CaCl_2$ + H_2O) are subhedral to anhedral and present with subtle rounding of

364 corners (Supp. Fig. 1h). Sub-micrometer monazite-(Ce) grains fill fractures with little evidence

365 of micrometer scale fluorapatite dissolution (Supp. Fig. 1h). Run product fluorapatite grains from

366 experiments FS1, FS4, and FS21 are homogenous in the high-contrast BSE images (Supp. Fig.

367   1a,d,h). Average run product concentrations for S, Fe, and Ce from experiments FS1, FS4, and

368   FS21 are below EPMA detection limits (Table 2).

369

370   Run product fluorapatite grains from experiment FS9 (Table 1; 800 °C, 1 GPa; FlAp + 1M

371   H_2SO_4 + $FeCl_3$ + $CaCl_2$ + H_2O) are subhedral to anhedral and homogenous in the high-contrast

372   BSE and CL images (Figs. 4a,b). Occasional aggregates of subhedral grains overgrown by larger

373   anhedral masses of fluorapatite are visible in the grain mount. In contrast to the BSE and CL

374   imagery, there exists a distinct element zonation and a strong positive spatial correlation for

375   elevated Fe, S, and Cl in the WDS maps of the run product fluorapatite (Figs. 4d,e,f). The

376   composition of fluorapatite grains from FS9 exhibit a decrease of P to 18.16 wt.%, measurable S

377   at 154 μg/g, Na and Si are slightly greater at 0.03 wt.% and 48 μg/g, respectively, and

378   measurable Fe at 0.09 wt.% (Table 2). Run product halogen concentrations in apatite grains from

379   FS9 exhibit a decrease of F to 3.34 wt.%, an increase of Cl to 0.58 wt.%, and an estimated OH

380   concentration of 0.20 wt.% (Table 2). The S atomic proportion exhibits a weak negative

381   correlation with the reported trace amounts of Na (ρ = -0.36) for all plotted data with the

382   majority on or above the 1:1 atomic ratio line. When ion pairs with S concentrations below

383   detection limits are removed, the Na-S correlation coefficient increases to ρ = +0.27. Data points

384   for Si plot near and near-parallel to the X-axis (Fig. 4g), indicating no relationship with the

385   incorporated S. The S concentrations exhibit a strong positive correlation with Fe (ρ = +0.75) for

386   all points measured (Fig. 4h). The reported correlation coefficient for Fe and S includes the data

387   points that present with independent Fe and S concentrations (Fig. 4h; box outline). There is a

388   cluster of plotted Fe concentrations that present with a linear trend that is subparallel and above

389   the 1:1 atomic ratio line (Fig. 4h). Run product fluorapatite grains from experiment FS10 (Table

390 1; 800 °C, 1 GPa; FlAp + 1M H_2SO_4 + $CeCl_3$ + $CaCl_2$ + H_2O) are euhedral to anhedral, with a

391 bi-modal grayscale in the high-contrast BSE and CL imagery (Figs. 5a,b). The darker, inclusion-

392 free regions in the BSE image are marked by a sharp reaction front that is traced by micrometer

393 to sub-micrometer scale monazite-(Ce) inclusions that separate brighter regions with numerous ≤

394 5 μm monazite inclusions and/or grains mantling the run product fluorapatite (Fig. 5a). In the

395 WDS maps of the run product fluorapatite grains, there exists a distinct element zonation and a

396 positive spatial correlation for elevated Ce and S (Figs. 5c,d). The composition of the BSE darker

397 regions in experiment FS10 exhibit a decrease in P to 18.32 wt.%, S is below EPMA detection

398 limits, subtle increases to average Na and Si concentrations, and measurable Ce at 0.34 wt.%

399 (Table 2). The halogen concentrations in the BSE darker regions exhibit a decrease of F to 3.43

400 wt.%, an increase of Cl to 0.48 wt.%, and an estimated OH concentration of 0.21 wt.% (Table 2).

401 The average concentrations of the brighter regions in fluorapatite grains from experiments FS10

402 exhibit a further decrease in P to 18.11 wt.%, measurable S at 153 μg/g, a decrease of Ca to

403 37.93 wt.%, and measurable Ce at 2.03 wt.% (Table 2). The Na and Si concentrations in the BSE

404 brighter regions are comparable to the starting fluorapatite composition (Table 2). There halogen

405 concentrations in the brighter BSE regions exhibit a further decrease of F to 3.18 wt.%, an

406 increase of Cl to 0.83 wt.%, and an estimated OH concentration of 0.19 wt.% (Table 2). There is

407 no statistical correlation between S and Na (ρ = +0.20) or a positive correlation with Si (ρ = -

408 0.61) (Figs. 5d,e,f,g). There is weak statistical correlation for Ce with Na (ρ = +0.31) and a

409 negative correlation with Si (ρ = -0.51) in the run-product fluorapatite concentrations. There is a

410 strong positive spatial and chemical correlation between Ce and S (ρ = +0.95) (Figs. 5c,d,h). Run

411 product fluorapatite grains from experiment FS14 (Table 1; 800 °C, 1 GPa; FlAp + Na_2SO_4 +

412 $SrCl_2$ + H_2O) are subhedral to anhedral with a bi-modal grayscale in the high-contrast BSE

413   images where the brighter regions are mantling darker cores and sometimes fluorapatite grains

414   are mantled by masses of Cl rich $SrSO_4$ (Fig. 6a). The brighter fluorapatite regions in BSE

415   images sometimes exhibit subtle and/or sharp zonation and can be found filling healed fractures

416   in the darker regions. In contrast with the CL imagery, the brighter fluorapatite regions in BSE

417   images have a strong positive spatial correlation with elevated Sr, Na, and S and a subtle positive

418   spatial correlation with Si in the WDS maps (Figs. 6c-f). The composition of the darker

419   fluorapatite regions in BSE images of experiment FS14 exhibit an increase of Ca to 39.26 wt.%

420   and an estimated OH concentration of 0.21 wt.% (Table 2). The concentrations of P, Sr, Na, F,

421   and Cl in the darker cores of the experiment run products is comparable to the concentrations in

422   the starting fluorapatite grains and S is below the EPMA detection limit (Table 2). The

423   composition of the brighter regions in BSE images of fluorapatite grains from experiment FS14

424   exhibit a decrease in P to 17.17 wt.%, measurable S at 3,514 µg/g, a decrease of Ca to 32.30

425   wt.%, an increase of Na to 0.20 wt.%, an increase of Si to 59 µg/g, and an increase of Sr to 10.24

426   wt.% (Table 2). The halogen concentrations of the bright areas in the run product fluorapatite

427   grains from FS14 exhibit a decrease of F to 3.29 wt.%, an increase of Cl to 0.09 wt.%, and an

428   estimated OH concentration of 0.31 wt.% (Table 2). The darker core of the Sr-bearing

429   fluorapatite in the BSE images (Fig. 6a) is interpreted to be the starting synthetic fluorapatite

430   (Table 2) and the composition plots near the origin of the Na, Si, S atomic proportion plot (Fig.

431   6g). The Sr-rich fluorapatite rims exhibit a strong positive correlation between Na and S

432   concentrations ($\rho = +0.99$) with the data plotting below and subparallel to the 1:1 atomic ratio

433   line (Fig. 6g). The data points for the Si concentrations plot near or on the X-axis (Fig. 6g).

434   There exists a strong positive correlation between Sr and S concentrations in the run-product

435   fluorapatite ($\rho = +0.99$).

436

Results from sulfide reagent experiment

Run product fluorapatite grains from experiment FS6-2 (Table 1; 800 °C, 1 GPa; FlAp + FeS + H_2O) are anhedral, exhibit numerous, subparallel, dissolution pits 5 to 20 μm deep that extend into the grain (Fig. 7a). Two regions are visible in the high-contrast BSE images of the reacted grains, a darker homogenous core that shares a distinct reaction front with a brighter rim; the dissolution pits do not extend into the darker cores. The BSE-brighter rims exhibit a heterogenous grayscale on the micrometer scale with a combination of distinct and diffuse reaction fronts and have a strong positive spatial correlation with elevated Fe and S in the WDS maps (Figs. 7a,c,d). A minor phase consisting of 5 μm or less, bright, Fe-rich grains is present with the run product apatite grains. The Fe-rich phases are not present as inclusions in the metasomatized regions of the run product fluorapatite grains. The Fe-rich phases were not analyzed for their composition. The Fe concentration in the starting synthetic apatite is less than the LA-ICP-MS detection limit of ca. 3093 μg/kg and the S concentration is less than the EPMA detection limit of ca. 38 μg/g (Supplementary Tables 1 and 2), indicating that the observed Fe-rich phases formed from the FeS reagent added to the fluid and not from the starting synthetic apatite. The chemical composition of the BSE-darker run product fluorapatite cores from experiment FS6-2 exhibit a decrease of P to 18.40 wt.%, measurable S at 71 μg/g, an increase of Si to 57 μg/g, an estimated OH concentration of 0.21 wt.%, Ca and F concentrations comparable to the starting fluorapatite grains, and Na, Fe, and Cl concentrations below their respective EPMA detection limits (Table 2). The chemical composition of the brighter run product rims from experiment FS6-2 exhibit a decrease of P to 18.03 wt.%, measurable S at 461 μg/g, a decrease of Ca to 37.47 wt.%, measurable Fe at 2.45 wt.%, and an estimated OH concentration

459   of 0.24 wt.%. The concentrations of Na, Si, and F in the brighter rims are comparable to the

460   starting fluorapatite grains, and Cl in the brighter regions is below the EPMA detection limit

461   (Table 2). There is a weak-moderate correlation between Na and S concentrations in the run

462   products (ρ = +0.39) where the a.p.f.u. concentrations plot near the origin or near the X-axis

463   (Fig. 7g). There is no statistical correlation between S and Si (ρ = -0.17) nor for S with the

464   halogens F (ρ = +0.18), Cl (ρ = -0.03), or OH (ρ = -0.18). There is a strong positive correlation

465   between Fe and S concentrations in the FS6-2 run products (Fig. 7h).

466

467   **DISCUSSION**

468   **The role of Na and Si in hydrothermal sulfate substitution in fluorapatite**

469   Previous studies demonstrated the coupled substitutions of S^{6+} with Na^+ and/or Si^{4+} (Eqns. 1 and

470   2) for S-bearing fluorapatite crystallized from a silicate melt, whereas our experiments test the

471   feasibility of these substitutions via a fluid-mediated process. When the Na and Si ion

472   concentrations are compared with the S ion concentrations of run-product apatite grains from this

473   study, there is a clear and distinct near 1:1 relationship between S and the charge balancing

474   cation Na where the majority of data points cluster on or near the 1:1 line (Fig. 8a). The

475   calculated statistical correlation coefficient for Na-S ion pairs for all experiments is ρ = +0.88

476   (i.e. a strong correlation). The correlation coefficient was calculated for the entire data set as we

477   found that despite not adding a Na source to some experiments, the Na and S coupled

478   substitution still occurred using the trace amounts of Na in the starting synthetic fluorapatite

479   (Table 2). In contrast, when considering the Si-bearing fluid experiments there is weak evidence

480   for a relationship between Si and S, where the majority of the EPMA data points plot near and

481   parallel to the X-axis (Fig. 8b), indicating no substantial relationship between Si and S for the

482   experiment conditions chosen. For the aggregate Si-bearing data set a strong statistical

483   correlation coefficient was calculated (ρ = +0.79) and further increased to ρ = +0.95 when only

484   the experiments that indicated a Si-S coupled substitution were considered (FS12 and FS13).

485   This overall trend is consistent with those observed in natural apatite grains from a variety of

486   metamorphic P-T conditions as well as trends observed in experimentally crystallized apatite.

487   The black X-symbols in Figure 8 represent average a.p.f.u. concentrations for apatite grains in

488   metamorphic rocks from Huangmailing, Hubei and Jinping, Jiangsu, China, and apatite grains

489   from Wilberforce, Ontario, Canada (Liu and Comodi, 1993), apatite grains from the partially

490   metasomatized Sudbury Igneous Complex, Ontario, Canada (Warner et al., 1998), and for

491   partially metasomatized apatite grains found in the Kiirunavaara magnetite-apatite ore bodies

492   (Harlov et al., 2002b). These samples represent a range of metamorphic pressure and temperature

493   conditions from 0.5 to greater than 2.8 GPa and 350 to 829 °C (Xiaochun, 1993, Liu et al., 2004;

494   Moecher et al., 1997), which encompass the 1GPa and 800 °C experimental conditions of this

495   study. We find that our data exhibit overlap with the black symbols representing apatite

496   compositions from metamorphic terranes, where they cluster along and near the 1:1 line in the

497   Na-S atomic plot (Fig. 8a) and trace amounts plot on or near the 1:1 line in on the Si-S atomic

498   plot (Fig. 8b). The grey polygons in Figure 8 represent the approximate regions of plotted Na vs.

499   S and Si vs. S a.p.f.u. concentrations of run-product apatite grains (Parat et al., 2011) from the S

500   partitioning apatite-melt experiments of Parat and Holtz (2004, 2005) and Parat et al. (2008) that

501   exhibit much less overlap with our experimental results when compared to the metamorphic

502   apatite (Figs. 8a,b).

503

504   From the overall Na vs. S trend that is near-parallel to and straddles the 1:1 atomic proportion

505   line (Fig. 8a) and the reported Pearson correlation coefficients, it is clear that, for the fluid

506   compositions and P-T conditions chosen, a stronger relationship exists between S and the charge

507   balancing cation Na (Eqn. 1). Whereas for the Si and S atomic plot, the natural metamorphic

508   apatite plot near the origin or near and parallel to the Y-axis while the experiment run-product

509   apatite compositions plot near the origin or near and parallel to the X-axis, indicating the

510   independent incorporation of Si and/or S i.e. not through the Si-S coupled substitution (Eq. 2),

511   and few data points plot near the 1:1 line and up to ca. 0.035 a.p.f.u. (Fig. 8b), indicating that the

512   coupled substitution between Si and S is secondary (Eqn. 2).

513

514   We acknowledge that of our experiments testing the Si-S coupled substitution, few resulted in

515   appreciable concentrations of Si and S. We suspect that this is from the Si reagents chosen:

516   powdered $Na_2Si_2O_5$ and powdered crystalline SiO_2. Experiments FS12 and FS13 used $Na_2Si_2O_5$

517   and are the only two experiments that yielded appreciable Si-S concentrations (Table 2) and

518   exhibit Si-S trends that are comparable to the natural metamorphic apatite (Fig. 8b, cf. Fig.2 and

519   Supplementary Fig. 4). $Na_2Si_2O_5$ (Industrial reagent nomenclature: SKS-6) is a commercial grade

520   water softening agent that is readily soluble in H_2O at room temperature, saturates a fluid of

521   amorphous silica and aqueous Na (Coker and Rees, 1993), and is a synthetic analog of the

522   naturally occurring natrosilite. Thermodynamic models demonstrate that amorphous silica (e.g.

523   SKS-6) is more soluble than crystalline SiO_2 in pure H_2O, but the overlap in the P-T limitations

524   of the models do not include our experiment P-T conditions (Fournier and Rowe, 1977; Fournier

525   and Potter II, 1982; Manning, 1994; Dolejš and Manning, 2010; Karásek et al. 2013). However,

526 this does not change our conclusion of a Na-S coupled substitution being preferred to a Si-S

527 coupled substitution.

528

529 It is not uncommon for Na a.p.f.u. concentrations to plot above the stoichiometric 1:1 line

530 indicating an excess of Na with respect to the coupled, charge balanced element being

531 substituted in the apatite crystal structure, such as S or REEs (Fig. 8a). This can be corrected for

532 natural concentrations by subtracting the ionic influences of elements that compete with the

533 element of interest, e.g. ionic Si-(Ce+Na) vs. ionic S (Peng et al., 1997). However, correcting for

534 the trace amounts of the REEs and Y in the starting synthetic fluorapatite (Supplementary Table

535 2) does not completely account for the excess Na with respect to S. Therefore, we suggest the

536 known substitution of Na for Ca and a vacancy on the halogen site that allows for an overall

537 neutral charge balance ($Na^+ + Vac. = Ca^{2+} + X^-$; Pan and Fleet, 2002):

538

539 The results of our experiments demonstrate the successful Na and Si charge balanced sulfate

540 coupled substitutions (Eqns. 1 and 2) during hydrothermal alteration and precipitation of the

541 mineral apatite, affirming the mineral apatite as a recorder of S, Na, and Si in a hydrothermal

542 fluid. When comparing the initial S concentration in the starting fluids (Table 1) to the measured

543 average S concentration in the respective run-products (Table 2), it is clear that that the activity

544 of Na and Si in the fluid is the limiting factor. However, experimentation that further constrains

545 the concentrations of Na, Si, and S in the starting and run-product fluid and apatite grains is

546 required to quantify the partitioning of S, Na, and Si between metasomatized apatite and a

547 hydrothermal fluid as a function of their respective concentrations.

548

Fluorapatite as a recorder of metal content in hydrothermal fluids

Apatite supergroup minerals can substitute a variety of metals for Ca in the crystal structure (e.g. Pb^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Na^+, Ce^{3+}, La^{3+}, Y^{3+} and Bi^{3+}; Pasero et al., 2010). Experiment FS1 reacted the starting synthetic fluorapatite with an Fe-bearing fluid with no Na or Si added as a reagent, which yielded run-products with little textural or chemical evidence that the starting fluorapatite had reacted with the fluid (Supp. Fig. 1a; Table 2). Experiment FS9 further increased the Cl activity in the fluid with the addition of $CaCl_2$, which resulted in partially metasomatized fluorapatite with measurable concentrations of Fe and S in the altered areas (Table 2). For the calculated a.p.f.u. concentrations, there is no statistical correlation indicates a coupled substitution between S and the trace amounts of the charge balancing cations Na and Si that might be sourced from the dissolution of the synthetic apatite. However, there is a strong positive correlation between Fe and S (Fig. 4h), which we suggest implies a previously unexplored coupled substitution between ferric iron and sulfite:
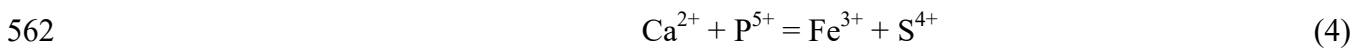
$$Ca^{2+} + P^{5+} = Fe^{3+} + S^{4+} \tag{4}$$

At the intrinsic fO_2 buffering of the 'Johannes type' piston cylinder apparatus is assumed to be between the graphite-carbon-carbon monoxide (CCO) buffer (imposed by piston cylinder graphite oven) and approximately the nickel – nickel oxide (NNO) buffer (Matjuschkin et al., 2015), ferrous and ferric iron exist. Due to the likely coexistence of Fe^{2+} and Fe^{3+} in the fluid, the observed correlation between Fe and S (Fig. 4h), and the lack of a significant correlation between S and the other known charge balancing cations (Fig. 4g), we propose Equation 4 to explain sulfite incorporation in apatite. This is supported by evidence that synthetic apatite grown from a fluid can be doped with Fe^{3+} (Low et al., 2008; Salviulo et al., 2010). We stress

572   that we were unable to determine the oxidation states of Fe in our run-product fluorapatite as this

573   requires the use of micro X-ray absorption near edge structure (μ-XANES) spectroscopy at the

574   Fe *K*-edge. However, these results highlight the ability of apatite to record fluid compositions

575   and potentially multiple species of redox sensitive metals. Further redox and crystal structure

576   analyses, which is beyond the scope of this study, will be required to better understand the site

577   occupancy (M1 vs. M2) and the effects of the smaller Fe^{2+} and Fe^{3+} cations (Shannon, 1976) on

578   the fluorapatite crystal structure.

579

580   If the 0.09 wt.% Fe incorporated into the run-product apatite for experiment FS9 is not some

581   ratio of Fe^{2+}/Fe^{3+}, then all must have been incorporated as a direct substitution of Fe^{2+} for Ca^{2+},

582   leaving one method for the incorporation of the measured S. Sulfur in magmatic-hydrothermal

583   fluids can be present as S^{2-}, S^{4+}, and S^{6+} where the proportion of each is controlled by fO_2

584   (Binder and Keppler, 2011; Binder et al., 2018). Konecke et al. (2017) reported the presence of

585   S^{4+} in the metasomatized regions of Mina Carmen fluorapatite and proposed the following

586   polyvalent S coupled substitution (Konecke et al., 2017a; Kim et al., 2017):

$$2P^{5+} = S^{6+} + S^{4+} \tag{5}$$
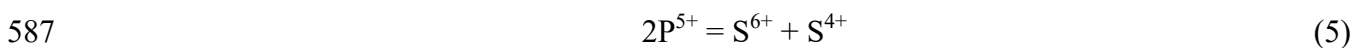
588

589   We suggest that this coupled sulfate-sulfite substitution explains the perceived excess S in all of

590   our run-products with respect to Equations 1 and 2 (i.e. more S than Na or Si allows). Without a

591   coupled substitution with Fe^{3+}, then the 154 $\mu g/g$ of measured S (Table 2) would be from the

592   sulfite-sulfate coupled substitution (Eq.5).

593

594   Strontium is a minor element commonly found in fluorapatite (Nash, 1984) and exhibits a unique

595   relationship with Na and the REEs in fluorapatite. When Sr is substituted into the apatite crystal

596   structure, it exhibits a preferential occupancy of the M2 site, which is normally occupied by the

597   smaller Ca^{2+}, while the also larger Na and the REEs (Shannon, 1976) alternate occupying the M1

598   site (Hughes et al., 1991; Rakovan and Hughes, 2000). Due to the positive spatial and statistical

599   correlations between Na and S enrichment, spatial correlations between Sr and S enrichment in

600   the run-product Sr-bearing fluorapatite (Figs. 6c,d,e,g), and the known site occupancies of Sr and

601   Na in strontian apatite we suggest that the presence of Sr in a hydrothermal fluid has significant

602   potential to promote Equation 1 over Equation 3, when the concentration of REEs in the

603   hydrothermal fluid are vanishingly low (i.e. REEs were not added to the experiment fluid and

604   vanishingly low concentrations as a potential source are present in the starting apatite; cf.

605   Supplementary Table 2), but is not a component in the charge balanced coupled substitution

606   formula of S. Experiment FS14 yielded texturally and compositionally zoned Sr-bearing

607   fluorapatite grains that yielded the greatest average S concentration for all experiments in this

608   study (3,514 µg/g; Table 2).

609

610   It is well known that the mineral apatite is one of the principal hosts of REEs in geologic systems

611   (Nash, 1984) and that they commonly substitute into the crystal structure via coupled substitution

612   with Na (Eqn. 1) and Si (Pan and Fleet, 2002):

613 $$REE^{3+} + Si^{4+} = Ca^{2+} + P^{5+} \qquad (6)$$
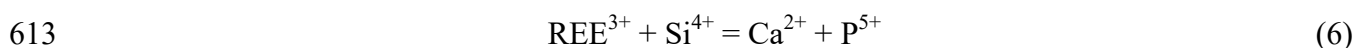
614   Experiment FS10, which reacted the starting synthetic fluorapatite with a S-, Ce-, and Cl-bearing

615   fluid, yielded a texturally and compositionally zoned run product fluorapatite (Fig. 5a; Table 2).

616   No observable spatial distribution or measured atomic proportions were observed that would

617 indicate a S coupled substitution with the trace amounts of Na and Si present in the starting

618 synthetic fluorapatite, nor for Ce with Na or Si (Figs. 5e,f,g). However, there is a strong positive

619 spatial and statistical chemical correlation between Ce and S (Figs. 5c,d,h). From these

620 observations, we propose the following coupled substitution between Ce^{3+} and S^{4+}:

621 $$Ca^{2+} + P^{5+} = Ce^{3+} + S^{4+} \tag{7}$$
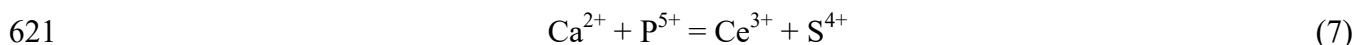
622

623 It is known that REE-bearing phosphates form at the expense of the host apatite grain via

624 coupled dissolution-reprecipitation of the host apatite by a hydrothermal fluid and that a coeval

625 decrease in Na, Si, and S can occur (Harlov et al., 2002a, 2005; cf. Our Eqns. 1,2,3, and 6).

626 During growth of secondary monazite-(Ce) from Ce- and S-bearing apatite grains, sulfate will

627 commonly substitute for phosphate in the monazite crystal structure (Laurent et al., 2016).

628 However, the dependence of both the REEs and S on Na and Si for coupled substitutions into the

629 apatite crystal structure, the need for ionic corrections to natural apatite REE and S a.p.f.u. plots

630 (Peng et al., 1997; Streck and Dilles, 1998), the known REE-sulfate complexes in a hydrothermal

631 fluid for transport and deposition (Banks et al., 1994; Migdisov et al., 2016), and the

632 aforementioned substitution of S during the growth of REE-phosphates, all indicate an intrinsic

633 and non-trivial relationship between S, the REEs, and the apatite supergroup.

634

635 The results of these metal-focused hydrothermal fluid alteration experiments demonstrate that

636 apatite records information about the metal budget of hydrothermal fluids. The results reported

637 here document previously unrecognized interdependencies between the substitution of S and the

638 metals Fe, Sr, and Ce into the apatite crystal structure. The mineral apatite records their presence

639 using the direct substitution of divalent cations, the coupled substitution of non-divalent cations

640   (e.g. Ce^{3+}) with Na^+ and/or Si^{4+}, and our proposed coupled substitutions with S. These

641   experiments underscore the necessity for further investigation into the redox state of Fe in the

642   run-product apatite grains and structural refinements of the run-product crystal structure to better

643   understand the site specific effects of these metal and S substitutions on the apatite crystal

644   structure.

645

646   **Effects of metasomatized fluorapatite halogen chemistry on fluid-mediated S substitutions**

647   Fluorapatite is the most common apatite end-member in magmatic systems (Piccoli and Candela,

648   2002; references therein) and changes to the apatite halogen chemistry reflects the composition

649   of the silicate melt during primary apatite crystallization (Webster and Piccoli, 2015; references

650   therein) and magmatic-hydrothermal fluids during metasomatic alteration (Harlov, 2015; Spear

651   and Pyle, 2002; Zhu and Sverjensky, 1991). Literature describing the apatite supergroup often

652   define members by their halogen chemistry (e.g. Sulphato-silicates $[Ca_{10}(SiO_4)_3(SO_4)_3(X)_2]$ -

653   ellestadite-(OH) and ellestadite-(F)) (Pasero et al., 2010), which leads to our hypothesis that

654   apatite halogen chemistry effects the substitution of S in fluorapatite.

655

656   Experiment FS11 is a control group experiment whereby saturating the fluid with a F source

657   (NaF) the run products remained a F-dominant apatite (Harlov, 2015; Spear & Pyle, 2002; Zhu

658   and Sverjensky, 1991). Experiment FS8 reacted the synthetic fluorapatite with a Na-free fluid

659   saturated with Si and Cl to explore the effects of Cl substitution on Equation 2. The run product

660   fluorapatite grains from experiment FS8 exhibit a minor incorporation of Cl and estimated OH

661   (Table 2). There is a weak negative correlation between S and Si, contrary to what was

662   anticipated. Instead, there is a weak correlation between S and Na which we suggest indicates

663   that the trace amounts of Na in the starting fluorapatite charge balanced the incorporation of S in

664   the run-products (Table 2). Experiment FS17 utilized $Ca(OH)_2$ to increase the activity of OH in

665   the fluid and promote the incorporation of OH into the apatite crystal structure to explore the

666   effects of OH on Equation 1. EPMA analyses indicate that we were able to successfully

667   incorporate OH into the run product apatite with a reduction of F, a minor Cl incorporation, and

668   an increase of the estimated OH content (Table 2). Experiment FS13 reacted synthetic

669   fluorapatite with a Na-, Si-, and Cl-bearing fluid in order to explore the effects of Cl substitution

670   on Equations 1 and 2. EPMA analyses reveal a decrease in F, no appreciable change to Cl, and

671   an increase of the estimated OH concentration (Table 2).

672

673   Of the experiments conducted testing the effects of the halogens F, Cl, and OH in the fluid on

674   Equations 1 and 2, FS11 retained halogen concentrations similar to the starting apatite grains and

675   yielded the greatest average measured S concentration (Fig. 9; Table 2). We suggest that in this

676   instance the reincorporation of Ca was suppressed during dissolution-reprecipitation by the

677   formation of CaF_2 using the excess F in the fluid (Harlov et al., 2006), thereby promoting the

678   substitution of Na and S in run products from experiment FS11 (Fig. 3g). Experiment FS13

679   exhibits the next greatest S concentration with a moderate estimated OH concentration and a

680   minor Cl concentration (Fig. 9; Table 2) Experiments FS17 and FS8 exhibit the lowest S

681   concentrations of the 4 experiments despite the greatest estimated OH and Cl concentrations,

682   respectively (Fig. 9; Table 2). We suggest that the moderate to strong correlations between S and

683   Cl concentrations, and the moderate correlation with estimated OH concentrations in the run

684   products demonstrate an effect of apatite halogen chemistry on the incorporation of S in apatite.

685   The halogen Cl has a larger ionic radius when compared to F and OH, is disordered above or

686   below the mirror planes in the unit cell which affects adjacent site occupancies, and has

687   cascading effects on interatomic bond lengths and forces (Hughes et al., 1989). The complex and

688   intricate effects of halogen site chemistry on the apatite crystal structure and the relatively

689   inconclusive results of our halogen alteration experiments stress the importance of conducting

690   detailed structural refinement studies to better understand the control of halogen site chemistry

691   on the substitution of minor and trace elements on the M- and T-sites in the apatite crystal

692   structure.

693

694   A positive relationship is observed between the initial S and Cl concentrations in the fluid (Table

695   1) and the S and Cl concentrations in the run-product apatite grains (Table 2) from experiments

696   FS11, FS13, FS17, and FS8. For these four experiments, FS11 had the greatest initial S content

697   in the fluid and yielded the greatest S concentration in the run-products while FS8 had the

698   greatest initial Cl content in the fluid and yielded the greatest Cl content in the run-products. This

699   trend for the F, Cl, and estimated OH concentrations in the experiment run-products agrees with

700   the dependence of apatite halogen site chemistry on the activity of F, Cl, and OH in a

701   hydrothermal fluid (Harlov, 2015; Spear and Pyle, 2002; Zhu and Sverjensky, 1991). However,

702   this trend is not true for S. Experiment FS14 run-products yielded the greatest average S content

703   of all experiments with ca. 7.6 wt.% S in the starting fluid composition while experiment FS6-2

704   yielded significantly less S in the run-products despite an initial fluid composition of ca. 22.3

705   wt.% S. These observations reinforce the hypothesis that the concentrations of charge balancing

706   elements is the limiting factor for S substitutions.

707

708   In the WDS maps of some experiments, the zonation of F or Cl is diffuse and in contrast to the

709   sharp reaction fronts visible for other elements (e.g. Figs. 2e,f). Sharp reaction fronts in

710   metasomatized fluorapatite are indicators of dissolution-reprecipitation and diffuse reaction

711   fronts are attributed to volume diffusion (Harlov et al. 2005; Putnis, 2002, 2009; Altree-Williams

712   et al., 2015), illustrating two distinct methods of re-equilibration. However, from the work of

713   others we know that electron beam induced diffusion of F and Cl in fluorapatite is common

714   (Stormer et al., 1993) and that the beam current affects the rate of diffusion (Goldoff et al.,

715   2012). This indicates that the alteration to the fluorapatite chemistry is a result of dissolution-

716   reprecipitation and that the diffuse reaction fronts visible in the F WDS map are a result of the

717   beam current and dwell time used for EPMA WDS data collection.

718

719   **Hydrothermal sulfide substitution in fluorapatite**

720   Experiment FS6-2, which reacted the starting synthetic apatite grains with an FeS-bearing

721   aqueous fluid to assess whether reduced S will substitute for F, Cl, and OH in apatite grains

722   reacted with a hydrothermal fluid. If the reduced S substituted for F in fluorapatite run-products,

723   we would expect to see an inverse relationship between S and F concentrations. However, no

724   statistically significant inverse correlation was observed for a.p.f.u. concentrations between S

725   and F, nor Cl or OH concentrations. Despite the textural differences, the results of experiment

726   FS6-2 (Figs. 7c,d) are similar to those of FS9 (Figs. 4d,e) where there is a clear positive spatial

727   correlation between Fe and S, and an unexpected strong positive correlation between the

728   calculated ionic concentrations of Fe and S in the run-product fluorapatite for experiment FS6-2

729   (Fig. 7h).

730

731 Given the possible range of intrinsic fO_2 buffering of the piston cylinder experiment apparatus

732 (CCO to NNO), it is reasonable to assume the coexistence of S^{2-}, S^{4+}, and S^{6+} in the fluid (Binder

733 and Keppler, 2011; Binder et al., 2018). However, without a clearly constrained intrinsic

734 buffering of the piston cylinder apparatus, it is impossible to infer an approximate ratio of $S^{6+}/\Sigma S$

735 for the hydrothermal fluid. Therefore, we cannot confirm whether S^{2-} or S^- were present in great

736 enough abundance to react with the synthetic fluorapatite. Due the strong positive correlation

737 between Fe and S, and the lack of an inverse correlation between S and F, we suggest that the

738 results of experiment FS6-2 provide additional evidence for a potential Fe^{3+} and S^{4+} coupled

739 substitution (Eqn. 4).

740

741 **IMPLICATIONS**

742 The data reported here document that fluorapatite, which experiences hydrothermal

743 metasomatism, preserves the chemical signature of the metasomatic fluid. Palma et al. (2019)

744 conducted textural, micro-analytical, and isotopic analyses on metasomatized primary

745 fluorapatite grains from the Mina Carmen IOA deposit in the Chilean iron belt. They propose

746 that an oxidized Cl-OH-S bearing magmatic-hydrothermal fluid reacted with the primary

747 magmatic fluorapatite and resulted in the partially metasomatized Cl-OH apatite rims that are

748 enriched in Na, S, Fe, and Sr. The results of our experiments are consistent with their hypothesis

749 that metasomatized fluorapatite will incorporate the volatiles Cl, OH, and S during the

750 dissolution-reprecipitation process and that the dominant S substitution in apatite occurs by

751 coupled substitution with Na (Eqn. 1; Fig.8a) and not with Si (Eqn. 2; Fig.8b). We suggest that

752 Sr in the magmatic-hydrothermal fluid likely promoted the Na-S coupled substitution as

753 evidenced by the coeval enrichment of Sr in the metasomatized regions of the Mina Carmen

754   apatite grains. We caution that the Na and S concentrations in the metasomatized regions of

755   Mina Carmen apatite should not be used to approximate Na or S concentrations in the fluid until

756   the influence of Sr on Equation 1 is better understood. The demonstrated fluid mediated Fe

757   incorporation in our experiment run-products suggest that the metasomatizing fluid was likely

758   enriched in Fe, supported by the reported cross-cutting relationship between magnetite veinlets

759   and the Fe-enriched Mina Carmen fluorapatite.

760

761   Boyce et al. (2014) proposed a fractional crystallization model to explain an observed core to rim

762   S enrichment and F-Cl-OH transition in apatite grains from lunar mare basalts. This model was

763   refuted by Konecke et al. (2017b) when they experimentally demonstrated that the proposed

764   lunar melt composition could not account for the S concentrations in the apatite grains. They

765   instead proposed a cryptic metasomatic event where the primary Cl-OH-S-poor lunar apatite

766   grains were altered by a S-Cl-bearing fluid that resulted in the enriched rims. The results of our

767   experiments demonstrate the metasomatic enrichment of Cl, OH, and S in a relatively S- and Cl-

768   free primary fluorapatite and support the cryptic metasomatism hypothesis of Konecke et al.

769   (2017b). Boyce et al. (2014) also reported the apparent coeval enrichment of Fe, Si, and Ce with

770   the volatiles Cl and OH. This core to rim enrichment is similar to that reported by Palma et al.

771   (2019) for the metasomatized Mina Carmen fluorapatite grains and our experiments demonstrate

772   the fluid-mediated enrichment of these elements in metasomatized run-product fluorapatite

773   grains.

774

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783

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1097   **Figure 4: a)** High-contrast BSE image of a grain from experiment FS9. Grains are subhedral to

1098   anhedral and homogenous in high-contrast BSE image grayscale. **b)** Monochromatic CL image

1099   of representative grain. Grid pattern is artifact of data processing. **c-f)** Wavelength dispersive

1100   spectroscopy elemental maps of Na, Fe, S, and Cl. A positive spatial correlation is visible for Fe,

1101   S, and Cl. Note the diffuse zonation of Cl. **g)** Atoms per formula unit (a.p.f.u.) scatter plot where

1102   red symbols compare S on the x-axis and Na on the y-axis, and blue symbols compare S on the

1103   x-axis and Si on the y-axis. The 1:1 line represents the sulfate coupled substitutions from

1104   Equations 1 and 2. **h)** Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S

1105   on the x-axis and Fe on the y-axis. Error bars for a.p.f.u. scatter plots represent X-ray counting

1106   error and can be smaller than the symbols. Detection limits are indicated by dashed lines. Black

1107   square indicates cluster with independent Fe and S concentrations. Dashed red line indicates

1108   approximate trend of data points for the proposed $Fe^{3+} + S^{4+} = Ca^{2+} + P^{5+}$ coupled substitution.

1109

1110   **Figure 5: a)** High-contrast BSE image of a grain from experiment FS10. Grains are euhedral to

1111   anhedral with a bi-modal grayscale in high-contrast BSE imagery where darker, inclusion-free

1112   regions are marked by a sharp reaction front traced by micrometer to sub-micrometer scale bright

1113   monazite-(Ce) inclusions (Mnz) that separate brighter regions with numerous ≤ 5 μm inclusions.

1114   **b)** Monochromatic CL image of representative grain. Negative black regions are an artifact from

1115   non-optimized brightness/contrast settings during automated electron microprobe data collection.

1116   **c-f)** Wavelength dispersive spectroscopy elemental maps of distinctly zoned Ce and S, and Na

1117   and Si that exhibit subtle zoning. Cerium and S exhibit strong positive spatial correlation with a

1118   more subtle Na and Si spatial correlation. **g)** Atoms per formula unit (a.p.f.u.) scatter plot where

1119   red symbols are S vs. Na on the y-axis and blue symbols are S vs. Si on the y-axis for analyses of

1120   the darker regions visible in BSE grayscale. Green symbols are S vs. Na on the y-axis and purple

1121   symbols are S vs. Si on the y-axis for analyses of the brighter regions visible in BSE grayscale.

1122   The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2. **h)** Atoms per

1123   formula unit (a.p.f.u.) scatter plot where blue symbols are S vs. Ce for the BSE-dark regions and

1124   red symbols are S vs. Ce for the BSE-bright regions. Error bars for a.p.f.u. scatter plots represent

1125   the X-ray counting error and can be smaller than the symbols. Detection limits are indicated by

1126   dashed lines.

1127

1128   **Figure 6: a)** High-contrast BSE image of a grain from experiment FS14. The red dashed line is

1129   the approximate location of the apatite grain boundary. Grains are subhedral to anhedral with a

1130   bi-modal grayscale in high-contrast BSE imagery where the brighter regions are mantling darker

1131   cores. Fluorapatite grains are sometimes mantled by masses of Cl-rich $SrSO_4$. **b)** Monochromatic

1132   CL image of representative grain where CL brightness presents inverse to BSE image intensity.

1133   The red dashed line is the approximate location of the apatite grain boundary. **c-f)** Wavelength

1134   dispersive spectroscopy elemental maps of Na, S, Sr, and Si. Sodium, S, and Sr exhibit a strong

1135   positive correlation in the zoned apatite. The bright green dashed line in (c) is the approximate

1136   location of the apatite grain boundary. **g)** Atoms per formula unit (a.p.f.u.) scatter plot where red

1137   symbols are S vs. Na on the y-axis and blue symbols are S vs. Si on the y-axis for analyses of the

1138   darker regions visible in BSE grayscale. Green symbols are S vs. Na on the y-axis and purple

1139   symbols are S vs. Si on the y-axis for analyses of the brighter regions visible in BSE grayscale.

1140   The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2. Error bars for

1141   a.p.f.u. scatter plots represent X-ray counting error and are smaller than the symbols. Detection

1142   limits are indicated by dashed lines.

1143

1144   **Figure 7: a)** High-contrast BSE image of a grain from experiment FS6-2. Grains are anhedral

1145   and exhibit numerous, subparallel, dissolution pits that extend into the grain. Two regions are

1146   visible in high-contrast BSE imagery, a darker homogenous core that shares a distinct reaction

1147   front with brighter grain margins. The brighter grain margins exhibit a heterogenous grayscale on

1148   the micrometer scale with a combination of distinct and diffuse reaction fronts. **b)**

1149   Monochromatic CL image of representative grain where CL brightness presents inverse to BSE

1150   image intensity. **c-f)** Wavelength dispersive spectroscopy elemental maps of Fe, S, Si, and F.

1151   Iron and S exhibit a strong positive spatial correlation in the zoned apatite. **g)** Atoms per formula

1152   unit (a.p.f.u.) scatter plot where red symbols are S vs. Na on the y-axis and blue symbols are S

1153   vs. Si on the y-axis for analyses of the darker regions visible in BSE grayscale. Green symbols

1154   are S vs. Na on the y-axis and purple symbols are S vs. Si on the y-axis for analyses of the

1155   brighter regions visible in BSE grayscale. The 1:1 line represents the sulfate coupled

1156   substitutions from Equations 1 and 2. **h)** Atoms per formula unit (a.p.f.u.) scatter plot where blue

1157   symbols are S vs. Fe for the darker BSE regions and yellow symbols are S vs. Fe for the brighter

1158   BSE regions. Error bars for a.p.f.u. scatter plots represent X-ray counting error and can be

1159   smaller than the symbols. Detection limits are indicated by dashed lines.

1160

1161   **Figure 8: a)** Atoms per formula unit (a.p.f.u.) scatter plot where red circles represent S and Na

1162   concentrations for all S-bearing run products, the black X-symbols are representative of reported

1163   S and Na concentrations in metamorphic apatite grains (Liu and Comodi, 1993; Warner et al.,

1164   1998; Harlov et al., 2002b), the inverted black triangles are representative of reported S and Na

1165   concentrations in the Mina Carmen apatite grains (Palma et al., 2019), and the grey polygon with

1166   the dashed outline is the approximate region of reported S and Na concentrations in apatite

1167   grains from apatite-melt partition experiments (modified from Parat et al., 2011; references

1168   therein). **b)** Atoms per formula unit (a.p.f.u.) scatter plot where open circles represent the 'low S'

1169   concentration experiments FS3 and FS20, the open squares represent the 'moderate S'

1170   concentration experiments FS8 and FS15, the blue symbols represent experiments FS12 and

1171   FS13 that plot on or near the 1:1 atomic ratio line, the black X-symbols are representative of

1172   reported S and Si concentrations in metamorphic apatite grains (Liu and Comodi, 1993; Warner

1173   et al., 1998; Harlov et al., 2002b), the inverted black triangles are representative of reported S

1174   and Si concentrations in the Mina Carmen apatite grains (Palma et al., 2019), and the grey

1175   polygon with the dashed outline is the approximate region of reported S and Si concentrations in

1176   apatite grains from apatite-melt partition experiments (modified from Parat et al., 2011;

1177   references therein). The 1:1 line represents the ideal sulfate coupled substitutions from Equations

1178   1 and 2.

1179

1180   **Figure 9:** Ternary plot illustrating F-Cl-OH halogen site occupancy in percent for experiment

1181   run products assessing the effects of halogen site chemistry on S incorporation and the starting

1182   synthetic apatite grains (APS-102). The chemical formula for run products is calculated using 5

1183   cations and 26 oxygens; assuming that the halogen site (X) is occupied by F, Cl, OH and that the

1184   S present in the fluorapatite is oxidized and occupies the tetrahedral site (T).

1185

1186   **List of Supplementary Figure Captions**

1187   **Supplementary Figure 1:** BSE images of representative fluorapatite grains from experiments

1188   where average S concentrations are below electron microprobe (EMP) detection limits. **a)**

1189   Representative grain from experiment FS1. Run-product apatite grains are homogenous in BSE

1190   image grayscale, subhedral to anhedral, with few rounded grain margins. **b)** Representative grain

1191   from experiment FS2. Run-product apatite grains are homogenous in BSE image grayscale,

1192   dominantly anhedral, and occasionally fractured. **c)** Representative grain from experiment FS3.

1193   Grains are homogenous in BSE image grayscale, subhedral to anhedral, slightly rounded, and

1194   occasionally mantled by a silicate glass that was not analyzed for its chemical composition.

1195   Brighter spots, indicated by a red arrow, on apatite grain are beam damage from EMP analyses.

1196   **d)** Representative grain from experiment FS4. Grains are homogenous in BSE image grayscale,

1197   subhedral to anhedral, slightly rounded from dissolution, with sub-micrometer monazite (Mnz)

1198   grains found in partially healed fractures and mantling the fluorapatite (Ap) grains. Brighter

1199   spots, indicated by a red arrow, on apatite grain are beam damage from EMP analyses. **e)**

1200   Representative grain from experiment FS7. Grains are homogenous in BSE image grayscale and

1201   anhedral with slightly concave margins from conchoidal fracturing. **f)** Representative grain from

1202   experiment FS16. Grains are homogenous in BSE image grayscale, and subhedral to anhedral

1203   with partially healed fractures. **g)** Representative grain from experiment FS20. Grains of

1204   fluorapatite (Ap) are homogenous in BSE image grayscale, subhedral to anhedral, with shallow

1205   etch pits, and occasional subtle rounding of corners. Aggregate masses of small (≤ 50 μm)

1206   euhedral to subhedral secondary quartz grains (Si) are present but were not analyzed for their

1207   chemical composition. Brighter spots, indicated by a red arrow, on apatite grain are beam

1208   damage from EMP analyses. **h)** Representative grain from experiment FS21. Grains of

1209   fluorapatite (Ap) are homogenous in BSE image grayscale, and subhedral to anhedral with subtle

1210   rounding of corners. Sub-micrometer monazite-(Ce) (Mnz) grains can be found filling fractures.

1211   Brighter spots, indicated by a red arrow, on apatite grain are beam damage from EMP analyses.

1212

1213   **Supplementary Figure 2: a)** High-contrast BSE image of a grain from experiment FS15. Grains

1214   are euhedral to anhedral, slightly rounded and exhibit a subtle greyscale zonation. White dashed

1215   line indicates approximate location of zonation boundary between overgrowth and seed crystal.

1216   **b)** diffuse boundary zonation in monochromatic CL image. **c-f)** Wavelength dispersive

1217   spectroscopy elemental maps of spatially correlated Na, Si, S, and F. Note the distinct zonation

1218   boundary for Na and S, and the diffuse boundary for F. Bright spots in Na and Si map are Na-Si

1219   glass spheroids. **g)** Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S on

1220   the x-axis and Na on the y-axis, and blue symbols compare S on the x-axis and Si on the y-axis.

1221   Error bars represent X-ray counting error and can be smaller than the symbols. Detection limits

1222   are indicated by dashed lines. The 1:1 line represents the sulfate coupled substitutions from

1223   Equations 1 and 2.

1224

1225   **Supplementary Figure 3: a)** High-contrast BSE image of a grain from experiment FS8. Grains

1226   are euhedral to anhedral, slightly rounded and homogenous in BSE grayscale. Bright spots on the

1227   apatite grain are beam damage from previous analyses. **b)** Monochromatic CL image with no

1228   apparent zonation. Beam damage visible as dark spots. **c-f)** Wavelength dispersive spectroscopy

1229   elemental maps of spatially correlated Na, Si, S, and Cl. Note the distinct zonation boundary for

1230   S and the diffuse boundary for Cl. Bright spots in Si map are silicate glass spheroids. **g)** Atoms

1231   per formula unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Na on the

1232   y-axis, and blue symbols compare S on the x-axis and Si on the y-axis. Error bars represent X-

1233 ray counting error and can be smaller than the symbols. Detection limits are indicated by dashed

1234 lines. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2.

1235

1236 **Supplementary Figure 4: a)** High-contrast BSE image of fluorapatite grain (Ap) from

1237 experiment FS13. Grains are subhedral to anhedral and homogenous in BSE image grayscale.

1238 Elongate grains of accessory wollastonite (Wol) and spheroids of sodium silicate glass (Na-Si)

1239 are present but were not analyzed for their chemical compositions. Dashed white line indicates

1240 approximate c-axis orientation. Bright spots on the apatite grain are from electron beam damage.

1241 **b)** Distinct zonation boundaries in monochromatic CL imagery. **c-f)** Wavelength dispersive

1242 spectroscopy elemental maps of Cl and spatially correlated Na, Si, and S. **g)** Atoms per formula

1243 unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Na on the y-axis, and

1244 blue symbols compare S on the x-axis and Si on the y-axis. Error bars represent X-ray counting

1245 error are smaller than the symbols. Detection limits are indicated by dashed lines. The 1:1 line

1246 represents the sulfate coupled substitutions from Equations 1 and 2.

1247

1248 **Supplementary Figure 5: a)** High-contrast BSE image of a grain from experiment FS17. Grains

1249 are dominantly subhedral to anhedral with partially healed fractures, and larger masses (> 100

1250 μm) of smaller (≤ 15μm) grain aggregates. Grains are euhedral to subhedral and exhibit grain to

1251 grain variation in BSE images. **b)** Subtle zonation in monochromatic CL imagery. **c-f)**

1252 Wavelength dispersive spectroscopy elemental maps of spatially correlated Na and S, and

1253 inversely correlated F and Cl. **g)** Atoms per formula unit (a.p.f.u.) scatter plot where red symbols

1254 compare S on the x-axis and Na on the y-axis, and blue symbols compare S on the x-axis and Si

1255 on the y-axis. Error bars represent X-ray counting error are smaller than the symbols. Detection

1256   limits are indicated by dashed lines. The 1:1 line represents the sulfate coupled substitutions

1257   from Equations 1 and 2.

Table 1. Summary of experimental results

Experiment	P (GPa)	T(°C)	Time (days)	Synthetic fluorapatite	H$_2$O	1M H$_2$SO$_4$	Na$_2$SO$_4$	FeCl$_3$	SrCl$_2$	CeCl$_3$	SiO$_2$
FS1	1	800	5	19.12		5.16		5.5			
FS2	1	800	5	19.28	4.95		4.3				
FS3	1	800	5	20.14		4.88					4.4
FS4	1	800	5	20.3		5.01				4.2	
FS6-2	1	800	8 hrs.	20.6	5.98						
FS7	1	800	5	20.96	5.72		5.03				
FS8	1	800	5	21.21		5.39					5.91
FS9	1	800	5	19.45		5.59		4.96			
FS10	1	800	5	21.14		5.37				5.06	
FS11	1	800	5	22.6	5.73		6.01				
FS12	1	800	5	20.18	5.84		5.21				
FS13	1	800	5	20.2	5.98		6.73				
FS14	1	800	5	20.32	5.18		5.97		6.52		
FS15	1	800	5	6.41	5.15		2.63				1.42
FS16	1	800	5	20.16	6.03		6.38				
FS17	1	800	5	19.56	5.97		5.38				
FS20	1	800	5	20.7	5.06		5.19				5.45
FS21	1	800	5	19.81	5.52		5.45			5.38	

Solids and liquids in mg. In high contrast BSE images of run products: all grains from a single experiment are equivalent in grayscale intensity and

Na₂Si₂O₅	β-Ca₃(PO₄)₂	FeS	CaCl₂	NaF	Ca(OH)₂	Initial Wt% S*	Initial Wt.% Cl*	Results
						4.4	11.3	Run product apatite grains are sub-hedral to anhedral, with fe...
						10.5		Run product apatite grains are occasionally fractured and dom...
						4.8		Run product apatite grains are slightly rounded and sub-hedra...
						4.9	6.6	Run product apatite grains are sub-hedral to anhedral and slig... mantling fluorapatite grains.
	9.45					22.3		Run product apatite grains are anhedral, have numerous sub-p... contrast BSE images. Sharp reaction front is visible in gray sc... Reprecipitated fluorapatite on rims are sometimes faceted.
		5.1				7.2	10.3	Run product apatite grains are anhedral with slightly concave...
		5.17				3.0	10.0	Run product apatite grains are anhedral, dominantly rounded...
		5.16				3.2	17.4	Run product apatite grains are sub-hedral to anhedral, with ag...
		5.45				3.1	15.5	Run product apatite grains are euhedral to anhedral, with num... show a bi-modal grayscale; darker, inclusion free, regions and... front.
				1.92		9.9		Run product apatite grains are sub-hedral to anhedral, are slig...
7.35						6.4		Run product apatite grains are sub-hedral to anhedral and are...
8.23		2.74				6.4	3.7	Run product apatite grains are sub-hedral to anhedral with agg... fluorapatite grains, including aggregates, are homogenous in g...
						7.6	8.3	Run product apatite grains are sub-hedral to anhedral with a b... the darker grains. Brighter regions sometimes exhibit subtle a...
	11.22			0.95		2.8		Run product apatite grains are euhedral to anhedral, 10s to 10... mantled by aggregates of smaller grains that have grown toge...
					5.38	8.1		Run product apatite grains are sub-hedral to anhedral, with pa...
		5.37			5.05	5.6	7.9	Run product apatite grains are dominantly sub-hedral to anhe... (≤15μm) euhedral to sub-hedral grains.
		5.77				5.5	8.6	Run product apatite grains are sub-hedral to anhedral, concav... aggregate masses of small (≤50μm) euhedral to sub-hedral se...
		4.73				5.8	10.8	Run product apatite grains are sub-hedral to anhedral with sub... little evidence of fluorapatite dissolution.

d individual grains are homogenous in grayscale, unless otherwise noted. * = wt.% of element relative to total mass of starting liquid and reagents.

w lobate margins.

ninantly anhedral.

l to anhedral. Fluorapatite is occasionally mantled by silicate glass.

htly rounded from dissolution reprecipitation. Sub-micron monazite grains are found in partially healed fractures and

parallel dissolution pits 5-20 µm deep that extend into the grain, with minor 5 µm or less bright iron sulfide grains in high
cale of BSE images separating darker cores from brighter rims; dissolution pits do not extend into darker cores.

margins from conchoidal fracturing.

margins with occasional facets.

gregates of sub-hedral grains overgrown by larger anhedral masses.

erous ≤5 µm Monazite-(Ce) inclusions and/or grains mantling the fluorapatite. In high contrast BSE images, some grains
d a sharp reaction front separating brighter regions. Micron to sub-micron scale monazite inclusions trace the reaction

htly rounded with partially healed fractures.

slightly rounded.

gregates of smaller (≤15µm) grains growing together to form larger anhedral grains. In high contrast BSE images the
grayscale. Elongate grains of accessory Wollastonite and spheroids of sodium silicate glass are present.

i-modal grayscale in high constrast BSE images. Brighter regions are found mantling darker cores and filling fractures of
nd/or sharp zonation in grayscale. Few fluorapatite grains are mantled by large (>200µm) masses of Cl rich $SrSO_4$.

0s of microns across, and present a homogenous grayscale in high contrast BSE images. Fluorapatite seed grains are
ther and have an undiscernible boundary with the seed crystals.

rtially healed fractures, and clusters of small (≤15µm) fluorapatite grains found on rims of larger grains.

dral with partially healed fractures, and occasionally larger grains (>100µm) are comprised of aggregates of smaller

e grain margins from conchoidal fracturing, and occasionally subtle rounding of corners. Large (>300µm) elongate
condary quartz grains.

otle rounding of corners. Sub-micron monazite-(Ce) grains can be found filling fractures of fluorapatite grains despite

Table 2. Chemical composition of run products from EPMA analyses

Exp	P (MPa)	T (°C)	time	area	# pts.	P (%)	Si (µg/g)	S (µg/g)	Ce (%)	Ca (%)	Fe (%)	Sr (%)	Na (%)	F (%)	Cl (%)
Synthetic fluorapatite used in this study					65	18.54	38			39.14		0.02	0.02	3.70	0.01
						0.01	*1*			*0.05*		*0.00*	*0.00*	*0.01*	*0.00*
FS1	1000	800	5 days		42	18.53	51			39.19		0.03	0.02	3.74	0.01
						0.02	*2*			*0.04*		*0.00*	*0.00*	*0.03*	*0.00*
FS2	1000	800	5 days		56	18.32	62			39.51		0.03	0.01	3.60	
						0.01	*2*			*0.04*		*0.00*	*0.00*	*0.03*	
FS3	1000	800	5 days		34	18.53	53			39.49		0.03	0.02	3.64	
						0.02	*3*			*0.06*		*0.00*	*0.00*	*0.04*	
FS4	1000	800	5 days		18	18.35	54			39.16		0.02	0.02	3.62	0.07
						0.05	*3*			*0.09*		*0.00*	*0.00*	*0.05*	*0.02*
FS6-2	1000	800	8 hrs.	dark	30	18.40	57	71		39.26		0.03		3.65	
						0.03	*2*	*4*		*0.06*		*0.00*		*0.03*	
				light	4	18.03	44	461		37.47	2.45	0.01	0.01	3.58	
						0.07	*4*	*103*		*0.72*	*0.81*	*0.00*	*0.00*	*0.17*	
FS7	1000	800	5 days		40	18.42	56			39.66		0.03	0.02	3.52	0.01
						0.02	*2*			*0.05*		*0.00*	*0.00*	*0.04*	*0.00*
FS8	1000	800	5 days		30	18.29	43	105		39.16		0.02	0.03	3.40	0.44
						0.02	*2*	*21*		*0.04*		*0.00*	*0.00*	*0.04*	*0.07*
FS9	1000	800	5 days		27	18.16	48	154		39.16	0.09	0.02	0.03	3.34	0.58
						0.03	*4*	*26*		*0.05*	*0.01*	*0.00*	*0.00*	*0.06*	*0.06*
FS10	1000	800	5 days	dark	24	18.32	48		0.34	39.22		0.02	0.03	3.43	0.48
						0.03	*3*		*0.15*	*0.12*		*0.00*	*0.00*	*0.05*	*0.06*
				light	14	18.11	39	153	2.03	37.93		0.02	0.03	3.18	0.83
						0.13	*6*	*58*	*1.32*	*0.89*		*0.00*	*0.00*	*0.08*	*0.06*
FS11	1000	800	5 days		32	18.24	68	452		39.74		0.03	0.07	3.63	
						0.03	*2*	*53*		*0.08*		*0.00*	*0.00*	*0.03*	
FS12	1000	800	5 days		52	18.22	228	347		39.22		0.03	0.03	3.22	
						0.03	*28*	*57*		*0.05*		*0.00*	*0.00*	*0.07*	
FS13	1000	800	5 days		21	18.21	440	416		39.14		0.04	0.02	3.34	0.01
						0.06	*153*	*176*		*0.09*		*0.00*	*0.01*	*0.12*	*0.00*
FS14	1000	800	5 days	dark	41	18.52	47			39.26		0.02	0.03	3.66	0.01
						0.02	*2*			*0.05*		*0.00*	*0.00*	*0.03*	*0.00*
				light	15	17.17	59	3514		32.30	10.24	0.20	3.29	0.09	
						0.06	*3*	*87*		*0.25*	*0.39*	*0.00*	*0.03*	*0.01*	
FS15	1000	800	5 days		53	18.43	55	436		39.34		0.03	0.07	3.71	0.01
						0.02	*2*	*43*		*0.05*		*0.00*	*0.00*	*0.02*	*0.00*
FS16	1000	800	5 days		20	18.35	46			39.78		0.02	0.02	3.64	
						0.03	*2*			*0.09*		*0.00*	*0.00*	*0.08*	
FS17	1000	800	5 days		31	18.22	39	156		39.38		0.02	0.03	3.21	0.03
						0.03	*10*	*98*		*0.05*		*0.00*	*0.00*	*0.15*	*0.01*
FS20	1000	800	5 days		30	18.37	40			39.09		0.02	0.01	3.64	0.01

					0.02	*3*	*0.04*	*0.00*	*0.00*	*0.03*	*0.00*
FS21	1000	800	5 days	38	18.32		39.73	0.03		3.65	0.04
					0.02		*0.05*	*0.00*		*0.03*	*0.01*

Standard error (/√n) in *italics*. Blank = below EPMA detection limit. * = calculated from EPMA data. † = site vacancy.

O* (%)	Sum (%)	est. OH* (%)	F	Cl	OH
38.02	99.46		1.90	0.00	0.10[†]
0.03			*0.01*	*0.00*	*0.01*
38.01	99.53	0.15	1.91	0.00	0.08
0.03			*0.01*	*0.00*	*0.01*
37.95	99.45	0.25	1.85		0.14
0.03			*0.02*		*0.02*
38.18	99.90	0.24	1.86		0.14
0.04			*0.02*		*0.02*
37.81	99.06	0.21	1.86	0.02	0.12
0.06			*0.02*	*0.01*	*0.02*
37.93	99.30	0.21	1.88		0.12
0.04			*0.01*		*0.01*
37.52	99.11	0.24	1.86		0.14
0.16			*0.08*		*0.08*
38.15	99.81	0.32	1.81	0.00	0.19
0.04			*0.02*	*0.00*	*0.02*
37.76	99.12	0.21	1.76	0.12	0.12
0.04			*0.02*	*0.02*	*0.02*
37.62	99.03	0.20	1.73	0.16	0.11
0.04			*0.03*	*0.02*	*0.02*
37.85	99.70	0.18	1.76	0.13	0.10
0.06			*0.02*	*0.02*	*0.02*
37.39	99.54	0.19	1.66	0.23	0.11
0.27			*0.03*	*0.02*	*0.02*
38.00	99.78	0.23	1.87		0.13
0.04			*0.01*		*0.01*
37.93	98.72	0.55	1.68		0.32
0.04			*0.04*		*0.04*
37.86	98.71	0.46	1.73	0.00	0.26
0.06			*0.06*	*0.00*	*0.06*
38.07	99.59	0.21	1.88	0.00	0.12
0.04			*0.01*	*0.00*	*0.01*
36.14	99.79	0.31	1.78	0.03	0.19
0.09			*0.01*	*0.00*	*0.01*
38.05	99.69	0.17	1.90	0.00	0.10
0.03			*0.01*	*0.00*	*0.01*
38.06	99.89	0.24	1.87		0.13
0.06			*0.04*		*0.04*
37.93	98.84	0.56	1.66	0.01	0.33
0.06			*0.08*	*0.00*	*0.07*
37.80	98.95	0.20	1.88	0.00	0.11

0.03			*0.01*	*0.00*	*0.01*
37.99	99.78	0.20	1.88	0.01	0.11
0.04			*0.01*	*0.00*	*0.01*

Figure 1

Figure 2

FS12: FlAp + Na_2SO_4 + $Na_2Si_2O_5$ + H_2O
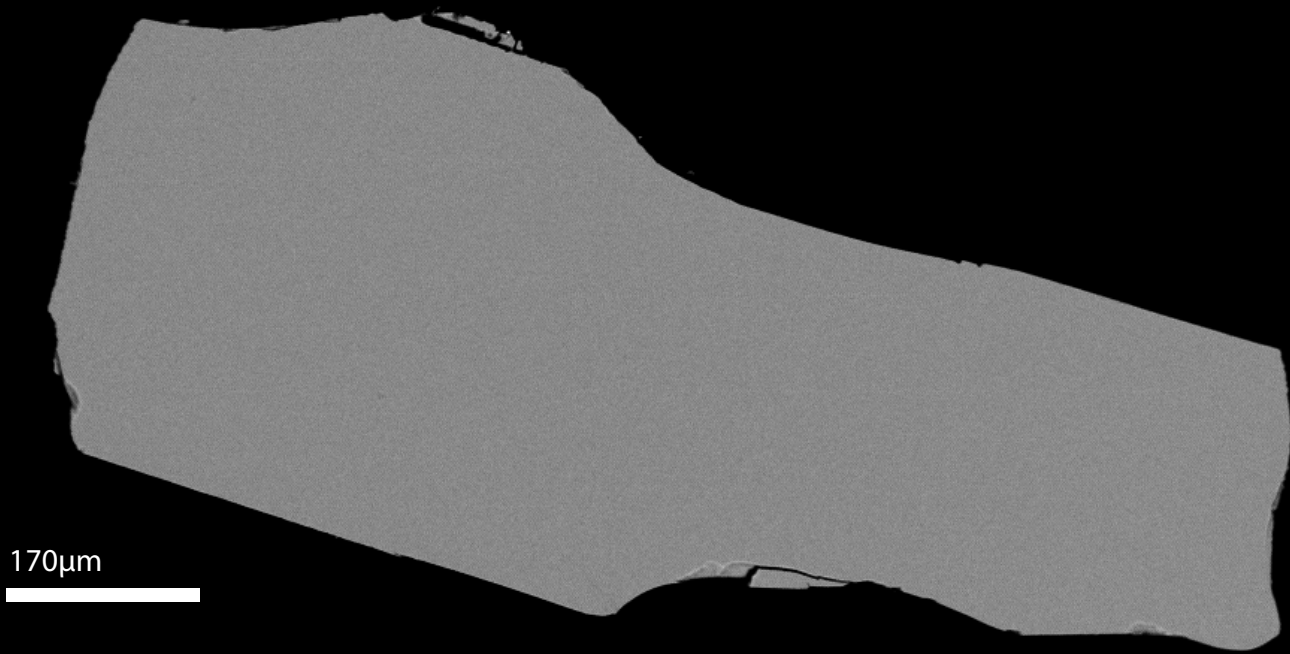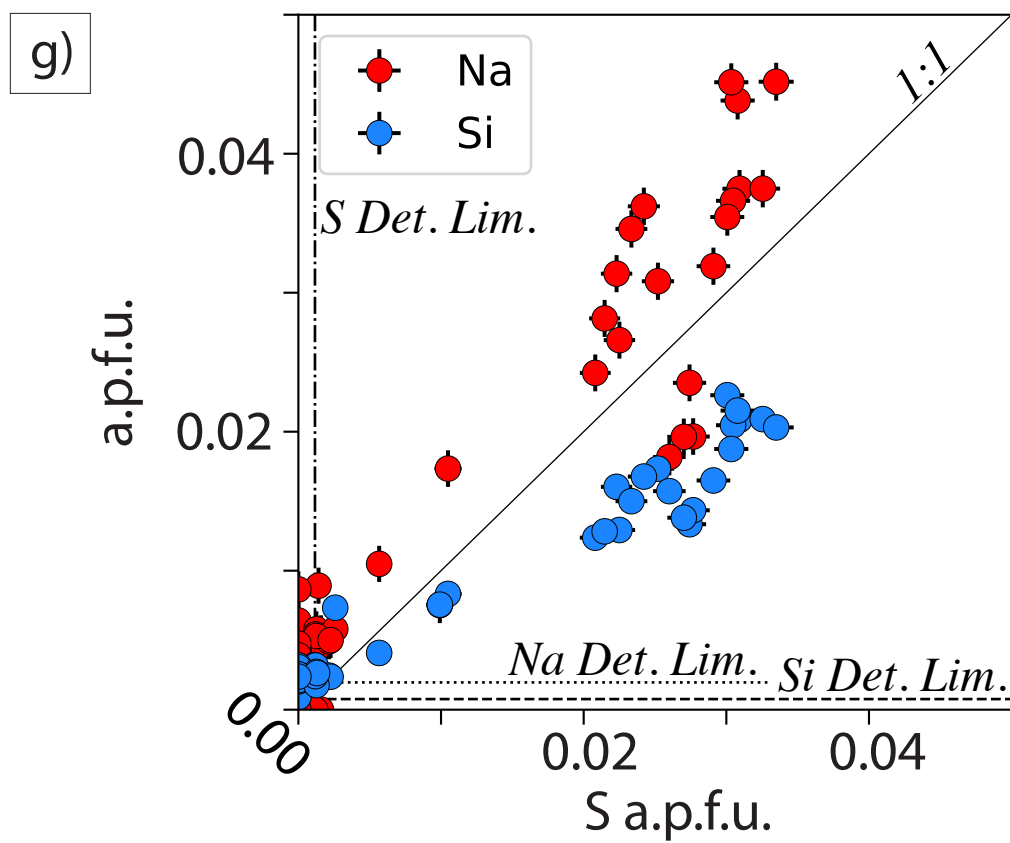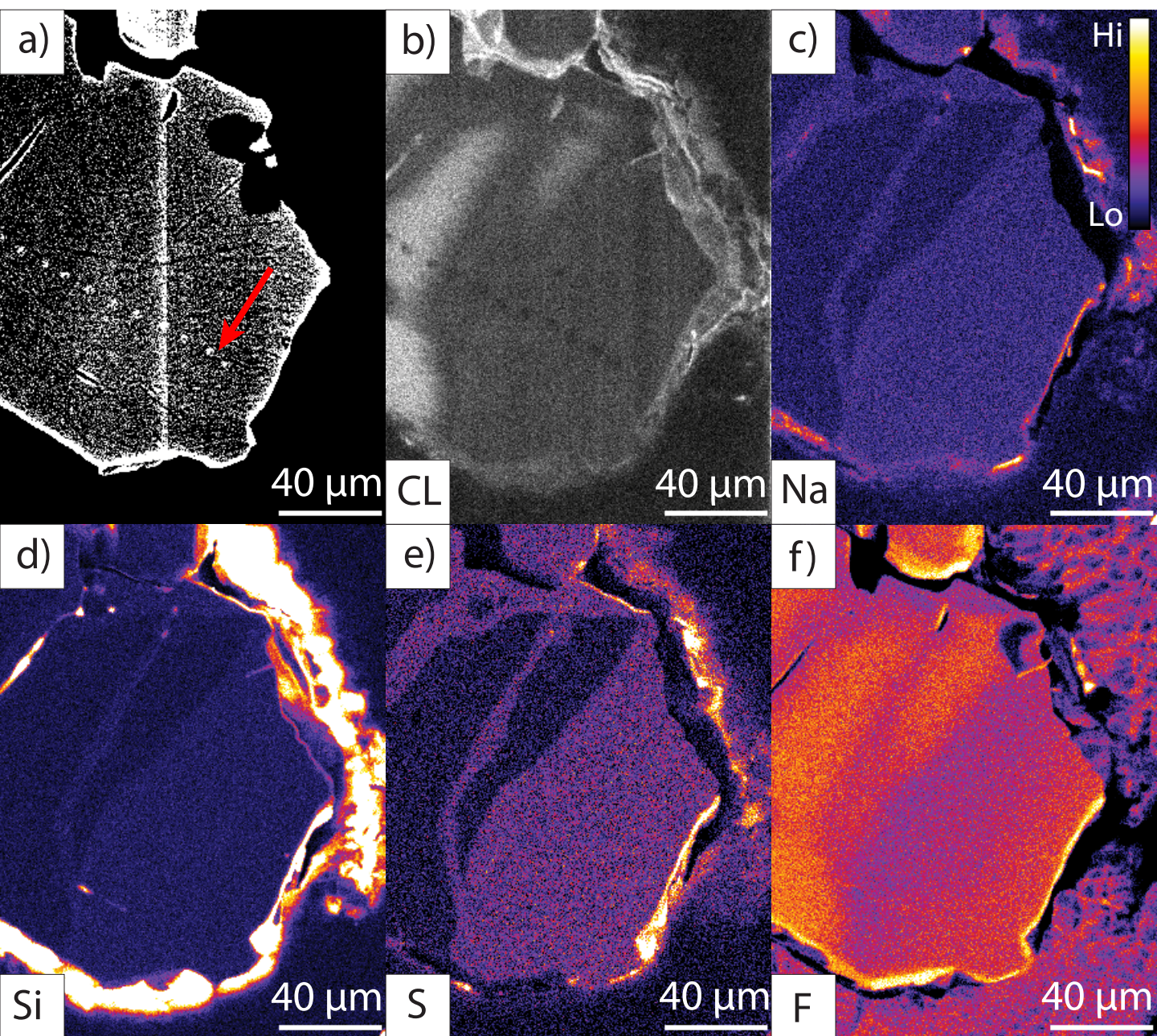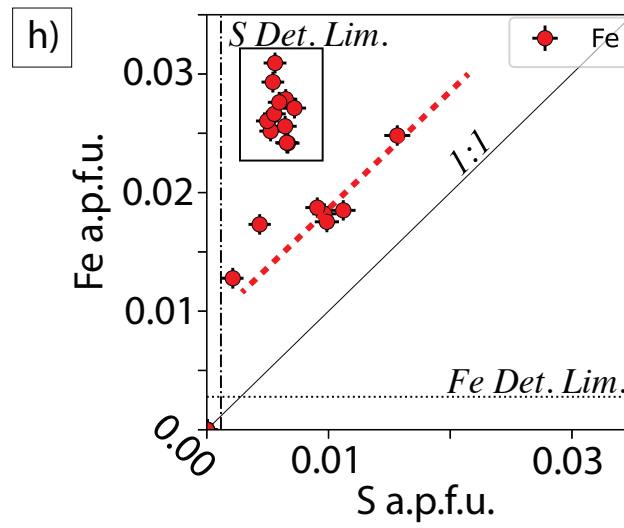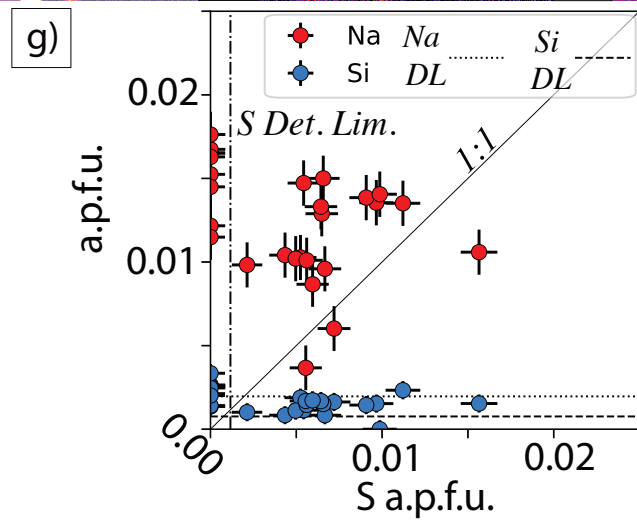
Figure 3
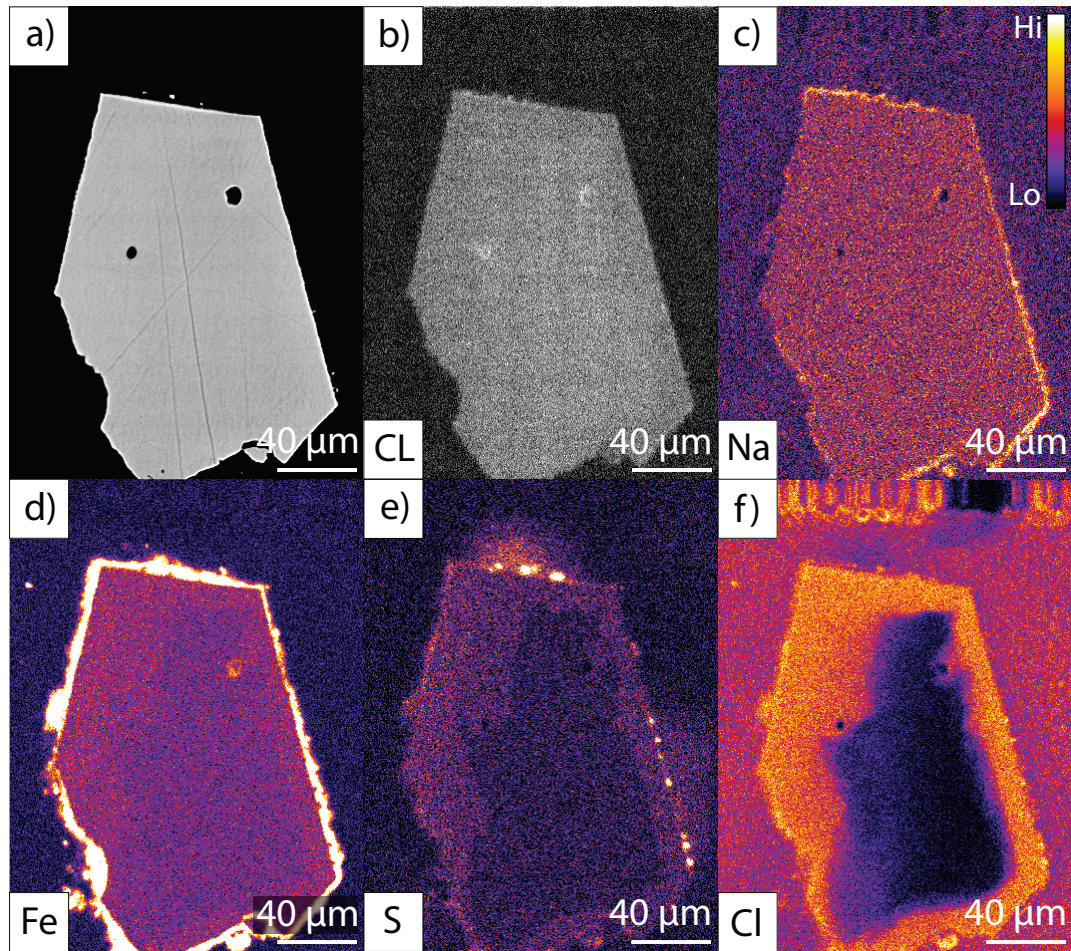
FS11: FlAp + Na2SO4 + NaF + H2O
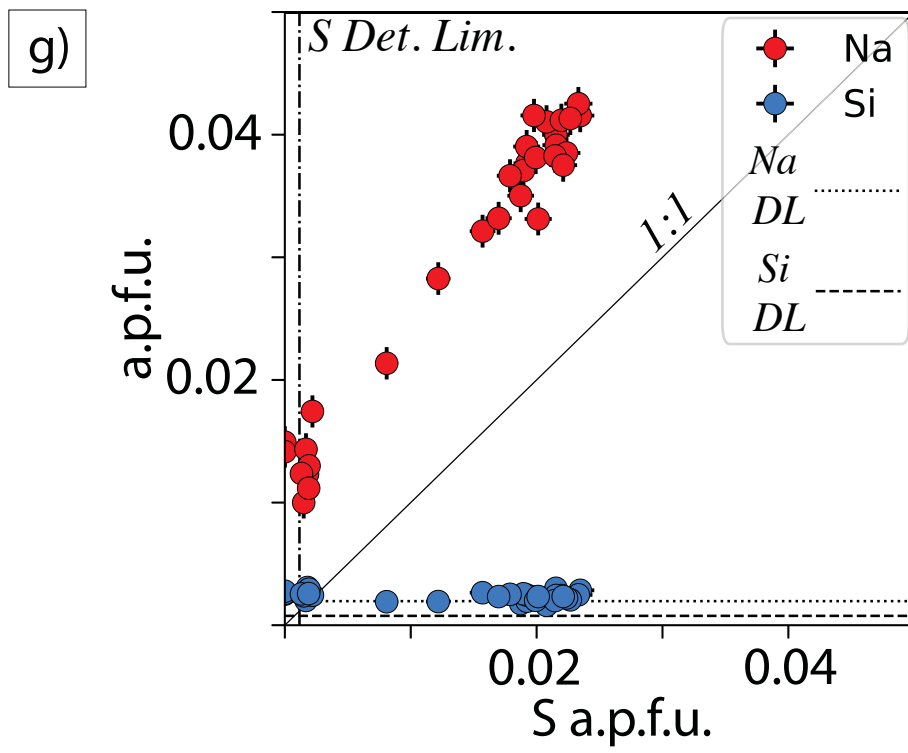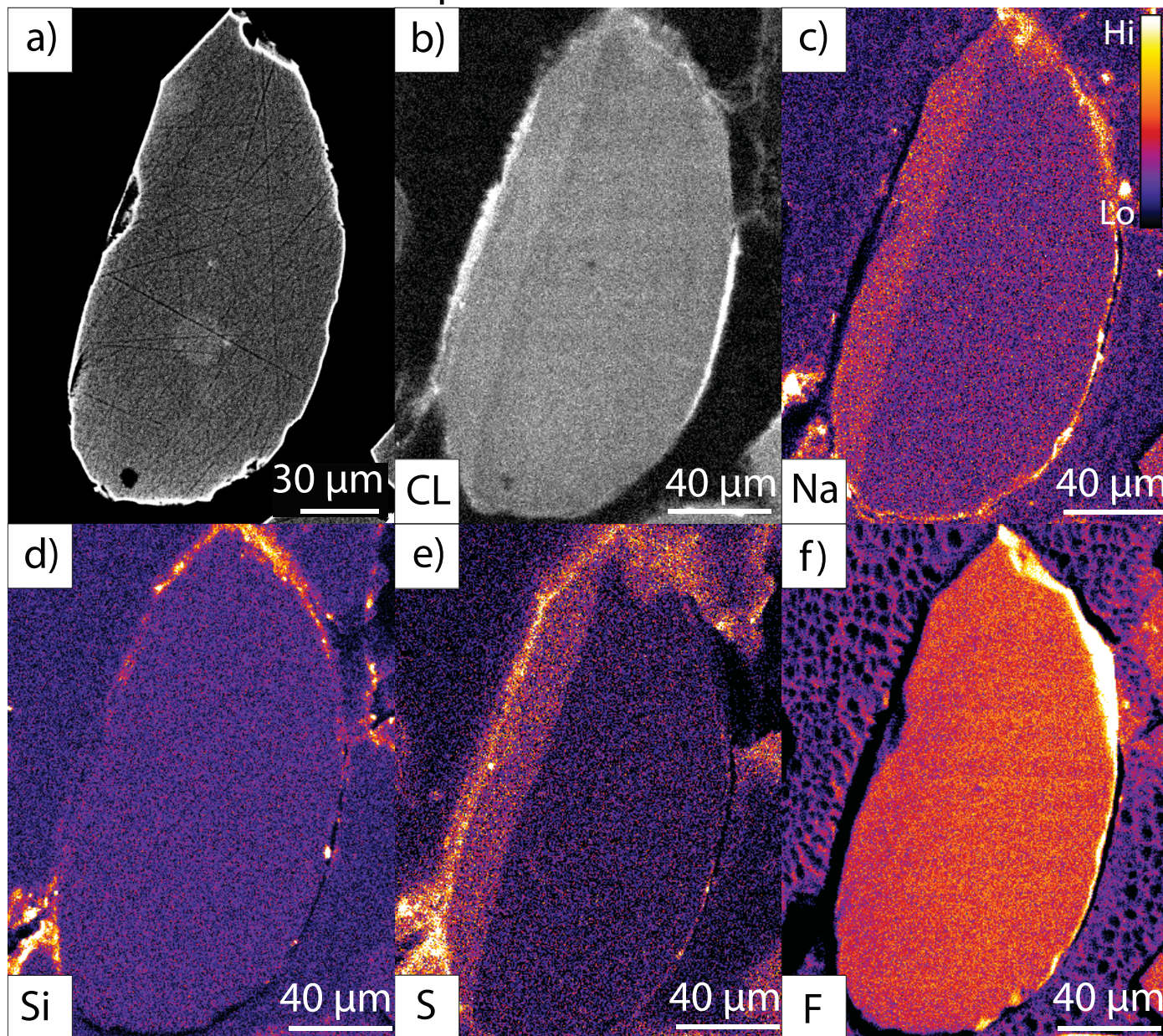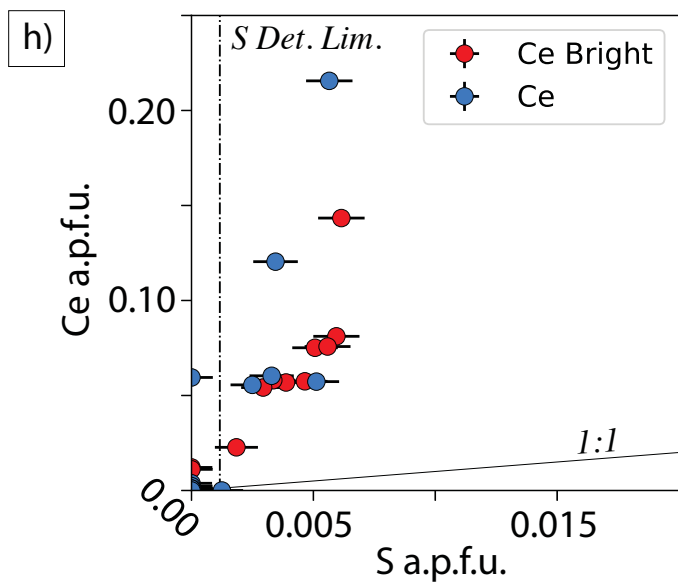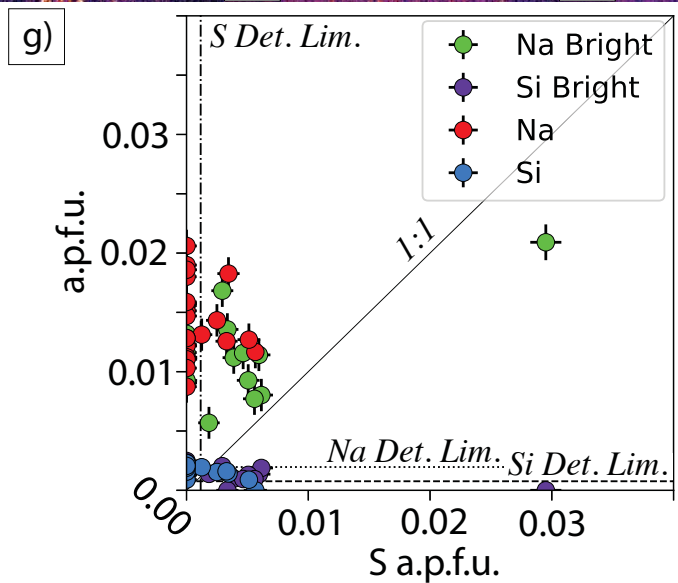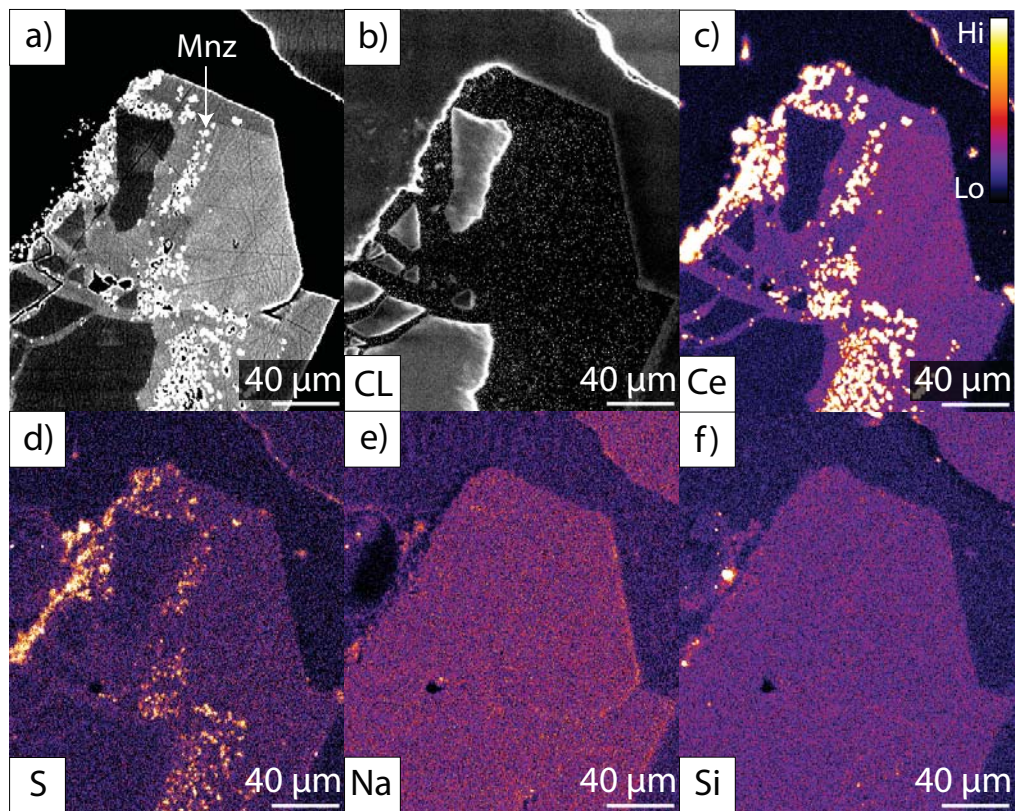
Figure 4

FS9: FlAp +1M H_2SO_4 + $FeCl_3$+ $CaCl_2$+ H_2O

Figure 5

FS10: FlAp +1M H_2SO_4+ $CeCl_3$+ $CaCl_2$+ H_2O

Figure 6

FS14: FlAp + Na_2SO_4 + $SrCl_2$ + H_2O

a) $SrSO_4$ — 40 μm

b) CL — 40 μm

c) Na — Hi / Lo — 40 μm

d) S — 40 μm

e) Sr — 40 μm

f) Si — 40 μm

g)

- Na Bright
- Si Bright
- Na
- Si

a.p.f.u. vs S a.p.f.u.

1:1

Figure 7

FS6-2: FlAp + FeS + H_2O

Figure 8

Figure 9