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

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Abstract

The mineral apatite [Ca_{10}(PO_{4})_{6}(F,Cl,OH)_{2}] is ubiquitous in terrestrial geologic systems. The apatite supergroup is capable of incorporating a significant portion of the periodic table of elements. As such, apatite is commonly used as a tool for, *inter alia*, U-Pb and fission track dating of processes in igneous and metamorphic systems, determining the water content of silicate melts at the time of apatite crystallization, and using Sr-Nd isotope systematics fingerprinting the source of magmas and possible assimilation of crustal rocks. Despite apatite
being ubiquitous in igneous and magmatic-hydrothermal systems, there is a dearth of data that constrain the partitioning of trace elements between apatite and aqueous hydrothermal fluids. Here, we report results from hydrothermal alteration and crystallization experiments at 800 °C and 1 GPa that constrain the partitioning of sulfur, iron, strontium, and the rare earth element (REE) cerium between fluorapatite and fluids of variable compositions. The data demonstrate that sulfur is incorporated in apatite through a balanced coupled substitution with Na and Si. The data also demonstrate that the presence of Sr in the aqueous fluid promotes the incorporation of Na and S in apatite. Our data reveal a previously unknown intrinsic relationship among Fe, Ce, and S in metasomatized fluorapatite that is explained by coupled substitutions between Fe$^{3+}$ and Ce$^{3+}$ with S$^{4+}$. The concentrations of Cl, OH, and S in run-produce apatite are positively correlated with each other, which indicates that the halogen chemistry of apatite plays a determinative role in the incorporation of S in apatite. Overall, the data demonstrate that incorporation of sulfate and sulfite into apatite during metasomatism depends on the abundance of charge-balancing cations in the hydrothermal fluid.

**Keywords:** Fluorapatite, hydrothermal, sulfur, iron, strontium, rare earth element

**INTRODUCTION**

Apatite is a common accessory mineral in sedimentary, igneous, and metamorphic rocks. The apatite supergroup crystal chemical formula is $^{IX}\text{M}_1^{IV}\text{M}_2^{VI}X_2 (Z = 1)$, where the M sites are most commonly occupied by Ca, the T site by P, and the X site by F, Cl or OH. The Roman numeral superscripts indicate the ideal coordination numbers. Apatite can structurally 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$^{6+}$/ΣS, in magmatic apatite can be used to quantify oxygen fugacity ($f_{O2}$) 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...
magnetite-apatite deposit in northern Sweden resulted in decreased concentrations of Na, S, Fe, Sr, and Ce concentrations in regions of individual grains that were metasomatized by a Cl-OH-fluid. Contrarily, Palma et al. (2019) reported that hydrothermal alteration of fluorapatite in samples from the Mina Carmen iron oxide-apatite (IOA) deposit of northern Chile resulted in an increase in the concentrations of Na, S, Fe, and Sr in regions of apatite grains that were metasomatized by a Cl-OH-S-fluid. Konecke et al. (2017) reported that the same metasomatized fluorapatite grains studied by Palma et al. (2019) contain \( S^{6+}, S^{4+}, \) and \( S^{2-} \), in the metasomatized regions of individual grains.

A limited number of experimental studies have been conducted in order to better understand how the composition of apatite is affected by hydrothermal (metasomatic) alteration. Harlov et al. (2002a) experimentally reacted unaltered Ødegårdens Verk chlorapatite grains with pure \( H_2O \), a 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 GPa. They report that hydrothermal alteration of the chlorapatite grains with pure \( H_2O \) resulted in a depletion of Na, Si, and (Y + REE) in apatite and concomitant growth of monazite and xenotime inclusions. Those authors also reported that hydrothermal alteration of chlorapatite grains with a F-bearing fluid resulted in the enrichment of F and Si in apatite and sparse growth of monazite. Those authors reported that reaction of chlorapatite with a \( CO_2 \)-bearing fluid resulted in no measurable changes to the starting apatite. Harlov and Förster (2003) experimentally reacted natural light REE (LREE) enriched Durango fluorapatite grains with pure \( H_2O \), brines bearing Na, Ca, or K, and \( CO_2 \) bearing fluids at 300 – 900 °C and 0.5 – 1 GPa. Those authors reported increased fluorapatite reactivity with increased temperature and the leaching of the LREEs, Na, and Si from metasomatized regions of the run-product fluorapatite.
grains. They also reported that the increased activity of Na and Ca in the fluids stabilized the LREEs in the Durango fluorapatite grains and prevented the formation of accessory monazite. Harlov et al. (2005) experimentally reacted natural LREE enriched Durango fluorapatite grains with 1 and 2 N HCl and H$_2$SO$_4$ solutions at 300 – 900 °C and 0.5 – 1 GPa and reported the depletion of the REEs, Na, Si, S, and Cl in the metasomatized regions and the formation of accessory monazite, consistent with Harlov and Förster (2003). The aforementioned experiments elucidated the formation of REE-bearing monazite commonly observed in magmatic and hydrothermal systems.

There is a dearth of published experimental data that elucidate the formation of Na-, S-, Fe- and Sr-bearing apatite in hydrothermal systems (Konecke et al., 2017; Palma et al., 2019). Existing experimental data demonstrate a relationship among Na, Si, and S in magmatic apatite that is explained by coupled substitution of Na and/or Si ions with S$^{6+}$ according to the following charge balanced coupled substitutions (Rouse and Dunn, 1982; Liu and Comodi, 1993; Tepper and Kuehner, 1999; Parat et al., 2011):

$$S^{6+} + Na^+ = P^{5+} + Ca^{2+} \quad (1)$$

$$S^{6+} + Si^{4+} = 2P^{5+} \quad (2)$$

Palma et al. (2019) also reported that the concentrations of S, Fe, and Sr in fluorapatite from the magmatic-hydrothermal Mina Carmen iron oxide-apatite deposit were positively correlated with each other and that fluorapatite grains contained secondary inclusions of monazite. That the monazite is secondary is evinced by the consistent presence of hydrothermal magnetite veinlets that crosscut primary fluorapatite. Those authors did not propose an explanation for the elevated Sr concentrations in metasomatized fluorapatite from Mina Carmen, but Hughes et al. (1991) and
Rakovan and Hughes (2000) reported that Sr\(^{2+}\) prefers to substitute for Ca\(^{2+}\) on the M2 site in apatite while Na\(^{+}\) and REE\(^{3+}\) alternate occupying the M1 site. In this instance, the Na charge balances the REE via the following coupled substitution for Ca (Pan and Fleet, 2002):

\[ \text{Na}^+ + \text{REE}^{3+} = 2\text{Ca}^{2+} \]  

(3)

Palma et al. (2019) reported an overall decrease of REE concentrations in the metasomatized fluorapatite grains, which suggests an influence of Sr on the coupled substitution of Na and S described in Equation 1 rather than Equation 3. Apatite in natural magmatic and magmatic-hydrothermal systems is commonly zoned with respect to F, Cl, and OH, and there is often a positive correlation among the concentrations of Cl, OH, and S contents in the metasomatized fluorapatite grains from Mina Carmen (Palma et al., 2019).

To our knowledge, there are no published experimental studies that constrain the partitioning of S and REEs between apatite and a hydrothermal fluid. Here, we report the results of a series of experiments wherein synthetic fluorapatite grains were reacted with a series of hydrothermal fluids with different compositions to assess the effects of coupled dissolution-reprecipitation and hydrothermal crystallization on the incorporation of S in metasomatized apatite. Experiments were conducted at 800 °C and 1 GPa wherein synthetic S-free fluorapatite grains were reacted with a variety of aqueous solutions containing dissolved S, Si, Fe, Ce, Sr, Na, Cl, F, and OH in varying amounts (Table 1). The new data reported here provide insight into the incorporation of S into fluorapatite that precipitates from, or re-equilibrates with, a S-bearing hydrothermal fluid.

**METHODS**

**Experimental Methods**
Endmember fluorapatite (APS-102) grains used in the experiments were synthesized using the molten flux method outlined by Schettler et al. (2011) (see also Cherniak, 2000). Starting synthetic fluorapatite grains were euhedral, elongate, and homogenous in back scattered electron (BSE) image grayscale (Fig. 1). Experimental charges for metasomatism experiments consisted of 20 mg of starting synthetic fluorapatite grains (APS-102), 5 mg of H₂O, 5 mg of a powdered S-bearing compound or a S-bearing solution source, and compounds possessing the necessary elements to effect charge balance for the coupled substitutions defined by Equations 1 and 2 (Table 1). Experimental charges for the hydrothermal crystal growth experiments consisted of H₂O, synthetic fluorapatite (APS-102) seed crystals, powdered β-Ca₃(PO₄)₂ (Fluka, LOT 4558807/1-223043209) as a Ca and P source, and powdered NaF as a Na and F source. Here, Na₂SO₄ served as the S source as well as providing the charge balancing cation Na⁺ (Eqn. 1), whereas SiO₂ served as the source of the charge balancing cation Si⁴⁺ (cf. Eqn. 2) (Table 1).

Charges were loaded either into 3 mm wide, 1 cm long Pt capsules for oxidized S sources or into 3 mm wide, 1 cm long Au capsules for reduced S sources, and then micro arc-welded shut. Capsules were checked for leaks by first weighing, then placed in a drying oven at 110 °C for a minimum of 8 hours and then weighing again. Platinum capsules have been known to react with S to form sulfide complexes, resulting in embrittlement and/or corrosion of capsules, which can potentially result in capsule failure (Webster and Botcharnikov, 2011). In our experiments, Pt capsules containing sulfate-bearing reagents maintained capsule integrity over a 5-day duration of the experimental run.
Experiments at 800 °C and 1 GPa for 5 days were conducted for 4 Au or 4 Pt capsules at the same time using a ‘Johannes Type’ non-end load piston cylinder apparatus (Johannes et al., 1971; Johannes, 1973), a solid CaF₂ assembly as the pressure medium, and a cylindrical graphite oven (Angiboust and Harlov, 2017; see their Fig.3 for assembly cross section). The capsules were gently flattened and loaded vertically into an approximately 5 x 5 x 12 mm pocket in the CaF₂ assembly. The capsules were separated by biotite sheets to prevent them from welding together and packed with powdered CaF₂. A Ni-Cr thermocouple was inserted into the CaF₂ assembly with the tip halfway up along the side of the experimental charges. A thermal gradient along the length of the 1 cm experiment capsule meant that either end of the capsule was approximately 20 °C lower than the temperature measured at the center. Once the CaF₂ assembly was loaded into the apparatus, the pressure was increased to approximately 15% below the final pressure. The temperature was increased to the final 800 °C, such that thermal expansion increased the pressure to near the desired 1 GPa. Minor adjustments were then made to achieve the final pressure, which was maintained automatically within a preset range of ± 0.015 GPa for the duration of the experiments. Experiments were quenched non-isobarically by turning off the heating current and automatic pressure control, which allowed the water cooling jackets and mass of the apparatus to cool the experiments to below 100 °C in approximately 30 seconds. The capsules were then extracted from the CaF₂ assembly, cleaned, and weighed to determine whether capsule integrity was maintained. Cleaned capsules that did not maintain their starting mass were discarded.

All experiment capsules were punctured, placed in a drying oven at 110 °C for 24 hrs., and weighed again to determine the amount of fluid present. The dried run products were removed
from the experiment capsules and rinsed three times in DI H₂O to remove any solutes. A random sampling of run product grains (i.e. a literal scoop) for each experiment were then dried, mounted in epoxy, and polished for scanning electron microscopy (SEM), BSE imaging, and quantitative EPMA.

Analytical Methods

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

Carbon-coated epoxy grain mounts were first analyzed on a JEOL JSM-7800FLV SEM using an accelerating voltage of 20 kV at the Robert B. Mitchell Electron Microbeam Analysis Lab (EMAL), University of Michigan, Ann Arbor, Michigan, USA. High-contrast BSE imagery was utilized to record mineral textures of the experiment run-product fluorapatite. EPMA quantitative analyses of run-product fluorapatite compositions were conducted on a Cameca SX-100 electron microprobe (EMP) at EMAL, using a 15 keV electron beam and a beam current of 20 nA. Counting times were 10 seconds on-peak and 5 seconds off-peak for all elements measured using the mean atomic number (MAN) continuum X-ray correction method outlined in Donovan and Tingle (1996). Because of the F and Cl X-ray count rate variation in response to electron beam exposure (Goldoff et al., 2012), F and Cl were measured first as well as using Time-Dependent Intensity (TDI) corrections incorporated into ProbeForWindows software (Donovan et al., 2007). Quantitative analyses were conducted prior to the collection of representative BSE images. Multiple points on multiple grains from each experiment were selected so as to obtain a random dataset large enough for statistical consideration. Concentrations were obtained from raw counts using a ZAF intensity correction. EPMA data and standards used for peak positions are listed in the Supplementary Table 1. Wavelength dispersive spectroscopy (WDS) maps and
Cathodoluminescence (CL) monochromatic grayscale images were collected post-quantitative analyses on the Cameca SX-100 EMP using a 15 keV electron beam, a beam current of 40 nA, a 0.5 μm step size, and a 60 ms dwell time.

**Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).** The concentrations of Sc, Mn, Fe, Y, Ba and REEs in the starting synthetic fluorapatite grains (APS-102) were measured by LA-ICP-MS using an ESI NWR193 laser ablation system attached to an Agilent Technologies 7900s quadrupole ICP-MS, housed at the Holder Laser Ablation ICP-MS Laboratory, University of Michigan, Ann Arbor, Michigan, USA (Supplementary Table 2). Analyses were conducted by using a 70 μm spot size, a fluence of 1.4 J/cm², at 6 Hz repetition, 30 sec of ablation, and a 20 sec baseline. The analyte in a He carrier gas was transported from the LA system to a glass mixing bulb where the sample aerosol was mixed with Ar gas prior to the ICP-MS. Trace element concentrations and detection limits were calculated using the method outlined by Longerich et al. (1996), with the Ca concentration from EPMA analyses (Table 2) as an internal standard, and using NIST610 glass as a secondary standard. The glass standards NIST610 and NIST612 were analyzed throughout the session to correct for instrument drift.

**RESULTS**

Major and trace element concentrations of the starting synthetic fluorapatite grains measured by EPMA are reported in Table 2. The chemical formula for run product apatite grains was calculated using 5 cations and 26 oxygens (Ketcham, 2015); with the halogen site (X) occupied by F, Cl, OH, and sulfur as $S^{6+}$ and $S^{4+}$ in the tetrahedral site (T). It is understood and acknowledged by the geochemical community that nano scale inclusions below a polished grain
surface may be present in the electron beam excitation volume. In order to address this potential issue, points selected for EPMA avoided cracks, intact and compromised fluid inclusions, and avoided regions with pervasive accessory phases (i.e. Monazite). EPMA points which yielded non-stoichiometric apatite chemical formula, insufficient sums, or indicated a secondary phase were discarded and not used in this study. Pearson correlation coefficients ($\rho$) were calculated from EPMA point analyses for ion pairs of interest (Pearson, 1895). A correlation coefficient speaks to the linearity of data such that a coefficient of unity would plot on a straight line. However, a correlation coefficient does not inform on the slope of the data trend (e.g. ratios in ionic substitutions) or the extent of the data trend (e.g. minimum and maximum concentrations). We define a strong correlation as $\rho > 0.75$, a moderate correlation as $0.5 < \rho < 0.75$, and a weak correlation as $0.25 < \rho < 0.5$.

**Results from sulfate reagent experiments**

**Experiments at 800°C and 1 GPa involving H$_2$O + S $\pm$ Na $\pm$ Si.** Run product fluorapatite grains from experiment FS2 (Table 1; 800 °C, 1GPa; FlAp + Na$_2$SO$_4$ + H$_2$O) are dominantly anhedral, occasionally fractured, present with little evidence for dissolution, and are homogenous in high-contrast BSE images (Supp. Fig. 1b). Run product fluorapatite grains from experiment FS3 (Table 1; 800 °C, 1GPa; FlAp + 1M H$_2$SO$_4$ + SiO$_2$ + H$_2$O) are homogenous in high-contrast BSE images, show minor evidence of dissolution with slightly rounded grains that are subhedral to anhedral and are occasionally mantled by a silicate glass that was not analyzed for its chemical composition (Supp. Fig. 1c). The compositions of run product fluorapatite grains from FS2 and FS3 are equivalent to the starting synthetic fluorapatite grains (Table 2); notably the S concentration is below the EPMA detection limit. Run product fluorapatite grains from
experiment FS12 (Table 1; 800 °C, 1 GPa; FlAp + Na₂SO₄ + Na₂Si₂O₅ + H₂O) are slightly rounded, subhedral to anhedral, exhibit a subtle greyscale zonation in the high-contrast BSE image, and a diffused zonation in the CL image (Fig. 2b) where darker regions are spatially correlated with increased Na, Si, and S in the WDS maps (Figs. 2c,d,e). Run product fluorapatite grains from experiment FS12 exhibit a 0.32 wt.% decrease in P to 18.22 wt.%, measurable S at 347 μg/g, an increase of Na to 0.03 wt.%, and an increase of Si to 228 μg/g (Table 2). For experiment FS12 there exists a strong positive correlation between S with Na (ρ = +0.95), and S with Si (ρ = +0.98) for the calculated atomic proportions (Fig. 2g). The data points for Na vs. S are above and nearly straddle the stoichiometric 1:1 line whereas the Si vs. S data points with elevated S concentrations are below and subparallel to the 1:1 line (Fig. 2g). Data clusters that plot above the stoichiometric 1:1 line indicate an excess of the charge balancing cation and data clusters that plot below the 1:1 line indicate an excess of S with respect to the charge balancing cation. Run product fluorapatite grains from experiment FS15 (800 °C, 1GPa; FlAp + Na₂SO₄ + SiO₂ + β-Ca₃(PO₄)₂ + NaF + H₂O) are euhedral to anhedral, and tens to hundreds of micrometers in diameter. Aggregates of small euhedral fluorapatite grains coalesce into larger subhedral grains, where the larger grains present with subtle zonation in the high-contrast BSE and CL images (Supp. Figs. 2a,b) that is spatially correlated with elevated Na and S in the WDS maps (Supp. Figs. 2c,e). In the WDS maps of Na and S, the zonation is more apparent and exhibits a sharp reaction front separating a distinct core from the rim (Supp. Figs. 2c,e). The core appears elongate, ca. 30 μm in diameter, subhedral with distinct parallel facets, and presents topotaxial to the crystal habit of the rim. The Na and S poor core is the remnant parent crystal that has been overgrown by a new Na and S bearing daughter material that precipitates from the fluid. Run product fluorapatite grains from experiment FS15 exhibit measurable S with an average of 436
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 two distinct populations for Na, Si, and S concentrations in the run-product fluorapatite; a S below detection limit group that plots on or near the Y-axis from measurements of grain cores and a group where S concentrations range from ca. 0.011 to 0.027 a.p.f.u. for rim measurements (Supp. Figs. 2g). There is a strong positive correlation between Na and S ($\rho = +0.98$) and no correlation between Si and S ($\rho = +0.04$) (Fig. 4g). The Na vs. S trend plots above and subparallel to the 1:1 atomic ratio line (Supp. Figs. 2g).

Experiments at 800 °C and 1 GPa involving $H_2O + S \pm Na \pm Si \pm Cl \pm F \pm OH$. Run product fluorapatite grains from experiment FS7 (Table 1; 800 °C, 1 GPa; FlAp + Na$_2$SO$_4$ + CaCl$_2$ + H$_2$O) are subhedral to anhedral and homogenous in high-contrast BSE imagery (Supp. Fig. 1e). Run product fluorapatite grains from experiment FS16 (800 °C, 1 GPa; FlAp + Na$_2$SO$_4$ + Ca(OH)$_2$ + H$_2$O) are subhedral to anhedral, homogenous in high-contrast BSE imagery, with partially healed fractures and clusters of small ($\leq$ 15μm) fluorapatite grains found on rims of larger grains (Supp. Fig. 1f). Run product fluorapatite grains from experiment FS20 (Table 1; 800 °C, 1 GPa; FlAp + Na$_2$SO$_4$ + SiO$_2$ + CaCl$_2$ + H$_2$O) are subhedral to anhedral, with shallow etch pits, and occasional subtle rounding of corners (Supp. Fig. 1g). Large (> 300 μm) elongate aggregate masses of small ($\leq$ 50 μm) euhedral to subhedral secondary quartz grains are present but were not analyzed for their chemical composition. The compositions of the run product fluorapatite grains from FS7, FS16, and FS20 are comparable to the starting synthetic fluorapatite grains (Table 2); notably, S is below the EPMA detection limit.
Run product fluorapatite grains from experiment FS8 (Table 1; 800 °C, 1 GPa; FlAp + 1M H2SO4 + SiO2 + CaCl2 + H2O) are subhedral to anhedral with rounded margins, are homogenous in the high-contrast BSE and CL images (Supp. Figs. 3a,b) with spatially correlated elevated S and Cl in the WDS maps (Supp. Figs. 3d,f). Experiment FS8 run product fluorapatite grains exhibit a 0.25 wt.% decrease in P to 18.29 wt.%, measurable S at 105 μg/g, and an increase in Na and Si to 0.03 wt.% and 43 μg/g, respectively (Table 2). The run product halogen chemistry of experiment FS8 exhibit a 0.30 wt.% decrease of F to 3.40 wt.%, an increase of Cl to 0.44 wt.%, and an estimated OH concentration of 0.21 wt.% (Table 2). There is a weak negative statistical correlation between measured S and Si concentrations (\(\rho = -0.38\)) and a weak positive correlation between S and Na (\(\rho = +0.36\)). When the below detection limit data points are removed from consideration, the Na-S correlation coefficient increases to \(\rho = +0.42\) and the Si-S correlation coefficient increases to \(\rho = -0.34\). There is a strong positive correlation between S and Cl (\(\rho = +0.91\)) concentrations and a weak negative correlation with the estimated OH content (\(\rho = -0.31\)). Run product fluorapatite grains from experiment FS11 (Table 1; 800 °C, 1 GPa; FlAp + Na2SO4 + NaF + H2O) are subhedral to anhedral, slightly rounded with partially healed fractures, homogenous in the high-contrast BSE images (Fig. 3a), and a subtle zonation in the CL image where brighter areas are spatially correlated with elevated Na and S in the WDS maps (Figs. 3b,c,e). Run product fluorapatite grains from experiment FS11 exhibit a 0.30 wt.% decrease in the P concentration to 18.24 wt.%, measurable S at 452 μg/g, a 0.05 wt.% increase of Na to 0.07 wt.%, and a 30 μg/g increase of Si to 68 μg/g (Table 2). Experiment FS11 run product halogen chemistry exhibits a 0.07 wt.% decrease of F to 3.63 wt.% and an estimated OH concentration of 0.23 wt.% (Table 2). There is a strong positive correlation for Na and S concentrations (\(\rho = +0.98\)) that plot above and subparallel to the 1:1 line and a weak inverse...
correlation for Si and S ($\rho = -0.31$) that plot on or near the X-axis (Fig. 3g). There is no statistical
correlation for S concentrations with those of F ($\rho = -0.22$), Cl ($\rho = -0.23$), or OH ($\rho = +0.22$).
Run product fluorapatite grains from experiment FS13 (Table 1; 800 °C, 1 GPa; FlAp + Na₂SO₄
+ Na₂Si₂O₅ + CaCl₂ + H₂O) are subhedral to anhedral, homogenous in high-contrast BSE image
grayscale (Supp. Fig. 4a) with occasional aggregates of smaller (≤ 15μm) grains coalescing to
form larger anhedral grains. Elongate grains of accessory wollastonite (Ca₃(Si₅O₁₅)) and
spheroids of sodium silicate glass are present (Supp. Fig. 4a) but were not analyzed for their
chemical compositions. Distinct zonation in the high-contrast CL image is visible with a spatial
correlation between brighter CL areas and elevated Na, Si, and S in the WDS maps (Supp. Figs.
4b,c,d,e). Run product fluorapatite grains from FS13 exhibit a 0.33 wt.% decrease of P to 18.21
wt.%, measurable S at 416 μg/g, Ca and Na average concentrations are unchanged with an
increase of Si to 440 μg/g (Table 2). Experiment FS13 run product fluorapatite grain halogen
chemistry exhibits a 0.36 wt.% decrease of F to 3.34 wt.%, Cl is unchanged at 0.01 wt.%., and an
estimated OH concentration of 0.46 wt.% (Table 2). There exists a strong positive correlation
between S with Na ($\rho = +0.96$) and Si ($\rho = +0.99$) concentrations (Supp. Fig. 4g), and a
moderate positive correlation with Cl ($\rho = +0.70$) and estimated OH ($\rho = +0.55$). The Si vs. S
a.p.f.u. concentrations plot on the atomic ratio 1:1 line while the Na vs. S a.p.f.u. concentrations
plot below and subparallel (Supp. Fig. 4g). Run product fluorapatite grains from experiment
FS17 (Table 1; 800 °C, 1 GPa; FlAp + Na₂SO₄ + CaCl₂ + Ca(OH)₂ + H₂O) are dominantly
subhedral to anhedral with partially healed fractures. Larger grains (> 100 μm) are occasionally
an aggregate of smaller (≤ 15μm) euhedral to subhedral grains (Fig. 8a). Experiment FS17 run
products exhibit grain to grain variation in the high-contrast BSE image grayscale (Supp. Fig. 5a)
that does not display a clear and consistent correlation with zonation in the CL image or zonation
in the WDS maps (Supp. Figs. 5b-f). There is a distinct zonation in the run-product WDS map of F that exhibits an inverse relationship with Cl (Supp. Figs. 5e,f) and a Na and S spatial correlation of elevated concentrations along fractures and grain margins (Supp. Figs. 5c,d). Run product fluorapatite grains from experiment FS17 exhibit a 0.32 wt.% decrease of P to 18.22 wt.%, measurable S at 156 μg/g, an increase of Na to 0.03 wt.%, and Si remains unchanged (Table 2). The Na and S concentrations plot below and appear subparallel to the 1:1 atomic ratio line while Si data points plot near the X-axis (Supp. Fig. 5g). Halogen concentrations of run products from experiment FS17 exhibit a 0.49 wt.% decrease of F to 3.21 wt.%, an increase of Cl to 0.03 wt.%, and an estimated OH concentration of 0.56 wt.% (Table 2). There is a moderate positive correlation between S and Cl ($\rho = +0.58$) and between S and the estimated OH content ($\rho = +0.55$).

**Experiments at 800 °C and 1 GPa involving H$_2$O + S + Cl ± Na ± Fe ± Sr ± Ce.** Run product fluorapatite grains from experiment FS1 (Table 1; 800 °C, 1 GPa; FlAp + 1M H$_2$SO$_4$ + FeCl$_3$ + H$_2$O) are subhedral to anhedral, with few rounded grain margins (Supp. Fig. 1a). Run product fluorapatite grains from experiment FS4 (Table 1; 800 °C, 1 GPa; FlAp + 1M H$_2$SO$_4$ + CeCl$_3$ + H$_2$O) are subhedral to anhedral, slightly rounded from dissolution, with sub-micrometer monazite grains found in partially healed fractures and mantling the fluorapatite grains (Supp. Fig. 1d). Run product fluorapatite grains from experiment FS21 (Table 1; 800 °C, 1 GPa; FlAp + Na$_2$SO$_4$ + CeCl$_3$ + CaCl$_2$ + H$_2$O) are subhedral to anhedral and present with subtle rounding of corners (Supp. Fig. 1h). Sub-micrometer monazite-(Ce) grains fill fractures with little evidence of micrometer scale fluorapatite dissolution (Supp. Fig. 1h). Run product fluorapatite grains from experiments FS1, FS4, and FS21 are homogenous in the high-contrast BSE images (Supp. Fig.
Average run product concentrations for S, Fe, and Ce from experiments FS1, FS4, and FS21 are below EPMA detection limits (Table 2).

Run product fluorapatite grains from experiment FS9 (Table 1; 800 °C, 1 GPa; FlAp + 1M \( \text{H}_2\text{SO}_4 + \text{FeCl}_3 + \text{CaCl}_2 + \text{H}_2\text{O} \)) are subhedral to anhedral and homogenous in the high-contrast BSE and CL images (Figs. 4a,b). Occasional aggregates of subhedral grains overgrown by larger anhedral masses of fluorapatite are visible in the grain mount. In contrast to the BSE and CL imagery, there exists a distinct element zonation and a strong positive spatial correlation for elevated Fe, S, and Cl in the WDS maps of the run product fluorapatite (Figs. 4d,e,f). The composition of fluorapatite grains from FS9 exhibit a decrease of P to 18.16 wt.%, measurable S at 154 μg/g, Na and Si are slightly greater at 0.03 wt.% and 48 μg/g, respectively, and measurable Fe at 0.09 wt.% (Table 2). Run product halogen concentrations in apatite grains from FS9 exhibit a decrease of F to 3.34 wt.%, an increase of Cl to 0.58 wt.%, and an estimated OH concentration of 0.20 wt.% (Table 2). The S atomic proportion exhibits a weak negative correlation with the reported trace amounts of Na (\( \rho = -0.36 \)) for all plotted data with the majority on or above the 1:1 atomic ratio line. When ion pairs with S concentrations below detection limits are removed, the Na-S correlation coefficient increases to \( \rho = +0.27 \). Data points for Si plot near and near-parallel to the X-axis (Fig. 4g), indicating no relationship with the incorporated S. The S concentrations exhibit a strong positive correlation with Fe (\( \rho = +0.75 \)) for all points measured (Fig. 4h). The reported correlation coefficient for Fe and S includes the data points that present with independent Fe and S concentrations (Fig. 4h; box outline). There is a cluster of plotted Fe concentrations that present with a linear trend that is subparallel and above the 1:1 atomic ratio line (Fig. 4h). Run product fluorapatite grains from experiment FS10 (Table
1; 800 °C, 1 GPa; FlAp + 1M H$_2$SO$_4$ + CeCl$_3$ + CaCl$_2$ + H$_2$O) are euhedral to anhedral, with a bi-modal grayscale in the high-contrast BSE and CL imagery (Figs. 5a,b). The darker, inclusion-free regions in the BSE image are marked by a sharp reaction front that is traced by micrometer to sub-micrometer scale monazite-(Ce) inclusions that separate brighter regions with numerous ≤ 5 μm monazite inclusions and/or grains mantling the run product fluorapatite (Fig. 5a). In the WDS maps of the run product fluorapatite grains, there exists a distinct element zonation and a positive spatial correlation for elevated Ce and S (Figs. 5c,d). The composition of the BSE darker regions in experiment FS10 exhibit a decrease in P to 18.32 wt.%, S is below EPMA detection limits, subtle increases to average Na and Si concentrations, and measurable Ce at 0.34 wt.% (Table 2). The halogen concentrations in the BSE darker regions exhibit a decrease of F to 3.43 wt.%, an increase of Cl to 0.48 wt.%, and an estimated OH concentration of 0.21 wt.% (Table 2).

The average concentrations of the brighter regions in fluorapatite grains from experiments FS10 exhibit a further decrease in P to 18.11 wt.%, measurable S at 153 μg/g, a decrease of Ca to 37.93 wt.%, and measurable Ce at 2.03 wt.% (Table 2). The Na and Si concentrations in the BSE brighter regions are comparable to the starting fluorapatite composition (Table 2). There halogen concentrations in the brighter BSE regions exhibit a further decrease of F to 3.18 wt.%, an increase of Cl to 0.83 wt.%, and an estimated OH concentration of 0.19 wt.% (Table 2). There is no statistical correlation between S and Na ($\rho = +0.20$) or a positive correlation with Si ($\rho = -0.61$) (Figs. 5d,e,f,g). There is weak statistical correlation for Ce with Na ($\rho = +0.31$) and a negative correlation with Si ($\rho = -0.51$) in the run-product fluorapatite concentrations. There is a strong positive spatial and chemical correlation between Ce and S ($\rho = +0.95$) (Figs. 5c,d,h). Run product fluorapatite grains from experiment FS14 (Table 1; 800 °C, 1 GPa; FlAp + Na$_2$SO$_4$ + SrCl$_2$ + H$_2$O) are subhedral to anhedral with a bi-modal grayscale in the high-contrast BSE
images where the brighter regions are mantling darker cores and sometimes fluorapatite grains are mantled by masses of Cl rich SrSO₄ (Fig. 6a). The brighter fluorapatite regions in BSE images sometimes exhibit subtle and/or sharp zonation and can be found filling healed fractures in the darker regions. In contrast with the CL imagery, the brighter fluorapatite regions in BSE images have a strong positive spatial correlation with elevated Sr, Na, and S and a subtle positive spatial correlation with Si in the WDS maps (Figs. 6c-f). The composition of the darker fluorapatite regions in BSE images of experiment FS14 exhibit an increase of Ca to 39.26 wt.% and an estimated OH concentration of 0.21 wt.% (Table 2). The concentrations of P, Sr, Na, F, and Cl in the darker cores of the experiment run products is comparable to the concentrations in the starting fluorapatite grains and S is below the EPMA detection limit (Table 2). The composition of the brighter regions in BSE images of fluorapatite grains from experiment FS14 exhibit a decrease in P to 17.17 wt.%, measurable S at 3,514 μg/g, a decrease of Ca to 32.30 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 wt.% (Table 2). The halogen concentrations of the bright areas in the run product fluorapatite grains from FS14 exhibit a decrease of F to 3.29 wt.%, an increase of Cl to 0.09 wt.%, and an estimated OH concentration of 0.31 wt.% (Table 2). The darker core of the Sr-bearing fluorapatite in the BSE images (Fig. 6a) is interpreted to be the starting synthetic fluorapatite (Table 2) and the composition plots near the origin of the Na, Si, S atomic proportion plot (Fig. 6g). The Sr-rich fluorapatite rims exhibit a strong positive correlation between Na and S concentrations (ρ = +0.99) with the data plotting below and subparallel to the 1:1 atomic ratio line (Fig. 6g). The data points for the Si concentrations plot near or on the X-axis (Fig. 6g). There exists a strong positive correlation between Sr and S concentrations in the run-product fluorapatite (ρ = +0.99).
**Results from sulfide reagent experiment**

Run product fluorapatite grains from experiment FS6-2 (Table 1; 800 °C, 1 GPa; FlAp + FeS + H₂O) 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 heterogeneous 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 productapatite 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
of 0.24 wt.%. The concentrations of Na, Si, and F in the brighter rims are comparable to the starting fluorapatite grains, and Cl in the brighter regions is below the EPMA detection limit (Table 2). There is a weak-moderate correlation between Na and S concentrations in the run products ($\rho = +0.39$) where the a.p.f.u. concentrations plot near the origin or near the X-axis (Fig. 7g). There is no statistical correlation between S and Si ($\rho = -0.17$) nor for S with the halogens F ($\rho = +0.18$), Cl ($\rho = -0.03$), or OH ($\rho = -0.18$). There is a strong positive correlation between Fe and S concentrations in the FS6-2 run products (Fig. 7h).

**DISCUSSION**

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

Previous studies demonstrated the coupled substitutions of $S^{6+}$ with Na$^+$ and/or Si$^{4+}$ (Eqns. 1 and 2) for S-bearing fluorapatite crystallized from a silicate melt, whereas our experiments test the feasibility of these substitutions via a fluid-mediated process. When the Na and Si ion concentrations are compared with the S ion concentrations of run-product apatite grains from this study, there is a clear and distinct near 1:1 relationship between S and the charge balancing cation Na where the majority of data points cluster on or near the 1:1 line (Fig. 8a). The calculated statistical correlation coefficient for Na-S ion pairs for all experiments is $\rho = +0.88$ (i.e. a strong correlation). The correlation coefficient was calculated for the entire data set as we found that despite not adding a Na source to some experiments, the Na and S coupled substitution still occurred using the trace amounts of Na in the starting synthetic fluorapatite (Table 2). In contrast, when considering the Si-bearing fluid experiments there is weak evidence for a relationship between Si and S, where the majority of the EPMA data points plot near and parallel to the X-axis (Fig. 8b), indicating no substantial relationship between Si and S for the
experiment conditions chosen. For the aggregate Si-bearing data set a strong statistical correlation coefficient was calculated ($\rho = +0.79$) and further increased to $\rho = +0.95$ when only the experiments that indicated a Si-S coupled substitution were considered (FS12 and FS13). This overall trend is consistent with those observed in natural apatite grains from a variety of metamorphic P-T conditions as well as trends observed in experimentally crystallized apatite. The black X-symbols in Figure 8 represent average a.p.f.u. concentrations for apatite grains in metamorphic rocks from Huangmailing, Hubei and Jinping, Jiangsu, China, and apatite grains from Wilberforce, Ontario, Canada (Liu and Comodi, 1993), apatite grains from the partially metasomatized Sudbury Igneous Complex, Ontario, Canada (Warner et al., 1998), and for partially metasomatized apatite grains found in the Kiirunavaara magnetite-apatite ore bodies (Harlov et al., 2002b). These samples represent a range of metamorphic pressure and temperature conditions from 0.5 to greater than 2.8 GPa and 350 to 829 °C (Xiaochun, 1993, Liu et al., 2004; Moecher et al., 1997), which encompass the 1GPa and 800 °C experimental conditions of this study. We find that our data exhibit overlap with the black symbols representing apatite compositions from metamorphic terranes, where they cluster along and near the 1:1 line in the Na-S atomic plot (Fig. 8a) and trace amounts plot on or near the 1:1 line in on the Si-S atomic plot (Fig. 8b). The grey polygons in Figure 8 represent the approximate regions of plotted Na vs. S and Si vs. S a.p.f.u. concentrations of run-product apatite grains (Parat et al., 2011) from the S partitioning apatite-melt experiments of Parat and Holtz (2004, 2005) and Parat et al. (2008) that exhibit much less overlap with our experimental results when compared to the metamorphic apatite (Figs. 8a,b).
From the overall Na vs. S trend that is near-parallel to and straddles the 1:1 atomic proportion line (Fig. 8a) and the reported Pearson correlation coefficients, it is clear that, for the fluid compositions and P-T conditions chosen, a stronger relationship exists between S and the charge balancing cation Na (Eqn. 1). Whereas for the Si and S atomic plot, the natural metamorphic apatite plot near the origin or near and parallel to the Y-axis while the experiment run-product apatite compositions plot near the origin or near and parallel to the X-axis, indicating the independent incorporation of Si and/or S i.e. not through the Si-S coupled substitution (Eq. 2), 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 coupled substitution between Si and S is secondary (Eqn. 2).

We acknowledge that of our experiments testing the Si-S coupled substitution, few resulted in appreciable concentrations of Si and S. We suspect that this is from the Si reagents chosen: powdered Na$_2$Si$_2$O$_5$ and powdered crystalline SiO$_2$. Experiments FS12 and FS13 used Na$_2$Si$_2$O$_5$ and are the only two experiments that yielded appreciable Si-S concentrations (Table 2) and exhibit Si-S trends that are comparable to the natural metamorphic apatite (Fig. 8b, cf. Fig.2 and Supplementary Fig. 4). Na$_2$Si$_2$O$_5$ (Industrial reagent nomenclature: SKS-6) is a commercial grade water softening agent that is readily soluble in H$_2$O at room temperature, saturates a fluid of amorphous silica and aqueous Na (Coker and Rees, 1993), and is a synthetic analog of the naturally occurring natrosilite. Thermodynamic models demonstrate that amorphous silica (e.g. SKS-6) is more soluble than crystalline SiO$_2$ in pure H$_2$O, but the overlap in the P-T limitations of the models do not include our experiment P-T conditions (Fournier and Rowe, 1977; Fournier and Potter II, 1982; Manning, 1994; Dolejš and Manning, 2010; Karásek et al. 2013). However,
this does not change our conclusion of a Na-S coupled substitution being preferred to a Si-S coupled substitution.

It is not uncommon for Na a.p.f.u. concentrations to plot above the stoichiometric 1:1 line indicating an excess of Na with respect to the coupled, charge balanced element being substituted in the apatite crystal structure, such as S or REEs (Fig. 8a). This can be corrected for natural concentrations by subtracting the ionic influences of elements that compete with the element of interest, e.g. ionic Si-(Ce+Na) vs. ionic S (Peng et al., 1997). However, correcting for the trace amounts of the REEs and Y in the starting synthetic fluorapatite (Supplementary Table 2) does not completely account for the excess Na with respect to S. Therefore, we suggest the known substitution of Na for Ca and a vacancy on the halogen site that allows for an overall neutral charge balance (Na$^+$ + Vac. = Ca$^{2+}$ + X$^-$; Pan and Fleet, 2002):

The results of our experiments demonstrate the successful Na and Si charge balanced sulfate coupled substitutions (Eqns. 1 and 2) during hydrothermal alteration and precipitation of the mineral apatite, affirming the mineral apatite as a recorder of S, Na, and Si in a hydrothermal fluid. When comparing the initial S concentration in the starting fluids (Table 1) to the measured average S concentration in the respective run-products (Table 2), it is clear that the activity of Na and Si in the fluid is the limiting factor. However, experimentation that further constrains the concentrations of Na, Si, and S in the starting and run-product fluid and apatite grains is required to quantify the partitioning of S, Na, and Si between metasomatized apatite and a hydrothermal fluid as a function of their respective concentrations.
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:

\[
\text{Ca}^{2+} + \text{P}^{5+} = \text{Fe}^{3+} + \text{S}^{4+} \tag{4}
\]

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
that we were unable to determine the oxidation states of Fe in our run-product fluorapatite as this requires the use of micro X-ray absorption near edge structure (μ-XANES) spectroscopy at the Fe K-edge. However, these results highlight the ability of apatite to record fluid compositions and potentially multiple species of redox sensitive metals. Further redox and crystal structure analyses, which is beyond the scope of this study, will be required to better understand the site occupancy (M1 vs. M2) and the effects of the smaller Fe$^{2+}$ and Fe$^{3+}$ cations (Shannon, 1976) on the fluorapatite crystal structure.

If the 0.09 wt.% Fe incorporated into the run-product apatite for experiment FS9 is not some ratio of Fe$^{2+}$/Fe$^{3+}$, then all must have been incorporated as a direct substitution of Fe$^{2+}$ for Ca$^{2+}$, leaving one method for the incorporation of the measured S. Sulfur in magmatic-hydrothermal fluids can be present as S$^{2-}$, S$^{4+}$, and S$^{6+}$ where the proportion of each is controlled by $fO_2$ (Binder and Keppler, 2011; Binder et al., 2018). Konecke et al. (2017) reported the presence of S$^{4+}$ in the metasomatized regions of Mina Carmen fluorapatite and proposed the following polyvalent S coupled substitution (Konecke et al., 2017a; Kim et al., 2017):

$$2P^{5+} = S^{6+} + S^{4+} \quad (5)$$

We suggest that this coupled sulfate-sulfite substitution explains the perceived excess S in all of our run-products with respect to Equations 1 and 2 (i.e. more S than Na or Si allows). Without a coupled substitution with Fe$^{3+}$, then the 154 μg/g of measured S (Table 2) would be from the sulfite-sulfate coupled substitution (Eq.5).
Strontium is a minor element commonly found in fluorapatite (Nash, 1984) and exhibits a unique relationship with Na and the REEs in fluorapatite. When Sr is substituted into the apatite crystal structure, it exhibits a preferential occupancy of the M2 site, which is normally occupied by the smaller Ca$^{2+}$, while the also larger Na and the REEs (Shannon, 1976) alternate occupying the M1 site (Hughes et al., 1991; Rakovan and Hughes, 2000). Due to the positive spatial and statistical correlations between Na and S enrichment, spatial correlations between Sr and S enrichment in the run-product Sr-bearing fluorapatite (Figs. 6c,d,e,g), and the known site occupancies of Sr and Na in strontian apatite we suggest that the presence of Sr in a hydrothermal fluid has significant potential to promote Equation 1 over Equation 3, when the concentration of REEs in the hydrothermal fluid are vanishingly low (i.e. REEs were not added to the experiment fluid and vanishingly low concentrations as a potential source are present in the starting apatite; cf. Supplementary Table 2), but is not a component in the charge balanced coupled substitution formula of S. Experiment FS14 yielded texturally and compositionally zoned Sr-bearing fluorapatite grains that yielded the greatest average S concentration for all experiments in this study (3,514 μg/g; Table 2).

It is well known that the mineral apatite is one of the principal hosts of REEs in geologic systems (Nash, 1984) and that they commonly substitute into the crystal structure via coupled substitution with Na (Eqn. 1) and Si (Pan and Fleet, 2002):

$$\text{REE}^{3+} + \text{Si}^{4+} = \text{Ca}^{2+} + \text{P}^{5+}$$  \hspace{1cm} (6)

Experiment FS10, which reacted the starting synthetic fluorapatite with a S-, Ce-, and Cl-bearing fluid, yielded a texturally and compositionally zoned run product fluorapatite (Fig. 5a; Table 2). No observable spatial distribution or measured atomic proportions were observed that would
indicate a S coupled substitution with the trace amounts of Na and Si present in the starting synthetic fluorapatite, nor for Ce with Na or Si (Figs. 5e,f,g). However, there is a strong positive spatial and statistical chemical correlation between Ce and S (Figs. 5c,d,h). From these observations, we propose the following coupled substitution between Ce$^{3+}$ and S$^{4+}$:

$$\text{Ca}^{2+} + \text{P}^{5+} = \text{Ce}^{3+} + \text{S}^{4+} \quad (7)$$

It is known that REE-bearing phosphates form at the expense of the host apatite grain via coupled dissolution-reprecipitation of the host apatite by a hydrothermal fluid and that a coeval decrease in Na, Si, and S can occur (Harlov et al., 2002a, 2005; cf. Our Eqns. 1,2,3, and 6). During growth of secondary monazite-(Ce) from Ce- and S-bearing apatite grains, sulfate will commonly substitute for phosphate in the monazite crystal structure (Laurent et al., 2016). However, the dependence of both the REEs and S on Na and Si for coupled substitutions into the apatite crystal structure, the need for ionic corrections to natural apatite REE and S a.p.f.u. plots (Peng et al., 1997; Streck and Dilles, 1998), the known REE-sulfate complexes in a hydrothermal fluid for transport and deposition (Banks et al., 1994; Migdisov et al., 2016), and the aforementioned substitution of S during the growth of REE-phosphates, all indicate an intrinsic and non-trivial relationship between S, the REEs, and the apatite supergroup.

The results of these metal-focused hydrothermal fluid alteration experiments demonstrate that apatite records information about the metal budget of hydrothermal fluids. The results reported here document previously unrecognized interdependencies between the substitution of S and the metals Fe, Sr, and Ce into the apatite crystal structure. The mineral apatite records their presence using the direct substitution of divalent cations, the coupled substitution of non-divalent cations...
(e.g. Ce$^{3+}$) with Na$^+$ and/or Si$^{4+}$, and our proposed coupled substitutions with S. These experiments underscore the necessity for further investigation into the redox state of Fe in the run-product apatite grains and structural refinements of the run-product crystal structure to better understand the site specific effects of these metal and S substitutions on the apatite crystal structure.

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

Fluorapatite is the most common apatite end-member in magmatic systems (Piccoli and Candela, 2002; references therein) and changes to the apatite halogen chemistry reflects the composition of the silicate melt during primary apatite crystallization (Webster and Piccoli, 2015; references therein) and magmatic-hydrothermal fluids during metasomatic alteration (Harlov, 2015; Spear and Pyle, 2002; Zhu and Sverjensky, 1991). Literature describing the apatite supergroup often define members by their halogen chemistry (e.g. Sulphato-silicates [Ca$_{10}$(SiO$_4$)$_3$(SO$_4$)$_3$(X)$_2$] - ellestadite-(OH) and ellestadite-(F)) (Pasero et al., 2010), which leads to our hypothesis that apatite halogen chemistry effects the substitution of S in fluorapatite.

Experiment FS11 is a control group experiment whereby saturating the fluid with a F source (NaF) the run products remained a F-dominant apatite (Harlov, 2015; Spear & Pyle, 2002; Zhu and Sverjensky, 1991). Experiment FS8 reacted the synthetic fluorapatite with a Na-free fluid saturated with Si and Cl to explore the effects of Cl substitution on Equation 2. The run product fluorapatite grains from experiment FS8 exhibit a minor incorporation of Cl and estimated OH (Table 2). There is a weak negative correlation between S and Si, contrary to what was anticipated. Instead, there is a weak correlation between S and Na which we suggest indicates
that the trace amounts of Na in the starting fluorapatite charge balanced the incorporation of S in the run-products (Table 2). Experiment FS17 utilized Ca(OH)$_2$ to increase the activity of OH in the fluid and promote the incorporation of OH into the apatite crystal structure to explore the effects of OH on Equation 1. EPMA analyses indicate that we were able to successfully incorporate OH into the run product apatite with a reduction of F, a minor Cl incorporation, and an increase of the estimated OH content (Table 2). Experiment FS13 reacted synthetic fluorapatite with a Na-, Si-, and Cl-bearing fluid in order to explore the effects of Cl substitution on Equations 1 and 2. EPMA analyses reveal a decrease in F, no appreciable change to Cl, and an increase of the estimated OH concentration (Table 2).

Of the experiments conducted testing the effects of the halogens F, Cl, and OH in the fluid on Equations 1 and 2, FS11 retained halogen concentrations similar to the starting apatite grains and yielded the greatest average measured S concentration (Fig. 9; Table 2). We suggest that in this instance the reincorporation of Ca was suppressed during dissolution-reprecipitation by the formation of CaF$_2$ using the excess F in the fluid (Harlov et al., 2006), thereby promoting the substitution of Na and S in run products from experiment FS11 (Fig. 3g). Experiment FS13 exhibits the next greatest S concentration with a moderate estimated OH concentration and a minor Cl concentration (Fig. 9; Table 2) Experiments FS17 and FS8 exhibit the lowest S concentrations of the 4 experiments despite the greatest estimated OH and Cl concentrations, respectively (Fig. 9; Table 2). We suggest that the moderate to strong correlations between S and Cl concentrations, and the moderate correlation with estimated OH concentrations in the run products demonstrate an effect of apatite halogen chemistry on the incorporation of S in apatite. The halogen Cl has a larger ionic radius when compared to F and OH, is disordered above or...
below the mirror planes in the unit cell which affects adjacent site occupancies, and has cascading effects on interatomic bond lengths and forces (Hughes et al., 1989). The complex and intricate effects of halogen site chemistry on the apatite crystal structure and the relatively inconclusive results of our halogen alteration experiments stress the importance of conducting detailed structural refinement studies to better understand the control of halogen site chemistry on the substitution of minor and trace elements on the M- and T-sites in the apatite crystal structure.

A positive relationship is observed between the initial S and Cl concentrations in the fluid (Table 1) and the S and Cl concentrations in the run-product apatite grains (Table 2) from experiments FS11, FS13, FS17, and FS8. For these four experiments, FS11 had the greatest initial S content in the fluid and yielded the greatest S concentration in the run-products while FS8 had the greatest initial Cl content in the fluid and yielded the greatest Cl content in the run-products. This trend for the F, Cl, and estimated OH concentrations in the experiment run-products agrees with the dependence of apatite halogen site chemistry on the activity of F, Cl, and OH in a hydrothermal fluid (Harlov, 2015; Spear and Pyle, 2002; Zhu and Sverjensky, 1991). However, this trend is not true for S. Experiment FS14 run-products yielded the greatest average S content of all experiments with ca. 7.6 wt.% S in the starting fluid composition while experiment FS6-2 yielded significantly less S in the run-products despite an initial fluid composition of ca. 22.3 wt.% S. These observations reinforce the hypothesis that the concentrations of charge balancing elements is the limiting factor for S substitutions.
In the WDS maps of some experiments, the zonation of F or Cl is diffuse and in contrast to the sharp reaction fronts visible for other elements (e.g. Figs. 2e,f). Sharp reaction fronts in metasomatized fluorapatite are indicators of dissolution-reprecipitation and diffuse reaction fronts are attributed to volume diffusion (Harlov et al. 2005; Putnis, 2002, 2009; Altree-Williams et al., 2015), illustrating two distinct methods of re-equilibration. However, from the work of others we know that electron beam induced diffusion of F and Cl in fluorapatite is common (Stormer et al., 1993) and that the beam current affects the rate of diffusion (Goldoff et al., 2012). This indicates that the alteration to the fluorapatite chemistry is a result of dissolution-reprecipitation and that the diffuse reaction fronts visible in the F WDS map are a result of the beam current and dwell time used for EPMA WDS data collection.

Hydrothermal sulfide substitution in fluorapatite

Experiment FS6-2, which reacted the starting synthetic apatite grains with an FeS-bearing aqueous fluid to assess whether reduced S will substitute for F, Cl, and OH in apatite grains reacted with a hydrothermal fluid. If the reduced S substituted for F in fluorapatite run-products, we would expect to see an inverse relationship between S and F concentrations. However, no statistically significant inverse correlation was observed for a.p.f.u. concentrations between S and F, nor Cl or OH concentrations. Despite the textural differences, the results of experiment FS6-2 (Figs. 7c,d) are similar to those of FS9 (Figs. 4d,e) where there is a clear positive spatial correlation between Fe and S, and an unexpected strong positive correlation between the calculated ionic concentrations of Fe and S in the run-product fluorapatite for experiment FS6-2 (Fig. 7h).
Given the possible range of intrinsic $fO_2$ buffering of the piston cylinder experiment apparatus (CCO to NNO), it is reasonable to assume the coexistence of $S^{2-}$, $S^{4+}$, and $S^{6+}$ in the fluid (Binder and Keppler, 2011; Binder et al., 2018). However, without a clearly constrained intrinsic buffering of the piston cylinder apparatus, it is impossible to infer an approximate ratio of $S^{6+}/\Sigma S$ for the hydrothermal fluid. Therefore, we cannot confirm whether $S^{2-}$ or $S^-$ were present in great enough abundance to react with the synthetic fluorapatite. Due the strong positive correlation between Fe and S, and the lack of an inverse correlation between S and F, we suggest that the results of experiment FS6-2 provide additional evidence for a potential $Fe^{3+}$ and $S^{4+}$ coupled substitution (Eqn. 4).

**IMPLICATIONS**

The data reported here document that fluorapatite, which experiences hydrothermal metasomatism, preserves the chemical signature of the metasomatic fluid. Palma et al. (2019) conducted textural, micro-analytical, and isotopic analyses on metasomatized primary fluorapatite grains from the Mina Carmen IOA deposit in the Chilean iron belt. They propose that an oxidized Cl-OH-S bearing magmatic-hydrothermal fluid reacted with the primary magmatic fluorapatite and resulted in the partially metasomatized Cl-OH apatite rims that are enriched in Na, S, Fe, and Sr. The results of our experiments are consistent with their hypothesis that metasomatized fluorapatite will incorporate the volatiles Cl, OH, and S during the dissolution-reprecipitation process and that the dominant S substitution in apatite occurs by coupled substitution with Na (Eqn. 1; Fig.8a) and not with Si (Eqn. 2; Fig.8b). We suggest that Sr in the magmatic-hydrothermal fluid likely promoted the Na-S coupled substitution as evidenced by the coeval enrichment of Sr in the metasomatized regions of the Mina Carmen
apatite grains. We caution that the Na and S concentrations in the metasomatized regions of Mina Carmen apatite should not be used to approximate Na or S concentrations in the fluid until the influence of Sr on Equation 1 is better understood. The demonstrated fluid mediated Fe incorporation in our experiment run-products suggest that the metasomatizing fluid was likely enriched in Fe, supported by the reported cross-cutting relationship between magnetite veinlets and the Fe-enriched Mina Carmen fluorapatite.

Boyce et al. (2014) proposed a fractional crystallization model to explain an observed core to rim S enrichment and F-Cl-OH transition in apatite grains from lunar mare basalts. This model was refuted by Konecke et al. (2017b) when they experimentally demonstrated that the proposed lunar melt composition could not account for the S concentrations in the apatite grains. They instead proposed a cryptic metasomatic event where the primary Cl-OH-S-poor lunar apatite grains were altered by a S-Cl-bearing fluid that resulted in the enriched rims. The results of our experiments demonstrate the metasomatic enrichment of Cl, OH, and S in a relatively S- and Cl-free primary fluorapatite and support the cryptic metasomatism hypothesis of Konecke et al. (2017b). Boyce et al. (2014) also reported the apparent coeval enrichment of Fe, Si, and Ce with the volatiles Cl and OH. This core to rim enrichment is similar to that reported by Palma et al. (2019) for the metasomatized Mina Carmen fluorapatite grains and our experiments demonstrate the fluid-mediated enrichment of these elements in metasomatized run-product fluorapatite grains.

Acknowledgements
This research was funded by the U.S. National Science Foundation (NSF) grants 1924142 and 2214119 and an NSF Graduate Research Fellowship to J.C. We thank Monika Koch-Müller for graciously hosting J.C. at the GFZ, Potsdam, DE. We thank Owen K. Neill for his assistance with microprobe analysis at the Robert B. Mitchell Electron Microbeam Analysis Lab, University of Michigan, Ann Arbor, Michigan, USA, and Robert Holder for his assistance with laser ablation inductively coupled plasma mass spectrometry analysis at the Holder Laser Ablation ICP-MS Laboratory, University of Michigan, Ann Arbor, Michigan, USA.
References Cited


Webster, J.D., and Botcharnikov, R.E. (2011) Distribution of sulfur between melt and fluid in SOHC-Cl-bearing magmatic systems at shallow crustal pressures and temperatures. Reviews in Mineralogy and Geochemistry, 73(1), 247-283.


List of In Text Figure Captions

Figure 1: BSE image of a representative grain of the starting synthetic fluorapatite (APS 102). Starting synthetic fluorapatite grains are euhedral, elongate, and homogenous in BSE image grayscale. Scale bar represents 170 μm.

Figure 2: a) High-contrast BSE image of a grain from experiment FS12. Grains are subhedral to anhedral, slightly rounded, exhibit a subtle greyscale zonation with diffuse boundaries. The red arrow indicates traces of beam damage visible in the BSE and CL images. b) Diffuse zonation in monochromatic CL image. c-f) Wavelength dispersive spectroscopy elemental maps of spatially correlated Na, Si, S, and F. Note the diffuse zonation boundaries for F. g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Na on the y-axis, and blue symbols compare S on the x-axis and Si on the y-axis. Error bars represent X-ray counting error and can be smaller than the symbols. Detection limits are indicated by dashed lines. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2.

Figure 3: a) High-contrast BSE image of a grain from experiment FS11. Grain is anhedral and slightly rounded with partially healed fractures. b) Distinct zonation boundary in monochromatic CL image. c-f) Wavelength dispersive spectroscopy elemental maps of Si and F, and spatially correlated Na and S. g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Na on the y-axis, and blue symbols compare S on the x-axis and Si on the y-axis. Error bars represent X-ray counting error and can be smaller than the symbols. Detection limits are indicated by dashed lines. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2.
Figure 4: a) High-contrast BSE image of a grain from experiment FS9. Grains are subhedral to anhedral and homogenous in high-contrast BSE image grayscale. b) Monochromatic CL image of representative grain. Grid pattern is artifact of data processing. c-f) Wavelength dispersive spectroscopy elemental maps of Na, Fe, S, and Cl. A positive spatial correlation is visible for Fe, S, and Cl. Note the diffuse zonation of Cl. g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Na on the y-axis, and blue symbols compare S on the x-axis and Si on the y-axis. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2. h) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Fe on the y-axis. Error bars for a.p.f.u. scatter plots represent X-ray counting error and can be smaller than the symbols. Detection limits are indicated by dashed lines. Black square indicates cluster with independent Fe and S concentrations. Dashed red line indicates approximate trend of data points for the proposed $\text{Fe}^{3+} + \text{S}^{4+} = \text{Ca}^{2+} + \text{P}^{5+}$ coupled substitution.

Figure 5: a) High-contrast BSE image of a grain from experiment FS10. Grains are euhedral to anhedral with a bi-modal grayscale in high-contrast BSE imagery where darker, inclusion-free regions are marked by a sharp reaction front traced by micrometer to sub-micrometer scale bright monazite-(Ce) inclusions (Mnz) that separate brighter regions with numerous $\leq 5$ μm inclusions. b) Monochromatic CL image of representative grain. Negative black regions are an artifact from non-optimized brightness/contrast settings during automated electron microprobe data collection. c-f) Wavelength dispersive spectroscopy elemental maps of distinctly zoned Ce and S, and Na and Si that exhibit subtle zoning. Cerium and S exhibit strong positive spatial correlation with a
more subtle Na and Si spatial correlation. g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols are S vs. Na on the y-axis and blue symbols are S vs. Si on the y-axis for analyses of the darker regions visible in BSE grayscale. Green symbols are S vs. Na on the y-axis and purple symbols are S vs. Si on the y-axis for analyses of the brighter regions visible in BSE grayscale. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2. h) Atoms per formula unit (a.p.f.u.) scatter plot where blue symbols are S vs. Ce for the BSE-dark regions and red symbols are S vs. Ce for the BSE-bright regions. Error bars for a.p.f.u. scatter plots represent the X-ray counting error and can be smaller than the symbols. Detection limits are indicated by dashed lines.

Figure 6: a) High-contrast BSE image of a grain from experiment FS14. The red dashed line is the approximate location of the apatite grain boundary. Grains are subhedral to anhedral with a bi-modal grayscale in high-contrast BSE imagery where the brighter regions are mantling darker cores. Fluorapatite grains are sometimes mantled by masses of Cl-rich SrSO₄. b) Monochromatic CL image of representative grain where CL brightness presents inverse to BSE image intensity. The red dashed line is the approximate location of the apatite grain boundary. c-f) Wavelength dispersive spectroscopy elemental maps of Na, S, Sr, and Si. Sodium, S, and Sr exhibit a strong positive correlation in the zoned apatite. The bright green dashed line in (c) is the approximate location of the apatite grain boundary. g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols are S vs. Na on the y-axis and blue symbols are S vs. Si on the y-axis for analyses of the darker regions visible in BSE grayscale. Green symbols are S vs. Na on the y-axis and purple symbols are S vs. Si on the y-axis for analyses of the brighter regions visible in BSE grayscale. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2. Error bars for
Figure 7: a) High-contrast BSE image of a grain from experiment FS6-2. Grains are anhedral and exhibit numerous, subparallel, dissolution pits that extend into the grain. Two regions are visible in high-contrast BSE imagery, a darker homogenous core that shares a distinct reaction front with brighter grain margins. The brighter grain margins exhibit a heterogenous grayscale on the micrometer scale with a combination of distinct and diffuse reaction fronts. b) Monochromatic CL image of representative grain where CL brightness presents inverse to BSE image intensity. c-f) Wavelength dispersive spectroscopy elemental maps of Fe, S, Si, and F. Iron and S exhibit a strong positive spatial correlation in the zoned apatite. g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols are S vs. Na on the y-axis and blue symbols are S vs. Si on the y-axis for analyses of the darker regions visible in BSE grayscale. Green symbols are S vs. Na on the y-axis and purple symbols are S vs. Si on the y-axis for analyses of the brighter regions visible in BSE grayscale. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2. h) Atoms per formula unit (a.p.f.u.) scatter plot where blue symbols are S vs. Fe for the darker BSE regions and yellow symbols are S vs. Fe for the brighter BSE regions. Error bars for a.p.f.u. scatter plots represent X-ray counting error and can be smaller than the symbols. Detection limits are indicated by dashed lines.

Figure 8: a) Atoms per formula unit (a.p.f.u.) scatter plot where red circles represent S and Na concentrations for all S-bearing run products, the black X-symbols are representative of reported S and Na concentrations in metamorphic apatite grains (Liu and Comodi, 1993; Warner et al.,
1998; Harlov et al., 2002b), the inverted black triangles are representative of reported S and Na concentrations in the Mina Carmen apatite grains (Palma et al., 2019), and the grey polygon with the dashed outline is the approximate region of reported S and Na concentrations in apatite grains from apatite-melt partition experiments (modified from Parat et al., 2011; references therein). b) Atoms per formula unit (a.p.f.u.) scatter plot where open circles represent the ‘low S’ concentration experiments FS3 and FS20, the open squares represent the ‘moderate S’ concentration experiments FS8 and FS15, the blue symbols represent experiments FS12 and FS13 that plot on or near the 1:1 atomic ratio line, the black X-symbols are representative of reported S and Si concentrations in metamorphic apatite grains (Liu and Comodi, 1993; Warner et al., 1998; Harlov et al., 2002b), the inverted black triangles are representative of reported S and Si concentrations in the Mina Carmen apatite grains (Palma et al., 2019), and the grey polygon with the dashed outline is the approximate region of reported S and Si concentrations in apatite grains from apatite-melt partition experiments (modified from Parat et al., 2011; references therein). The 1:1 line represents the ideal sulfate coupled substitutions from Equations 1 and 2.

Figure 9: Ternary plot illustrating F-Cl-OH halogen site occupancy in percent for experiment run products assessing the effects of halogen site chemistry on S incorporation and the starting synthetic apatite grains (APS-102). The chemical formula for run products is calculated using 5 cations and 26 oxygens; assuming that the halogen site (X) is occupied by F, Cl, OH and that the S present in the fluorapatite is oxidized and occupies the tetrahedral site (T).

List of Supplementary Figure Captions
Supplementary Figure 1: BSE images of representative fluorapatite grains from experiments where average S concentrations are below electron microprobe (EMP) detection limits. 

a) Representative grain from experiment FS1. Run-product apatite grains are homogenous in BSE image grayscale, subhedral to anhedral, with few rounded grain margins.

b) Representative grain from experiment FS2. Run-product apatite grains are homogenous in BSE image grayscale, dominantly anhedral, and occasionally fractured.

c) Representative grain from experiment FS3. Grains are homogenous in BSE image grayscale, subhedral to anhedral, slightly rounded, and occasionally mantled by a silicate glass that was not analyzed for its chemical composition. Brighter spots, indicated by a red arrow, on apatite grain are beam damage from EMP analyses.

d) Representative grain from experiment FS4. Grains are homogenous in BSE image grayscale, subhedral to anhedral, slightly rounded from dissolution, with sub-micrometer monazite (Mnz) grains found in partially healed fractures and mantling the fluorapatite (Ap) grains. Brighter spots, indicated by a red arrow, on apatite grain are beam damage from EMP analyses.

e) Representative grain from experiment FS7. Grains are homogenous in BSE image grayscale and anhedral with slightly concave margins from conchoidal fracturing.

f) Representative grain from experiment FS16. Grains are homogenous in BSE image grayscale, and subhedral to anhedral with partially healed fractures.

g) Representative grain from experiment FS20. Grains of fluorapatite (Ap) are homogenous in BSE image grayscale, subhedral to anhedral, with shallow etch pits, and occasional subtle rounding of corners. Aggregate masses of small (≤ 50 μm) euhedral to subhedral secondary quartz grains (Si) are present but were not analyzed for their chemical composition. Brighter spots, indicated by a red arrow, on apatite grain are beam damage from EMP analyses.

h) Representative grain from experiment FS21. Grains of fluorapatite (Ap) are homogenous in BSE image grayscale, and subhedral to anhedral with subtle
rounding of corners. Sub-micrometer monazite-(Ce) (Mnz) grains can be found filling fractures. Brighter spots, indicated by a red arrow, on apatite grain are beam damage from EMP analyses.

**Supplementary Figure 2:** a) High-contrast BSE image of a grain from experiment FS15. Grains are euhedral to anhedral, slightly rounded and exhibit a subtle greyscale zonation. White dashed line indicates approximate location of zonation boundary between overgrowth and seed crystal.

b) diffuse boundary zonation in monochromatic CL image. c-f) Wavelength dispersive spectroscopy elemental maps of spatially correlated Na, Si, S, and F. Note the distinct zonation boundary for Na and S, and the diffuse boundary for F. Bright spots in Na and Si map are Na-Si glass spheroids.

g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Na on the y-axis, and blue symbols compare S on the x-axis and Si on the y-axis. Error bars represent X-ray counting error and can be smaller than the symbols. Detection limits are indicated by dashed lines. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2.

**Supplementary Figure 3:** a) High-contrast BSE image of a grain from experiment FS8. Grains are euhedral to anhedral, slightly rounded and homogenous in BSE grayscale. Bright spots on the apatite grain are beam damage from previous analyses. b) Monochromatic CL image with no apparent zonation. Beam damage visible as dark spots. c-f) Wavelength dispersive spectroscopy elemental maps of spatially correlated Na, Si, S, and Cl. Note the distinct zonation boundary for S and the diffuse boundary for Cl. Bright spots in Si map are silicate glass spheroids.

g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Na on the y-axis, and blue symbols compare S on the x-axis and Si on the y-axis. Error bars represent X-
ray counting error and can be smaller than the symbols. Detection limits are indicated by dashed lines. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2.

**Supplementary Figure 4:** a) High-contrast BSE image of fluorapatite grain (Ap) from experiment FS13. Grains are subhedral to anhedral and homogenous in BSE image grayscale. Elongate grains of accessory wollastonite (Wol) and spheroids of sodium silicate glass (Na-Si) are present but were not analyzed for their chemical compositions. Dashed white line indicates approximate c-axis orientation. Bright spots on the apatite grain are from electron beam damage. b) Distinct zonation boundaries in monochromatic CL imagery. c-f) Wavelength dispersive spectroscopy elemental maps of Cl and spatially correlated Na, Si, and S. g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Na on the y-axis, and blue symbols compare S on the x-axis and Si on the y-axis. Error bars represent X-ray counting error are smaller than the symbols. Detection limits are indicated by dashed lines. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2.

**Supplementary Figure 5:** a) High-contrast BSE image of a grain from experiment FS17. Grains are dominantly subhedral to anhedral with partially healed fractures, and larger masses (> 100 μm) of smaller (≤ 15μm) grain aggregates. Grains are euhedral to subhedral and exhibit grain to grain variation in BSE images. b) Subtle zonation in monochromatic CL imagery. c-f) Wavelength dispersive spectroscopy elemental maps of spatially correlated Na and S, and inversely correlated F and Cl. g) Atoms per formula unit (a.p.f.u.) scatter plot where red symbols compare S on the x-axis and Na on the y-axis, and blue symbols compare S on the x-axis and Si on the y-axis. Error bars represent X-ray counting error are smaller than the symbols. Detection
limits are indicated by dashed lines. The 1:1 line represents the sulfate coupled substitutions from Equations 1 and 2.
### Table 1. Summary of experimental results

<table>
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<tr>
<th>Experiment</th>
<th>P (GPa)</th>
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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...
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<th>FeS</th>
<th>CaCl$_2$</th>
<th>NaF</th>
<th>Ca(OH)$_2$</th>
<th>Initial Wt% S*</th>
<th>Initial Wt.% Cl*</th>
<th>Results</th>
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</table>
| 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 don-
| 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-
|                |                 |     |         |     |             |                 | 9.45 22.3     | mantling fluorapatite grains. |
| 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-
|                |                 |     |         |     |             |                 | 1.92 9.9      | show a bi-modal grayscale; darker, inclusion free, regions anc-
| 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 ag-
|                |                 |     |         |     |             |                 | 7.6 8.3       | fluorapatite grains, including aggregates, are homogenous in j-
| 11.22          | 0.95            | 2.8 |         |     |             |                 |                | Run product apatite grains are sub-hedral to anhedral with a b-
|                |                 |     |         |     |             |                 | 5.38 8.1      | the darker grains. Brighter regions sometimes exhibit subtle a-
| 5.37           | 5.05            | 5.6 | 7.9     |     |             |                 |                | Run product apatite grains are euhedral to anhedral, 10s to 10-
|                |                 |     |         |     |             |                 | 5.77 5.5      | mantled by aggregates of smaller grains that have grown toge-
| 4.73           | 5.8             | 10.8 |         |     |             |                 |                | Run product apatite grains are sub-hedral to anhedral, concav-
|                |                 |     |         |     |             |                 |                | aggregate masses of small (≤50μm) euhedral to sub-hedral se-
|                |                 |     |         |     |             |                 |                | Run product apatite grains are sub-hedral to anhedral with sul-
|                |                 |     |         |     |             |                 |                | little evidence of fluorapatite dissolution. |

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

unantly anhedral. Fluorapatite is occasionally mantled by silicate glass.

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

arallel dissolution pits 5-20 μm deep that extend into the grain, with minor 5 μm or less bright iron sulfide grains in high

ale 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.

eryous ≤5 μm Monazite-(Ce) inclusions and/or grains mantling the fluorapatite. In high contrast BSE images, some grains

a sharp reaction front separating brighter regions. Micron to sub-micron scale monazite inclusions trace the reaction

htly rounded with partially healed fractures.

ightly rounded.

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

-modal grayscale in high contrast BSE images. Brighter regions are found mantling darker cores and filling fractures of

do/or sharp zonation in grayscale. Few fluorapatite grains are mantled by large (>200μm) masses of Cl rich SrSO₄.

os 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.

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

ral 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

dondary quartz grains.

rle 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

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Figure 2

FS12: FIAp + Na$_2$SO$_4$ + Na$_2$Si$_2$O$_5$ + H$_2$O

- a) 40 μm
- b) CL 40 μm
- c) Na 40 μm
- d) Si 40 μm
- e) S 40 μm
- f) F 40 μm
- g) Figure 2

Table: S a.p.f.u.

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Figure 3

FS11: FlAp + Na2SO4 + NaF + H2O

a) 30 μm

b) CL

c) Na

d) Si

e) S

f) F

g) S Det. Lim.
Figure 4

FS9: FLAp +1M H₂SO₄ + FeCl₃ + CaCl₂ + H₂O

(a) 40 μm  (b) 40 μm  (c) 40 μm

(d) CL  40 μm  (e) Na  40 μm  (f) S  40 μm  (g) Cl  40 μm

(g) 0.00  0.01  0.02  0.03

(h) 0.00  0.01  0.02  0.03
Figure 5
FS10: FlAp +1M H₂SO₄ + CeCl₃ + CaCl₂ + H₂O

- a) Mnz
- b) CL
- c) Ce
- d) S
- e) Na
- f) Si
- h) Ce Bright, Ce
Figure 6

FS14: FLAp + Na₂SO₄ + SrCl₂ + H₂O

a) SrSO₄

b) CL

c) Na

d) Si

e) S

f) Sr

g) Si, Na Bright

1:1

S a.p.f.u.
a.p.f.u. 0.05 0.10 0.15

0.00 0.02 0.06 0.10 0.14
Figure 7

FS6-2: FlAp + FeS + H₂O
Figure 9