

Experimental metasomatic incorporation of sulfur into fluorapatite

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The mineral apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{F},\text{Cl},\text{OH})_2]$ is ubiquitous in most geologic systems and can incorporate many elements including S as S^{2-} , S^{4+} , and S^{6+} . A plethora of experimental studies have demonstrated that the oxidation state of S plays a fundamental role in controlling ore metal solubilities in parental silicate melts and partitioning of ore metals between melt and magmatic-hydrothermal ore fluids. It has also been experimentally demonstrated that the relative abundances of S^{2-} , S^{4+} , and S^{6+} in igneous melts record the oxygen fugacity at the time of crystallization [1,2]. Here, we report results from a series of piston cylinder alteration and recrystallization experiments (CaF₂ setup, graphite oven) involving fluorapatite and a series of different fluids at 800 °C and 1 GPa that constrain the partitioning of S, Fe, Sr, and Ce between fluorapatite and these fluids. The new data demonstrate that S can be incorporated into fluorapatite via the possible coupled substitutions $\text{S}^{6+} + \text{Na}^+ = \text{P}^{5+} + \text{Ca}^{2+}$ and $\text{S}^{6+} + \text{Si}^{4+} = 2\text{P}^{5+}$. The data indicate that incorporation of S and Na into fluorapatite was enhanced by the presence of Sr and also suggest the existence of two previously unknown coupled substitutions in metasomatized areas of fluorapatite involving Fe, Ce, and S, i.e., $\text{Ca}^{2+} + \text{P}^{5+} = \text{Fe}^{3+} + \text{S}^{4+}$ and $\text{Ca}^{2+} + \text{P}^{5+} = \text{Ce}^{3+} + \text{S}^{4+}$. The concentrations of Cl, OH, and S in the run-product fluorapatite are positively correlated with each other, which suggests that the presence of Cl and OH facilitates the incorporation of S in fluorapatite, plausibly on the halogen site as S^{2-} as described by [3,4]. Overall, the data demonstrate that fluorapatite can incorporate S during metasomatic processes and that the concentration of S is positively correlated with the charge balancing cations Na and Si. Future work will use S-XANES to measure the relative abundances of S^{2-} , S^{4+} , and S^{6+} in the experimentally metasomatized fluorapatite.

[1] Konecke et al. (2017) *American Mineralogist*, 102(3), 548-557.

[2] Konecke et al. (2019) *Geochimica et Cosmochimica Acta*, 265, 242-258.

[3] Kim et al. (2017) *American Mineralogist*, 102, 1646-1656.

[4] Kim et al., (2022) *American Mineralogist*, 102(8), 1646-1656.