

Metasomatic incorporation of S⁶⁺ and S⁴⁺ into fluorapatite as a function of coupled substitutions with Na, Si, Fe, and Ce

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Apatite [Ca₁₀(PO₄)₆(F,Cl,OH)₂] is a ubiquitous mineral in many metamorphic, igneous, and magmatic-hydrothermal systems, and can incorporate a wide range of elements including S as S²⁻, S⁴⁺, and S⁶⁺. It has been experimentally demonstrated that the relative abundances of S²⁻, S⁴⁺, and S⁶⁺ in apatite from 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 alkali-, Cl-, F-, and S-bearing fluids at 800 °C and 1 GPa that constrain the partitioning of S, Fe, Sr, and Ce (as a proxy for the REE) between fluorapatite and these fluids. The data from these experiments demonstrate that S can be incorporated in apatite by the two known coupled substitutions S⁶⁺ + Na⁺ = P⁵⁺ + Ca²⁺ and S⁶⁺ + Si⁴⁺ = 2P⁵⁺ via a coupled dissolution-reprecipitation process. The data also demonstrate that the presence of Sr in hydrothermal fluids promotes the incorporation of Na and S in apatite via the coupled substitution S⁶⁺ + Na⁺ = P⁵⁺ + Sr²⁺. Our data also reveal a previously unknown intrinsic relationship between Fe and S, and Ce and S in metasomatized fluorapatite that can be explained by coupled substitutions Ca²⁺ + P⁵⁺ = Fe³⁺ + S⁴⁺ and Ca²⁺ + P⁵⁺ = Ce³⁺ + S⁴⁺, respectively. The concentrations of Cl, OH, and S in run-produce apatite are positively correlated with each other, which indicates that the presence of Cl and OH can play a determinative role in the incorporation of S in apatite [3,4]. Overall, the data from these metasomatism experiments involving S and apatite demonstrate that incorporation of sulfate and sulfite into apatite during metasomatism depends on the abundance of charge-balancing cations in the fluid.

[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.