

Empirically investigating the sulfur and rare earth element mobility between apatite and hydrothermal fluids as a function of temperature (500-800 °C) and fluid composition (mHCl-mH₂SO₄)

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The mineral apatite $\text{-Ca}_{10}(\text{PO}_4)_6(\text{F,Cl,OH})_2\text{-}$ is nearly ubiquitous in terrestrial geologic systems and can incorporate nearly one-third of the periodic table of elements, including sulfur (S) and rare earth elements (REEs). The multiple oxidation states of S (e.g., S^{6+} , S^{2-}) are critical for the transport and enrichment of base and precious metals in igneous and hydrothermal mineral deposits. Because of their magnetic and luminescent properties, REEs are important for the manufacturing and development of renewable energy and consumer technologies. Published experimental studies elucidated the partitioning behavior of S and REEs between apatite and silicate melts, demonstrated that igneous apatite incorporates $\text{S}^{6+} > \text{S}^{2-} > \text{S}^{4+}$, and that oxygen fugacity ($f\text{O}_2$) is the master variable controlling the $\text{S}^{6+}/\Sigma\text{S}$ ratio in silicate melt and igneous apatite. Studies of metasomatized apatite in natural systems revealed the presence of secondary REE phases, intra-apatite zoning of REEs, and the depletion or enrichment of polyvalent S within natural apatite. Experimental studies have constrained the factors controlling the formation of metasomatic secondary monazite. To our knowledge, no experimental studies have explored the effects of temperature, fluid composition, and $f\text{O}_2$ on S and REE mobility between apatite and hydrothermal fluids at PTX conditions relevant for upper crustal systems.

Here, we will discuss results from new experiments performed at 100 MPa, 500–800 °C and variable fluid compositions (mHCl, mH₂SO₄) buffered at NNO designed to constrain the mobility of S and REEs between fluid and fluorapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2]$; Durango fluorapatite was used as starting material. Run product apatite grains were analyzed by EPMA, SEM EDX element mapping and CL images. The data revealed altered regions of apatite that exhibit Na, Si, and S concentrations lower than the starting material and often below detection limits (308, 154, and 44 ppm, respectively). Leaching of REEs via dissolution-precipitation of starting apatite resulted in the growth of secondary REE phases, e.g., monazite. The data also reveal that the extent of apatite-fluid reactivity decreases with increasing temperature, which is plausibly explained by decreasing acid dissociation, demonstrating the importance of temperature and fluid composition for REE mobilization in apatite-saturated systems.