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Rare Earth Element and Sulfur Partitioning Between Apatite and Hydrothermal Fluids as a Function of Temperature, Fluid Composition, and Oxygen Fugacity

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The mineral apatite— $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}, \text{Cl}, \text{OH})_2$ —is nearly ubiquitous in terrestrial and lunar geologic systems and can incorporate nearly one-third of the periodic table of elements, including polyvalent sulfur (S) and as much as 10 wt % rare earth elements (REEs). Polyvalent S (e.g., S^{6+} , S^{2-}) is 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. Work by Sadove et al. (2019) on metasomatized apatite from the magnetite-sulfide Philips Mine in New York revealed regions with secondary REE-rich phases and elevated REE and S concentrations associated with dominantly S^{6+} (as determined by S-XANES). They propose that the elevated concentrations of S and REEs are the result of apatite metasomatism by an oxidized hydrothermal fluid. To our knowledge, no experimental studies have explored the effects of temperature, fluid composition, and oxygen fugacity ($f\text{O}_2$) on S and REE partitioning between apatite and hydrothermal fluids at PTX conditions relevant for upper crustal systems.

Here, we will discuss results from experiments performed at 100 MPa, 500°–800°C and variable fluid compositions (mHCl, mH₂SO₄, Na₂Si₂O₅) buffered at the Ni-NiO mineral equilibrium (where S is present as both reduced and oxidized sulfur) and new data from experiments buffered at M-H (where the S present is dominantly oxidized) and Co-CoO (where the S present is dominantly reduced). The experiments are designed to constrain the partitioning of S and REEs between fluid and fluorapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{F})_2$]. Run product apatite grains were analyzed by EPMA, SEM EDX mapping, S-XANES maps of S oxidation states, and CL images. The data from experiments buffered at NNO revealed altered regions of apatite that exhibit depleted Na, Si, and S concentrations and leaching of REEs via dissolution-reprecipitation of the starting apatite, which resulted in the growth of secondary REE phases, e.g., monazite. The apatite was more reactive with HCl-bearing fluids than H₂SO₄-bearing fluids, and the leaching of Na, Si, S, and the REEs was buffered by the presence of Na and Si in the fluid. The data from experiments buffered at NNO also reveal that apatite-fluid reactivity decreases with increasing temperature for mHCl-bearing fluids, which can be explained by the increased association of HCl at elevated temperatures. The mineral apatite is not currently sought after as a source of REEs; however, as the need for these energy-critical metals is projected to increase, an understanding of the PTX conditions that result in REE-rich apatite is of interest.