

Sulfur-in-apatite: The redox evolution of ore fluids during the formation of the Phillips Mine sulfide ore deposit, New York, USA

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The oxidation state of sulfur plays a critical role in the formation of certain igneous and magmatic-hydrothermal ore deposits. For instance, the presence of reduced sulfur (i.e., sulfide) is efficient at complexing with and transporting gold in aqueous fluid, whereas oxidized sulfur (sulfite or sulfate) is an inefficient complexing ligand for gold. Constraining the oxidation state of sulfur in igneous and magmatic-hydrothermal systems can be a valuable tool to help understand mineralizing processes. Apatite (commonly $\text{Ca}_{10}[\text{PO}_4]_6[\text{F,OH,Cl}]_2$) is an ubiquitous accessory mineral in igneous and magmatic-hydrothermal ore-forming systems, and can incorporate nearly half of the periodic table of elements, including redox sensitive elements such as Fe, Mn, and S. Owing to its sensitivity to changes in coexisting fluid or melt composition, the elemental zonation of apatite may record the chemical and redox evolution of the system. In this study, micro X-ray absorption near edge structure (μ -XANES) spectroscopy at sulfur *K*-edge, was used to measure the oxidation states of S in natural apatite from the Phillips Mine magnetite-sulfide ore body in Putnam County, New York. The studied apatite grains contain inclusions of euhedral pyrite, pyrrhotite, magnetite, ferroan carbonate, pyroxene, and monazite, the presence of the latter mineral is indicative of metasomatic alteration. Four μ -XANES transects were collected within two apatite grains starting near the edge of (1) a pyrrhotite inclusion (transects = 75 - 94 μm), and (2) a pyrite - ferroan carbonate - pyroxene- magnetite inclusion (transects = 80 - 104 μm), moving away from the inclusions and into the apatite host. Nine electron probe micro-analysis (EPMA) transects were performed parallel to the four μ -XANES transects to correlate changes in S oxidation state to compositional variations. The analyses reveal that apatite contains S^{6+} , S^{4+} , S^{1-} and S^{2-} , with corresponding peak absorption energies observed by use of XANES; 2482 eV (S^{6+}), 2478 eV (S^{4+}), 2471 eV (S^{1-}), and 2470 eV (S^{2-}). Sulfur peak areas, determined for the different S oxidation states in apatite, demonstrate systematic variations in $\text{S}^{6+}/\sum\text{S}$, where elevated $\text{S}^{6+}/\sum\text{S}$ ratios typically coincide with higher concentrations of S and rare earth elements (REEs). This finding of multiple oxidation states of sulfur, and the presence of monazite inclusions that record secondary dissolution-reprecipitation of apatite, indicate differences in sulfur and oxygen fugacity during primary mineralization and metasomatism. This study demonstrates that the oxidation state of sulfur in apatite may provide valuable geochemical information regarding the redox evolution of igneous and magmatic-hydrothermal systems.