Multiple oxidation states of sulfur in apatite from the Philips Mine magnetite - apatite deposit, New York

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Sulfur is a polyvalent element (S^{2-}, S^{4+}, S^{6+}) and the third most abundant volatile element in magmatic systems. A growing number of studies indicate that the sulfur oxidation state is related to the genesis of ore deposits and related magmatic, and magmatic-hydrothermal systems. For instance, redox conditions have a major control on metal partitioning between a magmatic-hydrothermal system and the ore fluid(s). Apatite (commonly $Ca_5(PO_4)_3(F,OH,Cl)$) is an ubiquitous accessory mineral in igneous and 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 is believed to record the chemical and redox evolution of the system. In this study, natural apatite samples from the Philips Mine IOA deposit in the Adirondack Mountains, NY were analysed by micro X-ray absorption near edge structures (XANES) spectroscopy at the S *K*-edge to determine the formal S oxidation state. The studied apatite contains inclusions of euhedral pyrite, up to 800 µm in diameter, and ~10-15 µm sized monazite ($[REE]PO_4$) grains, an observation consistent with metasomatic alteration. We collected a 40 µm XANES transect, positioned near the edge of the pyrite inclusion, moving into the apatite host. Electron probe micro-analysis (EPMA) transects were positioned parallel to the XANES transect in order to link changes in S oxidation state to compositional variations. Analyses conducted away from the pyrite (~20 microns) and into the apatite matrix, demonstrate variation in sulfur content; initially 472 ppm to 60 ppm and plateauing at 128 ppm. The XANES spectra reveal the presence of S^{2-} and S^{6+} in the apatite structure, with a gradual decrease of the S^{6+}/S^{2-} peak intensities in apatite moving away from the sulfide inclusion. A systematic decrease in the XANES peak intensities is proportional to an observed decrease in the sulfur concentration. This variability points to the chemical history of the system, suggesting changes in sulfur and oxygen fugacity. A recent experimental study documents that apatite is the first mineral to contain varying proportions of oxidized (S^{6+}) and reduced (S^{2-}) oxidation states of sulfur. Upon further research, the oxidation state of sulfur in apatite may provide valuable geochemical information regarding the redox evolution of magmatic and magmatic-hydrothermal systems during apatite crystallization.