

SPECIAL COLLECTION: APATITE: A COMMON MINERAL, UNCOMMONLY VERSATILE

Co-variability of S^{6+} , S^{4+} , and S^{2-} in apatite as a function of oxidation state: Implications for a new oxybarometer

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ABSTRACT

In this study, we use micro-X-ray absorption near-edge structures (μ -XANES) spectroscopy at the S *K*-edge to investigate the oxidation state of S in natural magmatic-hydrothermal apatite (Durango, Mexico, and Mina Carmen, Chile) and experimental apatites crystallized from volatile-saturated lamproitic melts at 1000 °C and 300 MPa over a broad range of oxygen fugacities [$\log(f_{O_2}) = \text{FMQ}$, $\text{FMQ}+1.2$, $\text{FMQ}+3$; FMQ = fayalite-magnetite-quartz solid buffer]. The data are used to test the hypothesis that S oxidation states other than S^{6+} may substitute into the apatite structure. Peak energies corresponding to sulfate S^{6+} (~2482 eV), sulfite S^{4+} (~2478 eV), and sulfide S^{2-} (~2470 eV) were observed in apatite, and the integrated areas of the different sulfur peaks correspond to changes in f_{O_2} and bulk S content. Here, multiple tests confirmed that the S oxidation state in apatite remains constant when exposed to the synchrotron beam, at least for up to 1 h exposure (i.e., no irradiation damages). To our knowledge, this observation makes apatite the first mineral to incorporate reduced (S^{2-}), intermediate (S^{4+}), and oxidized (S^{6+}) S in variable proportions as a function of the prevailing f_{O_2} of the system.

Apatites crystallized under oxidizing conditions ($\text{FMQ}+1.2$ and $\text{FMQ}+3$), where the S^{6+}/S_{Total} peak area ratio in the coexisting glass (i.e., quenched melt) is ~1, are dominated by S^{6+} with a small contribution of S^{4+} , whereas apatites crystallizing at reduced conditions (FMQ) contain predominantly S^{2-} , lesser amounts of S^{6+} , and possibly traces of S^{4+} . A sulfur oxidation state vs. S concentration analytical line transect across hydrothermally altered apatite from the Mina Carmen iron oxide-apatite (IOA) deposit (Chile) demonstrates that apatite can become enriched in S^{4+} relative to S^{6+} , indicating metasomatic overprinting via a SO_2 -bearing fluid or vapor phase. This XANES study demonstrates that as the f_{O_2} increases from FMQ to $\text{FMQ}+1.2$ to $\text{FMQ}+3$ the oxidation state of S in igneous apatite changes from S^{2-} dominant to $S^{6+} > S^{4+}$ to $S^{6+} \gg S^{4+}$. Furthermore, these results suggest that spectroscopic studies of igneous apatite have potential to trace the oxidation state of S in magmas. The presence of three S oxidation states in apatite may in part explain the non-Henrian partitioning of S between apatite and melt. Our study reveals the potential to use the S signature of apatite to elucidate both oxygen and sulfur fugacity in magmatic and hydrothermal systems.

Keywords: Apatite, sulfur oxidation state, XANES, oxybarometer, apatite crystallization experiments