

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 ( $\mu$ -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 [ $\log(f_{O_2}) = \text{FMQ}$ ,  $\text{FMQ}+1.2$ ,  $\text{FMQ}+3$ ;  $\text{FMQ}$  = 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 (FMQ+1.2 and FMQ+3), where the  $S^{6+}/S_{\text{Total}}$  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  $\text{SO}_2$ -bearing fluid or vapor phase. This XANES study demonstrates that as the  $f_{O_2}$  increases from FQM to FMQ+1.2 to 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