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($f_{O2}$)] = FMQ, FMQ+1.2, 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 inapatite, and the integrated areas of the different sulfur peaks correspond to changes in $f_{O2}$ 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 $f_{O2}$ of the system.

Apatites crystallized under oxidizing conditions (FMQ+1.2 and 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 $S^{4+}$, and possibly traces of $S^{6+}$. 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 $f_{O2}$ increases from FQM to FMQ+1.2 to FMQ+3, the oxidation state of S in igneous apatite changes from $S^{2–}$ dominant to $S^{6+}$ to $S^{4+}$. 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

INTRODUCTION

Sulfur is the third most abundant volatile in magmatic systems released during volcanic eruptions and degassing processes (cf. Faure 1986; Métrich and Mandeville 2010; Mandeville 2010) and is the fundamental chemical anomaly in arc-related magmatic-hydrothermal porphyry-type ore deposits, which are an important source of Cu, Au, Ag, and Mo (Gustafson and Hunt 1975; Candela and Piccoli 2005). A growing body of data suggests that the oxidation state of S (e.g., $S^{2–}$, $S^{4+}$, $S^{6+}$) plays a fundamental role in controlling ore metal solubilities in parental silicate melts and partitioning of ore metals between melt and magmatic-hydrothermal ore fluids (Simon and Ripley 2011). Sulfur oxidation state in silicate melts and magmatic-hydrothermal fluids is intrinsically linked to oxygen fugacity ($f_{O2}$), where sulfur is present as sulfate ($S^{6+}$) and sulfide ($S^{2–}$) in oxidized and reduced silicate melts, respectively (Jugo et al. 2010). While sulfur in aqueous fluids that exsolved from oxidized and reduced silicate melts exists as sulfate ($S^{6+}$; SO$_4^{2–}$), sulfide ($S^{2–}$; H,S; Burgisser et al. 2015), and a trisulfur ion (S$_3$; Pokrovski and Dubrovinsky 2011; Pokrovski and Dubessy 2015).

The mineral apatite, commonly Ca$_5$(PO$_4$)$_3$(F,Cl,OH), is an ubiquitous phase in terrestrial (Webster and Piccoli 2015) and extraterrestrial (McCubbin and Jones 2015) magmatic and magmatic-hydrothermal systems and incorporates redox sensitive elements such as Fe, Mn, and S. Mainly based on the observation that S-rich (terrestrial) apatite is typically observed...