A New S-in-Apatite Oxybarometer for Magmatic Systems

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Apatite—generally $Ca_{10}(PO_4)_6(F,Cl,OH)_2$—is a common accessory phase in terrestrial and extraterrestrial geologic systems [1], and can structurally incorporate about 1/3 of the periodic table of elements, including volatile and redox sensitive elements such as sulphur (S) [2]. Considering apatite's ability to crystallize from melts and magmatic-hydrothermal fluids [2], the intra- and inter-crystalline zonation with respect to S contents and oxidation states (e.g., S^{6+}, S^{4+}, S^{2-}) may serve as a proxy to reconstruct redox processes, and the budget of S in magmatic systems [3,4].

In this study, we performed apatite crystallization experiments at fixed T-P-X (i.e., $1000^{\circ}C$; 300 MPa; mafic silicate melt, containing ~0.35 wt.% bulk S), and variable fO_2 (e.g., where log fO_2 [ΔFMQ] = -1, +0, +0.25, +0.8, +1.2, and +3), in order to test the hypothesis that the integrated peak area ratios of S oxidation states ($S^{6+}/\Sigma[S^{6+} + S^{4+} + S^{2-}]$) in apatite can be used as a oxybarometer. Micro X-ray absorption near-edge structures (µ-XANES) spectroscopy at the S K-edge was used to measure the oxidation state(s) of S in experimental crystallized apatite. The integrated $S^{6+}/\Sigma S$ peak area ratios of the apatite were calculated following the methodology of [4], where: $S^{6+}/\Sigma S$ = 0.134 (FMQ-1), 0.137 (FMQ), 0.504 (FMQ+0.25), 0.962 (FMQ+0.8), 0.958 (FMQ+1.2), and 0.964 (FMQ+3). The integrated $S^{6+}/\Sigma S$ peak area ratios vs. ΔFMQ results were fitted using a (Boltzmann) sigmoidal function (adjusted r^2 = 0.99). The calibration curve exhibits a sharp transition (e.g., slope of inflection point) from low $S^{6+}/\Sigma S$ to high $S^{6+}/\Sigma S$, indicating that the S-in-apatite oxybarometer is highly sensitive with respect to redox conditions from ~FMQ+0 to ~FMQ+0.8. This redox range is particularly relevant for MORB systems, and relatively reduced (e.g., <FMQ+1) arc related basalts, that can oxidize upon degassing of a S-bearing fluid [5]. Although the S-in-apatite calibration can be applied for the conditions investigated in this study, future work will focus on the extension of the calibration over a broader range of T-P-X.

[1] Parat et al. (2011), Rev. Mineral. Geochem. 73, 285–314.
[2] Webster and Piccoli (2015), Elements. 11, 177-182. [3] Streck and Dilles (1998), Geology. 26, 523-526. [4] Konecke et al. (2017), Amer. Miner. 102, 548-557. [5] Burgisser and Scaillet (2007), Nature. 445, 194-197.

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