

Sulfate (S⁶⁺), sulfite (S⁴⁺), and sulfide (S²⁻) partitioning into apatite: Its potential and limitations

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Apatite is a common accessory phase in magmatic and hydrothermal environments, and can contain several thousand $\mu\text{g/g}$ of the redox sensitive element sulfur. The recent work by Konecke et al. [1] revealed the presence of three different oxidation states of sulfur (S⁶⁺, S⁴⁺, S²⁻) in the apatite structure as a function of oxygen fugacity (fO₂). Here, we present new experimental and computational results that further constrain the incorporation of sulfur into apatite and its potential application as an oxybarometer.

Apatite crystallization experiments in rhyolitic and lamproitic systems were performed at 1000°C, 300 MPa and at fO₂ = FMQ-1 to FMQ+3. The apatite-melt partitioning coefficient of sulfur $D_{\text{S}^{\text{ap/m}}}$ increases gradually over the studied range of fO₂; from ~0.2 at FMQ-1 to ~3.0 at FMQ+3. Smaller variations in $D_{\text{S}^{\text{ap/m}}}$ were observed with changing sulfur fugacity and melt composition. The data indicate that $D_{\text{S}^{\text{ap/m}}}$ may decrease further at fO₂ < FMQ-1, whereas a plateau seems to be reached at \geq FMQ+2. Thus, $D_{\text{S}^{\text{ap/m}}}$ seems to be redox sensitive over a wider range of fO₂ when compared to the S oxidation state in the coexisting melt [2]. This is consistent with sulfur XANES spectra collected on the experimental apatite grains and with ab-initio calculations, which model the incorporation of S into end-members F-, Cl-, OH-apatite. For instance, XANES reveals the presence of appreciable amounts of S⁶⁺ in a S²⁻ dominated apatite grown at FMQ-1 and our computational results indicate a general preference of apatite for S⁶⁺ > S²⁻ > S⁴⁺. Here, S⁶⁺ and S⁴⁺ are replacing P⁵⁺ in the apatite structure, whereas S²⁻ favors the column anion site. Notably, the probability for S²⁻ incorporation is highest for Cl-apatite.

Hence, a S-in-apatite oxybarometer may be applicable over a wide range of fO₂, but may require careful calibration for specific apatite (and melt) compositions.

[1] Konecke, B.A., Fiege, A., Simon, A.C., Parat, F., Stechern, A. (2017). *American Mineralogist*, 102, 548-557.

[2] Jugo, P.J., Wilke, M., Botcharnikov, R.E. (2010). *Geochimica et Cosmochimica Acta*, 74, 5926-5938.