

Manganese speciation in apatite: a tool for determining redox conditions in magmas?

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Apatite is a common accessory in many igneous rocks, and also found in many sedimentary and metamorphic rocks. Despite having the general formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F},\text{Cl},\text{Br})_2$ apatite group minerals are remarkably tolerant to structural distortion and chemical substitution, and are consequently diverse in composition. The potential of apatite to readily incorporate multivalent elements such as Fe, Mn, Eu and Ce in multiple oxidation states means that it has potential as a proxy for quantifying the oxidation state of the magmas from which it crystallised. Recent observations from the zoned Criffell granitic pluton (southern Scotland) support the use of manganese incorporation in apatite as a tool for determining oxygen fugacity. Variations in Mn concentrations of apatites across this body are independent of changes in whole-rock Mn content, and instead appear to correlate with the increased compatibility of Mn in apatite under more reducing conditions.

In order to explore the potential for a Mn in apatite 'oxygeobarometer' we have characterised Mn incorporation in a series of natural and synthetic apatites grown in the lab under controlled conditions using X-ray absorption spectroscopy at the Diamond Light Source, Oxfordshire (UK). Spectra clearly indicate that Mn is readily incorporated into the apatite structure as Mn²⁺, Mn³⁺ or Mn⁴⁺, with mixed valence of Mn noted in most samples studied. Clearly differences in near-edge absorption features are noted in samples with Mn contents as low as a few hundred ppm, which provides a ready means for calibrating proportions of different valence states. We discuss possible mechanisms for Mn incorporation in the apatite structure based on this work and present the first data on the influence of $f\text{O}_2$ on apatite-silicate melt partitioning of Mn in a model silica-rich system.