Apatite trace element chemistry as a tool for determining oxidation state in magmas in the early solar system

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Oxygen fugacity… why should we care?

- Oxygen fugacity (fO₂) is a measure of how reducing or oxidising an environment is, and is essentially the effective partial pressure of oxygen.
- fO₂ controls mineral stability, dictates gas species released from volcanoes, controls metallogenesis in igneous ore bodies, and dictates how volatile species are incorporated in planetary interiors.
- fO₂ is highly variable across the inner solar system; it has varied systematically throughout Earth’s history, with changes in mantle fO₂ linked to planetary processes and atmospheric evolution.
- Despite its importance, fO₂ is one of the least well constrained geological variables, especially in ancient rocks.

Why the Mn-in-Apatite oxybarometer doesn’t work.

- Miles et al. (2014) suggested that apatite Mn content can be used to determine fO₂ in host magmas, based on published data and observations of apatite chemistry in the zoned Criffel pluton.
- Here, we test the Mn-in-apatite oxybarometer by (1) determining variation in Mn valence state in silicate melt and apatite with varying fO₂, and (2) measuring apatite-melt Mn partitioning.

But an oxybarometer based on REE in apatite shows real potential.

- Apatite readily incorporates significant (1000s ppm) quantities of Rare Earth Elements (REEs), which substitute onto the Ca²⁺ site; most REEs in magmatic systems are present only as ³⁺ cations, although Ce can be Ce⁴⁺ and/or Ce⁵⁺, and Eu can be Eu⁴⁺ and Eu⁵⁺, depending on fO₂.
- We have conducted preliminary work to test the potential for an oxybarometer based on trends in Eu and Ce apatite-melt partitioning.

Progressive changes in Eu⁴⁺/Eu³⁺ in silicate melt as a function of fO₂, determined from XANES spectra (gas-mixing experiments). Melt composition (presence of Fe and/or degree of polymerisation) has an additional influence.

- Eu⁴⁺/Eu³⁺ increases systematically in silicate melts with increasing fO₂, although also depends on melt chemistry, as noted by Burnham et al. (2015).
- Trends in Ce⁴⁺/Ce⁵⁺ in melts as a function of fO₂ are not under more oxidising conditions (FMQ upwards), although these can only be determined in Fe-free systems.
- There are no trends in Eu or Ce redox state in apatite with fO₂, implying that Eu and Ce apatite-melt partitioning should be strongly fO₂ dependent.
- Based on this, we are conducting experiments to formulate an Eu/Ce in apatite oxybarometer…. watch this space!


- Mn K edge XANES spectra from glasses synthesised in a gas-mixing furnace verify this. Mn in all glasses is Mn⁴⁺ over a wide range in fO₂ (numbers in figure: for reference, NNO = 6.5 at 1300 °C). In contrast, Fe⁴⁺/Fe³⁺ ratios vary systematically. Changes in Mn speciation in melt as a function of fO₂ are required to drive changes in Mn apatite-melt partitioning as a function of fO₂.

There is no change in Mn D⁴⁺ in apatite with δfO₂. Melt chemistry does have an influence (trend in BMT samples due to changes in melt chemistry).

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