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

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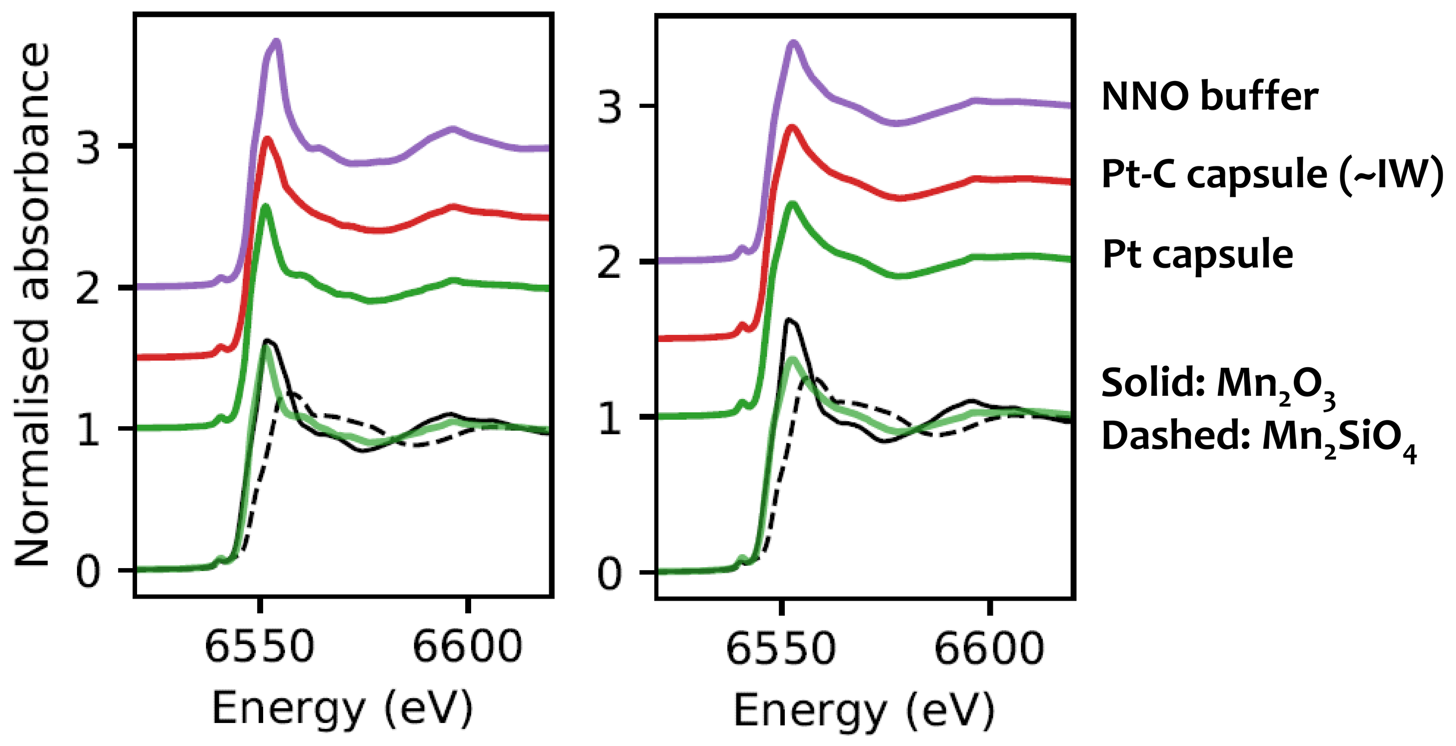
Oxygen fugacity… ..why should we care?

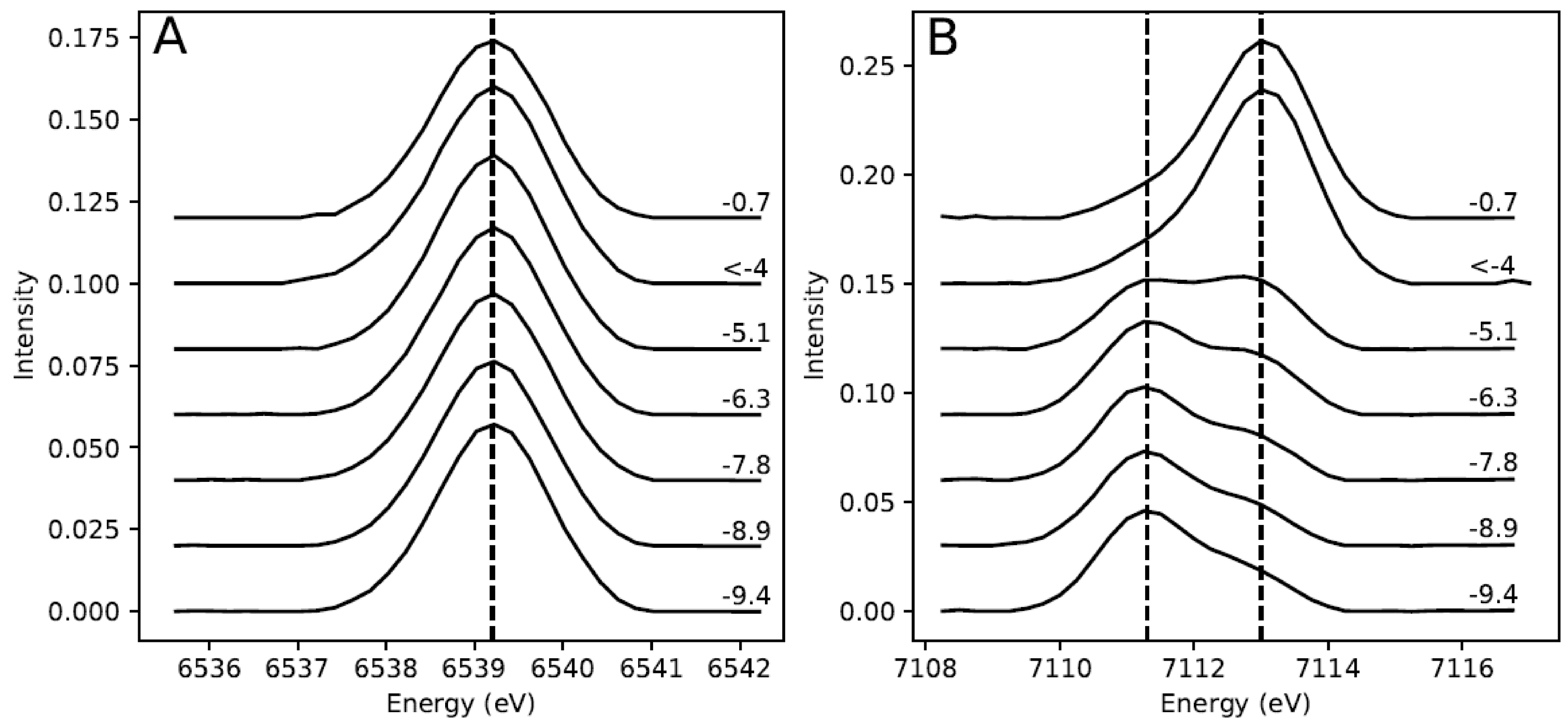
- Oxygen fugacity (fO_2) is a measure of how reducing or oxidising an environment is, and is essentially the effective partial pressure of oxygen.
- fO_2 controls mineral stability, dictates gas species released from volcanoes, controls metallogenesis in igneous ore bodies, and dictates how volatile species are incorporated in planetary interiors.
- fO_2 is highly variable across the inner solar system; it has varied systematically throughout Earth's history, with changes in mantle fO_2 linked to planetary processes and atmospheric evolution.
- Despite its importance, fO_2 is one of the least well constrained geological variables, especially in ancient rocks.

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

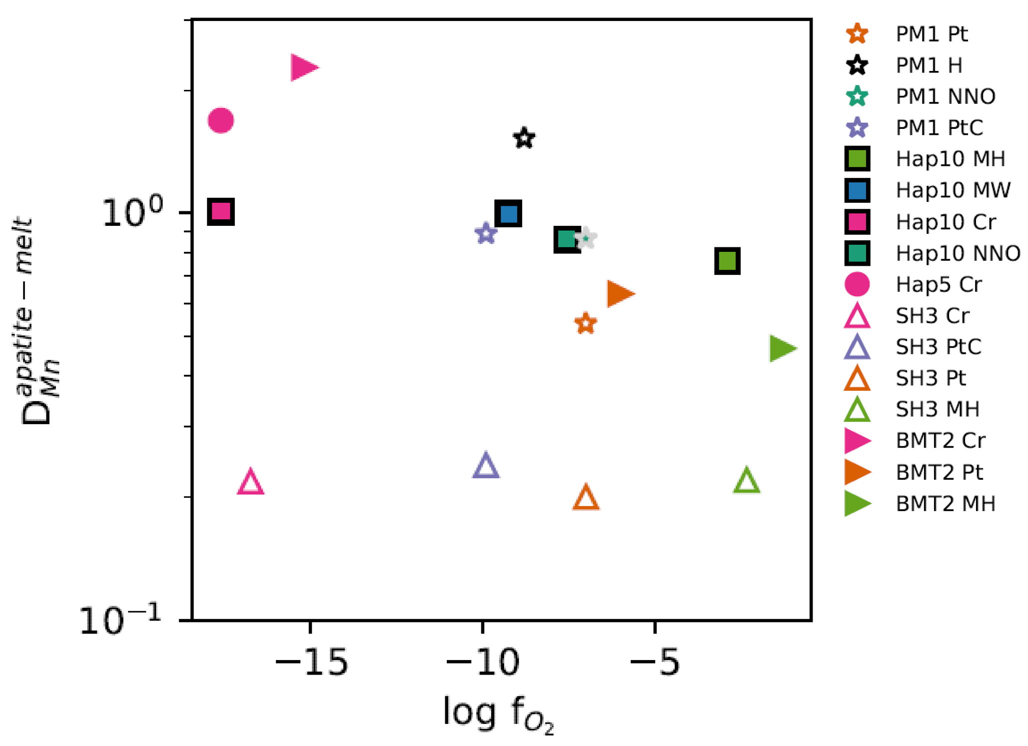
- Miles et al. (2014) suggested that apatite Mn content can be used to determine fO_2 in host magmas, based on published data and observations of apatite chemistry in the zoned Criffel pluton.
- Here, we test the Mn-in-apatite oxybarometer by (1) determining variation in Mn valence state in silicate melt and apatite with varying fO_2, and (2) measuring apatite-melt Mn partitioning.



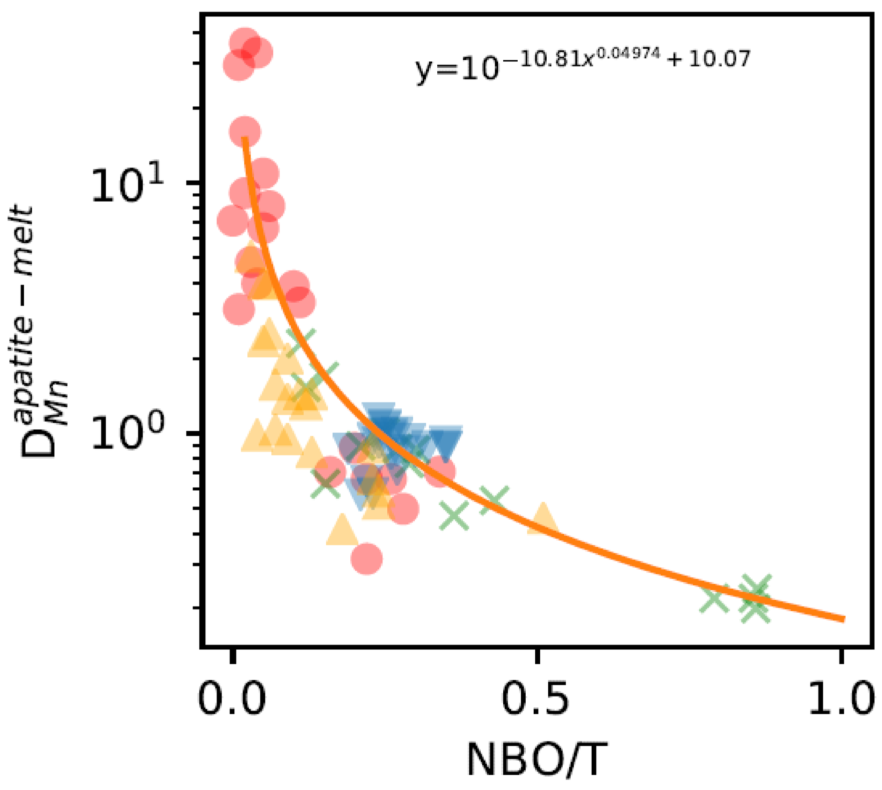
Mn K edge XANES spectra (i18, Diamond Light Source) from coexisting apatite (left) and silicate melt (right), (synthesised at 1 GPa, 1450 to 1250/1200/1100°C) show that both contain only Mn^{2+}, independent of changes in fO_2, for various melt compositions.

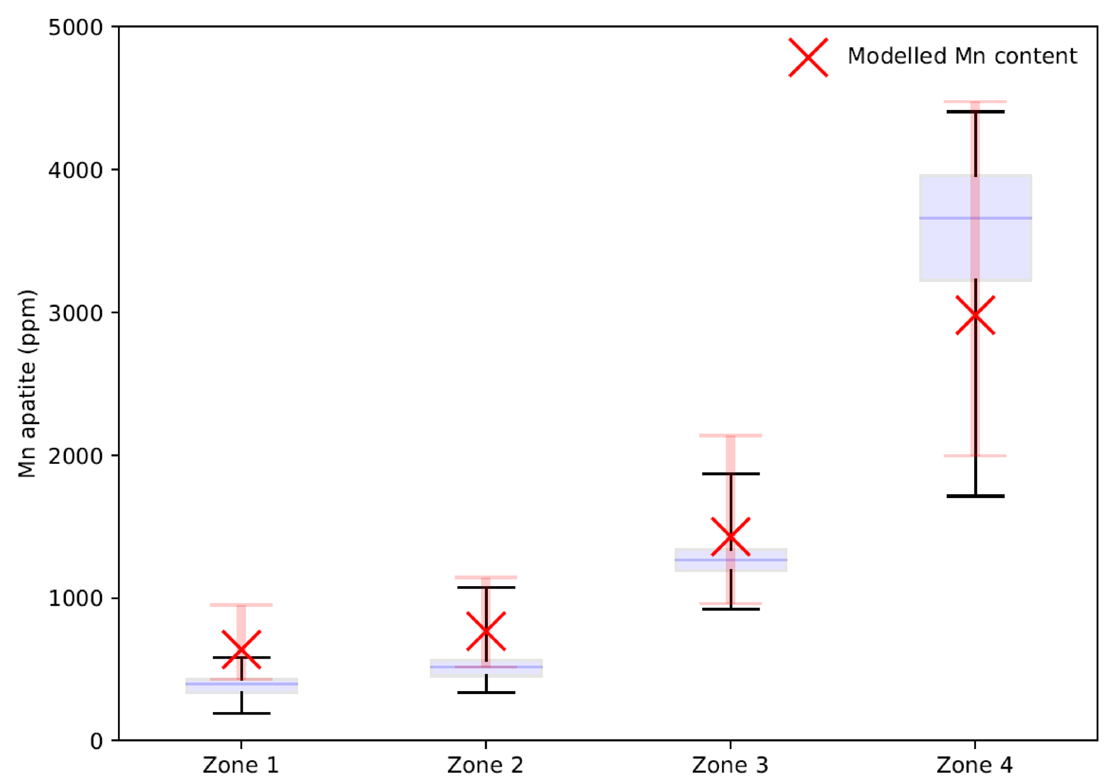


K edge XANES spectra from glasses synthesised in a gas-mixing furnace verify this. Mn in all glasses is Mn^{2+} (A) over a wide range in fO_2 (numbers in figure: for reference, NNO=-6.5 at 1300°C). In contrast, Fe^{2+}/Fe^{3+} ratios vary systematically (B). Changes in Mn speciation in melt as a function of fO_2 are required to drive changes in Mn apatite-melt partitioning as a function of fO_2.



There is no change in Mn $D^{apatite\text{-}melt}$ with ΔfO_2. Melt chemistry does have an influence (trend in BMT samples due to changes in melt chemistry).

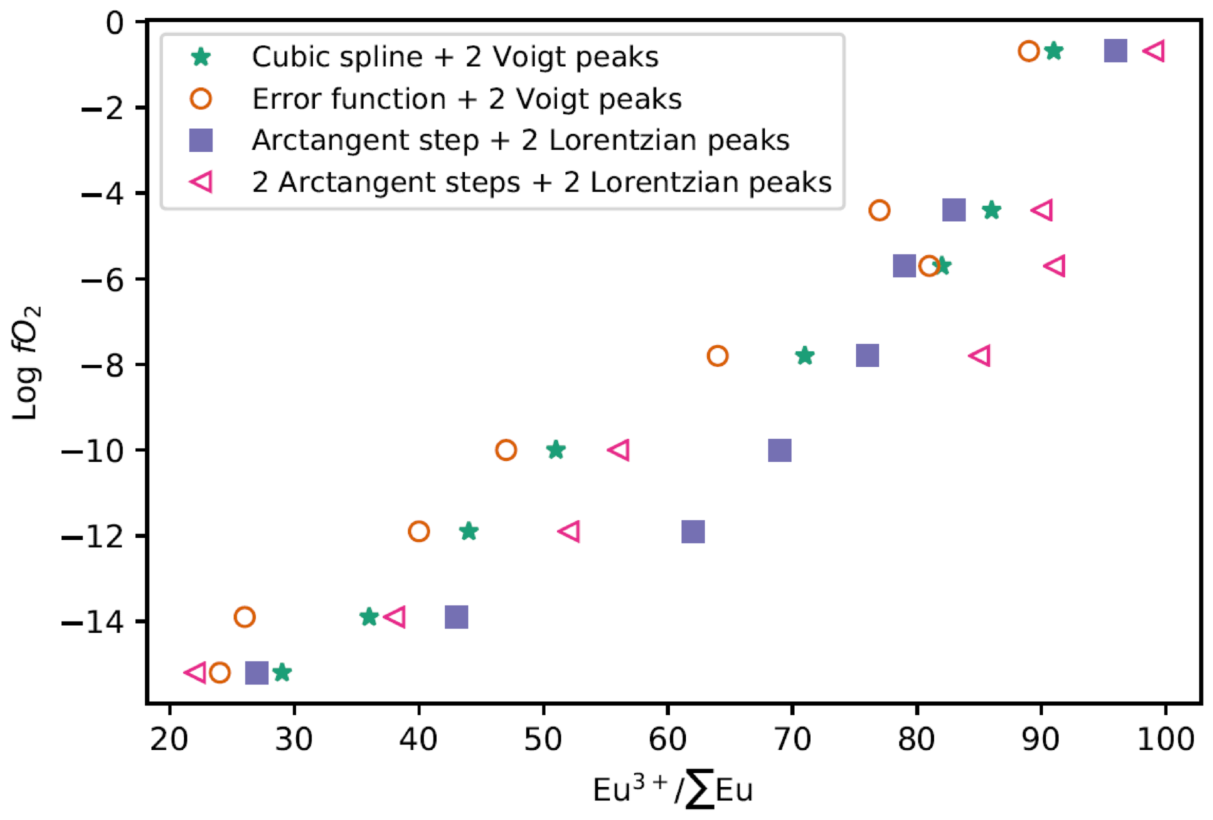




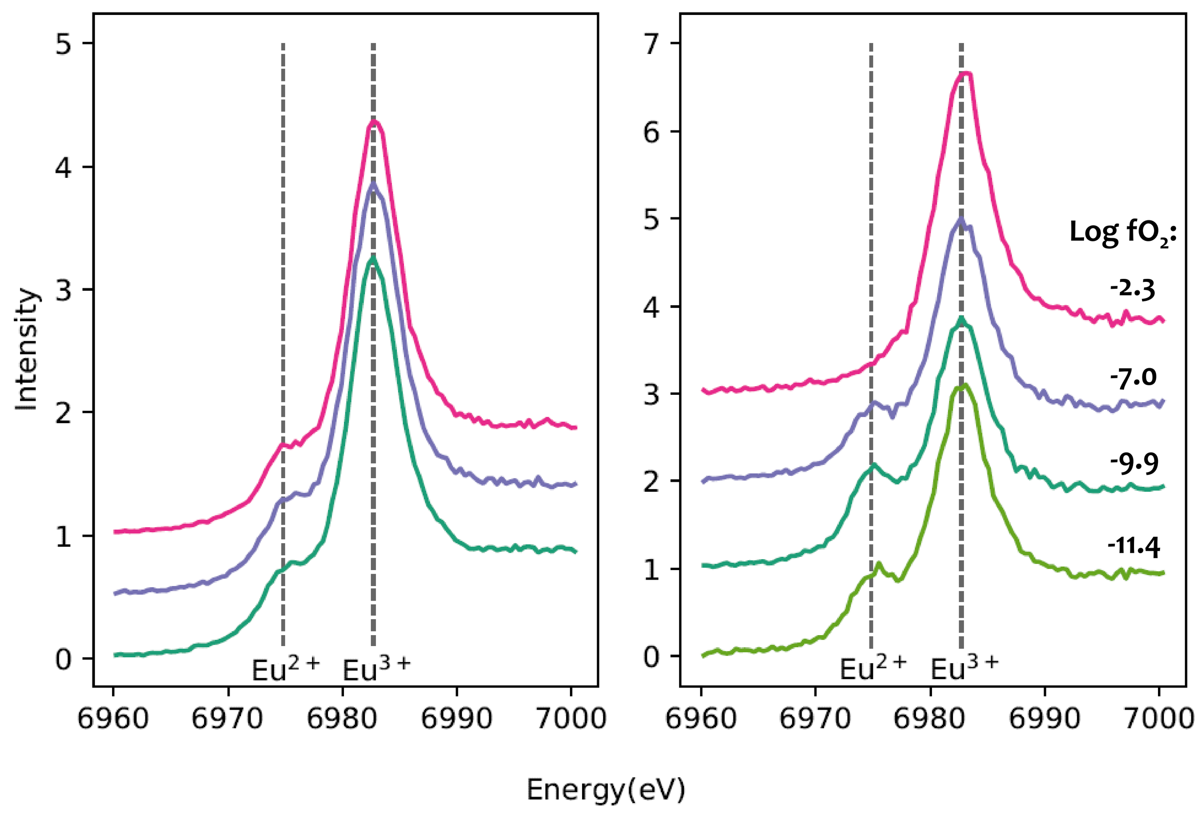
Mn partitioning varies systematically with extent of melt polymerization (left). We can use this relationship to explain trends in Mn apatite content across the Criffel pluton which were used by Miles et al. (2014) to propose their oxybarometer (right).

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

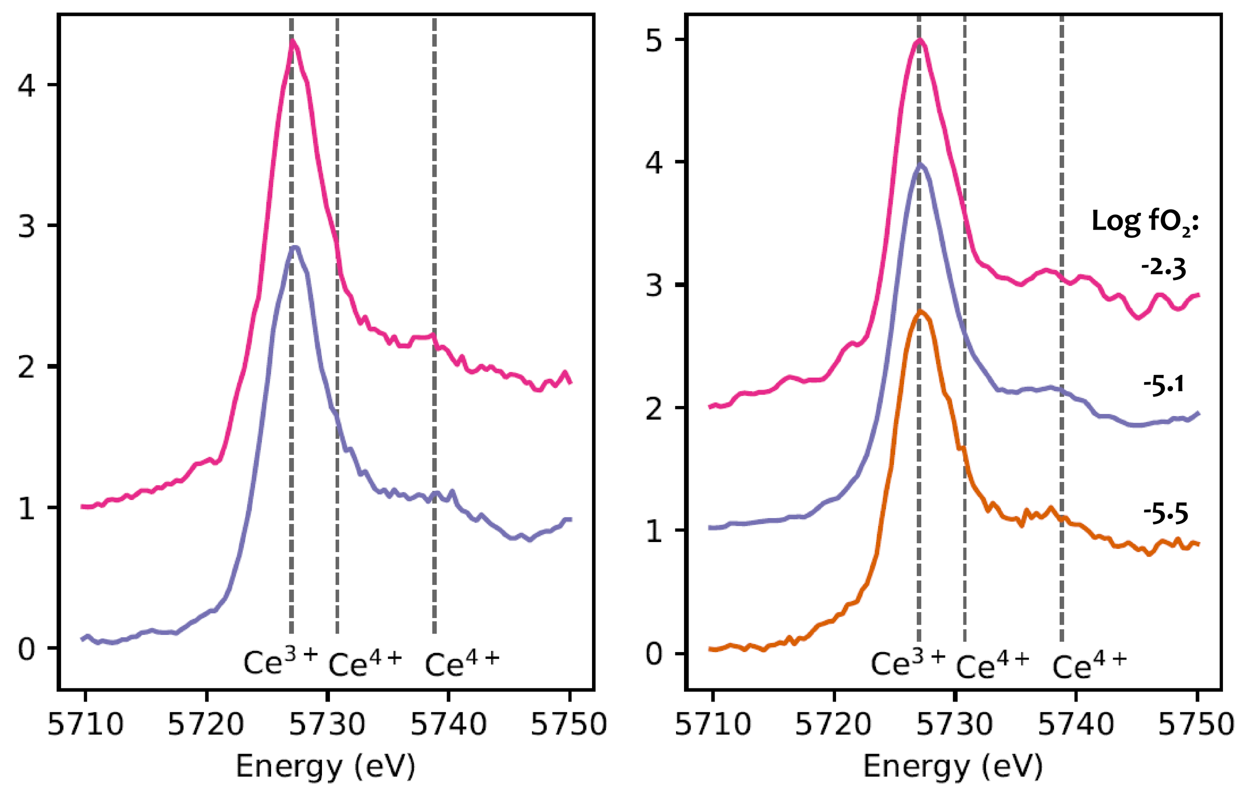
- Apatite readily incorporates significant (1000s ppm) quantities of Rare Earth Elements (REEs), which substitute onto the Ca2 site; most REEs in magmatic systems are present only as 3+ cations, although Ce can be Ce^{3+} and/or Ce^{4+}, and Eu can be Eu^{3+} and Eu^{2+}, depending on fO_2.
- We have conducted preliminary work to test the potential for an oxybarometer based on trends in Eu and Ce apatite-melt partitioning.



Progressive changes in $Eu^{3+}/\Sigma Eu$ in silicate melt as a function of fO_2, determined from XANES spectra (gas-mixing experiments). Melt composition (presence of Fe and/or degree of polymerisation) has an additional influence.



Eu L_3 edge XANES spectra show that 90% of Eu in apatite is Eu^{3+}, independent of fO_2. Systematic trends in $Eu^{3+}/\Sigma Eu$ in coexisting melt are again observed (synthesised at 1 GPa, 1400-1250°C in a piston-cylinder device using solid fO_2 buffers and 2 different melt comps).



Ce L_3 edge XANES spectra demonstrate that 90% of Ce in apatite is Ce^{3+}, again independent of fO_2. Ce redox state can only be determined in Fe-free melts due to coupled Fe-Ce redox reactions during quenching.

- $Eu^{3+}/\Sigma Eu$ increases systematically in silicate melts with increasing fO_2, although also depends on melt chemistry, as noted by Burnham et al. (2015).
- Trends in $Ce^{3+}/\Sigma Ce$ in melts as a function of fO_2 are noted 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 fO_2, implying that Eu and Ce apatite-melt partitioning should be strongly fO_2 dependent.
- Based on this, we are conducting experiments to formulate an Eu/Ce in apatite oxybarometer… ..watch this space!

Burnham et al. (2015) Chem Geol 411: 248-259; Papike et al. (2016) Am. Min. 101(4): 907-918; Miles et al. (2014) GCA 132; 101-119. Mn in apatite work: Stokes et al. (2019) Chem Geol (in press).

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