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Apatite: a new redox proxy for silicic magmas?

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The oxidation states of magmas provide valuable information about the release and speciation of volatile elements during volcanic eruptions, metallogenesis, source rock compositions, open system magmatic processes, tectonic settings and potentially titanium (Ti) activity in chemical systems used for Ti-dependent geothermometers and geobarometers. In this presentation we explore the use of Mn in apatite as an oxybarometer in intermediate and silicic igneous rocks. Increased Mn concentrations in apatite in granitic rocks from the zoned Criffell granitic pluton (southern Scotland) correlate with decreasing Fe_2O_3 (Fe^{3+}) and Mn in the whole-rock and likely reflect increased $Mn^{2+}/Mn^{3+}$and greater compatibility of Mn^{2+} relative to Mn^{3+} in apatite under reduced conditions. Fe^{3+}/Fe^{2+} ratios in biotites have previously been used to calculate oxygen fugacities (fO_2) in the outer zone granodiorites and inner zone granites where redox conditions have been shown to change from close to the magnetite-hematite buffer to close to the nickel-nickel oxide buffer respectively[1]. This trend is apparent in apatite Mn concentrations from a range of intermediate to silicic volcanic rocks that exhibit varying redox states and are shown to vary linearly and negatively with log fO_2, such that

$\log fO_2$=-0.0022($\pm$0.0003)Mn(ppm)-9.75($\pm$0.46)

Variations in the Mn concentration of apatites appear to be largely independent of differences in the Mn concentration of the melt. Apatite Mn concentrations may therefore provide an independent oxybarometer that is amenable to experimental calibration, with major relevance to studies on detrital mineral suites, particularly those containing a record of early Earth redox conditions, and on the climatic impact of historic volcanic eruptions[2].

[1] Stephens, W. E., Whitley, J. E., Thirlwall, M. F. and Halliday, A. N. (1985) The Criffell zoned pluton: correlated behaviour of rare earth element abundances with isotopic systems. Contributions to Mineralogy and Petrology, 89, 226–38.

[2] Miles, A.J., Graham, C.M., Hawkesworth, C.J., Gillespie, M.R., Hinton, R.W., 2014, Mn in apatite: A new redox proxy for silicic magmas?: Geochimica et Cosmochimica Acta v. 132, p. 101-119.