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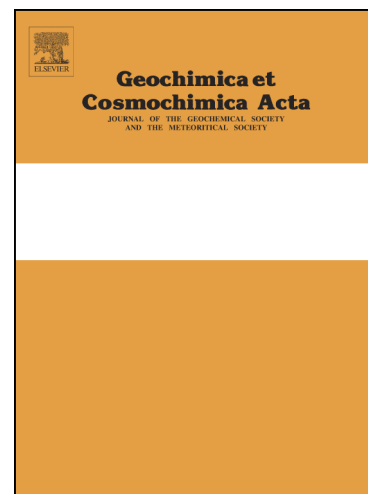
Reply to comment by Marks et al. (2016) on 'Apatite: A new redox proxy for silicic magmas?'

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Introduction

Marks et al. (2016) investigate the applicability of the Mn-in-apatite oxybarometer proposed by Miles et al. (2014) across a range of magma compositions using published data on well-characterised samples. The authors show that for magma compositions outside of the calc-alkaline and intermediate to silicic range used in the preliminary calibration, fO_2 values calculated from Mn-in-apatite vary significantly from independently constrained estimates. These data are used to reiterate our warnings that other controls that are additional to oxygen fugacity are likely to affect Mn partitioning into apatite in some rock types, and particularly so in magmas that lie outside of the range of compositions and conditions used in the calibration. Marks et al. (2016) highlight that temperature may have an especially important effect on Mn partitioning in apatite in some rock types.

We thank the authors for their contribution and would welcome further investigations of published work and new experimental data. Here we simply wish to clarify a few points regarding the preliminary calibration and to offer some comments and suggestion about why the oxybarometer in its current form is unlikely to be applicable to some magma compositions referred to in their comment without further experimental refinement.

Discussion

The empirical negative relationship reported by Miles et al (2014) between Mn-in-apatite and fO_2 was calibrated using independently constrained estimates of redox conditions in a number of calc-alkaline, intermediate to evolved samples between 660 and 920°C. These compositions and conditions are appropriate for the majority of upper continental igneous rocks on Earth. For samples that fit the compositional criteria such as the amphibole-bearing granites from the Aegean (Teiber et al., 2014), we are encouraged that fO_2 values calculated from Mn in apatite are broadly consistent with other, qualitative estimates of redox conditions (Figure 1 in Marks et al., 2016).

Of the two experimental studies mentioned by the authors, only Webster et al. (2009) conducted experimental work on felsic magmas similar to the natural samples used for the preliminary calibration. Although the range of redox conditions and Mn concentrations in apatite (all < 500 ppm) are limited by comparison to other studies, these data lie broadly on our calibration (Figure 1 in Marks et al., 2016). The experimental data of Mathez and Webster (2005) were measured using a mafic silicate melt composition and shows large deviations from the calibration curve (Figure 1 in Marks et al., 2016). As with natural mafic samples, the deviations clearly point to additional controls on Mn partitioning into apatite in basic magma compositions, or to marked differences in the relative timing of apatite saturation in such magmas compared to silicic magmas. Unlike in silicic magmas, apatite commonly saturates at a late stage in basic magmas (e.g. Watson, 1979) within interstitial melts. Bulk-magma compositions (including redox conditions) may differ substantially from late-stage, small-volume interstitial melts. Furthermore, interstitial magmas may evolve independently resulting in large compositional differences between apatite crystals in such rock types. This, together with other possible compositional controls on Mn partition in basic magmas may contribute to the wide variations in apatite Mn concentrations.

The influence of melt composition on Mn partition coefficients is poorly constrained. However, melt chemistry has been shown to exert a significant influence on REE partition coefficients (Klemme and Dalpe, 2003; Prowatke and Klemme, 2005; Prowatke and Klemme, 2006). In particular, the coordination of some trace elements, including redox-sensitive elements such as Th, have been shown to vary with increasing polymerisation in the melt (Wilke et al., 2005), and especially as a function of the aluminium saturation index (ASI: molar ratio $Al_2O_3/(Na_2O+K_2O)$) which is a useful proxy for melt polymerisation (Prowatke and Klemme, 2005). ASI varies significantly over a range of bulk compositions even when SiO_2, K_2O and CaO contents remain relatively constant. The influence of ASI on

Mn partitioning may be especially important in highly peraluminous magmas such as the muscovite-bearing granites from Bohemia highlighted by Marks et al. (2016).

The absence or reduced modal abundance of other Mn-bearing minerals such as magnetite, biotite and amphibole was shown to increase the proportion of Mn in apatite by a factor of *c.* 2 between metaluminous and weakly peraluminous zones of the Criffell pluton (Miles et al., 2014). However, this could not explain the *c.* 27 fold increase observed in the Mn content of some apatites between these samples. Whilst competing Mn-bearing minerals are likely to have an influence on the Mn content of apatites, we consider it secondary to other influences such as fO_2 and possibly the ASI of a melt and temperature. Furthermore, in many granitic systems, apatite saturation temperatures (Harrison and Watson, 1984) are commonly > 900°C, suggesting that apatite saturates early and possibly before many other Mn-bearing phases. Early apatite saturation is often consistent with petrographic observations such as apatite being included in multiple host mineral phases, including other accessory minerals (Miles et al., 2013).

Marks et al. (2016) are correct to emphasise the possible important effect of temperature on Mn partitioning in apatite. However, without further experimental constraints, it remains frustratingly difficult to quantify the temperature effect on Mn partitioning. High apatite saturation temperatures (Harrison and Watson, 1984; Piccoli and Candela, 1994; Streck and Dilles, 1998) together with significant variations in the trace element compositions of apatites (Miles et al., 2013) suggest that apatite crystallises over a significant part of the crystallisation history of granitic magmas. The implication is that different crystals record different stages of magma evolution, and presumably magma temperatures and melt compositions. As pointed out by Marks et al. (2016), many of the deviations seen from the calibration for some samples may well relate to temperature effects and further quantification of this effect is required.

Preliminary evidence for differences in the valency of Mn observed by Bromiley et al. (2015) in apatites from variously oxidised magmas of the Criffell pluton are encouraging, and tentatively support the idea that in more reduced magmas the proportion of Mn^{2+} increases relative to more oxidised forms of Mn (e.g. Mn^{3+}, Mn^{4+} or Mn^{5+}). Mn^{2+} is more easily incorporated into the apatite structure, probably in place of Ca^{2+} (Sha and Chappell., 1999; Miles et al., 2014). It remain less clear how more oxidised forms of Mn such as Mn^{3+} are structurally bound, but this presumably that involves either coupled substitutions with other

ions or the existence of cation vacancies (or both). For the former, melt chemistry will likely be an additional controlling factor in determining the total Mn concentration of apatite. Further experimental work is again required to fully quantify these compositional parameters.

In conclusion, we agree with Marks et al. (2016) that further empirical and experimental work is required to fully investigate the potential of Mn in apatite as a redox proxy. We agree that temperature and melt composition in particular are likely to have a significant role and that these factors need careful experimental investigation. Nevertheless, we consider that our empirical study shows that there is great potential in using Mn and other multi-valent elements in apatite to better constrain conditions during magma crystallisation.

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