

Experimental calibration of a new oxybarometer for silicic magmas based on the partitioning of vanadium between magnetite and silicate melt

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Oxygen fugacity is an important parameter in magmatic systems that affects the stability of mineral phases and fluid species. However, there is no well-established method to reconstruct the oxygen fugacity of slowly cooled magmas such as granite, for example, because existing oxybarometers (e.g., magnetite-ilmenite method) are susceptible to re-equilibration processes during slow cooling and thus lead to erroneous results when applied for granitic rocks. In this study, we aim at developing an oxybarometer that is based on the partitioning of vanadium (a redox-sensitive element) between magnetite inclusions and silicate melt inclusions preserved in quartz phenocrysts, where they were protected from subsolidus alteration and can be measured as entities by LA-ICP-MS.

In the first – experimental – part of this study we investigated the effects of temperature (800-950 °C), pressure (1-2 kbar), oxygen fugacity (from $\Delta FMQ+0.7$ to $\Delta FMQ+4.0$), magnetite composition, and melt composition on the partition coefficient of vanadium between magnetite and melt ($D_{V_{mgt-melt}}$). The experiments were carried out in cold-seal pressure vessels and the starting material was a mixture of V-doped haplogranite glasses or natural obsidian powder with variable aluminum saturation index (ASI), and synthetic, V-free magnetite of 10-20 μm grain size. The vanadium partition coefficient was found to depend strongly on oxygen fugacity, and to lesser (but still considerable) degrees on melt composition and temperature. A more than 1.5 log unit decrease in $D_{V_{mgt-melt}}$ values with increasing oxygen fugacity can be explained by a change of the dominant valence state of V in the silicate melt. For a given oxygen fugacity buffer $D_{V_{mgt-melt}}$ decreases with increasing temperature, but this reflects mostly the change in absolute fO_2 values while the net temperature effect is in fact positive. $D_{V_{mgt-melt}}$ depends significantly on melt composition, resulting in higher D-values with increasing aluminum saturation index (ASI). This seems to reflect less favorable incorporation of V into peraluminous melts compared to depolymerized, peralkaline melts. Changing pressure from 1 to 2 kbar had an effect only at NNO, causing 0.3 log unit increase in D, whereas the Ti-content of magnetite turned out to have negligible effect on the V partitioning. In summary, the dependence of $D_{V_{mgt-melt}}$ on temperature, ASI and oxygen fugacity can be described by the following regression equation:

$$\log D(V)_{mgt/melt} = -1.22 + 0.31 * 10^5 / T(^{\circ}K) + 1.73 * ASI - 0.49 * \Delta FMQ$$

First tests of the equation on natural samples were carried out on rapidly cooled tuffs and vitrophyres from variable tectonic settings, for which fO_2 could be constrained independently by the magnetite-ilmenite method. All calculated fO_2 values fall within ± 0.75 log unit within those suggested by the Fe-Ti oxybarometer, whereas 12 out of 16 samples agree within 0.5 log units .