

## Effects of water on the oxidation state of iron in hydrous rhyolites

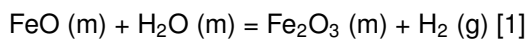
Donald G. Fraser, Madeleine C.S. Humphreys

Department of Earth Sciences, University of Oxford, UK

E-mail: don@earth.ox.ac.uk

Understanding the interaction of water with silicic magmas is of key importance in the assessment and prediction of volcanic hazards. Magmas produced by partial melting of the sub-arc mantle undergo significant degassing and crystallization near the earth's surface. This also makes it difficult to use eruptive products to estimate the oxidation state of sub-arc mantle, because components such as H<sub>2</sub>O, are themselves volatile oxide components with acid-base properties that affect oxidation states such as Fe(III)/Fe(II).

The effect of H<sub>2</sub>O on Fe oxidation state is still unclear. Some theoretical arguments have suggested that shallow degassing leads to increasing Fe<sup>3+</sup>/ΣFe as a result of preferential diffusion of H<sub>2</sub> out of the melt:



However understanding redox behaviour must take account of the overall acid-base properties of the hydrous melt. In particular, the dominantly basic behaviour of FeO the amphoteric behaviour of Fe<sub>2</sub>O<sub>3</sub> and changes in melt basicity relating to dissolution of H<sub>2</sub>O, can explain increasing Fe(III/FeII) with increasing H<sub>2</sub>O. Similar arguments might lead us to predict that dissolution of CO<sub>2</sub> should show the opposite effect, i.e. decreasing melt Fe(III/FeII) The predicted amphoteric behavior of H<sub>2</sub>O itself has been shown by NMR spectroscopy with even dominantly acidic behaviour observed, as predicted, in diopside rich melts.

Recent measurements by XANES of Fe(III/FeII) in rhyolitic obsidian hydrated in gold capsules in cold-seal apparatus, show a positive correlation between Fe<sup>3+</sup>/ΣFe and the H<sub>2</sub>O content of the glass. The observed increase in Fe oxidation state with increasing a(H<sub>2</sub>O) in these acidic melts is consistent with the addition of H<sub>2</sub>O as a predominantly Lux-Flood basic oxide. Hydrogen species in an oxide melt include molecular H<sub>2</sub>O, OH. OH<sup>-</sup> and hydroxylated silicate anions. The H<sub>2</sub> fugacity in [1] is defined thermodynamically by reactions involving water and the oxide/silicate melt and is likely to be low. Moreover it is experimentally well-known that the oxidation state of redox ions in silicate melts increases with addition of basic oxides at constant fO<sub>2</sub>. H<sub>2</sub> loss is thus unnecessary as a driver of oxidation change in these systems. As with the addition of other basic oxides, e.g. Na<sub>2</sub>O, the Fe(III/FeII) in hydrous acid melts adjusts along with activities of other components, including those containing hydrogen, as the result of acid-base equilibria in the melt at constant fO<sub>2</sub>.

References:

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