Fe oxidation state in hydrous magmas during ascent and degassing

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Arc magmas erupted at the earth's surface are commonly observed to be more oxidised than those produced at mid-ocean ridges. One possible cause for this is that the transfer of fluids during subduction results in direct oxidation of the sub-arc mantle wedge. However, an alternative hypothesis is that crustal processes, including fractionation and degassing of volatile-rich magmas, control the oxidation state of the arc magmas. This study sets out to isolate the effect of dynamic changes in H_2O content on Fe oxidation state in partially hydrated and degassed, sulphur-free rhyolites.

Rhyolites hydrated at both low and high temperatures show $Fe^{3+}/\Sigma Fe$ increasing strongly with increasing H_2O concentration. The overall change in oxidation state is broadly consistent with changes in water activity at constant fH_2. In the low-temperature samples, this implies that the rate of hydration is not controlled by reaction-diffusion of hydrogen, but by water diffusion at constant fH_2. During hydration at high temperatures, the melt may also undergo structural changes involving Fe and other network-modifying cations.

Degassing results in clear spatial variations in H_2O concentration, and samples show increasing $Fe^{3+}/\Sigma Fe$ with decreasing H_2O concentration. This can be explained by loss of H_2 as well as H_2O into the coexisting fluid, and is consistent with the predictions of thermodynamic models, taking into account the volume of fluid present in the experimental capsules.

These new data raise further questions about the controls on fO_2 during the generation, fractionation, storage and ascent of magmas in arc settings, in particular relation to the attainment of equilibrium in a dynamic system. We explore the effectiveness of potential solid and gas buffers in different parts of the sub-volcanic environment, and the importance of kinetic factors and partial disequilibrium in determining the quality of the petrologic record of fO_2 changes during the generation and eruption of arc magmas.