Iron oxidation state in volcanic rocks, from magma generation to eruption

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Destructive plate margins, where the Earth's oceanic crust is forced down beneath another tectonic plate, are sites where formation and differentiation of continental crust takes place by the generation, storage and eruption of new magma. Known as subduction zones, these sites are particularly important because they are the primary location for most of the explosive volcanic eruptions that occur globally. Lavas erupted at subduction zones are typically more oxidised than those produced at mid-ocean ridges, where the tectonic plates spread apart. Iron oxidation state is a fundamental parameter for magma - it controls which minerals crystallise, the development of the some rock series, and the compositions of gas species that are released from volcanoes. The latter has been linked to the changing composition of the mantle and atmosphere with time during Earth's history. One possible cause for the high oxidation state observed at subduction zones is that the transfer of fluids during the subduction process results in direct oxidation of the Earth's mantle, where melting occurs. Another possibility is that crustal processes, including crystallisation and degassing of magmas rich in dissolved gases such as H_2O, control the oxidation state of the arc magmas.

This study sets out to investigate the effect of dynamic changes in H_2O content on Fe oxidation state in rhyolites (viscous magmas, rich in SiO_2) that were partially hydrated or degassed experimentally. The iron oxidation state, $Fe^{3+}/\Sigma Fe$, was measured directly in the experimental samples using XANES on beamline I18. Firstly, partial hydration of rhyolites results in strongly increasing $Fe^{3+}/\Sigma Fe$ with increasing H_2O concentration. The overall change in oxidation state is broadly consistent with changes in water activity at constant fH_2, which results in increased availability of oxygen within the silicate melt. The hydration experiments are analogous to the storage and transport of H_2O-undersaturated magmas within the crust. This implies that the Earth's crust may develop crustal-scale gradients in Fe oxidation state, with more oxidized melts in the shallow to mid-crust and more reducing conditions in the deep crust. This would have important implications for the segregation and transfer of metals to form ore systems.

Secondly, degassing of H_2O from magma results in systematically increasing $Fe^{3+}/\Sigma Fe$ with decreasing H_2O concentration. This can be explained by with loss of H_2 as well as H_2O into bubbles, and is consistent with the predictions of thermodynamic models, taking into account the volume of fluid present in the experimental capsules. This process is analogous to the rise of magma underneath volcanoes, with the gases released at the surface in a plume. The composition of the gas is commonly measured during monitoring of active volcanoes but this will be controlled by the kinetics of the magma's ascent and may not provide an accurate record of magma storage conditions within the crust. We explore the effectiveness of potential magma oxygen buffers, and the significance of disequilibrium in determining the quality of the rock record of fO_2 changes during the generation and eruption of subduction zone magmas.

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