

Reduction of mercury by surface Fe(II) and the formation of Hg⁰ in hydromorphic soils

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Hydrous ferric oxide (HFO) colloids formed in strictly anoxic conditions upon oxidation of Fe²⁺ ions adsorbed on mineral surfaces were investigated under *in situ* conditions by contact mode atomic force microscopy (AFM). Freshly cleaved and acid etched large single crystals of near endmember phlogopite were pre-equilibrated with dissolved Fe(II) and then reacted with Hg(II) at 25°C and 1 atm. HFO structures are found to be round (25 nm) microcrystallites located predominantly on the layer edges, and are indicative of an accelerated Fe(II) oxidation rate upon formation of Fe(II) innersphere surface complexes with the phyllosilicate edge surface sites.

Kinetic measurements at the nano molar level of Hg⁰ formed upon reduction of Hg(II) by Fe(II) in presence of phlogopite particles provide convincing evidence for reduction of Hg(II)_{aq} coupled to the oxidation of Fe(II) adsorbed at the phlogopite-fluid interface, and indicate that sorption of Fe(II) to mineral surfaces enhances the reduction rate of Hg(II) species. The Hg(II) reduction reaction appears to be driven by the high reactivity of adsorbed Fe(II), and follows a first order kinetic law. Under our experimental conditions, which were representative of many natural systems, 80% of the mercury is transferred to the atmosphere as Hg⁰ in less than 2h.

In tropical South America, this phenomenon appears to occur in water saturated soils. Compared to nearby Hg rich oxisols, hydromorphic soils are mercury depleted and have a large concentration of atmospheric Hg⁰ just above the soil surface. Therefore such pedologic and kinetic data and reaction pathways are important in predicting the fate and transport of mercury in natural systems.

Differentiation processes in a high-silica rhyolite as recorded in plagioclase crystals from Taupo volcano, New Zealand

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In many volcanic arcs, the erupted products represent the integrated effects of differentiation mechanisms, which act to modify primary magma(s) as they ascend from their source region(s). Radiogenic isotope systematics aid discrimination among various differentiation processes if the different end-members have contrasting isotopic signatures. The use of crystal isotope microstratigraphy, which employs microanalysis for Sr isotopes, shows that intra-crystalline isotopic and compositional heterogeneities exist within many volcanic rocks (Davidson et al., 1998).

Whilst intra-crystal Sr-isotope heterogeneities are well established for andesitic to dacitic volcanic systems, application to rhyolites has lagged. Here we present preliminary ⁸⁷Sr/⁸⁶Sr microanalysis data for feldspar crystals separated from representative rhyolite of the ~530km³, caldera-forming, 26.5 ka Oruanui eruption.

The Oruanui eruption is the largest known from Taupo volcano in the central North Island of New Zealand. Rhyolite from the eruption is mildly zoned, dominantly 73-76% SiO₂, but was non-systematically tapped. Within some rhyolite pumices, 1-5% of the plagioclase feldspars have blue-grey cores mantled by clear rims. High resolution electron microprobe traverses and Normarski imaging reveal a growth history punctuated by magmatic events that are manifested as unconformities and inclusion rich zones within the crystals. The opaque feldspar cores have ⁸⁷Sr/⁸⁶Sr of 0.70540, whereas rims are 0.70562, the latter being compatible with the whole-pumice values for Oruanui rhyolite. These variations are accompanied by changes from ~An₃₀ at the rim (in equilibrium with the host pumice) to ~An₆₅ in the core. Associated timescales of the magmatic variations recorded by these phenocrysts may be attainable by SHRIMP analyses of zircons within some of the growth zones, which can be compared with the age spectrum of zircons present as free microphenocrysts within the host pumice.

Davidson, J.P., Tepley, F.J.III, and Knesel, K.M., (1998), *EOS*. **79** (15), 185, 189, 193.