The influence of magmatic differentiation on the oxidation state of Fe in arc magmas

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Many studies of the redox conditions recorded by arc basalts indicate that arc magmas contain a higher proportion of oxidized Fe (i.e. $Fe^{3+}/\sum Fe$) than do basalts from mid-ocean ridge settings. Arc magmas could become oxidized through shallow differentiation processes, or instead may inherit oxidized signatures from their mantle sources. Here, we present new measurements of naturally glassy olivine-hosted melt inclusions from a single eruption of Agrigan volcano, Marianas, in order to test the effects of fractional crystallization and magmatic degassing on redox conditions. We determined $Fe^{3+}/\sum Fe$ ratios in glass inclusions using μ-XANES [1] and couple these data with major elements and S by EMP and dissolved volatiles (H_2O, CO_2) by FTIR.

After correcting for post-entrapment crystallization, $Fe^{3+}/\sum Fe$ ratios in the Agrigan melt inclusions (0.21-0.28) are uniformly more oxidized than normal MORB, and preserve a portion of the liquid line of descent of the magma from 5.7 to 3.2 wt.% MgO. Fractionation of olivine should increase $Fe^{3+}/\sum Fe$ and decrease MgO in the melt, but the data show an overall decrease in $Fe^{3+}/\sum Fe$ ratios as MgO decreases. The data trends are also inconsistent with magnetite crystallization, which would drive both $Fe^{3+}/\sum Fe$ and total FeO* down sharply. Crystallization cannot explain the extent and evolution of Fe oxidation in the Agrigan magma. Degassing is often invoked to cause redox changes in magmas, but neither H_2O nor CO_2 correlate with changes in $Fe^{3+}/\sum Fe$ in the Agrigan melts. Sulfur concentration, on the other hand, correlates positively with $Fe^{3+}/\sum Fe$, suggesting that S degassing may relate most closeley to the $Fe^{3+}/\sum Fe$ variations in the melt. The large exchange of electrons involved with converting dissolved S^{2-} in the melt into SO_2 (S^{4+}) vapor may drive magma reduction during S degassing. Shallow differentiation of magmas may modify magmatic redox conditions, but these processes are not ubiquitously oxidizing, and the uniformly oxidized condition of the Agrigan magma is likely inherited from its mantle source [2].

[1] Cottrell & Kelley (2009) *Chem. Geol.* **268**, 167–179.
[2] Kelley & Cottrell (2009) *Science*, **325**, 605–607.

Redox transformations of uranium near the mineral-microbe interface

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The vast majority of microorganisms in the subsurface are thought to exist in a surface-adhered state. However, the region within ~10 μm of the mineral-microbe interface is a fundamental, yet poorly understood, spatial regime that exerts critical control on contaminant transformations. Reactions that occur in this region can dominate subsurface reactivity, often exerting the greatest effect on transformations of a contaminant and the biogeochemical milieu in which it resides. We have used x-ray (150 nm spatial resolution) and electron microscopy to probe the spatial distribution of uranium and its valence state on a thin film of lepidocrocite with actively respiring surface-adhered bacteria (*Shewanella oneidensis* MR-1 and *Anearomyxobacter* spp.). Results of x-ray microspectroscopy experiments with *S. onedensis* MR-1 identify U (VI) associated with the surface-adhered cells and partially reduced uranium associated with the solid phase just a few microns away from the surface-adhered cells. Preliminary results of x-ray fluorescence and optical microscopy experiments with *Anaeromyxobacter* spp. on lepidocrocite thin films imply respiration and growth of the organism and the chance to investigate redox transformations of uranium under a microbial physiological state different from our previous studies. The implications of these results towards understanding transformations of uranium near surface-adhered bacteria will be presented.