Fate of U(IV) during microbially-driven Mn(II) oxidation in sediments

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Uranium is a toxic radionuclide and its contamination of soil and groundwater is a worldwide problem. The oxidized form of U, hexavalent uranium (U (VI)), is the most soluble and mobile form of uranium and therefore, an understanding of its behavior in contaminated environments is of utmost importance. It is known that U (VI) can be biologically reduced to less soluble U (IV) species such as the mineral uraninite (UO_2) or monomeric U (IV) and the stimulation of biological activity to this end is a salient remediation strategy; however, it is as yet unknown if these materials remain stable in their subsurface formation environments. Manganese oxides, also formed biogenically in the subsurface, are capable of rapidly oxidizing U (IV) to U (VI) [1].

Here, we evaluate the effect of Mn redox cycling on the mobility and stability of U in contaminated subsurface environments on various scales. Batch experiments were conducted in which agarose gels, containing Mn-oxidizing spores and biogenic UO_2, were exposed to Mn (II). After optimization of experimental variables using these batch reactors, the redox reactions were analyzed in sediment from a U-contaminated site in Rifle, Colorado USA. Results to date indicate biogenic UO_2 oxidation to U (VI) by nano-scale bio Mn oxides. The U (VI) product is retained within the agarose gel or the sediment matrix suggesting the formation of U (VI) precipitates or strong surface complexes. Various methods, including inductively coupled plasma mass spectroscopy (ICPMS), transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS), are used to pinpoint the speciation and spatial distribution of U (VI) relative to Mn. The feasibility of bioreduction as a strategy to immobilize uranium in the contaminated subsurface is contingent on the long-term stability of immobilized U. Hence it is critical that the role of Mn–present at sufficiently high concentrations at Rifle–in this stability be assessed. This study furthers our knowledge of the coupled U/Mn system and therefore is expected to inform future remediation efforts.

[1] Chini (2008) *Environ. Sci. Technol.* **42**, 8709–8714.

Thermal state of subducting plate beneath Kamchatka inferred from H_2O/Ce in melt inclusions

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We measured water and trace element contents in a new large set of naturally quenched and reheated melt inclusions in olivine from volcanoes along the Eastern Volcanic Front of Kamchatka (Zhupanosky, Karymsky, Vysokiy, Zavaritsky, Zheltovsky, Ksudach and others), which are located 100-190 km above the subducting plate. H_2O/Ce ratios in the least degassed inclusions correlate inversely with the distance from volcano to slab surface (fig. 1b) and suggest a systematic a change in the composition of slab component with increasing slab depth [1]. This data is used to estimate the temperature of equilibrium of water-bearing components with subducting sediments at the slab top [2].

The data indicate sharp temperature increase (740-800º) at relatively shallow depths (100-110 km) and less efficient slab heating at greater depths (800-950 ºC, 110-190 km). These results are in qualitative agreement with modern numeric SZ models (e.g. [3]) though our petrologic data predict ~50ºC hotter slab for 110-190 km depths beneath Kamchatka.
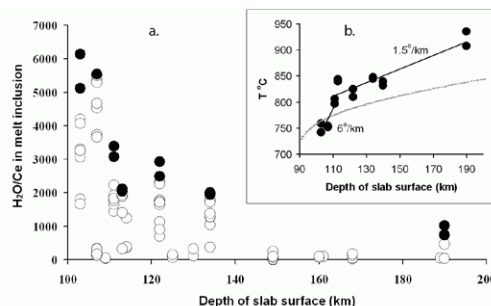

Figure 1: (a)

H_2O/Ce ratios in melt inclusions from Kamchatkan volcanoes and (b) calculated temperature of slab fluids [2] versus slab depth beneath volcanoes. Filled circles denote the least degassed inclusions. Gray line in (b) shows a model depth-temperature path of the Pacific plate surface beneath Kamchatka [3].

[1] Portnyagin *et al.* (2007) *EPSL* **255**, 53–69. [2] Plank *et al.* (2009) *Nature Geoscience* **2**, 611–615. [3] Van Keken *et al.* (2011) *JGR* **116**, B01401.