Abiotic U(VI) reduction by biogenic mackinawite

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Biostimulation of dissimilatory metal and/or sulfate reducing bacteria (DMRB and DSRB) has been extensively researched as a remediation strategy for mitigating subsurface uranium [U(VI)] contamination. These bacteria derive energy by reducing oxidized metals as terminal electron acceptors by utilizing organic substrates as electron donors. Iron [Fe(III)], an abundant subsurface element, represents a substantial sink for electrons from DMRB, and the reduction of Fe(III) leads to the presence of dissolved Fe(II) and/or reactive biogenic Fe(II)- and mixed Fe(II)/Fe(III)- mineral phases. Likewise, reduction of other electron acceptors such as sulfates by DSRB leads to the formation of sulfide-bearing minerals in subsurface environments. Thus, when evaluating the potential for *in-situ* uranium remediation in heterogeneous subsurface media, it is important to understand how the presence of alternative electron acceptors such as Fe(III) and sulfate affect U(VI) remediation and the long term behavior and reactivity of reduced uranium. Consequently, abiotic U(VI) reduction by reactive forms of biogenic Fe(II) and sulfide-bearing minerals will be a potentially important process for uranium immobilization.

In this study, amendment of Fe(III) and sulfate to a culture of *Shewanella putrefaciens* CN32 (DMRB) bacterium, resulted in the production of biogenic mackinawite, a Fe(II)-bearing sulfide mineral. This biogenic mineral was systematically characterized by X-ray powder diffraction (XRD), electron microscopy (SEM, TEM, HRTEM) and Mössbauer spectroscopy. Batch experiments involving biogenic mackinawite and U(VI) were carried out at room temperature under strict anoxic conditions. Following complete reduction of uranium (determined by ICP analysis), the biogenic mackinawite was analyzed by a suite of analytical techniques including X-ray absorption spectroscopy (XAS), SEM, HRTEM and Mössbauer spectroscopy to determine the speciation of uranium and concomitant phase transformation(s) with respect to mackinawite. SEM and selected area electon diffraction (SAED) analyses showed reduction of U(VI) to nanoparticulate UO_2 on the surface of biogenic mackinawite. These findings are consistent with XANES analysis that indicate reduction of U(VI) to U(IV) and µXRF analysis that was used to map iron and uranium in the sample. Determining the speciation of uranium is critical to success of a remediation strategy. The present work elucidates abiotic molecular scale redox interactions between biogenic mackinawite and uranium.

Extreme microbial sulfur isotope fractionation in a Mars analogue environment at Rio Tinto, SW Spain

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Sulfur isotopes are likely to be a key tool for the detection of past or present life on Mars, where abundandt sulfate minerals are present. To investigate the link between the activity of sulfate reducing microortanisms and sulfur isotope fractionation, we incubated sediments from a modern hyper-acidic, Fe-rich subareal environment at Rio Tinto, SW Spain.This site has frequently been used as a geochemical anologue of Mars.

Sediments were sampled from the upper part of the Rio Tinto (Marismilla) as well as the estuary (Moguer). Laboratory incubation were carried out at 30° C using an artificial input solution with sulfate in excess and following techniques developed by Stam et al. [1]. The experiments were performed with an input solution at pH 7 and pH 3 and electron donors were provided by the natural substrate. Duplicate reactors were incubated for a total of 10 weeks. Initial data indicate moderate sulfate reduction rates of between 5 and 90 nmol cm^{-3} h^{-1} in Marismilla and between 5 and 45 nmol cm^{-3} h^{-1} in Moguer, independently of the inflow solution pH. Outflow solutions showed pH close to 7, regardless of inflow pH of 3 or 7, suggesting buffering within the sediments. Sulfur isotope fractionation was extreme in the Moguer estuary, extending beyond the maximun of 47‰ as predicted by the starndard Rees model [2] of microbial sulfur isotope fractionation, suggesting that additional fractionation is possible [3] or indicating multiple cycles of reduction and oxidation of sulfate within the reactors. These data indicate that sulfur isotopes may have a potential to be sensitive indicators of biotic activity on Martian sulfate minerals.

[1] Stam (2010) *Chemical Geology* **278#**, 23-30.
[2] Rees (1973) *GCA* **37#**, 1141-1161.
[3] Brunner (2005) *GCA* **69#**, 4759-4771.