Impact of groundwater composition and diffusive transport limitations on uraninite stability

D.E. Giammar[1]*, J.M. Cerrato[1], C.J. Barrows[1], Z. Wang[1], V. Mehta[1], J.S.-Lezama-Pacheco[2] and J.R. Bargar[2]

[1]Department of Energy, Environmental and Chemical Engineering, Washington University, St. Louis, MO 63130, USA (*correspondence: giammar@wustl.edu)
[2]Stanford Synchrotron Radiaion Lightsource, SLAC National Accelerator Laboratory, CA, USA

The long-term stability of biogenic uraninite in sediments and groundwater are important to the performance of *in situ* bioremediation strategies for uranium-contaminated sites. Stability is influenced by subsurface biogeochemistry, structure and composition of uraninite (UO_2), and coupling with pore scale transport processes. Laboratory measurements of UO_2 dissolution rates under well-mixed and diffusion-limited regimes were integrated with direct characterization of the solid phase to investigate the effects of groundwater cations on UO_2 stability.

Groundwater contains abundant ions that can moderate U release from biogenic uraninite. Experiments were performed with Ca^{2+} and Zn^{2+} as model non-redox active groundwater cations with differing affinities for adsorption to metal oxides. Calcium only slightly inhibited UO_2 dissolution, but zinc had a much greater inhibitory effect. Complementary sorption experiments verified that Zn^{2+} adsorbed more strongly than Ca^{2+} to the uraninite surface. The inhibition of dissolution by the cations is orders of magnitude stronger for oxic conditions than for anoxic conditions, which suggests that the adsorbing or surface-precipitating cation is acting to block the access of oxygen to the UO_2 surface or inhibit the electron transfer from the UO_2 to a soluble oxidant. The molecular-scale structure around calcium and zinc species present at UO_2 –water interfaces were determined using X-ray absorption spectroscopy.

To examine UO_2 dissolution under diffusion-limited conditions, experiments separated the reacting UO_2 from the bulk solution by placing it in a tube covered with a membrane that allowed diffusive exchange of solutes. Slower net release rates of uranium from the tubes were caused by modest diffusive limitations to oxygen transfer to the UO_2. Experiments were performed in both simple aqueous solutions and synthetic groundwaters to further explore the role of groundwater cations on the dissolution process.

Cu speciation in coastal waters using a vibrating gold microwire electrode

K. B. Gibbon-Walsh, P. Salaün and C.M.G. Van Den Berg*

Marine Electrochemistry, School of Environmental Sciences, University of Liverpool, Liverpool, L69 3GP, UK (*correspondence: vandenberg@liv.ac.uk)

Cu speciation by pseudopolarography

Pseudopolarography (PP) was developed and optimised for use on a vibrating gold microwire electrode with the intention of developing a more sensitive technique for the speciation of Cu in seawater, with potential for in-situ application. The method was optimised and a desorption potential and conditioning sequence improved the electrodes reproducibility. Model ligands, including glutathione and other well characterised ligands[1] were studied in order to estimate the strength and class of Cu complexing ligands in Liverpool Bay.

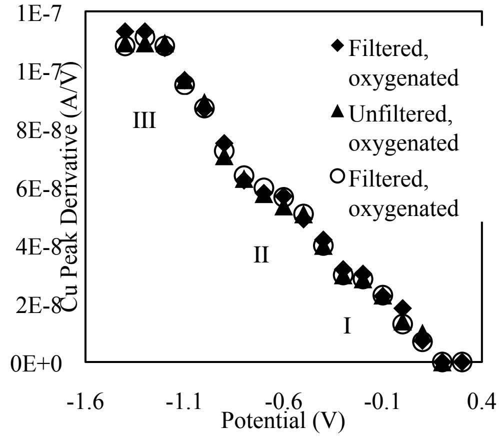

Figure 1: On-board PP analysis in oxygenated coastal sea water (Liverpool Bay)

Cu pseudopolarograms performed on-site, in coastal sea water from Liverpool Bay always show a succession of waves (Fig 1.). The most positive wave corresponds to free+labile Cu complexes while wave II and III represents more strongly bound complexes. Only minor variations were observed between filtered/unfiltered sample and oxygen is not an interference highlighting the potential of the technique to be used in-situ.

[1] Croot *et al.* (1999) *Marine Chemistry* **67,** 219-232.