Microbial reduction of U(VI) at alkaline pH relevant to geological disposal

ADAM J. WILLIAMSON,[1*] KATHERINE MORRIS,[1] GARETH T. W. LAW,[2] SAMUEL SHAW,[3] AND JONATHAN R. LLOYD[1]

[1] Research Centre for Radwaste and Decommissioning and Williamson Research Centre, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, adam.williamson-2@postgrad.manchester.ac.uk (* presenting author), katherine.morris@manchester.ac.uk, and jon.lloyd@manchester.ac.uk

[2] Research Centre for Radwaste and Decommissioning and Centre for Radiochemistry Research, School of Chemistry, The University of Manchester, gareth.law@manchester.ac.uk

[3] School of Earth Sciences, University of Leeds, s.shaw@see.leeds.ac.uk

The UK's intermediate level radioactive wastes (ILW) will be disposed of in a deep geological disposal facility (GDF) [1]. Here, one likely scenario for disposal in the UK GDF is mixing ILW with cement, grouting into stainless steel canisters followed by further backfilling with cement. Post-closure, re-saturation of the cementitious GDF over time will form a hyperalkaline chemically disturbed zone (CDZ) within the host rock.

Microbial processes, especially Fe(III) reduction, may immobilise redox active radioactive contaminants in the waste either through direct enzymatic reduction or via interactions with biogenic Fe(II) [2]. Here, we explore the extent of microbiologically-mediated U(VI) reduction under GDF relevant alkaline conditions. Microcosms were set up using sediments taken from legacy lime works, adjusted to pH 10, augmented with electron donor (organic acids with yeast extract) and systems were run with and without added Fe(III) oxyhydroxides. Systems were established with lower (20 ppm) and higher (100 ppm) concentrations of UO_2^{2+} and allowed to progress through a series of redox processes, potentially including metal reduction, and to assess sorption of U(VI), uranium biotransformations and to prepare samples for XAS analysis.

A cascade of microbial redox processes occurred at high pH in all microbially active systems with U(VI)-removal occurring in sediments with and without added Fe(III) oxyhydroxides. In Fe(III) augmented systems, which displayed high levels of Fe(III)-reduction, magnetite was the dominant Fe(II) bearing bio-mineral product. XANES analyses of all microbially active sediment end-members confirmed reduction of U(VI) to U(IV). Interestingly, controls using pre-reduced, autoclaved sediments showed no sign of U(VI) reduction, suggesting that U(VI) reduction in these systems is predominantly enzymatic. Overall, these results show that microbial metal reduction can occur in a high pH environment analogous to that of an evolved GDF and demonstrates the reductive removal of U(VI) from solution in such systems is likely mediated by direct enzymatic processes.

[1] Morris, K. Law, G.T. & Bryan, N.D. (2011). *Issues in Environmental Science and Technology* **32,** 129-151.
[2] Lloyd, J.R. (2003). *FEMS Microbiology Reviews* **27,** 411-425.

SIMS carbon isotope analysis of Proterozoic microfossils

KENNETH H. WILLIFORD[1*], TAKAYUKI USHIKUBO[1], J. WILLIAM SCHOPF[2], KEVIN LEPOT[1], KOUKI KITAJIMA[1], JOHN W. VALLEY[1]

[1]WiscSIMS, NASA Astrobiology Institute, Dept of Geoscience, University of Wisconsin, Madison, WI, USA, kwilliford@geology.wisc.edu (* presenting author)

[2]Dept of Earth and Space Sciences, University of California, Los Angeles, CA, schopf@ess.ucla.edu

We present new in situ carbon isotope ($\delta^{13}C$) data from permineralized microfossils in the stromatolitic cherts of the Gunflint (~1880 Ma), Bitter Springs (~830 Ma), Chichkan (~775 Ma), and Min'yar (~740 Ma) Formations. Specimens were selected for their excellent preservation and analyzed in thin section with a reproducibility of 1–2‰ (2 SD) using secondary ion mass spectrometry (SIMS). The range of $\delta^{13}C$ values (–34.6 to –22.1‰ VPDB) exhibited among the 46 specimens is consistent with photoautotrophic carbon fixation by ribulose bisphosphate carboxylase (RuBisCO), the acetyl-CoA pathway, or heterotrophic assimilation. In light of the morphologies, however, the $\delta^{13}C$ values support taxonomic assignments of these specimens as photoautotrophs using RuBisCO. Fossil cyanobacteria from the Gunflint, Bitter Springs, and Min'yar Formations, for which available carbonate $\delta^{13}C$ data can be used to estimate $\delta^{13}C$ of dissolved organic carbon (DIC), exhibit a consistent ~20‰ total fractionation ($\delta^{13}C_{DIC} - \delta^{13}C_{org}$) similar to that observed in living cyanobacteria. Morphologically diverse microfossils in a ~1 mm^2 part of a microbial mat from the Min'yar Formation exhibit $\delta^{13}C$ values that correlate with morphology-based taxonomy and cellular anatomy, suggesting that isotopic signatures of their original biosynthetic processes are preserved. Carbon isotopic compositions consistent with the different fractionations observed in modern cyanobacterial and eukaryotic RuBisCO are preserved in a colonial cyanobacterium and a phytoplanktonic protistan acritarch situated < 1 cm apart in in the stromatolitic Chichkan chert.

Due to the low total organic carbon (TOC) of permineralized microfossils, analyses were conducted using a relatively large (15 μm) spot, high (2.5 nA) intensity primary beam, an electron multiplier to collect ^{13}C, and standardized with a low TOC carbonaceous chert PPRG 215-1 [1,2]. This is distinct from our technique for $\delta^{13}C$ analysis of high TOC materials (e.g., kerogen in shales) which employs a 6 μm spot, two faraday cup collectors, an anthracite coal standard, and has a reproducibility of 0.4‰ (2 SD) [3]. Standardization of microfossils with kerogen in a low TOC carbonaceous chert avoids potential barriers to accuracy (different instrumental bias) presented by standardization with crystalline materials that have a high C content (e.g., graphite), and along with analyses of microfossils from the Gunflint and Bitter Springs Formations, the PPRG 215-1 standard enables a direct interlaboratory comparison with the first study of this kind [2].

Results from these exceptionally well-preserved Proterozoic microfossil specimens provide a baseline for a more extensive study of the effect of organic matter preservation on carbon isotope composition in a large suite of Proterozoic microfossils [4], and they demonstrate that it is possible to distinguish subtle differences between metabolic (e.g., eukaryotic vs. bacterial RuBisCO) and biosynthetic (e.g., peptidoglycan vs. lipid synthesis) pathways in individual ancient microbial fossils [5].

[1] Walter et al. (1983) *Earth's Earliest Biosphere: It's Origin and Evolution*. Princeton Univ. Press, 385–413. [2] House et al. (2000) *Geology* **28**, 707-710. [3] Williford et al. (2011) AGU Fall Meeting Abs. B21E-0323 [4] Schopf et al. (2005) *Astrobiology* 5, 333-371. [5] Williford et al. (in review) *EPSL*.