

Field-scale bioreduction of U(VI) to U(IV) in an alluvial aquifer: Evidence for microbially mediated precipitation of Uranium under both natural and biostimulated conditions

P.E. LONG

Pacific Northwest National Laboratory, Richland, WA 99354, USA (philip.long@pnl.gov)

Research at the U.S. Department of Energy's Integrated Field Challenge (IFC) site, at Rifle, Colorado, USA, is focused on developing a mechanistic understanding of microbially mediated reduction of soluble U(VI) to relatively insoluble U(IV) under Fe-reducing and sulfate-reducing conditions at the field scale. Experiments at the site in which low concentrations of acetate (3 to 5 mM) are amended to the subsurface show a decrease in U(VI) concentration in groundwater associated with growth of *Geobacter* sp. under conditions dominated by Fe-reduction. As an example of the approach used by the multidisciplinary team comprising the Rifle IFC, the most recent experiment has demonstrated the feasibility of measuring peptide abundances in groundwater samples as a means of estimating proteins produced by the microbial community under conditions of biostimulation. Results show that the groundwater population active during acetate amendment is dominated by a strain variant of *Geobacter* closely related to *G. M21* and *G. bemidjensis*. Other less abundant *Geobacter* strain variants are also present. Linkage of detailed information on proteins to the biogeochemistry of the groundwater at the time the samples were collected is expected to significantly enhance our understanding of metabolic processes controlling U(VI) bioreduction. While there is ample evidence that bioreduction of U(VI) produces nanoparticulate uraninite under laboratory conditions, naturally bioreduced sediments from the site collected prior to biostimulation, exhibit elevated concentrations of U(IV) in the <53 μm size fraction. Part of this U occurs at 0.1 to 0.2 wt. % in pyrite and magnetite. Since U was not introduced as a contaminant to the aquifer before ~1950, this suggests a process in which U is incorporated into magnetite and Fe sulfides during iron and sulfate reduction on a time scale of decades.

Mechanisms of crystal growth for birnessite at low temperatures

C.L. LOPANO^{1*}, P.J. HEANEY² AND J.E. POST³

¹RJ Lee Group, Inc., 350 Hochberg Rd., Monroeville, PA 15146 (*correspondence: CLopano@rjlg.com)

²Dept. Geosciences, Penn State University, University Park, PA, 16802 (heaney@geosc.psu.edu)

³Dept. Mineral Sciences, NMNH, Smithsonian Institution, Washington, D.C. 20013-7012 (postj@si.edu)

We investigated the evolution in morphology of birnessite, a highly adsorptive Mn oxide common to many soil environments [1], to infer mechanisms of crystal growth and to determine the effects of morphology on cation exchange reactions. Analyses were conducted using both environmental scanning electron microscopy (ESEM) at sufficiently high pressures to prevent dehydration and structural collapse, and field emission (FE) SEM, which provided higher resolution at high vacuum. We synthesized birnessite with formula $\text{Na}_{0.58}(\text{Mn}^{4+}_{1.42}, \text{Mn}^{3+}_{0.58})\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ and subsequently exchanged interlayer Na with Cs through immersion in aqueous solutions with dissolved CsCl.

Our SEM observations indicate that the birnessite growth mechanism occurs via two stages of oriented aggregation [2]. Birnessite initially grew as nanofibers with a strong morphological similarity to todorokite. These nanofibers assembled to form laths (aspect ratios of ~5:1), and the laths then aggregated as chevrons that expanded into the pseudo-hexagonal platelets characteristic of birnessite [3]. Our study of natural samples of ranciéite, a Ba- and Ca-rich variety of birnessite, yielded analogous textures and were suggestive of a similar mechanism. At all stages of Cs-exchange, platy morphologies were retained, but crystal edges revealed dissolution embayments and no nanofibers were observed.

- [1] Post (1999) *Proc Nat Acad Sci* **96**, 3447-3454. [2] Penn & Banfield (1999) *Geochim Cosmochim Acta* **63**, 1549-1557
[3] Post & Veblen (1990) *Am Mineral* **75**, 477-489.