

Extracellular *c*-Type Cytochromes from *Geobacter bemidjensis*

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The subsurface clade 1 of the *Geobacteraceae* often predominates during acetate-stimulated bioremediation of uranium-contaminated sites. The metabolic activity of this clade has been linked to solid phase U(VI) and Fe(III) reduction in the subsurface. Despite its importance for subsurface metal reduction, the complement of electron transfer proteins expressed by members of this clade have not been identified. *Geobacter bemidjensis* is a cultured representative of subsurface clade 1 and is an excellent model system to begin to understand electron transfer in the subsurface *Geobacteraceae* clade 1. Inspection of the genome of *G. bemidjensis* identified 84 proteins predicted to encode for *c*-type cytochromes. To identify the dominant *c*-type cytochromes expressed by *G. bemidjensis*, proteomics was performed on cultures grown with fumarate as an electron acceptor. A substantial fraction of *c*-type cytochromes were localized in the extracellular medium or were easily sheared from the outer-membrane. The most abundant of these *c*-type cytochromes was a flavocytochrome that clustered with fumarate reductases from *Shewanella* species. Other abundant *c*-type cytochromes included a homolog of OmcB, a cytochrome required for optimal reduction of Fe(III) oxides in *G. sulfurreducens*, and a nonheme cytochrome whose only homologs were found in *Geobacter* species from subsurface clade 1. Seven expressed *c*-type cytochromes were predicted to have >25 heme prosthetic groups. Peptides from the abundant *G. bemidjensis* cytochromes were also found in proteomic measurements of groundwater from a uranium-contaminated site at Rifle, CO undergoing acetate stimulation. The extracellular *c*-type cytochromes are distinct from those cytochromes identified for *G. sulfurreducens* and suggest that the *Geobacteraceae* from subsurface clade 1 may possess novel pathways for electron transfer.

Dissolution of uranyl precipitates in contaminated vadose zone sediments

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Metatorbernite, $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}_{(s)}$, was identified as the dominant form of uranium in contaminated sediments below former nuclear waste disposal ponds in the Hanford 300-Area (Washington State) in past microscopic and synchrotron-based spectroscopic and diffraction studies [1-3]. Uranium(VI) release from these sediments to groundwater, however, could not be explained by metatorbernite solubility determined from pure mineral studies at acidic conditions [4]. This work aims to reconcile these differences between known solid-phase speciation and the aqueous phase composition generated. Carbonate and synthetic groundwater extractions on metatorbernite and variable sediment:solution ratios and sediment sizes were performed in different experimental settings (e.g., batch, stir-flow) to quantify uranium(VI) release. Solid phase speciation before and after these extractions was investigated using scanning and transmission electron microscopy, micro X-ray diffraction and X-ray absorption techniques.

Preliminary results indicate that metatorbernite dissolution in synthetic groundwater is slow and is facilitated by secondary precipitation of an unidentified copper phase that limits the dissolved copper concentration (Figure 1). Metatorbernite in sediments may be gradually transforming to a uranyl carbonate phase as indicated by X-ray absorption spectroscopy. These results will be combined with other solid-phase characterization results and interpreted within a reaction-based modeling framework including dissolution-precipitation and aqueous speciation reactions.

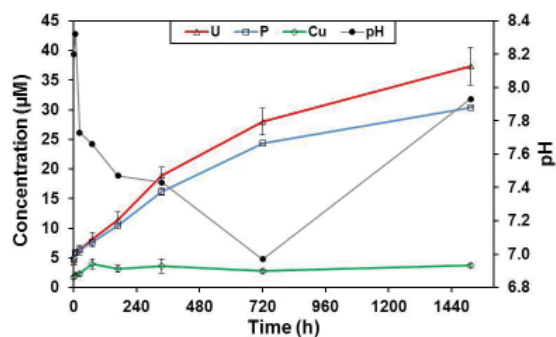


Figure 1: Measured dissolved concentrations and pH from metatorbernite dissolution in synthetic groundwater.

[1] Catalano et al. (2006) *Environmental Science & Technology* **40**, 2517-2524. [2] Arai et al. (2007) *Environmental Science & Technology* **41**, 4633-4639. [3] Stubbs et al. (2009) *Geochimica Et Cosmochimica Acta* **73**, 1563-1576. [4] Ilton et al. (2010) *Environmental Science & Technology* **44**, 7521-7526.