

## Geomicrobiological Controls on Metal Abundance and Speciation in the Environment

Jillian F. Banfield (jill@geology.wisc.edu)<sup>1</sup>, Thomas M. Gihring (tgihring@geology.wisc.edu)<sup>1</sup>, Anne E. Taunton<sup>1</sup>, Yohey Suzuki (yoheys@geology.wisc.edu)<sup>1</sup>, Philip L. Bond (bond@geology.wisc.edu)<sup>1</sup>, Susan A. Welch<sup>1</sup>, David Fowle (fowle@geology.wisc.edu)<sup>1</sup>, & Robert J. Hamers (hamers@chem.wisc.edu)<sup>2</sup>

<sup>1</sup> Department of Geology and Geophysics, University of Wisconsin Madison, Madison WI, USA

<sup>2</sup> Department of Chemistry, University of Wisconsin Madison, Madison WI, USA

Microorganisms can affect metal speciation and metal pollution in the environment in many ways. Some processes involve redox reactions that occur during chemolithotrophic energy generation, others result from utilization of metals as terminal electron acceptors (for example, during anaerobic respiration by heterotrophs). Some changes in metal abundance and speciation are the consequence of a toxicity response. Other reactions may be passive in nature, occurring due to changes in solution chemistry surrounding active cells or as the result of metal-organic interactions on the surfaces of inactive cells or cell fragments. Recent research in our group has explored how interactions between microorganisms and minerals control the fate of Fe, Zn, U, As, and Cu at sites of prior mining activity and in uncontaminated environments.

Microorganisms can affect the form and bioavailability of metals via intracellular or extracellular biomineralization. Examples of biomineralization reactions that lead to dramatic redistribution of Fe and Zn, both through formation of metal oxides and sulfide phases and via sorption of metals onto the surfaces of nanocrystalline biomineralization products, are provided in separate abstracts (Banfield et al.; Fowle et al.).

Microbial activity can alter the aqueous speciation of metals through organic exudate-metal complex formation and perturbation of solution equilibria. For example, results of field and experimental studies indicate that phosphorus and a variety of ions including lanthanides, Sr, Ba, U, etc., can be liberated from highly insoluble metal phosphate minerals via trivalent metal ion complexation by metabolic byproducts such as citrate and oxalate in combination with uptake of phosphate from solution by microorganisms.

Microorganisms can impact elemental speciation, toxicity, mobility, and rates of release of metals to the environment via catalysis of redox reactions. High arsenic concentrations are associated with hot springs, metal sulfide deposits, and fluids interacting with some sediments. Less toxic arsenate (pentavalent As) is reduced to arsenite (trivalent arsenic) or converted to a methylated organic form in most microbial toxicity response mechanisms. Arsenite can be oxidized to arsenate by microorganisms (e.g., Ehrlich 1996), a subset of which can generate energy from this reaction. Arsenic, especially arsenate, is strongly sorbed to ferrihydrite (e.g., Waychunas et al. 1993), which may be a byproduct of microbial iron oxidation. Arsenate, phosphate, and other metal ions, may be incorporated into goethite (and other iron oxyhydroxides formed from coarsening

of ferrihydrite), especially if crystal growth occurs via oriented aggregation (Banfield et al. 2000). Finally, arsenic can also be precipitated as arsenic sulfides in reducing environments (Newman et al. 1998). Uranium is utilized as a terminal electron acceptor during anaerobic respiration. The lower solubility of tetravalent compared to hexavalent U can lead to its precipitation as uranium minerals (e.g., Lovley and Phillips 1992). Uranium is also strongly adsorbed to cell surfaces (Fowle and Fein 2000). Electron microscopic characterization of bacterial, algal, and fungal cells indicates that U can be also be sequestered into precipitates located within cells.

Metal sulfide dissolution is a well known example of a process where microbial activity can dramatically increase the rate of release of metals to solution. An important environmental problem, acid mine drainage (AMD), results from the oxidative dissolution of metal sulfide minerals associated with ore deposits. Because the rate of ferric iron regeneration is an important rate limiting step in metal sulfide dissolution, microbes that catalyze ferrous iron oxidation play a fundamental role in controlling the rate of formation of acidity and release of elements such as Fe, Cu, Cd, Zn, Pb, and As to solution. Our work within the Richmond ore body at Iron Mountain, CA, has explored the nature of microbial communities involved in iron oxidation and the kinetics of microbial and inorganic reactions under the relevant field conditions (e.g., Edwards et al. 1998). Using DNA- and RNA-based approaches, we have shown that acidophilic microbial populations are dominated by novel microorganisms, including an iron-oxidizing archaeon with very high metal and acid tolerance. In ongoing work we are investigating the biochemistry of iron oxidation pathways, as well as the mechanisms by which microbes impact the chemistry of their environments as the result of acidity and metal resistance responses.

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