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Biomineralization and Geochemical Cycling in Subsurface Solutions: An Example

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It is well known that microorganisms can dramatically affect the mineralogy and solution chemistry of their surroundings. However, the distributions of microorganisms in aquifers, and the magnitudes of their roles in subsurface processes, are typically difficult to assess. In this talk we present initial results from a study of reactions occurring in flooded tunnels associated with an abandoned Pb, Zn mine located in southwestern Wisconsin, USA. Photography and sample collection by SCUBA divers, and the recent date of flooding, provide us with an unusual opportunity to evaluate the rates of biomineralization on monthly, annual, and decade time-scales. The geometry of the site permits investigation of how microbiological communities in specific microenvironments, and interactions between subsystem groups, impact groundwater geochemistry.

The interfaces created when reduced solutions carrying dissolved ferrous iron mix with more oxygenated, near-neutral pH solutions in the tunnels provide ideal environments for growth of iron oxidizing bacteria such as *Gallionella* spp. and *Leptothrix* spp. Over the period of 30 years since the tunnels were flooded, the activity of these and other iron-oxidizing microorganisms has generated tens of centimeter-thick slimes loaded with abundant ferrihydrite. Enormous reactive surface area associated with the extremely finely crystalline iron oxyhydroxide mineral products provides adsorption sites for metal ions (such as Zn). The products of this process: reduced carbon compounds (electron donors) and oxidized minerals (electron acceptors), are utilized by iron-reducing bacteria in more anaerobic regions. Thus, large quantities of carbon and iron (and Zn) appeared to be cycled across redox gradients in this groundwater system.

Centimeter-scale biofilms growing in more anaerobic portions of the tunnels are also sites of biomineralization reactions. Sulfide released by communities of sulfate-reducing bacteria belonging to the family *Desulfobacteriaceae* combines with Zn in solution (0.09 – 1.1 ppm) to form abundant ~ 3 nm sphalerite crystals that flocculate to form spherical, micron-scale aggregates. Scavenging of sulfide by Zn, which is continuously supplied by slowly moving groundwater, prevents accumulation of sulfide in solution. This precludes development of more anaerobic conditions consistent with lead sulfide or iron sulfide precipitation. The Eh established through ZnS precipitation is incompatible with communities of more anaerobic sulfate-reducing bacteria, emphasizing the delicate interconnection between microbial and geochemical processes.

Phenomena occurring in the tunnel system may provide insights into how microorganisms contribute to creation of ore deposits. The almost exclusive precipitation of large volumes of iron minerals in slightly oxygenated solutions provides an interesting analog for biological processes that may have been involved in generation of the banded iron formations. Precipitation of essentially monomineralic ZnS by sulfate-reducing bacteria is associated with an approximately one million times Zn enrichment in the biofilm relative to solution. Thus, the microbial and geochemical processes leading to ZnS accumulation may be relevant to ongoing efforts to understand how low-temperature metal sulfide ore deposits form.