Biogeochemical Cycling and Biomineralization in the Piquette Mine, Tennyson, WI

C. Chan, G. Druschel, S. Welch, M. Labrenz, J. Moreau, A. Skatvold, T. Thomsen-Ebert, and J. Banfield (the Banfield research group)

In 1999, a team of SCUBA divers led by Tamara Thomsen-Ebert brought to our attention an unusual community of microbes in an abandoned Mississippi Valley Type lead-zinc mine located in southwestern Wisconsin. In the 30 years since operations ceased and the mine was allowed to flood, microorganisms have colonized the floors and walls in the form of thick red fluffy biofilms and a few smaller white biofilms (Figure 1). The red biofilms, which are covered in iron oxyhydroxides (FeOOH), and the surrounding fluid provide an environment to study microbiallyinduced iron oxidation at circumneutral pH, a process which may be relevant to interpreting iron deposits in the geologic record and possibly on Mars. The white biofilms, which contain zinc sulfide, may give us insight into mechanisms concerning ore deposition and remediation techniques for metalcontaminated water. We have been using light and electron microscopy,

The group works closely with the divers to develop sampling methods and in situ experiments. In order to demonstrate the difficulties of underwater sampling while suited in SCUBA gear, Tami organized an outing to a local indoor pool where she dressed us in masks, flippers, and tanks (below). She had us "sample" golf balls and small foam balls with syringes, and attempt to swim through hoops with a bag full of empty (floating) sample bottles. We met with little success, but came away with a deeper appreciation for our underwater samplers' skills

microbiological techniques, geochemical analyses and geochemical modeling to investigate the role of these microorganisms in element cycling (e.g. Fe, Pb, Zn, and S) and biomineralization.

cycling (e.g. Fe, Pb, Zn, and S) and biomineralization. Regions of the tunnels exhibit distinguishable zones of clear (upper) and turbid (lower) water which correspond to a redox gradient, as evidenced by a transition from orange to gray on the tunnel walls (see Figure 2 for a schematic). Communities of iron oxidizing bacteria are often found at or near these interfaces because they are environments where significant quantities of reduced iron and oxygen are present. Light and electron microscope analyses show that the red biofilm is primarily

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composed of mineralized sheaths likely formed by Leptothrix sp. (often found in association with iron oxides) as well as some mineralized twisted stalks characteristic of Gallionella sp., a neutrophilic iron oxidizer (Figure 3). High-resolution transmission electron microscope analyses of these mineral coatings show that they are predominantly composed of two to three nm sized particles of ferrihydrite. Examination of water filtrate from both the clear and cloudy layers under the scanning electron microscope reveals intricately twisted mineralized filaments, some of which are associated with microorganisms (Figure 4). Energy dispersive spectral analyses of these filaments show that they are composed primarily of iron oxyhydroxides. It appears that these filaments and the associated minerals are formed by microbes, which suggests that the microbes in the water are involved in iron oxidation. However, we are currently trying to identify these organisms and elucidate their role in iron cycling at the mine.

The white biofilms differ from the red





biofilms in size and in that they are restricted to old timbers left in the mine. Sulfide released by sulfatereducing bacteria of the family *Desulfobacteriaceae*





Figure 2

combines with Zn in solution (1–3 ppm) to form abundant ~3 nm ZnS crystals that flocculate to form spherical, micron-scale aggregates (Figure 5).

Modeling of sulfate reduction associated with these microbial communities suggests a sequential order in which sulfide minerals are deposited. Precipitation of pure ZnS to the exclusion of other sulfides is closely linked to the supply of metals to the biofilm and the rate at which SRBs reduce sulfate. Thus, the microbial and geochemical processes leading to ZnS accumulation may be relevant to low-temperature metal sulfide ore deposit models and the design of wetland-based metal remediation.

The biofilms at the Piquette Mine also provide material for the study of nanocrystalline mineral formation and aging processes. Oriented attachment of nanoscale particles of both the ferrihydrite and ZnS has been observed in the red and white biofilms, respectively. We are also engaged in theoretical and experimental studies to investigate the mechanisms of nanocrystalline precipitation and mineral coarsening for ZnS.

Ongoing research will hopefully enable us to identify more of the microorganisms responsible for element cycling and to better understand the ecology of the biofilms, the mechanisms of nanocrystalline precipitation, and the geochemistry of oxyhydroxide and sulfide deposition. References: JF Banfield, SA Welch, H Zhang, T Ebert, and RL Penn. The role of aggregation in crystal growth and transformations in nanophase FeOOH biomineralization

Figure 1



Figure 3

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Figure 4



Figure 5