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The Effects Biogenic Nanoscale Iron Oxyhydroxides on Metal Mobilities in Near-Surface Water-Rock Systems

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Identifying and quantifying the controls on metal mobilities in weathering environments is critical in order to understand processes such as global element cycling, contaminant mass transport in near-surface water-rock systems, and sedimentary diagenesis. Micro-organisms are ubiquitous in low temperature geologic systems, and numerous laboratory and field studies demonstrate that micro-organisms can facilitate the formation of minerals. Despite the growing evidence that a significant proportion of mineral surface area exposed to fluids in many geological environments is associated with biogenic minerals, the majority of current metal sorption studies continue to focus on non-biogenic phases. To date there have been few systematic studies of the mechanisms by which biogenic iron oxyhydroxides control the fate of trace metals in near-surface environments. Several studies have demonstrated that biogenic Mn and Fe oxyhydroxides preferentially sequester metal ions over bacterial cell walls (Ferris et al. 1999, Nelson et al. 1999). However a quantitative model for the mechanism of metal sorption and incorporation into the biogenic minerals was not presented.

The carbonate-hosted Piquette Pb,Zn mine (Tennyson, Wisconsin) provides a unique field location for the study of the properties of minerals of biological origin. After the flooding of this mine 30 years ago biofilms ~20cm in thickness colonized and flourished on the floor and walls of mine. Characterization of the biofilms with HRTEM and SEM revealed that the stalks and sheaths the bacteria *Gallionella* and *Leptothrix* were coated with nanoscale iron oxyhydroxide phases formed through the biological oxidation of ferrous iron in the system. (Banfield et al., 2000). These ~ 2 - 3nm diameter, 2-line ferrihydrite and feroxyhite (FeOOH) particles aggregate in a crystallographically-controlled fashion to form porous pseudo-single crystals up to hundreds of nanometers in diameter. The presence of large quantities of nanoscale iron oxyhydroxides may have a tremendous impact on the aqueous geochemistry of the mine. Previous studies by our group demonstrate that the K_{ads} of nanoscale minerals significantly increases as a function of decreasing particle size (Zhang et al., 1999). In order to define and quantify the role of the biogenic nanoscale iron oxyhydroxide aggregates in controlling the long term fate of trace metals in this system we measured the surface properties of the minerals using acid-base titrations and the adsorption and desorption of metal ions as a function of pH, aqueous metal activity, and time.

Preliminary results of this study indicate that the surfaces of the iron oxyhydroxides have a high affinity for binding metalloids such arsenic (arsenate) and that adsorption can be quantitatively modeled utilizing a site-specific surface complexation approach. Furthermore, HRTEM data show that the 2-line ferrihydrite and feroxyhite (FeOOH) particles coarsen and recrystallize into the more stable phase goethite. If crystal growth occurs via oriented aggregation structural incorporation of surface adsorbed ions can lead to irreversible long term storage of toxic ions such as As or nutrients such as phosphate. Results of this study show that in the subsurface environment voluminous quantities of ferric iron minerals can be formed in association with micro-organisms. Preliminary experimental results indicate that biogenic mineral phases are may have a profound effect on the short and long term mobility and fate of metal ions in near-surface water-rock systems via sorption and structural incorporation mechanisms.

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