

Nanoparticulate bacteriogenic manganese oxides: Environmental reactivity and structural chemistry

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Bacteriogenic Mn oxides occur throughout (sub-)oxic marine and freshwater environments. These reactive natural materials serve as the primary sinks and sources for Mn(II), which plays a major role in photosynthesis, and profoundly impact ground water chemistry via their ability to sequester metals, oxidize a variety of recalcitrant organic and inorganic compounds, and act as terminal electron acceptors for microbial respiration. We seek to understand the key factors that control the reactivity of these reactive materials in aquatic environments.

Mn oxide production by *Bacillus* sp., strain SG-1 has been studied *in-situ* in sea water, fresh water, and in the presence of metal contaminants using synchrotron-based wide-angle x-ray scattering (WAXS), X-ray absorption spectroscopy (XAS), and complementary techniques, and has been compared to Mn biooxides collected at field sites. Laboratory studies indicate the initial Mn oxide product is a sub-nanoparticulate hexagonal phyllo-manganate, which is highly reactive and transforms to more stable secondary phases (including *c*-disordered birnessite and feitknechtite) in response to thermodynamic driving forces. Bacteriogenic Mn oxides from Pinal Creek, AZ and the Black Sea generally follow predictions based on our laboratory-based investigations. The bacteriogenically-derived Mn oxides can incorporate a surprisingly diverse number of metals into their structures, including copper(II), cobalt(II, III), zinc(II) and even uranium(VI). Thus, particle size, a propensity for mineralogic transformations, and a highly flexible solid-state structural chemistry appear to be fundamentally important to the interface between linked environmental cycles of Mn and other important elements.

Mössbauer spectroscopy of extracellular tabular magnetite formed during microbial iron reduction

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Mössbauer spectroscopy was employed to elucidate the transformation processes of nano-scale iron oxides by *Geobacter metallireducens* strain GS-15. During dissimilatory iron reduction, the quadrupole splittings and line widths of Fe(III) decreased systematically and a structural ordering of the crystallographic sites of iron took place, consistent with mineralogical transformation from ferrihydrite to magnetite with lepidocrocite as an intermediate phase (Fig. 1). We propose a solid-state conversion mechanism for this transformation, which would allow magnetite to inherit the tabular- and lath-like morphologies of the lepidocrocite precursor. Results of this study suggest that unusual forms of magnetite can be formed by a unique combination of chemical and biological processes during reduction of iron oxides. The results also support our TEM observation of the tabular magnetite formed by the same bacterium (Vali et al. PNAS 101, 16121-16126, 2004).

