

THEME 2: THE DYNAMIC INTERFACE

Session 2.3: In situ investigation of interface processes

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Interfacial processes play an important role in regulating and facilitating geo- and biogeochemical reactions. Interfaces between gases, liquids, solids and microbes influence reactive transport and geochemical transformations over a wide range of spatial and temporal scales. In recent years, significant insight has emerged on interface reactivity and many breakthroughs have been a direct result of advances in in-situ analytical, spectroscopic and imaging methods. Such techniques allow detailed measurement while maintaining environmentally-relevant conditions, allowing elucidation of previously intractable interface facilitated reaction mechanisms, such as sorption-desorption, mineral dissolution-transformation, oxidation-reduction, microbe-mineral interactions, etc. Such processes control biogeochemical reactivity and transport in multiphase systems and have been studied by coupling more conventional methods and novel reaction cell design with these advanced techniques. This symposium aims to bring together scientists who use in-situ analytical, spectroscopic and imaging techniques to complement classical methods for investigating geo- and biogeochemically relevant interfacial processes over a variety of temporal and spatial scales.

2.3.11

Structural chemistry and formation mechanisms of bacteriogenic manganese oxides

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Bacteriogenic manganese oxides occur as nanoparticles and grain coatings throughout marine and freshwater environments and profoundly impact ground water quality via their ability to degrade and sequester contaminants. Bacterial oxidation of Mn(II) is believed to be the dominant source of environmental Mn oxides. Mn(III) (produced during Mn(II) oxidation) and Mn(IV) are strong oxidants that impact nutrient cycling and oxidize a variety of recalcitrant organic and inorganic compounds. Thus, bacterial manganese cycling couples to nitrogen, carbon, iron, and sulfur environmental cycles.

We have utilized XAS and *in-situ* synchrotron-based transmission wide-angle x-ray scattering (WAXS) along with complementary wet chemical techniques to systematically characterize bacterial Mn(II) oxidation and to probe the structures of fully hydrated bacteriogenic Mn oxides produced by spores of the marine bacterium, *Bacillus* sp., strain SG-1. These studies indicate the primary solid-phase bacteriogenic reaction product to be an x-ray amorphous phyllo-manganate of very small particle size believed to have a hexagonal sheet symmetry and manganese oxidation state close to +4. This phase is highly reactive and rapidly transforms to more stable secondary phases, the nature and kinetics of which are dependent upon solution chemistry. Microbeam XAS and WAXS studies of bacteriogenic Mn oxides from the Black sea and manganese oxide coatings on sediments from Pinal Creek, AZ, an acid mine drainage-contaminated stream, are similar to those produced in our laboratory experiments. Because of the flexibility in Mn oxide structural motifs, the bacteriogenically-derived manganese oxides are strong metal scavengers, and can incorporate copper(II), cobalt(II, III), zinc(II) and even uranium(VI) at structural sites in the mineral.