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Mechanisms of trace metal sorption in *Pseudomonas putida*-birnessite assemblages

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Biogenic manganese oxides (MnO_2) are ubiquitous nanoparticulate minerals that contribute strongly to the adsorption of nutrient and toxicant metals in aquatic and terrestrial environments. The formation of these minerals is catalyzed by a diverse and widely-distributed group of bacteria and fungi, often through the enzymatic oxidation of aqueous Mn(II) to Mn(IV). The biogenic Mn(IV) oxide found in field settings, as well as that produced by model bacteria in laboratory culture, is typically layer-type hexagonal birnessite containing abundant cation vacancy sites and enmeshed in an organic matrix of bacterial cells and extracellular polymeric substances.

In this talk I summarize the results from laboratory-scale research designed to investigate the mechanisms of metal sorption by the bacterial biomass-birnessite assemblages formed by *Pseudomonas putida* GB-1 when grown in the presence of 1 mM Mn(II) at circumneutral pH values. The goals of this research were first, to identify the structure of the surface complexes formed by trace metals (e.g., Ni, Cu and Zn) on biogenic birnessite and second, to determine the conditions under which the bacterial cell surfaces and extracellular polymeric substances contribute to metal sorption. Macroscopic and spectroscopic experiments were performed at varying pH values (6 – 8) and over a wide-range of metal concentrations.

Extended X-ray absorption fine structure (EXAFS) spectroscopy and first-principles calculations based on density functional theory showed that cation vacancy sites in birnessite drive mineral reactivity, but that surface speciation varies from metal to metal. For, Ni we identified two species, Ni bonded to three surface oxygen atoms vacancy sites as a triple-corner-sharing (TCS) complex and Ni incorporated at vacancy sites, with surface speciation varying with pH and surface loading. Zinc formed TCS complexes at vacancy sites, with the proportion of Zn in tetrahedral or octahedral coordination geometry influenced by solution pH, background electrolyte, surface loading, and time of Zn addition relative to MnO_2 precipitation. Copper bonding at vacancy sites was found to be important as well, but the geometry of additional surface complexes, suggested by the EXAFS spectra, could not be identified. Based on the results from EXAFS spectroscopy, we concluded that the bacterial biomass does not limit Ni or Zn sorption at vacancy sites, contributing to metal sorption at very high surface loadings (> 0.1 mol Me mol^{-1} Mn). However, Cu, a transition metal with a high affinity for both organic and mineral functional groups and facile redox reactivity, was found to interact strongly with the biomass over all surface loadings investigated. This research advances our understanding of the surface reactivity of biogenic birnessite and sheds light on metal retention mechanisms in composite microbe-mineral assemblages, which regulate the concentrations and distribution of nutrient and toxicant metals in diverse ecosystems.