Environmental surface chemistry of manganese oxides: Impact on trace element and contaminant cylcing in surface environments

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Layer-type manganese oxides (MnOx) are among the most reactive mineral nanoparticles in aquatic and soil enviroments. From a structural point of view, they consist of sheets of edge-sharing Mn(IV) octahedra, which can accommodate a range of cations in layer and interlayer positions. Interlayer cations balance the charge deficit from layer Mn(III) atoms and abundant Mn(IV) vacancy sites.

Mn oxides impact numerous biogeochemical cycles including that of carbon, metals (e.g., Co, Ni, Cu, Zn and Pb) and metalloids (e.g., Cr, As, Sb, Se). These minerals exhibit among the highest metal sorption capacities (0.1 – 0.5 mol metal mol^{-1} Mn) and oxidative properties of any natural material. Furthermore, biological precipitation is the major pathway for Mn oxide formation under most environmental conditions. Thus, biogenic Mn oxides occur as mixtures of microbial cells, extracellular polymeric substances and mineral nanoparticles.

The physical, chemical and biological complexity of biogenic manganese oxides has rendered the study of their surface chemistry difficult. My group has overcome these challenges by integrating chemical and spectroscopic investigations of experimental systems of varying complexity, including chemically synthesized oxides, mixtures of microbial biomass and Mn oxides, and biogenic Mn oxides produced by model Mn-oxidizing bacteria and fungi. In addition, we have implemented routine wet-chemical methods to determine the redox state of the oxides through quantification of solid-phase Mn(III) content and/or average Mn oxidation number. Kinetic analysis of both sorption processes and evolution in Mn redox state—especially solid-phase Mn(III) content--have been key in advancing our understanding of their surface chemistry.

Here I will present our findings on three aspects of the surface chemistry of Mn oxides: 1) environmental parameters controling particle size, particle aggregation and redox state; 2) reactivity of particle edges and basal surfaces in the absence and presence of microbial biomass; and 3) the impact of Mn(III) on sorption processes and redox reactivity.