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Manganese oxides are versatile minerals in terms of their extensive applications in industry and environmentally important roles in biogeochemical elemental cycles. Manganese oxides with tunnel and layer structure can be used as cathodic materials in lithium batteries, ion sieves, molecular sieves, and catalysts. In the environment, manganese oxides can affect carbon cycling by oxidizing organic molecules and forming humic substances. Manganese oxides are also involved in nutrient transformations, such as oxidation of low oxidation states of nitrogen and phosphorous. Most importantly, mobility, toxicity and bioavailability of environmental contaminants, such as heavy metals (Pb, Cu, Zn, Ni, Co, Cr and Cd) and oxyanions (As and Se), are also strongly regulated by manganese oxides in natural settings even though the abundance of manganese oxides is lower in the environment compared to iron or aluminum oxides.

Biologically Mn(II) oxidation has been observed for many years and investigated extensively. Biogenic Mn(II) oxidation products, i.e., biogenic manganese oxides (BioMnOx), are recently believed to be the predominant forms of manganese oxides in ocean, aqueous and terrestrial environments. BioMnOx are poorly crystalline, which are expected to have high surface area and reactivity. BioMnOx are birnessite-like phyllomanganate; however, their secondary structures (i.e., the amount and distribution of inner-layer Mn(III) cations and vacancy sites) depend on geochemical solution conditions at which they are formed, such as coexisting cations (Ca, Na, etc.). The secondary structures are crucial because they determine the reactivity of layer manganese oxides.

My doctoral research focuses on the structure and reactivity of BioMnOx formed under various prevalent geochemical conditions using synchrotron-based techniques, such as X-ray absorption fine structure spectroscopy (XAFS), X-ray diffraction (XRD), and atomic pair distribution function (PDF) analysis as well as theoretical quantum chemical calculations. Our XAFS and XRD results showed that BioMnOx which were formed either under lower pH conditions or with Ni²⁺ as a coexisting cation tended to have lower amounts of lattice Mn(III) and higher amounts of vacancy sites. Further reactivity studies in terms of nickel sorption on BioMnOx indicated that heavy metal sorption capacity and affinity were determined by vacancy sites and lattice Mn(III) cations, respectively (*manuscript in preparation*).

The role of Mn(III) cations in arsenite (As(III)) oxidation is controversial in the research area of manganese oxides. In order to investigate the Mn(III) role in As(III) oxidation by layer manganese oxides, quantum chemical calculation was used. Our results indicated that Mn(III) cations are less reactive than Mn(IV) for As(III) oxidation due to their lower affinity for As(III) adsorption, higher potential to be blocked by As(V) complexes, and slower electron transfer rates with adsorbed As(III) (*ES&T*, 43(17):6655). This major finding is consistent with experimental observations in literature. Further experimental study will be planned to verify this conclusion.

Structures of hydrous manganese oxides (HMO), a synthetic analogue for BioMnOx, as well as naturally occurring vernadite, remain unclear because of poor crystalline composition and the difficulty to elucidate using XRD, which is the main tool for crystal structure determination. Recently, PDF has been shown as a powerful technique to reveal crystal structures of poorly crystalline or amorphous materials. We have collected PDF data from HMO and reference crystalline manganese oxides. These data indicate that HMO are hexagonal layered structures with R-3M space groups (*manuscript in preparation*).