

**STRUCTURE AND REACTIVITY STUDY OF BIOTIC AND ABIOTIC POORLY
CRYSTALLINE MANGANESE OXIDES**

by

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ABSTRACT

Manganese oxides (Mn-oxides) have environmental and economic significance. They can sequester large quantities of toxic heavy metals and promote transformation of toxic redox-active species, subsequently regulating bioavailability and toxicity of toxic elements in the environment. The most common Mn-oxides in the environment are fine grained and poorly crystalline, e.g. vernadite. The overall objective of this research was to utilize multiple experimental and theoretical approaches to improve our understanding of the structure and reactivity of biotic and abiotic poorly crystalline Mn-oxides which are analogues to naturally-occurring vernadite.

The crystal structure of three poorly crystalline Mn-oxides including δ -MnO₂, polymeric MnO₂ and a biogenic Mn-oxide (BioMnO_x), were investigated using atomic pair distribution function (PDF) analysis. Results indicate that these Mn-oxides are layered structure with nearly hexagonal layer symmetry, helping to resolve the controversy about whether these poorly crystalline materials are tunneled or layered structures. The best structural model for the simulation of the PDFs is a monoclinic structure in C2/m space group. The adjacent Mn-layers have significant shifts along the *a* axis with stacking vectors (β angle) between 95.8° – 98.9°. A high degree of disorder is present in the stacking direction. The proportions of vacant sites in Mn layers and coherent scattering domain (CSD) size were also estimated.

The formation of poorly crystalline Mn-oxides in the natural environment is largely mediated by Mn-oxidizing microorganisms whereas the geochemical conditions of natural settings are variable. The impacts of cations (H^+ , Ni(II), Na^+ and Ca^{2+}) during biotic Mn(II) oxidation on the structure of Mn octahedral layers of $BioMnO_x$ were investigated using solution chemistry and synchrotron X-ray techniques. Results demonstrate that the Mn octahedral layer symmetry and composition are sensitive to previous cations present during $BioMnO_x$ formation. Specifically, H^+ and Ni(II) enhance vacant site formation; whereas, Na^+ and Ca^{2+} favor formation of Mn(III) and its ordered distribution in Mn octahedral layers. This study emphasizes the importance of the abiotic reaction between Mn(II) and $BioMnO_x$ and the dependence of the crystal structure of $BioMnO_x$ on solution chemistry.

$BioMnO_x$ possess an extraordinary ability to sequester metals. $BioMnO_x$ are generally layered structures containing varying amounts of Mn(III) and vacant sites in the Mn layers. However the relationship between the varying structure of $BioMnO_x$ and metal sorption properties remains unclear. Ni(II) sorption mechanisms were determined for $BioMnO_x$ produced at either pH 6, 7 or 8 in $CaCl_2$ solutions by employing isotherms and extended X-ray absorption fine structure (EXAFS) spectroscopic analyses. Our data demonstrate that Ni(II) sorbs at vacant sites in the interlayer of the $BioMnO_x$ and the maximum Ni(II) sorption capacity increases as the formation pH decreases. This relation indicates that the quantity of $BioMnO_x$ vacant sites increases as formation conditions become more acidic, which is in good agreement with a previous $BioMnO_x$ structural study. Additionally, this study reveals, for the first time, that imidazole groups are involved in Ni(II) binding to biomaterials,

and have a higher Ni sorption affinity, but a lower site density compared to carboxyl groups.

Another important aspect in terms of reactivity of Mn-oxides is its oxidizing behavior. Density functional theory (DFT) calculations were used to investigate As(V) and As(III) surface complex structures and reaction energies on both Mn(III) and Mn(IV) sites in an attempt to better understand As(III) oxidation by layered Mn-oxides. Edge-sharing di-octahedral Mn(III) and Mn(IV) clusters with different combinations of surface functional groups ($>\text{MnOH}$ and $>\text{MnOH}_2$) were employed to mimic pH variability. Results show As(V) adsorption inhibits As(III) oxidation by blocking adsorption sites. Under simulated acidic pH conditions, Mn(IV) sites exhibited stronger adsorption affinity than Mn(III) sites for both As(III) and As(V). Overall, we hypothesize that Mn(III) sites are less reactive in terms of 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). Results from this study offer an explanation regarding the experimental observations of Mn(III) accumulation on birnessite and the long residence time of As(III) adsorption complexes on manganite ($\gamma\text{-MnOOH}$) during As(III) oxidation.