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699-29 Synthesis and Characterization of Nano-Mn(IV) Oxide Phases.

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Manganese(IV) oxides represent one of the main redox catalysts in subsurface environments, while also extensively sorbing anions and cations. Their wide-spread distribution in soil, combined with their highly reactive surfaces, allow manganese(IV) [Mn(IV)] oxides , even at low concentration, to oxidize trace metals. For example, they are capable of oxidizing mobile, toxic arsenite [As(III)] to arsenate [As(V)] which is less toxic and mobile. However, in environmental settings many, Mn(IV) oxide minerals form as nanometer-size particles, either through biological or surface catalyzed Mn(II) oxidation. The reactivity and surface chemistry of nano-Mn(IV) oxide phases is poorly understood and may be profoundly different than their more crystalline counterparts. In this paper we characterize nano-Mn(IV) minerals synthesized using both sol-gel and citrate ion reduction methods and compare these to bulk minerals of biogenic and abiotic origin. X-ray diffraction confirmed that the mixed Mn oxidation state mineral hausmanite was formed using both of these syntheses. The Mn oxidation state at the mineral surface is determined using X-ray photoelectron spectroscopy (XPS) and the bulk oxidation state and local structure will be determined using X-ray absorption spectroscopy (XAS). Additionally, mineral morphology has been analyzed using field emission gun scanning electron microscopy (FEG-SEM). A particle size of ~ 12 nm was determined via XRD, dynamic light scattering (DLS), and high-resolution transmission electron microscopy (HR-TEM). A comparison of the reactivity of these various particles will be presented in a companion paper.

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