742-3 Rates and Mechanisms of Arsenite Oxidation by Nano-Mn(IV) Oxide Mineral Phases.

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Arsenite [As(III)] oxidation to arsenate [As(V)] by manganese(IV) [Mn(IV)] oxides is an important reaction impacting the natural cycling of arsenic. The arsenite species is substantially more toxic and tends to bind more weakly to soils than As(V) does. Heterogeneous oxidation of As(III) on the surface of bulk Mn(IV) oxides has been well characterized; however, the formation of Mn(IV) oxide particles in the environment is thought to generally occur through either biologically or mineral-surface mediated Mn(II) oxidation. These two oxidation pathways result in the formation of nanometer-size Mn(IV) minerals. Compared with the bulk particles, the reactivity of these nano-oxides is poorly understood. In a companion paper we describe the synthesis and characterization of nano-Mn(IV) oxides using the sol-gel and citrate ion reduction methods. In this paper we use quick-scanning X-ray absorption near edge structure (XANES) spectroscopy to measure the rate of As(III) oxidation by these nano-oxides and compare it to the oxidation rate of bulk and biogenic Mn(IV) oxidation minerals. Additionally, we utilize quick-scanning extended X-ray absorption fine structure (EXAFS) spectroscopy coupled with electron microscopy to determine the As(III) oxidation mechanism and the potential for formation of inhibitory surface coatings on the Mn(IV) mineral surface.

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