

152 - Kinetics of arsenic oxidation by manganese oxide minerals: The influence of origin and structure on reactivity

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Manganese(IV) oxides are one of the main redox catalysts in the subsurface environment. Their highly reactive surfaces allow manganese minerals to oxidize trace metals such as arsenic from the mobile and toxic phase arsenite [As(III)], to a less mobile and toxic form, arsenate [As(V)]. In order to understand the many roles of manganese oxides in the natural world, it is essential to characterize the differences in their reactivities. Abiotic and biogenic manganese oxides are the two primary forms of manganese minerals found in natural systems. Five Manganese oxide minerals -- manganese oxide (HMO), hexagonal birnessite, random-stacked birnessite, acid birnessite, and biogenic manganese oxide were reacted under identical conditions with equal concentrations of manganese and arsenic(III) to determine arsenic oxidation kinetics. All five manganese oxides exhibited a biphasic oxidation reaction, with biogenic manganese oxides being the least reactive. Two synthetic manganese oxides, acid birnessite and HMO, oxidize arsenic(III) more rapidly than biogenic manganese oxide. This could be caused by interactions between the arsenic(III) and residual microbial biomass present in biogenic manganese oxide. Finally, arsenic concentration, pH, and temperature were varied with HMO and acid birnessite, the two most reactive manganese oxides. Under these conditions, only high arsenic concentrations decreased reactivity due to surface passivation. Understanding the reactivity of naturally occurring manganese oxide minerals provides key insight to the chemical processes that regulate manganese oxidation in the environment. This knowledge is invaluable in understanding how arsenic is naturally attenuated by manganese oxides in contaminated ecosystems.

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