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Impact of Structural Impurities in Manganese Oxides on Arsenic Oxidation

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Arsenic (As) is a well-known carcinogen and environmental contaminant. Manganese (Mn) oxides are widely studied for their ability to oxidize arsenite (As(III)) to arsenate (As(V)) and adsorb these As species onto the surfaces. However, our understanding of Mn oxide-As interactions is derived from laboratory studies with synthetic Mn oxides. These freshly-synthesized minerals, often lacking structural impurities, may not accurately reflect the properties of Mn oxides found in natural environments. Consequently, As oxidation and removal rates observed in laboratory studies with synthetic Mn oxides may overestimate the actual oxidation and sorption capacities of natural Mn minerals. In this study, we investigated both synthetic and natural Mn(III) oxides—hausmannite (Mn3O4) and hetaerolite (ZnMn2O4)—to compare their capacities for oxidizing As(III). While both minerals possess redox-active Mn(III), the oxidation capacity of hetaerolite toward As(III) had not been previously evaluated. The isostructural relationship between hausmannite and hetaerolite, with Zn(II) substituting for Mn(II) at the tetrahedral site in hetaerolite, enabled a systematic assessment of the influence of structural Zn on the minerals' oxidation potential. Analysis of solution and solid samples revealed that synthetic hausmannite exhibited a higher As(III) oxidation capacity than synthetic hetaerolite. The oxidation capacity decreased with increasing Zn substitution upto 5 wt%, but increased at 10 wt%. Natural minerals displayed a similar trend: natural hausmannite had a higher As(III) oxidation capacity than natural hetaerolite. However, isolating the Zn effect on As(III) oxidation in natural samples proved challenging due to the presence of additional structural impurities. Overall, both synthetic and natural minerals demonstrated a greater As(III) oxidation by hausmannite compared to hetaerolite. Notably, the oxidation magnitude was approximately 3 times higher for synthetic minerals than for natural specimens, even after normalization for surface area. This is likely due to the aged surfaces and lower surface area of natural minerals. These findings highlight the significant influence of structural impurities on the oxidation properties of Mn oxides, stress the importance of accounting for these factors when predicting the environmental reactivity of Mn minerals, and emphasize the need to recognize the limitations of using pristine, synthetic minerals to predict their behavior toward environmental contaminants in natural settings.