OXIDATION AND SORPTION KINETICS OF ARSENIC ON A POORLY CRYSTALLINE MANGANESE OXIDE

by

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ABSTRACT

Manganese oxides (Mn-oxides) are some of the most reactive minerals in the environment, and are known to readily oxidize toxic arsenite (As\textsuperscript{III}) to less toxic arsenate (As\textsuperscript{V}). However, As\textsuperscript{III} oxidation by Mn-oxides can be quite complex, involving many simultaneous reactions. Also, when As\textsuperscript{III} is oxidized by Mn-oxides, a reduction in the oxidation rate is often observed, which has been attributed to Mn-oxide surface passivation. Although As\textsuperscript{III} oxidation by Mn-oxides has been studied, fundamental understanding of the mechanisms of As\textsuperscript{III} oxidation, and subsequent Mn-oxide passivation by poorly crystalline, layered Mn-oxides (i.e. phyllomanganates), is lacking. In stirred-flow experiments, As\textsuperscript{III} oxidation by δ-MnO\textsubscript{2} (a poorly crystalline phyllomanganate) is initially rapid but slows appreciably as the mineral surface became passivated. Mn\textsuperscript{II} is the only reduced product of As\textsuperscript{III} oxidation by δ-MnO\textsubscript{2} during the initial period of the reaction, indicating that As\textsuperscript{III} oxidation does not proceed through a Mn\textsuperscript{III} intermediate. Also, X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) show that Mn\textsuperscript{II} sorption is the primary cause of δ-MnO\textsubscript{2} passivation during the early periods of As\textsuperscript{III} oxidation. There is also evidence that formation of Mn\textsuperscript{III} observed in previous studies is a result of conproportionation of Mn\textsuperscript{II} sorbed onto Mn\textsuperscript{IV} reaction sites of δ-MnO\textsubscript{2}. It is possible that Mn\textsuperscript{III} formed through Mn\textsuperscript{II} / Mn\textsuperscript{IV} conproportionation also plays a role in δ-MnO\textsubscript{2} passivation. Only As\textsuperscript{V} is observed bound to δ-MnO\textsubscript{2} during As\textsuperscript{III} oxidation, and it is present in several adsorption complexes that change as the Mn\textsuperscript{III} content in δ-MnO\textsubscript{2} increases. Although As\textsuperscript{V} is directly bound to the δ-MnO\textsubscript{2} surface, a significant fraction is quite mobile. These findings show that As\textsuperscript{III} oxidation by poorly crystalline δ-MnO\textsubscript{2} involves
several simultaneous reactions and emphasizes the importance of Mn oxidation state in the reactivity of Mn-oxides. Also demonstrated is the value of studying reaction mechanisms over a range of time scales.