

**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 ( $\text{As}^{\text{III}}$ ) to less toxic arsenate ( $\text{As}^{\text{V}}$ ). However,  $\text{As}^{\text{III}}$  oxidation by Mn-oxides can be quite complex, involving many simultaneous reactions. Also, when  $\text{As}^{\text{III}}$  is oxidized by Mn-oxides, a reduction in the oxidation rate is often observed, which has been attributed to Mn-oxide surface passivation. Although  $\text{As}^{\text{III}}$  oxidation by Mn-oxides has been studied, fundamental understanding of the mechanisms of  $\text{As}^{\text{III}}$  oxidation, and subsequent Mn-oxide passivation by poorly crystalline, layered Mn-oxides (i.e. phyllomanganates), is lacking. In stirred-flow experiments,  $\text{As}^{\text{III}}$  oxidation by  $\delta\text{-MnO}_2$  (a poorly crystalline phyllomanganate) is initially rapid but slows appreciably as the mineral surface became passivated.  $\text{Mn}^{\text{II}}$  is the only reduced product of  $\text{As}^{\text{III}}$  oxidation by  $\delta\text{-MnO}_2$  during the initial period of the reaction, indicating that  $\text{As}^{\text{III}}$  oxidation does not proceed through a  $\text{Mn}^{\text{III}}$  intermediate. Also, X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) show that  $\text{Mn}^{\text{II}}$  sorption is the primary cause of  $\delta\text{-MnO}_2$  passivation during the early periods of  $\text{As}^{\text{III}}$  oxidation. There is also evidence that formation of  $\text{Mn}^{\text{III}}$  observed in previous studies is a result of conproportionation of  $\text{Mn}^{\text{II}}$  sorbed onto  $\text{Mn}^{\text{IV}}$  reaction sites of  $\delta\text{-MnO}_2$ . It is possible that  $\text{Mn}^{\text{III}}$  formed through  $\text{Mn}^{\text{II}} / \text{IV}$  conproportionation also plays a role in  $\delta\text{-MnO}_2$  passivation. Only  $\text{As}^{\text{V}}$  is observed bound to  $\delta\text{-MnO}_2$  during  $\text{As}^{\text{III}}$  oxidation, and it is present in several adsorption complexes that change as the  $\text{Mn}^{\text{III}}$  content in  $\delta\text{-MnO}_2$  increases. Although  $\text{As}^{\text{V}}$  is directly bound to the  $\delta\text{-MnO}_2$  surface, a significant fraction is quite mobile. These findings show that  $\text{As}^{\text{III}}$  oxidation by poorly crystalline  $\delta\text{-MnO}_2$  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.