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XPS study of reductive dissolution of birnessite by H_2SeO_3 with constraints on reaction mechanism

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ABSTRACT

Reductive dissolution of 7 Å birnessite $[Mn^{2+}_{0.05}Mn^{3+}_{0.25}Mn^{4+}_{0.7}O_{1.7}(OH)_{0.25}]$ by selenious acid (H_2SeO_3) produces Mn^{3+} and Mn^{2+} surface reaction products (here represented as S-MnOOH and S-MnO, respectively) and $Mn^{2+,3+}$-selenite surface complexes at the solution-mineral interface.

$Mn2p_{3/2}$, Se3d, and O1s X-ray photoelectron spectra of reacted surfaces reveal that Mn^{4+} of birnessite is reduced simultaneously to Mn^{3+} and Mn^{2+} while Se^{6+} is oxidized to Se^{4+} according to the probable stoichiometric reactions:

$$2MnO_2 + H_2SeO_3 + H_2O \rightarrow 2S\text{-}MnOOH + H_2SeO_4$$

$$MnO_2 + H_2SeO_3 \rightarrow S\text{-}MnO + H_2SeO_4$$

There is no XPS evidence for reduction of surface Mn^{3+} to Mn^{2+} in the presence of selenite. Whereas this reaction proceeds in the presence of arsenite, selenite apparently inhibits reduction of Mn^{3+}, perhaps through formation of a strong Mn-selenite surface complex.

The rate of release of Mn^{2+} to dilute selenious acid (1.5×10^{-3} M) is considerably lower than the rate of release to aerated, distilled water at similar pH. This behavior suggests that adsorbed selenite complexes impede the proton promoted dissolution of the soluble Mn^{2+} component of birnessite.