

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

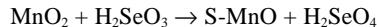
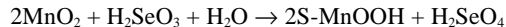
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ABSTRACT

Reductive dissolution of 7 Å birnessite [$\text{Mn}_{0.05}^{3+}\text{Mn}_{0.25}^{3+}\text{Mn}_{0.7}^{4+}\text{O}_{1.7}(\text{OH})_{0.25}$] 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 $\text{Mn}^{2+},^{3+}$ -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:



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 ($1.5 \times 10^{-3} M$) 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.