

Interpretation of XPS Mn(2p) spectra of Mn oxyhydroxides and constraints on the mechanism of MnO₂ precipitation

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ABSTRACT

Calculated Mn(2p_{3/2}) X-ray photoelectron spectra (XPS) of Mn²⁺, Mn³⁺, and Mn⁴⁺ free ions are strikingly similar to Mn(2p_{3/2}) spectra of Mn²⁺-, Mn³⁺-, and Mn⁴⁺-oxides and oxyhydroxides, indicating that these ions adopt high spin states in MnO, manganite, and birnessite. The Mn(2p) peak structures reveal the presence of only Mn³⁺ in manganite, but Mn²⁺, Mn³⁺, and Mn⁴⁺ are present in the near-surface of synthetic birnessite at about 5, 25, and 70%, respectively. Precipitation of birnessite by reaction of Mn²⁺(aq) with an oxidant includes two electron transfer steps: (1) oxidation of Mn²⁺(aq) to produce Mn³⁺-oxyhydroxide, an intermediate reaction product that forms on the surface of synthetic birnessite and (2) subsequent oxidation of Mn³⁺-oxyhydroxide surface species to produce synthetic birnessite. Some surface Mn³⁺, however, remains unoxidized and is incorporated into birnessite. As for this synthesis (KMnO₄ used as oxidant), oxidation may not proceed to completion in natural settings (as O₂ is the oxidant) leading to Mn³⁺ incorporation into Mn-oxides. The hypothesis explains the abundance of non-stoichiometric MnO₂ phases in sedimentary environments. The MnO₂ precipitation scheme proposed by Stumm and Morgan (1981) includes the surface species Mn²⁺·MnO₂. This and other studies indicate that the reactive intermediate is a Mn³⁺-bearing surface species. The formation rate of birnessite is probably controlled by one of these redox reactions. The proposed rate expression of Davies and Morgan (1989), however, needs no modification provided surface area is a reasonable measure of the surface density of the reactive intermediate.