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Photoreduction of Mn(IV) as a mechanism of Mn(III) accumulation in δ-MnO_2: Implications for mineral reactivity

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Birnessite, an ubiquitous mineral in most surface environments, is characterized by a strong reactivity towards the sorption and oxidation of many organic and inorganic compounds. This reactivity can be reduced by the presence of varying amounts of Mn(III). One pathway for the accumulation of Mn(III) in birnessite is photoreduction of Mn(IV in the absence of organic compounds. The Eh-pH stability of MnO_2 both shows a potential high enough to oxidize water over the whole pH range and increases to higher Mn reduction potentials with lower pH. However, the pH dependence of photoreduction has not been observed experimentally.

In this study, we investigated the mechanism and rate of Mn(III) photogeneration under 400 nm light irradiation in δ-MnO_2 at pH values of 4.0, 6.5 and 8.0 by coupling optical transient absorption spectroscopy with flow-through photoreactor experiments, respectively. Parallel dark-experiments were run under identical conditions.

Our results show that lower pH leads to small but detectable amounts of Mn(III) accumulation in the dark, confirming thermodynamic predictions. No pH dependence was observed in the photoexcitation decay dyanamics, but the accumulation of Mn(III) increased both with time and with decreasing suspension pH, reaching 6% at pH 4.0 vs 2% at pH 8.0 ater 4 days of irradiation. We interpret the pH dependence of photoreduction to the weakening of Mn-O bonds due to increased protonation of the mineral surface with decreasing pH, which promote Mn(III) stabilization in the interlayer region of the mineral.

The results from this study indicate that photoreduction of birnesite minerals in the absence of organic electron donors occurs over a broad range of pH values, and the resulting accumulation of Mn(III) can reduce the reactivity of birnessite in diverse environmental settings. A reduction in reactivity was confirmed by the release of adsorbed Ni on the mineral upon photogeneration of Mn(III).