pH-dependent photoreduction of δ-MnO_2

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Birnessite minerals (layer type Mn(III/IV) oxides) are linked to the biogeochemical cycle of carbon and many trace metals because of their small particle size, abundant sorption sites and redox properties. Photoreduction of these oxides contributes to the redox cycle of Mn in sunlit aquatic environments. We previously showed that δ-MnO_2, a fully oxidized synthetic birnessite, photoreduces in water under visible light irradiation at pH 6.5, whereby photogenerated Mn(III) migrates from the MnO_2 sheet into the interlayer [1]. However, natural sunlit environments are characterized by a broader range of pH conditions and thus we seek to understand the effect of pH on the photoreduction of birnessite minerals.

We investigated the rate, efficiency and mechanism, of δ-MnO_2 photoreduction at pH values of 4.0, 6.5 and 8.0. We coupled flow-through irradiation experiments with optical pump-probe spectroscopy to measure the rates and extent of irreversible Mn(III) generation on hour to day timescales and to probe electron-hole pair generation and recombination on picosecond to nanosecond timescales. We irradiated suspensions of δ-MnO_2 using 400 nm light and trapped photogenerated Mn(III) using pyrophosphate as a strong complexing ligand.

The results showed a four-fold increase in the yield of Mn(III) per photon absorbed (quantum yield) as suspension pH decreased from 8.0 to 4.0. Photoexcitation and recombination processes, however, were identical at all pH values. This comparison indicates that solution pH does not alter the fate or lifetime of photoexcited electrons or holes, rather it enhances the rate of one of the chemical steps. We propose that increased protonation of surface sites with acidic to circumneutral pK_a values promotes the release of Mn(III) ions into the interlayer. The results of this work expand our knowledge of the MnO_2 photoreduction mechanism, an important process in sunlit environmental systems.

1.Marafatto FF*, et al.* (2015) *Proc Natl Acad Sci USA* 112(15):4600-4605.