Physicochemical controls on the photoreduction of δ-MnO_2

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Layer-type Mn(III/IV) oxides (birnessites) are ubiquitous in environmental systems. These minerals are characterized by a high surface area, abundant vacancy sites and strong oxidizing capacity. These properties link birnessites to the biogeochemical cycle of carbon and trace metals. In sunlit aquatic environments, the main processes driving the Mn cycle are biogenic Mn(II) oxidation and photoreduction of particulate MnO_2. However, the environmental controls on the photoreduction mechanism remain poorly understood.

In our previous work, we elucidated the photoreduction mechanism for δ-MnO_2, a fully oxidized synthetic analog of natural birnessites, coupled to water oxidation at pH 6.5 [1]. Our results suggested that the stabilization of photogenerated Mn(III) in the interlayer may passivate further photoreactivity of the mineral. However, natural birnessites are formed under varying pH conditions and may contain significant fractions of Mn(III).

The objective of this work is to investigate the efficiency of δ-MnO_2 photoreduction as a function of pH and interlayer Mn(III) content. To this end, we carried out photoreduction experiments in a flow-through photoreactor setup under 400 nm irradiation on hour to day timescales using pyrophosphate to trap photogenerated Mn(III). We complemented the macroscopic rate measurements with optical pump-probe spectrsocopy to investigate the electron dynamics (electron-hole pair generation and recombination) on the pico- to nano-second timescale.

Our preliminary results show that the quantum yield for photoreduction decreases with increasing pH. A similar trend is expected with increasing interlayer Mn(III) due to passivation of mineral reactivity. The results from this study expand our current understanding of MnO_2 photoreduction pathways to include the effects of pH and Mn(III) as key geochemical constraints in natural settings.

[1] Marafatto F*, et al.* (2015) *Proceedings of the National Academy of Sciences of the United States of America.*