Photoreduction of δ-MnO_2 nanosheets

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The ability to cycle between the +4, +3 and +2 oxidation states and form species with high oxidizing potentials renders manganese (Mn) a key oxidant in environmental systems. Manganese oxide phases can oxidize a wide range of chemical species, including water, metals and organic matter. In sunlit environments, direct and indirect photochemical processes can enhance the reduction and dissolution of Mn oxide minerals. That MnO_2 photoreduction can occur under visible light irradiation has been suggested in studies using theoretical approaches and field- and laboratory-based measurements. However, direct Mn(IV) photoreduction in the absence of organic electron donors has not been investigated previously.

Recently we established macroscopic and spectroscopic approaches to investigate the photoreduction of δ-MnO_2 [1], a synthetic analog of biogenic Mn oxides that consists of randomly stacked MnO_2 nanosheets. We found that 400 nm irradiation of aqueous suspensions of δ-MnO_2 at pH 6.5 led to the irreversible accumulation of Mn(III) in the mineral over 72-h. Our measured rates of Mn(III) accumulation in the mineral and calculated quantum yields indicate that photoreduction of MnO_2 by water is an important environmental process with an efficiency comparable to that observed for Mn oxides in the presence of dissolved organic matter and greater than that reported for iron oxides in the presence of water. In addition, optical and X-ray transient absorption spectroscopy allowed us to follow the Mn chemistry following photoexcitation. We found that photon absorption creates a Mn(III) ion within 0.6 ps in the MnO_2 nanosheet; this species is unstable and migrates to the interlayer within 600 ps. This process, and subsequent irreversible changes in crystal chemistry, may represent a limiting step in multi-electron chemistry including water oxidation and environmental carbon cycling.

[1] Marafatto, F. F.; Strader, M. L.; Gonzalez-Holguera, J.; Schwartzberg, A.; Gilbert, B.; Pena, J., Rate and mechanism of the photoreduction of birnessite (MnO_2) nanosheets. *Proc Natl Acad Sci U S A* **2015**.