

**MARAFATTO Francesco Femi (2017) : The photoreduction of  $\delta$ -MnO<sub>2</sub>**

**Abstract**

Layer manganese(III,IV) oxides are amongst the most reactive transition metal oxides in surface environments. The high reactivity of these minerals towards sorption and oxidation of many organic and inorganic compounds arises from their high specific surface area and density of sorption sites, as well as from the high redox potential of the Mn(III,IV)/Mn(II) couples. Because of these mineral properties, Mn is linked to the biogeochemical cycle of carbon and many trace elements.

The reactivity of birnessite essentially depends on its structural and chemical stability. In particular, the dissolution of these minerals occurs through the reduction of Mn(III,IV), with the potential to mobilize associated compounds. One of the pathways for Mn oxide reduction in surface environments is photoreductive dissolution, a process in which sunlight initiates the electron transfer that leads to reductive dissolution of the mineral. Although this process is predicted to occur, it has never been observed in a system without components that themselves react to light. Therefore, the intrinsic photoreactivity of birnessite minerals in an environmental system lacks experimental evidence.

The objective of this dissertation was to identify the effect of visible light irradiation on the stability of  $\delta$ -MnO<sub>2</sub>, a fully oxidized synthetic birnessite. The rate and mechanism of photoreduction in aqueous mineral suspensions were determined by combining the rates measured on laboratory-based photoreactors with the molecular scale insights on electron transfer dynamics provided by pump-probe optical and synchrotron based techniques. The experiments were initially carried out in simple system containing only the mineral and water at a fixed pH. We then included the effect of environmentally relevant parameters, such as solution pH and the presence of the redox-inactive trace metal Ni(II) adsorbed onto the surface, on the photoreduction of birnessites. Our results show that irradiation of  $\delta$ -MnO<sub>2</sub> results in the formation of Mn(III), which is stabilized against chemical re-oxidation by migrating in the interlayer. The migration of Mn(III) to the interlayer is pH dependent, with a greater rate at lower pH. Furthermore, the higher amount of Mn(III) stabilized at low pH is also able to compete with Ni(II) adsorbed onto the surface by driving previously adsorbed Ni to solution.

The results from this dissertation provide experimental evidence to the thermodynamic predictions on the intrinsic photoreactivity of birnessite minerals, allowing us to predict the stability of Mn oxides in sunlit surface environments even in the absence of organic and inorganic electron donors. Furthermore, birnessite minerals have been studied recently as viable cost-effective candidates in water oxidation photocatalysis. Our results on the role of Mn(III) may be relevant to the material sciences community, providing better constraints for the design of efficient photoelectrocatalysts for water oxidation.