



Application for beam time at ESRF – Experimental Method

This document should consist of a **maximum of two A4 pages** (including references) with a minimal font size of **12 pt**.

Proposal Summary (should state the aims and scientific basis of the proposal):

The goal of this project is to investigate the effect of light on the structure and reactivity of metal-doped MnO₂ nanosheets (birnessite) by coupling wet chemical investigations with X-ray absorption spectroscopy (XAS). We hypothesize that birnessite photoreactivity will be modified by doping the mineral with transition metals. Because the band gap of semiconducting minerals such as MnO₂ is generally reduced upon metal doping, we expect that the rate of Mn(IV,III) photoreduction will be enhanced by Ni²⁺ (redox inert) and Co³⁺ (redox active) sorbed on the mineral surface. In addition, we expect that any changes in the photoreduction mechanism between un-doped and doped minerals may be manifest as changes in the mineral structure (probed by Mn K-edge XAS) or surface speciation of the sorbed metals (probed by Ni and Co K-edge XAS). The results from this study will provide a mechanistic understanding of the effect of sorbed metals on the photoreduction of MnO₂, an important chemical process both in environmental and catalytic systems.

Scientific background:

Layer-type Mn oxide nanosheets (birnessite) are among the most widespread Mn minerals in the environment. Due to their high redox reactivity and high sorption capacity, birnessite minerals play a crucial role in the biogeochemical cycle of carbon, trace metals, and organic contaminants⁽¹⁾. Manganese oxides are also known to have semiconducting properties, whereby visible light can promote electronic transitions. As a consequence, the photoreductive dissolution of MnO₂, which leads to the accumulation of Mn(III, II) in the environment, is an important geochemical process⁽²⁾. The photoreduction of Mn(IV,III) is also relevant to water oxidation catalysis and solar energy harvesting^(3, 4).

Although the photoreductive dissolution of Mn oxides is recognized to be an important process, very few mechanistic studies have been carried out to date. For instance no information is available on the effect of mineral structure and chemical composition on the rates of MnO₂ photoreduction. Moreover, the photochemistry of metal-doped Mn oxides has never been investigated. A recent study by our group measured the efficiency and timescales of Mn(IV) photoreduction by band gap excitation in aqueous suspensions of δ -MnO₂ nanosheets⁽⁵⁾. Based on both ultrafast optical and X-ray transient absorption spectroscopy, we found that 400 nm light promotes the reduction of Mn(IV) to Mn(III), with subsequent migration of Mn(III) from the MnO₂ sheet to the interlayer region, and formation of a Mn(IV) vacancy underneath. The migration of Mn(III) to the interlayer promotes greater sheet stacking along the crystallographic *c*-axis. In the absence of exogenous electron donors, the accumulation of Mn(III) in the interlayer may reduce further photoreduction of Mn in the nanosheets.

In natural settings, birnessite minerals accumulate a wide range of trace metals by adsorbing them at Mn(IV) vacancy sites or particle edges^(1, 6-8). Nickel and Co^(6, 8) serve as good probes of birnessite structure and reactivity: Ni forms triple corner sharing (TCS) complexes above Mn(IV) vacancy sites or becomes incorporated in the octahedral sheets⁽⁶⁾, whereas Co(II) can be oxidized by Mn(III/IV) and subsequently become incorporated into a Mn(IV) vacancy as Co(III)⁽⁷⁾. Sorbed metal species can also modify the mineral's electronic structure, creating new electronic states that narrow the band gap and thus increase photoreactivity. Thus, we expect the adsorbed or incorporated metals will enhance birnessite photoreduction rates, with the effect dependent on the sorption mechanism and electronic configuration of the sorbed species. In addition, the photoreduction of MnO₂ may induce changes in the structure and composition of the mineral phase, and thus in the average surface speciation of the sorbed metals.

Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc):

Metals will be adsorbed (48 h) onto MnO₂ nanosheets (δ -MnO₂) in the dark at pH 6.5 (pH STAT) and with 10 mM NaCl as the background electrolyte to achieve surface loadings of 3% and 10% on a Mn molar basis. After washing by centrifugation and resuspending in 10 mM NaCl, the suspension will be divided into two aliquots, one will be kept in the dark and the other will be irradiated by 400 nm light for 72 h. Before and after light irradiation, samples will be collected for analysis of total and aqueous metal concentrations (ICP-OES) and Mn(III) content, which will be quantified colorimetrically by extraction with sodium pyrophosphate. After 36 and 72 h of irradiation solids will be collected onto a filter membrane for XAS analysis.

The experiments with Ni-doped MnO₂ (Ni-MnO₂) will be used to investigate whether new reactive sites are generated upon light irradiation and whether these sites are located at Mn(IV) vacancy sites or particle edges, as inferred from changes in the average Mn and Ni bonding environments, which will serve as direct and indirect probes of mineral structure, respectively. The experiments with Co-doped MnO₂ (Co-MnO₂) will be used to investigate whether the presence of Co(III), by acting as an electron acceptor for MnO₂, decreases the net rate of birnessite photoreduction. Additionally, Co and Mn K-edge XAS will be used to determine if the average surface speciation of Co and the local structure of MnO₂ change as a consequence of photoreduction. X-ray absorption spectra will be measured from doped and un-doped minerals, both exposed to light and kept in the dark. A cryostat will be required to carry out measurements at 77 K to reduce beam damage to the sample, as well as a fluorescence detector for measurement of low Ni and Co loadings.

Beamline(s) and beam time requested with justification:

The proposed experiments require information on the speciation and local coordination environment of Mn, Co and Ni, with a level of detail that can only be obtained through XAS. At ESRF, the beamlines with XAS capabilities include BM01B, BM23 and ID26. A total of 25 experiments will be carried out, with 25 measurements on the Mn K-edge, 10 on the Co K-edge and 10 on the Ni K-edge. Considering an approximate of 30 minutes per scan and a minimum of 4 scans for sufficient statistics at the Mn K-edge, 5-7 scans on the Ni/Co K-edge, and additional time for changing samples, we are requesting 15 shifts of beamtime.

Results expected and their significance in the respective field of research:

The experiments proposed herein will confirm whether metal sorption increases the photoreduction rate of MnO₂, and how this process changes in the presence of redox active (Co) or redox inert (Ni) transition metals. Moreover, we have proposed previously that photoreduction results in the formation of Mn(IV) vacancies upon Mn(III) migration to the interlayer. This observation will be confirmed by an increase in Ni sorption at vacancy sites in light irradiated Ni-MnO₂ versus dark controls. Additionally, we expect that photoreduction of Co-MnO₂ will result in a decrease in incorporated Co and increase in Co sorbed at Mn(IV) vacancies. These results will allow us to better constrain both the effect of sorbed metals on the photoreactivity of MnO₂ (expanding our proposed model for MnO₂ photoreduction), with important implications on the fate and mobility of trace metals associated with Mn oxides in sunlit aquatic environments.

References

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- ³ R. K. Hocking *et al.*, *Nature chemistry* **2011**, 3, (6), pp. 461-466.
- ⁴ N. Sakai *et al.*, **2005**, 109, (19), pp. 9651-9655.
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