

# Using XAS to Understand the Formation, Structure, and Reactivity of Microbially Formed Mn Oxyhydroxides in Acid Rock Drainage Environments

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## Introduction

We have been using x-ray absorption spectroscopy (XAS) to evaluate two linked projects evaluating biominerals and metal behavior. Mn oxyhydroxides have been identified as key metal sorbents associated with microbial biofilms in an acid rock drainage (ARD) environment [1]. The biofilm-associated Mn oxyhydroxides are microbially formed, extremely fine-grained, and a key metal sequester, despite being a trace constituent of the bulk geochemical media. Wet geochemical analyses indicate that as much as 75% of the metals retained within these biofilm materials are directly associated with amorphous Mn oxyhydroxides. Cr is exclusively associated with the amorphous Mn oxyhydroxides and may be directly implicated in microbial formation of these biogenic Mn oxides. In contrast, Ni and Co also show high affinity for the biofilm organic matrix. We also observe that the biofilm Mn oxide pool undergoes diurnal dissolution and nocturnal formation over a 24-hour period, leading to significant fluctuations in the metals associated with these oxides. By using micro x-ray fluorescence (micro-XRF), we hope to resolve both the oxidation states of the elements involved and identify the types of surface complexes and precipitates/co-precipitates from these natural biofilm samples.

In our second XAS project, we have evaluated the structure and Ni scavenging behavior of synthetic Mn oxyhydroxides, variably, hydrologically conditioned. An important question that has not been addressed in the literature is the potential changes that might occur in mineral crystallinity and/or surface characteristics, given the amorphous nature and small size commonly observed for natural particles, which make them susceptible to changes in a variety of environmental conditions, such as water content, redox state, and temperature. The results of these two projects are keys to understanding the stability of the priority contaminants with respect to changing geochemical conditions and to developing bioremediation strategies that incorporate these microbial processes.

## Methods and Materials

In our biofilm study, our primary objective is to correlate Cr, Ni, Co, and Mn oxide distributions in biofilm samples that were collected on both seasonal and 24-hour timescales. Sample preparation reflects these objectives; the effects of high matrix Fe fluorescence were minimized by preparing <30- $\mu$ m-thick, micropolished thin sections of the natural biofilms adhered to glass slides. Additionally, use of laterally resolved micro-XRF will permit characterization of Ni partitioning within the biofilms.

The focus of the laboratory study was to quantitatively examine the influence of variable hydrologic conditions on the mineralogy, particle morphology, surface characteristics, and sorptive capacity of synthetic Mn oxyhydroxides (HMO) under three differing hydrologic regimes: (1) wet, freshly precipitated, amorphous HMO (wet); (2) dried HMO (dry); and (3) cyclically wet and dry exposed HMO (cycle). Ni sorption to the hydrologically conditioned HMO (wet, dry, and cycle) was examined at pH 2.0, 4.0 and 6.5, in batch experiments and by extended x-ray absorption fine structure (EXAFS) (10 mmol Ni<sup>2+</sup>, 0.250 g HMO dry weight).

## Results and Discussion

### *Biofilm Samples*

Initial characterization of biofilm thin sections (top 1 mm, collected two times per day at 7 a.m. and 7 p.m.) by using APS beamline 13-ID for micro-XAS has indicated that two Mn end-members occur in the biofilms: a mixed Mn(II/III-IV) phase and a Mn(II) sulfide. The particles of Mn are distinct from those of Fe, typically very small (<5  $\mu$ m) and heterogeneous. Cr was observed to be associated with the Mn(II/III-IV) end-member particles, consistent with the geochemical data, and supporting Cr redox coupling to Mn in these biofilms (Fig. 1) [2]. Small particle size and particle heterogeneity in the oxidation state, however, resulted in low reproducibility in the spectra generated, precluding exact characterization of the suite of Mn phases present. Future analyses will resolve the Mn end-members and evaluate diel and depth variation in biofilm Mn oxyhydroxide dynamics.

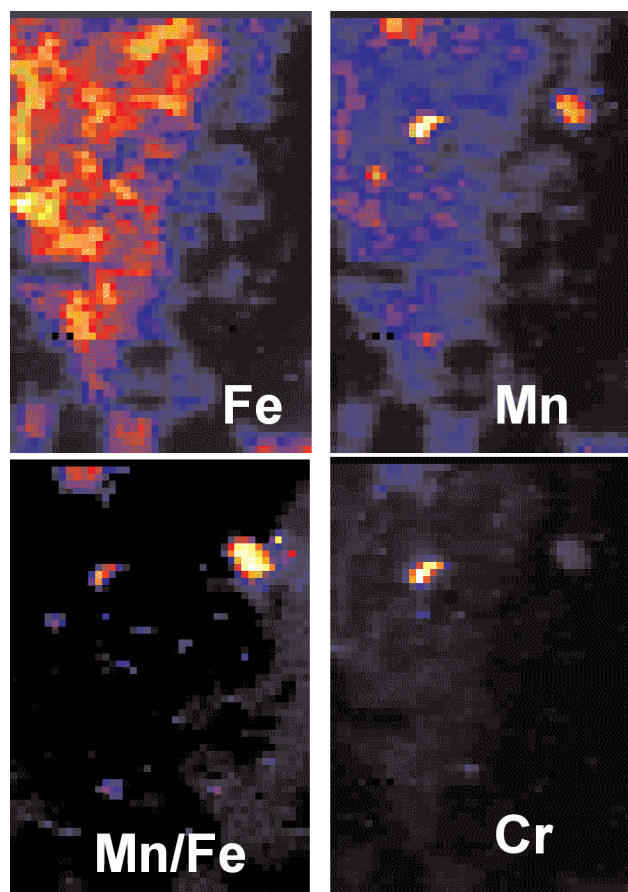


FIG. 1. Fe, Mn, Mn/Fe, and Cr elemental maps of biofilm samples by x-ray fluorescence microprobe (beamline 13-ID, APS). Results indicate that discrete hot spots of Mn occur, often overlapping Cr distribution. Preliminary x-ray absorption near-edge structure (XANES) indicates the presence of both reduced and oxidized Mn, as well as Cr III ( $200 \times 300 \mu\text{m}$  XRF maps).

### Synthetic Mn Oxyhydroxides

Significant differences in Ni sorptive capacity were not observed among the hydrologic treatments at pH 2.0, whereas at pH 4.0, the dry treatment sorbed significantly more than the other two treatments, reflecting the lower pH zero point of charge (ZPC) of the dry HMO compared to the other two treatments [3]. Ni sorptive capacity did not increase between pH 4.0 and 6.5, since all  $\text{Ni}^{2+}$  added was sorbed at pH 4.0. Mn K-edge EXAFS indicated that the pristine HMO samples were all birnessite-like: layer structures with few layer vacancies. The bulk oxidation state of HMO samples was determined to be 3.7 by using XANES spectra for model Mn compounds and the oxalate method; thus, Mn(III) could represent as much as 30%

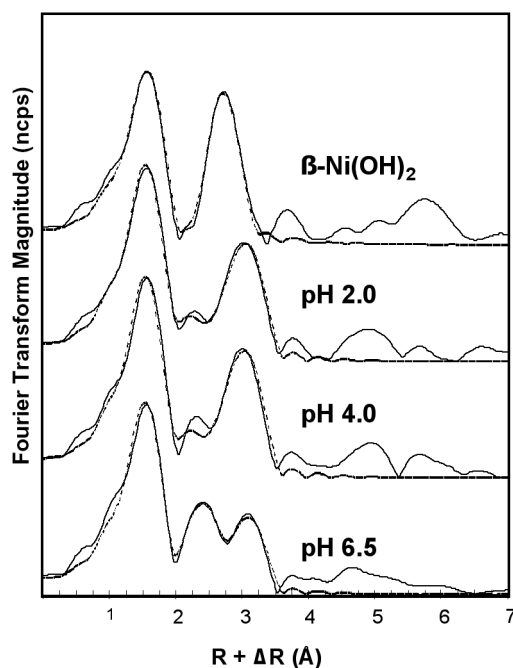


FIG. 2. Fourier transform magnitude of Ni dry HMO samples compared to  $\text{Ni}(\text{OH})_2$  standard. In all samples, the first peak indicates that Ni is octahedrally coordinated by six oxygen atoms. At pH 2.0 and 4.0, the second peak in the spectrum at  $\sim 3.1 \text{ \AA}$  (not corrected for phase shift [ncps]) corresponds to Ni-Mn corner-sharing distances. Approximately six Mn atoms surround the Ni at this distance, indicating that Ni is bound as an inner-sphere complex above/below a layer vacancy. At pH 6.5, there are two peaks due to neighboring cations. The peak at  $\sim 2.4 \text{ \AA}$  corresponds to Ni-Mn edge-sharing distances, suggesting that Ni substitutes for Mn in the  $\text{MnO}_6$  layer structure. The peak at  $\sim 3.1 \text{ \AA}$  again corresponds to Ni bound above/below layer vacancies.

of the Mn in the pristine HMO. Ni K-edge EXAFS indicated that at all pH values examined, Ni was octahedrally coordinated (by about six nearest oxygen neighbors) and sorbed in the interlayer above/below the vacant-layer octahedral sites, as a tridentate corner-sharing interlayer complex (Fig. 2). At pH 6.5, Ni also formed an edge-sharing complex, suggesting that it was substituted for Mn in the HMO layer structure (Fig. 2). These results show that while hydrologic treatment will affect the absolute amount of Ni sorbed to HMO, the crystallographic binding site is affected not by hydrologic treatment but by pH [4].

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