

The Importance of Manganese Sulfide Oxidation in Chromium Contaminated Sediments

Chromium (Cr) exists mainly under two oxidation states in natural sediments: chromium three and chromium six. The latter form of chromium is highly mobile and toxic, causing cancer, liver damage, and other health issues. Cr(III), conversely, is less toxic and forms relatively stable compounds. Studies have shown that this oxidation is slow with oxygen, but occurs faster when manganese is the oxidant, particularly manganite (MnOOH), a manganese three oxyhydroxide.¹ One potential source of a significant amount of this Mn(III) is the oxidation of manganese monosulfide (MnS). Therefore, I studied the reaction of MnS with oxygen and attempted to detect a Mn(III) byproduct via two approaches: 1) in-situ measurements, as the oxidation is occurring; 2) X-ray absorption spectroscopy (XAS) measurements of solid precipitates.

I first needed to design an experimental setup that would allow me to control the oxidation of MnS while simultaneously taking meaningful data of the reactions taking place. I used an airtight reaction cell with a removable lid that had five ports, providing the ability to insert a variety of apparatuses, such as a pH probe, without exposing the solution to air. I began my MnS oxidation experiments by adding 100 mL of a 5mM NaCl solution to the sealed reaction cell and bubbling it with zero grade, wet nitrogen gas to remove all the oxygen from solution and create an anoxic condition. I used a 5mM NaCl solution to replicate the ionic strength of the buffer solutions in order to make accurate pH calibrations and measurements. After a half-hour of N₂ bubbling to ensure that the solution is anoxic, green MnS powder was added to the cell very quickly, to minimize the solution's exposure to oxygen. The pH of solution was measured and recorded every 30 seconds. The solution was stirred vigorously under anoxic conditions until the pH stabilized, indicating complete dissolution of MnS. Then, the reaction cell was opened to expose the solution to the air and allow for oxidation. Once this step occurred, there was about a 0.3 increase in pH for about five minutes, and then it began to increase. This interesting change in pH suggests either an oxidation of Mn(II) to Mn(III), a reduction of S²⁻, or a combination of the two. It is unlikely that this peak in pH represents direct oxidation of Mn(II) to Mn(IV) because that would produce an increase in protons, and therefore a decrease in pH.

In an attempt to directly detect the presence of Mn(III) species, sodium pyrophosphate (PP) was added to the NaCl solution. Pyrophosphate (P₂O₇⁴⁻) is supposed to form a stable complex with Mn(III) that has a red color with a peak absorbance of 480nm. However, absorbance measurements unexpectedly decreased over time instead of increasing. In fact, without PP, as MnS oxidizes, it changes color from green to brown. With PP, though, the solution changed from green to colorless. After closer inspection of previous studies with PP and Mn(III), manganese oxides were used instead of manganese sulfides. Therefore, I hypothesized that the sulfides were inactivating the complex. To test this, I conducted the same experiment three more times, but replaced MnS with another Mn(III) compound that is lacking the sulfide component: Mn(III) acetyl-acetate. After waiting for it to dissolve, HNaS was added in excess (and under a hood) to examine how the addition of sulfides affected the complexation of PP with Mn(III). Unfortunately, this compound has a very low solubility constant, and many undissolved

particles colored the solution and interfered with absorbance measurements. Despite the lack of quantitative measurements, I analyzed the change in color of the solutions qualitatively, and I observed a similar change from brown, the initial color of the Mn(III) acetyl-acetate, to colorless. Therefore, this can be an indication that, as the Mn(II) oxidizes to Mn(IV), the PP complexes with Mn(III) intermediates, preventing it from fully oxidizing to the brown Mn(IV). Once the sulfides are added, it reacts with the Mn(III)-PP and inactivates the formation of the measurable red color. These experiments with PP could be additional evidence for the presence of Mn(III)

Finally, precipitates from oversaturated MnS oxidation were analyzed with X-ray absorption spectroscopy (XAS) with synchrotron radiation from the Advanced Photon Source (APS) at Argonne National Laboratory. The XAS technique utilizes high-energy X-rays at an element-specific wavelength to probe samples. As the X-rays strike the element of choice – in this case Mn – its core electrons will be ejected and backscattered by surrounding atoms, producing a characteristic absorption spectrum indicative of the speciation of the Mn. Precipitates from an oversaturated MnS oxidation experiment were collected on 0.2 micron filters and various times throughout the reaction, creating a time series of the oxidation process. These filters were then placed under the X-ray beam at the DND-CAT sector of the APS for XAS analysis. The X-Ray Absorption Near-Edge Structure (XANES) of the spectra were compared to the Mn 2+, 3+, and 4+ reference spectra. As the oxidation progresses, the spectra shows a shift from Mn(II) to Mn(III) and finally to Mn(IV).

In conclusion, the presence of Mn(III) byproducts from MnS oxidation has been suggested through direct pH measurements of the reaction and a time-series XAS spectra analysis. I also determined that PP cannot be used to identify Mn(III) from MnS oxidation, potentially because of sulfide chemistry. However, there is still more work that needs to be conducted before the presence of Mn(III) can be confidently identified. First, more XAS analysis must be performed. More XAS experiments should be run in order to determine whether the results are reproducible. It would be ideal if the oxidation experiments were run at the APS and samples were analyzed immediately after collection to minimize excess oxidation. Additionally, the sulfide chemistry is complex and needs to be studied further to determine its role in this reaction. It is crucial to study these types of reactions in order to better understand sediment chemistry, assess the toxicity of contaminated aquatic systems, and improve overall environmental health.

Sources

- 1) Johnson, C. A. and A. G. Xyla (1991). "THE OXIDATION OF CHROMIUM(III) TO CHROMIUM(VI) ON THE SURFACE OF MANGANITE (GAMMA-MN₂O₃·nH₂O)." Otero, X. L., T. O. Ferreira, et al. (2009). "Geochemistry of iron and manganese in soils and sediments of a mangrove system, Island of Pai Matos (Cananeia — SP, Brazil)." *Geoderma* **148**: 318 - 335.