

The Importance of Manganese Sulfide Oxidation in Chromium Contaminated Sediments By Michael Giannetto

In natural sediments, chromium (Cr) exists mainly under two oxidation states: chromium three and chromium six. The latter form of chromium is more mobile and more toxic, causing cancer, liver damage, and other health issues. In fact, Erin Brockovich famously exposed a natural gas company for polluting drinking water with Cr(VI), leading to the largest legal settlement in US history. Cr(III), conversely, is less toxic and an essential nutrient for metabolism at trace concentrations.¹ As a result of the contrasting characteristics of these two types of Cr, it is critical to understand the cycle between Cr(III) and Cr(VI) when assessing chromium pollution. In aquatic sediments, the conversion of Cr(III) into Cr(VI) is mediated by the presence of manganese oxyhydroxides (MnOOH). I will therefore study how this compound can be formed from the oxidation of manganese sulfide in order to assess its importance in chromium cycling in sediments.

Previous research on chromium-contaminated sediment from Baltimore Harbor, Maryland has shown that Cr(VI), when released into the environment, will quickly be reduced to Cr(III) in the presence of an anoxic, reducing environment that is typically found beneath sediment-water interfaces.² Once in the form of Cr(III), the metal is less soluble and will remain in the sediment where it is considered to be relatively harmless. However, the sediment is not a stable environment, and resuspension can be caused by storms, anthropogenic activities such as boating, and bioturbation from bottom-dwelling organisms. Once resuspended, the Cr(III)-containing sediment will be exposed to oxic conditions and could potentially be oxidized to toxic Cr(VI).³ See **Appendix A** for a basic diagram of Cr cycling in sediments and **Appendix B** for a more complete diagram of metal diagenesis. 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.⁴ One potential source of a significant amount of this Mn(III) is the oxidation of manganese monosulfide (MnS), and therefore it is the focus of my research.

Initially, most of the literature on Mn diagenesis has argued that MnS will not be present in most natural sediments because it is orders of magnitude more soluble than iron sulfides (e.g., FeS, Fe₃S₄, FeS₂). Since iron is frequently more abundant than Mn in sedimentary environments, it is thought that the iron will precipitate with any sulfides present in the sediments before Mn. Therefore, very limited research has been conducted on this presumably rare compound. According to the solubility products, MnS would only form if Mn concentrations were significantly higher than iron concentrations.^{5,6,7,8} Interestingly though, this condition seems to be met in Baltimore Harbor where researchers at Johns Hopkins University are studying chromium contamination, therefore suggesting the presence of MnS.⁹ MnS was additionally detected at significant levels at the site of a former Naval Air Station at Alameda, California, despite the low Mn concentrations in the sediments with respect to iron. The formation of MnS may in fact be more common than originally expected, and it may play a more significant role in the diagenesis of metal contaminants, including Cr.^{10,11} Therefore, I want to study the oxidation of MnS and attempt to detect Mn(III) oxides that will rapidly oxidize Cr(III) to Cr(VI).

I plan to use synchrotron radiation at the Advanced Photon Source (APS) at Argonne National Lab to conduct X-ray absorption spectroscopy (XAS) experiments to determine Mn coordination and speciation. 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

project it is Mn – its core electrons will be ejected and backscattered by surrounding atoms, producing a characteristic absorption spectrum. Manganese sulfide and manganese oxide compounds each have a unique spectrum, which have been measured by previous researchers.^{10,11} By comparing the spectra of my samples with the previously determined characteristic spectra, I should be able to determine the composition of my samples, which will contain the byproducts of MnS oxidation. My advisor, Professor Jean-Francois Gaillard, and his lab have been allotted time to use the XAS beam line DND-CAT at the APS for the week of December 5th, and he has given me permission to analyze my samples during this time.

Before going to the APS, however, I must run MnS oxidation experiments, take samples of this oxidation over time, and preserve the samples properly until XAS analysis. First, I need to ensure that the commercially bought MnS samples in the lab are in fact MnS and have not begun to oxidize. I plan on analyzing this commercially purchased MnS with the X-ray diffraction (XRD) facilities at Northwestern, which are commonly used to determine sample crystal structure and content. If these samples prove to be contaminated with other compounds, then I will have to search for another MnS chemical manufacturer or precipitate the MnS myself. Once I am certain I have pure manganese monosulfide samples, I will then design an experimental setup that will allow me to control the oxidation of MnS and also take samples over time in order to collect intermediate species. To preserve the samples and prevent further oxidation, I will store them in an anaerobic chamber in Professor Gaillard's lab. I will also use inductively coupled plasma (ICP) analysis to determine the total dissolved Mn concentration in my samples to compare them with the results from XAS. I plan to have samples ready for the December 5th XAS beam time, allowing me to focus on data analysis during winter quarter. Yet, if complications arise and my experiments are delayed, then may also have to use additional beam time at the end of winter quarter.

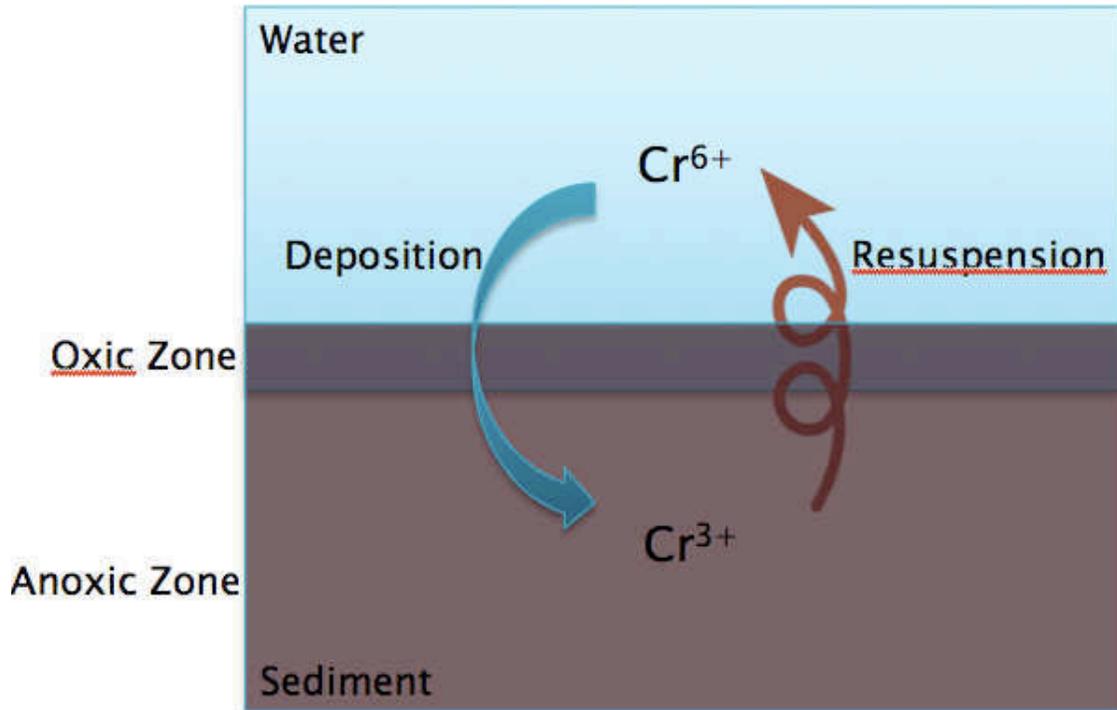
I have been working in Professor Gaillard's aquatic geochemistry lab as a research assistant since spring quarter of 2010 with graduate students Luciana Zanella and Brooke Jarrett, so I am very familiar with the lab's equipment and safety protocols. I have used the ICP-AES many times and I am very comfortable analyzing samples with this machine. I also have spent many hours working in the anaerobic chamber and maintaining its anoxic condition through catalyst rejuvenation. This past summer, I visited Argonne twice with my lab, so I have already received the required user badge and safety training to access the APS facilities. Although I have never analyzed XAS data before, I understand the process fairly well and I am confident that I can learn with the help of Cecile Cadoux, a post-doctoral associate in our lab who has had extensive experience with XAS analysis and with whom I have worked with before. I currently have no experience with XRD, but I will register for the necessary safety and training courses in order to learn how to operate the equipment and properly analyze its data.

I will use this research to write a senior honors thesis at the end of the school year, and I will create a poster to present my results at the Undergraduate Research Symposium. I am applying to PhD programs in environmental engineering for next year, and having first-hand experience in conducting my own research and writing a thesis will make me a more competitive candidate and prepare me for my future work.

References

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Appendix A: Basic Diagram of Chromium Cycling in Sediments



Appendix B: Diagram of General Metal Diagenesis in Sediments.

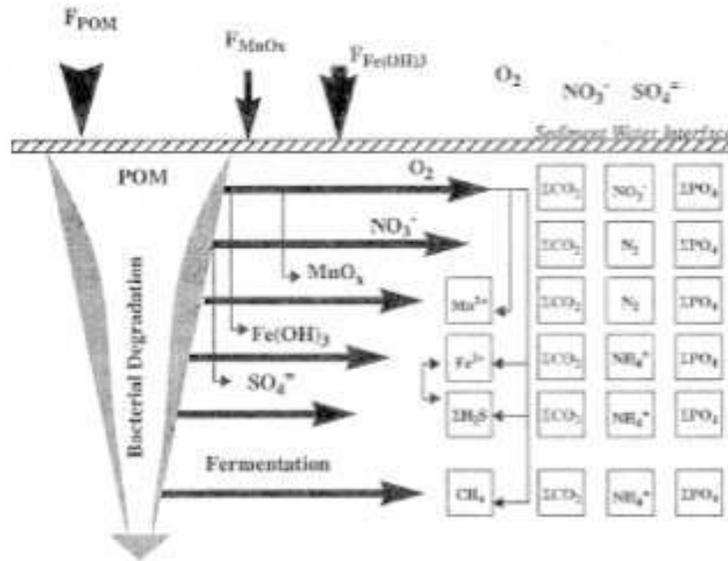


Fig 1: Schematic Diagram of the sequence of early diagenetic reactions occurring in surficial sediments. F_x represents the fluxes of the chemical species x reaching the water interface under particulate form, and POM the Particulate Organic Matter. The arrows indicate that the soluble by-products can diffuse in the porous medium and be re-oxidized in presence of electron acceptors (e.g. O_2).

Source:

Gaillard, J.-F. (1994). "Early diagenetic modeling: A critical need for process studies, kinetic rates, and numerical methods." *Trends in Chemical Geology* **1**: 239-252.