

**Manganese: Minerals, Microbes, and
the Evolution of Oxygenic
Photosynthesis**

Thesis by
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ABSTRACT

Oxygenic photosynthesis fundamentally transformed our planet by releasing molecular oxygen and altering major biogeochemical cycles, and this exceptional metabolism relies on a redox-active cubane cluster of four manganese atoms. Not only is manganese essential for producing oxygen, but manganese is also only oxidized by oxygen and oxygen-derived species. Thus the history of manganese oxidation provides a valuable perspective on our planet's environmental past, the ancient availability of oxygen, and the evolution of oxygenic photosynthesis. Broadly, the general trends of the geologic record of manganese deposition is a chronicle of ancient manganese oxidation: manganese is introduced into the fluid Earth as Mn(II) and it will remain only a trace component in sedimentary rocks until it is oxidized, forming Mn(III,IV) insoluble precipitates that are concentrated in the rock record. Because these manganese oxides are highly favorable electron acceptors, they often undergo reduction in sediments through anaerobic respiration and abiotic reaction pathways.

The following dissertation presents five chapters investigating manganese cycling both by examining ancient examples of manganese enrichments in the geologic record and exploring the mineralogical products of various pathways of manganese oxide reduction that may occur in sediments. The first chapter explores the mineralogical record of manganese and reports abundant manganese reduction recorded in six representative manganese-enriched sedimentary sequences. This is followed by a second chapter that further analyzes the earliest significant manganese deposit 2.4 billion years ago, and determines that it predated the origin of oxygenic photosynthesis and thus is supporting evidence for manganese-oxidizing photosynthesis as an evolutionary precursor prior to oxygenic photosynthesis. The lack of oxygen during this early manganese deposition was partially established using oxygen-sensitive detrital grains, and so a third chapter delves into what these grains mean for oxygen constraints using a mathematical model. The fourth chapter returns to processes affecting manganese post-deposition, and explores the relationships between manganese mineral products and (bio)geochemical reduction processes to understand how various manganese minerals can reveal ancient environmental conditions and biological metabolisms. Finally, a fifth chapter considers whether manganese can be mobilized and enriched in sedimentary rocks and determines that manganese was concentrated secondarily in a 2.5 billion-year-old example from South Africa. Overall, this thesis demonstrates how microbial processes, namely photosynthesis and metal oxide-reducing metabolisms, are linked to and recorded in the rich complexity of the manganese mineralogical record.

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Chapter 1

THE SOLAR SYSTEM

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Introduction

The invention of oxygenic photosynthesis was difficult – it only occurred once relatively late in Earth history – and yet the oxygen this metabolism released fundamentally and forever changed our planet. The emergence of oxygen altered the biogeochemical cycles of iron, sulfur, carbon, nitrogen, and manganese, and transformed the fitness landscape for life - laying the foundations for the evolution of complex multicellularity. Manganese is critically important for the functioning of oxygenic photosynthesis, and thus the history of manganese is linked to one of the most pivotal evolutionary innovations on ancient Earth. Manganese oxides are also uniquely sensitive as proxies for ancient oxygen, and thus the geologic record of manganese offers compelling insights into both the history of environmental oxygen and oxygenic photosynthesis.

The use of manganese in oxygenic photosynthesis and its specific reactivity with oxygen stem from the thermodynamic properties of manganese. Manganese has a very high reduction-oxidation (or redox) potential, and consequently the only common environmental oxidants that can oxidize manganese are oxygen and oxygen-derived products like superoxide (Figure 1). Its redox potential and multiple stable redox states also make it an ideal cofactor for oxygenic photosynthesis: four manganese atoms in the water-oxidizing complex each donate an electron to Photosystem II, building oxidizing potential until they can split water and generate an O-O bond to form O₂. The integral

role of manganese in water oxidation forms the basis of an evolutionary hypothesis that manganese-oxidizing photosynthesis was a transitional step between anoxygenic photosynthesis (PSI, RCI, RCII in Figure 1) and high-potential oxygenic photosynthesis (PSII in Figure 1).

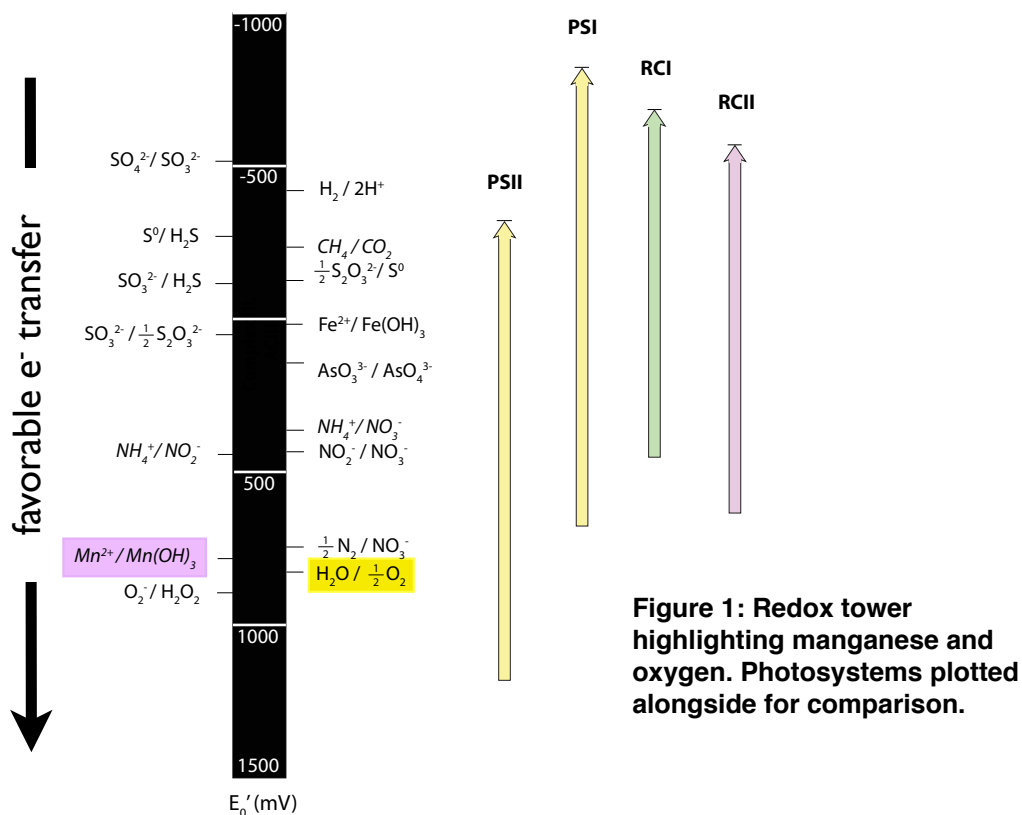


Figure 1: Redox tower highlighting manganese and oxygen. Photosystems plotted alongside for comparison.

Manganese has a further advantage: the dominant way for manganese to become concentrated in the sedimentary record is through oxidation, which requires oxygen or a high-potential photosystem to be present. So the presence of manganese oxides in the rock record can be understood as proxies for either oxygen or high-potential phototrophy using a photosystem oxidizing manganese (Figure 2). Without either of these two oxidation sources, manganese enters the fluid Earth from weathering of igneous rocks or

hydrothermal sources as Mn^{2+} and remains as an aqueous cation. The main sink for reduced manganese is substitution for calcium in carbonates, and this does not form a significant manganese enrichment (Figure 2).

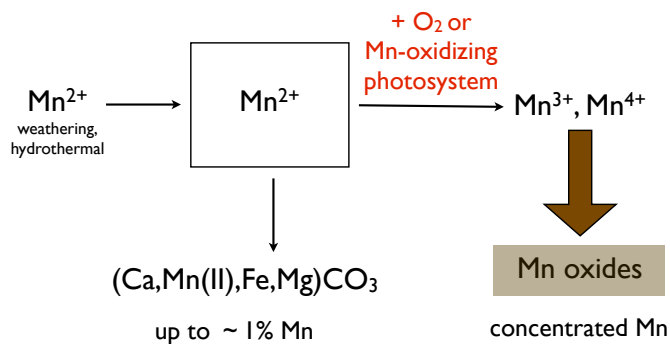


Figure 2: Schematic representation of manganese redox cycle, including how manganese enters the sedimentary record.

There are several potential problems with this simplified manganese model. Post-depositional processes (diagenesis) often affect the chemistry of sediments as they become lithified into a sedimentary rock, and the high redox potential of manganese makes manganese oxides an especially susceptible phase for diagenesis. Manganese oxides are highly favorable and reactive electron acceptors for a variety of organic carbon species, sulfur species, and iron species (Figure 1). Studying the geologic record of manganese therefore first requires an understanding of how diagenesis affects original deposits of manganese precipitates. Another potential complexity, especially important in very ancient sedimentary rocks, is that inferring manganese oxidation from manganese concentrates in the rock record only is accurate if manganese cannot enter the rocks another way. Secondary introduction of manganese needs to be always considered as an alternative hypothesis, and careful analysis is required to resolve whether manganese is

from original sedimentary processes or later introduction via metamorphic and metasomatic processes.

To study manganese in ancient, complicated rocks, we developed a multi-faceted approach applied throughout this dissertation. Inductively-coupled plasma mass spectrometry assessed bulk manganese concentrations. Synchrotron X-ray spectroscopic imaging and X-ray absorption spectroscopy were used to measure and map Mn redox and mineralogical state on a micron-scale. Textural relationships between mineral phases were established to understand relative timing of different manganese-bearing minerals using optical and electron microscopy, secondary ion mass spectrometry, and Raman spectroscopy. These whole-rock and *in-situ* techniques were all highly complimentary and proved essential to understanding the diagenetic history of the manganese minerals in ancient sediments.

The following dissertation focuses on how manganese minerals in the rock record can be proxies for diverse microbial processes, including photosynthesis and microbially-mediated manganese oxide reduction during diagenesis. Chapter 1 reviews the current literature on the various ways manganese can be oxidized and reduced, and presents a compilation of manganese-enriched sedimentary rock deposits ('manganese deposits') through geologic time. Selected manganese deposits were interrogated for manganese mineralogy and redox state, and these results led to a model proposing the mineralogical

changes induced during the diagenesis of manganese oxides. Chapter 2 employs South African drill cores obtained by the Agouron Drilling Project to investigate a hypothesis from evolutionary biology that Mn-oxidizing photosynthesis was a precursor to oxygenic photosynthesis. The cores had evidence of primary manganese oxides but two lines of evidence indicated oxygen was not present, and thus this manganese deposit is geologic evidence for a transitional Mn metabolism predicted by modern biology. One key observation to constrain oxygen levels here was redox-sensitive detrital pyrite, and so in Chapter 3 we expanded upon our findings and added the presence of a second oxygen-sensitive mineral, uraninite, and constructed a mathematical model to quantify the oxygen levels implied by these grains. Results from six ancient manganese deposits, presented in Chapter 1 and Chapter 2, all indicated that manganese is reduced during diagenesis, potentially via microbially-mediated mechanisms. These results inspired Chapter 4, in which a flow-through system at the synchrotron was developed to measure the phase transitions and mineralogical products during bacterial and abiotic manganese reduction. Chapter 5 returns to scrutinize the assumptions made in Figure 2 and uses a natural laboratory of correlated strata throughout South Africa that have seen dramatically different levels of heat, pressure, and hydrothermal fluids (i.e., metamorphism). Manganese concentrations increased and mineral speciation changed with increasing metamorphism, suggesting manganese can be mobilized and enriched by post-depositional processes but this can be understood using texture-specific techniques.