MANGANESE OXIDATION IN A NATURAL MARINE ENVIRONMENT- SAN ANTONIO BAY

A Thesis

by

ROSEMARY OGHENEOCHUKO NEYIN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Approved by:

Chair of Committee,	Michael Tice
Co-Chair of Committee,	Heath Mills
Committee Member,	Bruce Herbert
Head of Department,	Rick Giardino

May 2013

Major Subject: Geology

ABSTRACT

In the modern ocean, manganese is oxidized over a timescale of days. To better understand the mechanisms and driving factors for manganese oxidation in the natural environment, experiments were performed with surface water samples collected from the San Antonio Bay. In this study area, the formaldoxime assay was utilized to determine that manganese oxidation is catalyzed via multiple pathways utilizing various catalysts and proximal oxidants. The contribution of catalysts such as colloidal matter, microorganisms and the proximal oxidant superoxide were investigated in the San Antonio Bay. The study suggests that superoxide contributed about 30% of Mn oxidation. The microorganisms and colloids were equal in terms of catalysis and accounted for approximately 100% of Mn oxidation. This study is important because gaining more understanding on the mechanisms by which Mn is oxidized will contribute to its use as a geochemical redox indicator.

DEDICATION

To God and my family who made this possible.

ACKNOWLEDGEMENTS

I would like to thank my chair Michael Tice, my co-chair Heath Mills and committee member Bruce Herbert for their guidance and support throughout the course of my graduate program.

Thanks to Jian Gong, Ray Zeng and Gregory Neyin for their help in acquiring my samples for this research. Also, to the members of Team Tice and the staff and faculty of the Geology and Geophysics department, thank you for making graduate school a period filled with interesting experiences.

Finally, thanks to my parents, siblings and friends for their financial, emotional and spiritual support over the years.

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

Page

INTRODUCTION

Manganese (Mn) is a metal with the common oxidation states of +II, +III, +IV, +VI and +VII. Mn^{2+} is the reduced form of Mn and can be oxidized to any higher oxidation state, but Mn^{4+} is the most stable form first achieved (Stumm and Morgan 1996; Armstrong 2008). Mn^{3+} is a transitional/ metastable state that persists in nature before being further oxidized to the stable form of Mn^{4+}, which has also been described as a thermodynamic sink (Hem and Lind 1983; Stumm and Morgan 1996; Armstrong 2008). Mn oxides are found in the geologic record associated with other metal oxides such as iron (Fe) and cerium (Ce) (Braun et al 1990; Moffett 1990; Stumm and Morgan 1996). Iron oxides do not serve as a good indicator of oxygen in past environments since they can also be found in the top section of anoxic sediments (Berner 1981), while Mn oxides are only present in oxic conditions (Thamdrup et al 1994; Stumm and Morgan 1996).

Mn oxidation has been observed in various settings such as freshwater lakes (Chapnick et al 1982) and marine environments (Wollast et al 1979; Burdige and Gieskes 1983; Tebo and Emerson 1986). In general, environmental metal oxidation has two components: (1) a proximal oxidant such as oxygen or superoxide (Learman et al 2011), and (2) a catalyst such as a biological enzyme or a mineral surface (Froelich et al 1979; Stumm and Morgan 1996; Learman et al 2011). Mn oxidation has been attributed to a direct reaction with oxygen, microbial activity either directly via enzymatic catalysis

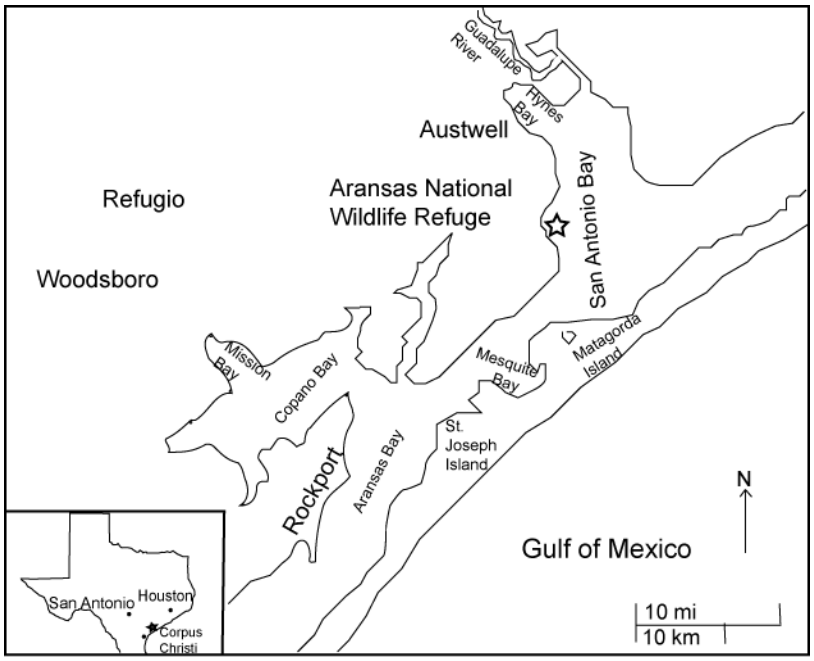
(Chapnick et al 1982; Diem and Stumm 1984; Nealson et al 1988; DePalma 1993; Stumm and Morgan 1996; Brouwers et al 1999) or by reaction with superoxide (Learman et al 2011), and autocatalytic reaction with Mn (IV) oxides (Coughlin and Matsui 1976; Stumm and Morgan 1996).

Microbially mediated oxidation of Mn has also been associated with Ce oxidation (Moffett 1994). Ce oxidation was observed using radioactive ^{139}Ce marker to trace the oxidation of Ce from Ce^{3+} to Ce^{4+} and the uptake of Ce onto filterable particles, while Mn oxidation was also occurring resulting in Mn oxide nodules containing Ce oxides (Elderfield and Greaves 1982; Braun et al 1990; Moffett 1990). Ce is a rare earth element (REE) that, unlike most REEs, participates in oxidation/ reduction reactions. The reduced form of Ce (Ce^{3+}) is soluble in water but upon oxidation to Ce^{4+}, it forms an insoluble oxide (cerianite, CeO_2) (Elderfield and Greaves, 1982; Braun et al, 1990). It has been suggested that Ce and Mn oxidation proceed via the same pathway, and each one competitively inhibits the oxidation of the other via kinetic competition (Moffett, 1994). Moffett (1994) suggests that Ce^{3+} and Mn^{2+} compete reversibly for a catalytic site but that once oxidized, Ce^{4+} could irreversibly bind to the reaction site.

Mn oxidation has been proposed as a critical geochemical tracer of oxygen in past environments (Kopp et al 2005). Mn oxides are only found in oxygenic conditions; as such their presence is an indicator of oxic conditions (Thamdrup et al 1994) Therefore, it is important to understand the importance of the various identified pathways by which Mn^{2+} is oxidized in natural systems. The purpose of this project is to determine the relative contributions of various catalysts and proximal oxidants, many of which were previously identified only in enrichment cultures or pure cultures, in fluids collected from a natural marine setting. The questions to be addressed for this environment are: (1) can Mn^{2+} be oxidized over a timescale of days in surface waters of the San Antonio Bay, Texas; (2) is Mn oxidation catalyzed by microorganisms, colloidal matter, mineral surfaces, or all three; and (3) is superoxide a significant proximal oxidant?

STUDY AREA

The area chosen for this study was located in the Aransas National Wildlife Refuge (ANWR) in San Antonio Bay, southeast Texas (Fig.1). The bay receives freshwater from the Guadalupe River and the San Antonio River. A local subenvironment was selected in order to maximize the likelihood of sampling from an active metal cycling profile (Wollast et al 1979; Klump and Martens 1981; Sunda et al 1983). Low energy environments with abundant sedimentary organic matter may produce steep environmental gradients between shallow reducing sediments and an oxidizing surface (Klump and Martens 1981), and thus have the potential to support active Mn redox cycling. Therefore, a low wave energy site dominated by fine-grained sediment, lacking visible sedimentary bedforms, and containing visible decaying organic matter coating the sediment surface was selected.



28°17′32.55″N, 96°48′33.63″W

Figure 1. Study Area in ANWR, San Antonio Bay, Texas. Sampling was performed in shallow water (30cm) within 5 m of the shore in a relatively protected, low energy environment (map modified from google maps).

METHODS

Microcosm experiments were performed to compare the reaction of Mn in fluids collected from the San Antonio Bay with their reaction in experimentally treated fluids. To test for biological catalysis of Mn oxidation, a comparison was made with microcosms containing experimentally sterilized fluids. Surface catalysis of Mn^{2+} oxidation by particulates was tested by microcosms that had particulates experimentally removed via prefiltration. To test for superoxide as the proximal oxidant of Mn, a comparison was made with samples from which superoxide had been scavenged.

Unfiltered water samples were collected in January in the morning above the sediment surface in 2 L autoclaved acid-washed polycarbonate bottles at a water depth of 30 cm. Ambient air temperatures during the week of collection ranged from 14- 23ºC. The bottles were wrapped in foil and transported to the lab on ice. Microcosms were set up in triplicate in autoclaved, acid-washed 50 mL polycarbonate conical tubes and amended with 100μM $MnCl_2$, with or without other metals or superoxide dismutase as described below. All experiments were performed at 23°C in the dark to prevent photoreduction of Mn oxides (Sunda et al 1983). Each tube was shaken vigorously by hand for 4 seconds prior to and after sampling for Mn measurements.

To estimate the abundances of particulate Mn, samples collected for measurement from each microcosm were split; half were processed unfiltered, and half were passed through a 0.2 μm filter (Tebo et al 2007). In the event that different treatments potentially affected more than one factor in each experiment, two different sets of treatments were crossed (Table 1). The first set was designed to affect microorganisms, particulates and colloidal oxides by physical removal or disruption. The second set was designed to add kinetic competition for catalytic sites or to remove superoxide via filtration (Table 1).

Physical Treatments

Prefiltration: Samples were passed through a 0.2 μm filter that eliminated microorganisms, colloidal matter and particulates greater than 0.2 μm in size. Colloids range in diameter from 0.001- 1μm (Krumbein and Sloss 1963), hence, prefiltration removed only the coarsest colloids.

Autoclave sterilization: Samples were heat-sterilized by autoclaving for 20 minutes at 121ºC. This treatment also potentially stimulated the oxidation of dissolved metals present before Mn amendation.

UV irradiation: Samples were UV-sterilized by exposure to 3.2 $\mu W/cm^2$ UVC under a Philips TUV 30W/G30 T8 mercury lamp for 11 hours. This not only eliminated microorganisms but also caused the dissolution of colloidal matter(Sunda et al 1983,

Stumm and Morgan 1996), which was confirmed visually by a reduction in the turbidity of the sample.

Chemical Treatments

Superoxide scavenging: Superoxide dismutase scavenges for superoxide by catalyzing the dismutation of superoxide to hydrogen peroxide and oxygen. A concentration of 5 μM of superoxide dismutase (from bovine erythrocytes, Sigma Aldrich) was added to specific microcosms (Learman et al 2011). Cu^{2+} was also added in superoxide experiments to scavenge for superoxide, and Zn^{2+} was added as a negative control because it has similar charge and ionic radius to Cu^{2+} but lacks superoxide scavenging activity.

Ce addition: A total of 100 μM of $CeCl_3$ was added to compete with Mn^{2+} for a catalytic sites on particle surfaces or organisms.

Cu addition: A total of 100 μM of $CuSO_4$ was added to specific microcosms. Cu^{2+} not only scavenges superoxide, but could also compete with Mn^{2+} for a catalytic site on mineral surfaces or organisms.

Table 1: Treatments. Key: microorganisms (m); particulates (p); oxides/ colloids (o); superoxide (s); competition (c)

Treatments	Control	+ Ce	+ Cu	+ Ce + Cu
	M P O S C	M P O S C	M P O S C	M P O S C
Control	+ + + +	+ + + + +	+ + + ?	+ + + +
Prefiltered (p^-, m^-)	+ +	+ + +	+ ?	+ +
Autoclaved (m^-)	+ + +	+ + + +	+ + ?	+ + +
UV irradiated (m^-, o^-)	+ +	+ + +	+ ?	+ +

Manganese Colorimetric Test

The formaldoxime assay was used to estimate total Mn abundances (dissolved and suspended particulate) (Goto et al 1962, Brewer and Spencer 1971, Armstrong et al 1979). The formaldoxime assay as described below was assembled from Brewer and Spencer (1971) with modifications from Goto et al, (1962), and Armstrong et al, (1979).

Formaldoxime: To make the formaldoxime reagent, 2 g of hydroxylamine hydrochloride and 1 mL of formaldehyde solution (37%) were combined in a beaker and diluted to a total volume of 50 mL using nanopure water. To make the formaldoxime mixture buffered with ammonium hydroxide prior to taking measurements, 10 mL of the

formaldoxime reagent was combined with 4 mL of NH_4OH. This was made on the same day the measurements were taken since it degrades after 24 hours. The EDTA solution consisting of 1.3 g of Mg EDTA and 30mL nanopure water and 10% hydroxylamine hydrochloride solution were also prepared. In a cuvette, 1 mL of the sample to be tested was added to 85.5 μL of the formaldoxime-NH_4OH and mixed well. After 3 minutes, 50 μL of the EDTA solution and 100 μL of the hydroxylamine hydrochloride solution were added. After 10 minutes, the absorbance was measured at 450 nm. The presence of Mn was indicated by a positive formaldoxime color change from clear to a deep purplish orange. Oxidized Mn abundances were estimated by filtering the samples with a 0.2 μm filter to measure the soluble Mn fraction (Mn^{2+}, dissolved and fine colloidal Mn), and then comparing it to the unfiltered formaldoxime assay which represented the total Mn concentration in the microcosm (Goto et al 1962, Brewer and Spencer 1971, Armstrong et al 1979, Tebo et al 2007). The filterable Mn fraction is the difference between the dissolved/ fine colloidal matter and the total Mn.

RESULTS

The water samples were collected at a water depth of 30 cm at approximately 5-10 cm above the sediment surface. When samples were initially collected, they were turbid with suspended sediment and the water itself was a light tan color. The coarsest suspended particles were allowed to settle prior to division of samples into microcosms.

Superoxide Treatments

Oxidation of Mn occurred in many treatments and was evidenced by decreasing soluble Mn concentrations and increasing filterable Mn abundances.

Mn oxidation was observed in the untreated microcosms over approximately two days, while prefiltration eliminated oxidative activity in the superoxide treatments. Addition of Cu and Zn reduced Mn oxidation by 83%. In the presence of superoxide dismutase (SOD), a total of 30% less Mn was oxidized when compared to the control (Fig 2). In the presence of microorganisms, superoxide and colloids greater than 0.2 μm, Cu and Zn inhibited the loss of Mn from solution (Fig. 2A).

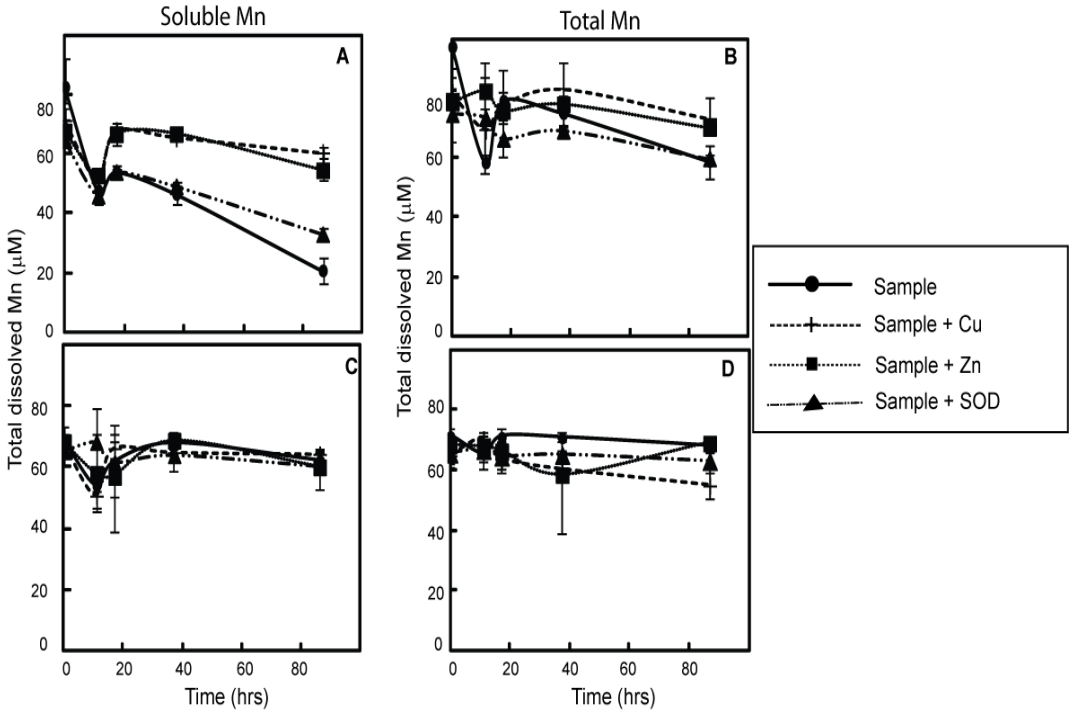


Figure 2. Superoxide Experimental Results. (A) Control of soluble Mn. (B) Control of total Mn. (C) Prefiltered sample of soluble Mn. (D) Prefiltered sample of total Mn. Measurement at the 10th hour showing a decrease in Mn concentration are likely erroneous due to prolonged sample processing time.

Fine sediments/ precipitates that accumulated on the walls and base of all tubes amended with Mn during the experiment were confirmed to be Mn bearing via acid digestion and formaldoxime tests. This accumulation is consistent with decreases in total Mn concentrations observed in all the microcosms (Fig. 3).

Control Treatments

Mn oxidation is evident when comparing the soluble Mn in Fig. 3A to the total Mn concentration in Fig. 3 B. Ce and Cu treatment effects are evident by day 5 based on the concentration of soluble Mn remaining. By day 5, the microcosms containing the sample and Mn had oxidized 70% of the total Mn while the microcosm with only Cu had oxidized 47%, Ce had oxidized 32% and the combination of Cu and Ce had oxidized 51% of the total Mn (Fig. 3 A & B).

Prefiltered Treatments

Prefiltered treatments with added Ce and Cu exhibited slower Mn oxidation rates than the controls by day 10 (Fig 3 A & C). The microcosm containing only Mn had 91% of the soluble Mn oxidized (Fig 3 C). The microcosms containing Cu oxidized 48% of the soluble Mn, the Ce microcosms oxidized 75% of the total Mn and the microcosms containing Cu and Ce oxidized 74% of the total Mn (Fig 3 C).

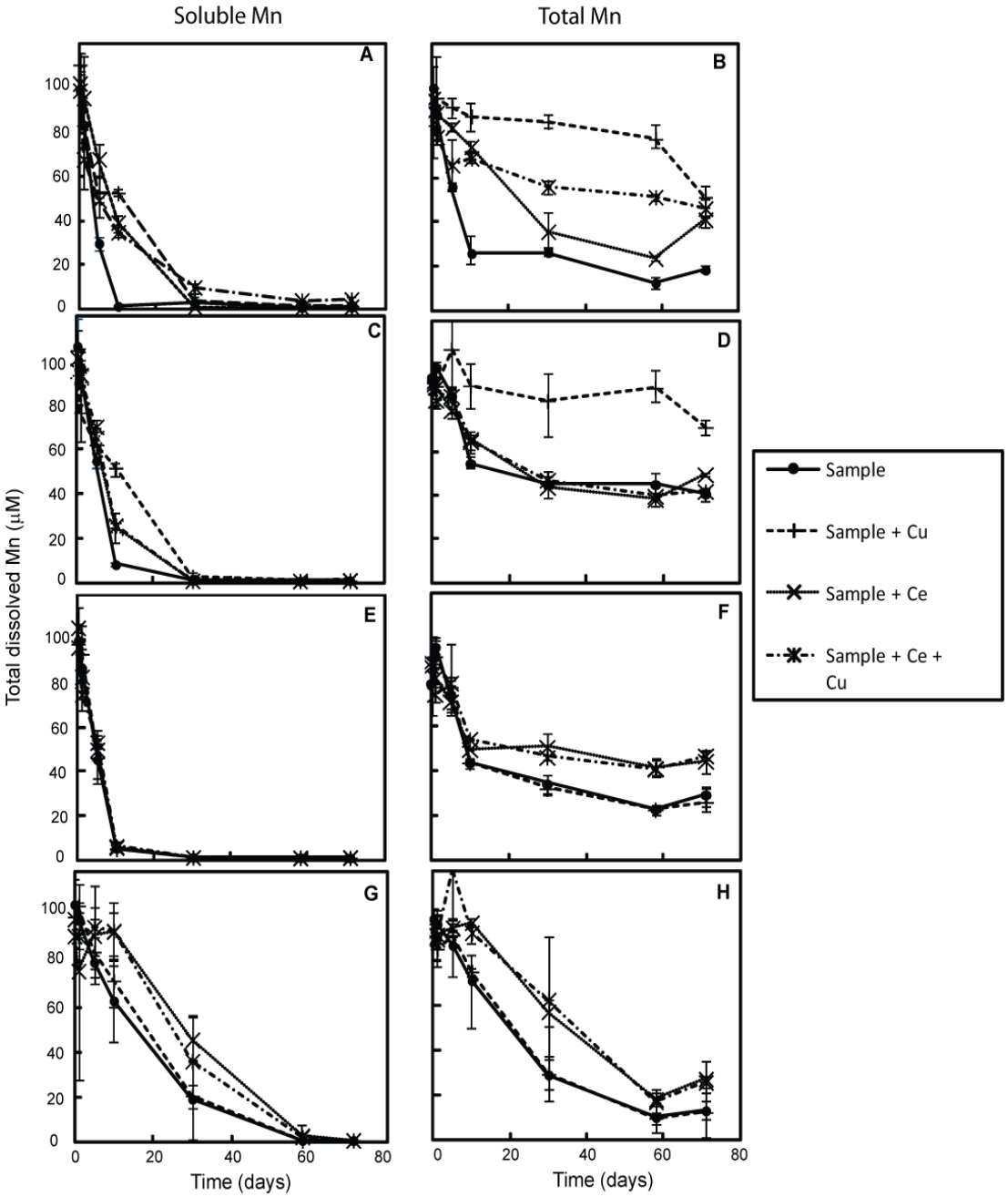
Autoclaved Treatments

Mn oxidation is observed in the autoclaved treatments (Fig. 3 E and 3 F). Over 90% of the soluble Mn was oxidized by day 10. All the soluble Mn graphs in the autoclaved microcosms overlapped.

UV Treatments

An initial lag is observed at the beginning of the experiment indicating a delay before Mn oxidation began (Fig. 3 G). Ce reduced oxidation rates by day 10. The UV microcosm containing Cu was similar to the UV microcosm containing only Mn, while the microcosm containing Ce and Mn was similar to the UV microcosm containing Ce, Cu and Mn.

Figure 3. Catalyst Experimental Results. (A) Control treatment exhibiting Ce and Cu effects which slow down the rate of Mn oxidation. (B) Control treatment exhibiting loss of total Mn suggests formation of larger particles and Mn binding to tube walls and base. (C) Prefiltered treatment of soluble Mn exhibiting Ce and Cu effects. (D) Total Mn of Prefiltered samples exhibiting a delay in the removal of total Mn from solution which suggests the inital formation of smaller Mn particles. (E) Soluble Mn of autoclaved treatments with no Ce or Cu effect. (F) Autoclaved treatments exhibiting loss of total Mn. (G) Soluble Mn concentrations of UV treatments exhibiting Ce and Cu effect. (H) Total Mn concentrations of UV treatments.


Soluble Mn
Total Mn
A
B
C
D
E
F
G
H
Total dissolved Mn (μM)
Time (days)
Time (days)
Sample
Sample + Cu
Sample + Ce
Sample + Ce + Cu

DISCUSSION

Based on the average temperature of the study area ranging between 14- 23ºC, the experiments were incubated at 23ºC.

Superoxide plays a role as a proximal oxidant of Mn in the microcosms since superoxide dismutase (SOD) slowed down Mn oxidation by 30% (Fig 2 A). Zn and Cu both inhibited the loss of Mn from the microcosms.

Rate Constants

Monte Carlo simulations were performed to compare Mn oxidation rates normalized to Mn abundances using a pseudo first order rate model:

$$C = (C_0 - C_\infty)e^{-rt} + C_\infty$$

Three hundred simulated data sets were generated for each treatment assuming observed means, standard deviations and normal distributions at each time step. Each resultant data set was fit by the first order rate model. The mean, 2.5 and 97.5 percentile values of the fitted first order pseudo rate constants (r) and asymptotic final concentrations (C_∞) were calculated. Treatments that did not fit the first order model are not reported here.

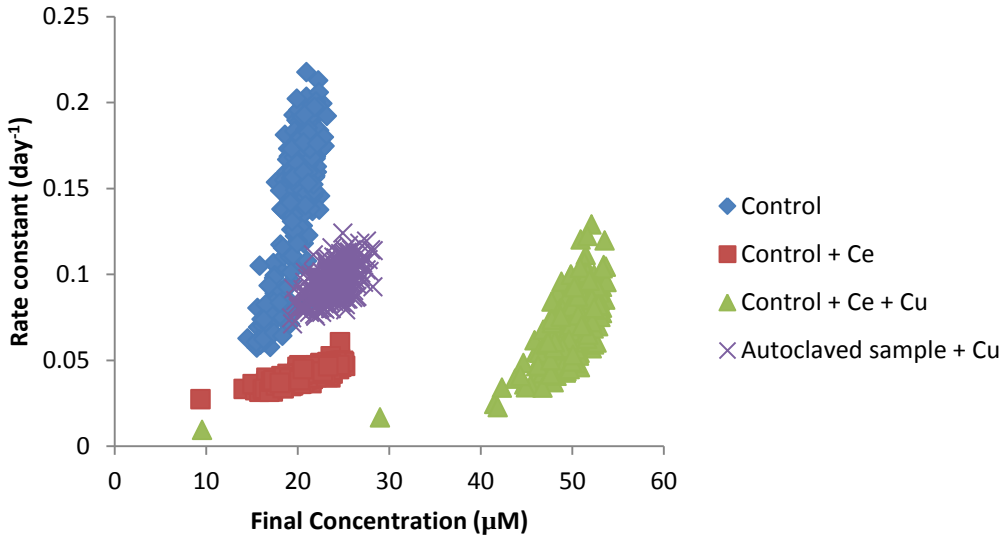


Figure 4. Monte Carlo Results Showing the Distribution of the Total Final Mn Concentrations and Rate Constants.

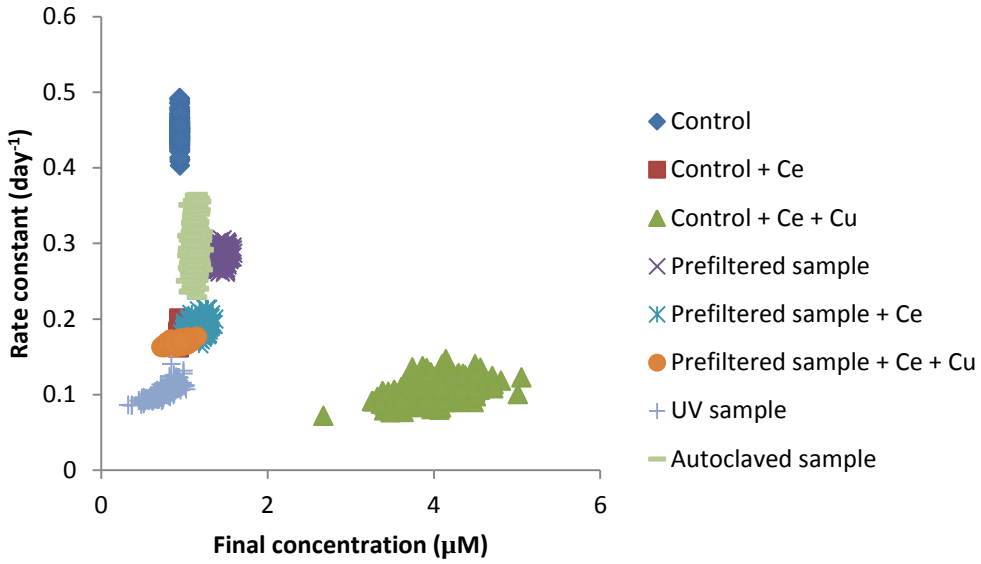


Figure 5. Monte Carlo Results Showing the Distribution of the Soluble Mn Final Concentrations and Rates.

Rate constants for loss of soluble Mn were greater than rate constants for loss of total Mn (Figs. 4 and 5). This implies growth in the suspended particulate Mn fraction throughout each treatment or possible assimilation into cells. However, the amount lost to assimilation into cells is not known.

Table 2. Estimated Rate Constants and Final Concentrations for Soluble Mn

Treatments	Rate (day^{-1})	$C_\infty(\mu M)$
Sample	0.45 (+0.05/-0.04)*	0.95 (+.006/-.003)*
Sample + Ce	0.18 (+0.014/-0.013)	0.94 (+0.002/-0.003)
Sample + Ce + Cu	0.11 (+0.041/-0.033)	4.102 (+0.96/-0.8)
Prefiltered sample	0.28 (+0.025/-0.021)	1.44 (+0.18/-0.15)
Prefiltered sample + Ce	0.19 (+0.03/-0.02)	1.16 (+0.17/-0.23)
Prefiltered sample + Ce + Cu	0.17 (+0.008/-0.006)	0.93 (+0.24/-0.19)
UV sample	0.103 (+0.04/-0.02)	0.78 (+0.34/-0.43)
Autoclaved sample	0.287 (+0.08/-0.053)	1.125 (+0.094/-0.099)
* Error estimates indicate 95% confidence intervals		

Microorganisms

Addition of Ce and Cu to the control microcosms resulted in a slower rate of Mn oxidation. Sterilization of the microorganisms via autoclaving decreased Mn oxidation by 36% ± 19% when compared to the control (Table 2). The UV treatment in which the microorganisms were eliminated and the colloidal matter was dissolved had the slowest rate of Mn oxidation by 77 % ± 9.26 % in comparison to the control (Table 2). Decreases in oxidation rates resulting from Ce and Cu addition in control microcosms but not in autoclaved microcosms suggest that much of this effect is the result of inhibition of a biological process. It is possible that Ce and Cu competed with Mn for enzymatic binding sites or that both metals were toxic to the relevant microbial populations.

Particulate Matter

Within the reproducibility of these experiments, the rate at which Mn was oxidized in the autoclaved microcosms was similar to that of the prefiltered microcosms (Table 2). The major difference between these two treatments was the presence of particulate matter with diameter >0.2 μm in the autoclaved microcosms. Therefore, there was no measureable effect of the presence of particulate matter on the rate at which Mn oxidation proceeded.

Colloids

Since particulates do not contribute significantly to Mn oxidation in the microcosms, colloids dominate Mn oxidation in the autoclaved microcosms. Colloids, therefore, oxidize Mn 36% ± 19% less than the control (Table 2).

Although UV treatment was designed to remove both microorganisms and colloids, the observation of a Ce treatment effect in these microcosms suggests that the microbial populations were not completely sterilized. Oxidation rates in the UV treated microcosms were the slowest observed in this study, consistent with suppression of both colloids and microorganisms. However, the rate at which Mn is oxidized cannot be specifically attributed to either catalyst. The apparent initial lag in the UV treated microcosms could be a result of the delayed recovery of the microbial population.

The loss of Mn from the initial concentration observed via the formaldoxime assay indicates Mn oxidation with an unknown fraction assimilated into biomass. The initial rate at which Mn oxidation occurred in the control was the fastest out of all the microcosms due to biological processes/ products, superoxide and colloids in the control. This was further stimulated by the autocatalytic effect of Mn oxides once the oxides were formed. Slowest reduction rates were observed in microcosms that removed or

suppressed both microorganisms and colloids. Colloidal matter and microorganisms each account for about 30% to 40% of the Mn oxidation observed.

Mn oxidation was slower in all Ce treatments except for the autoclaved treatments. However, final concentrations were similar. The fact that the final concentration does not change in the presence of Ce suggests that any competition for catalytic sites between Mn^{2+} and Ce^{3+} is reversible.

CONCLUSION

Mn was oxidized over a timescale of days in surface waters collected from San Antonio Bay, Texas. Mn oxidation was catalyzed by microorganisms, and colloids in the samples by similar amounts, and superoxide served as the proximal oxidant in up to 30% of the reaction. Ce^{3+} inhibited Mn^{2+} oxidation in some treatments, and may be especially important in competing reversibly for biological catalytic sites. However, further investigation of this mechanism is required. This can be done via developing better methods of identifying Ce (III) and Ce (IV) (non-oxidized vs. oxidized) in order to quantitatively compare oxidation rates.

This experiment sheds more light on the mechanisms involved in Mn oxidation. Future studies on reduction of Mn could contribute towards the use of Mn oxides as paleoredox indicators of oxygen levels in paleooceans in association with this study. Further investigation is needed to tie this to Ce anomalies and their use as paleoredox indicators.

REFERENCES

Armstrong P.B., Lyons W. B., Gaudette H.E. 1979. Application of Formaldoxime Colorimetric Method for the Determination of Manganese in the Pore Water of Anoxic Estuarine Sediments. Estuaries and Coast 2(3): 198-201.

Armstrong F.A. 2008. Why did Nature Choose Manganese to Make Oxygen? Philosophical Transactions of the Royal Society Biological Sciences 363: 1263-1270.

Berner R.A. 1981. A New Geochemical Classification of Sedimentary Environments. Journal of Sedimentary Petrology 51(2): 0359-0365.

Braun J., Pagel M., Muller J., Bilong P., Michard A., Guillet B. 1990. Cerium Anomalies in Lateritic Profiles. Geochemica et Cosmochimica Acta 54(3): 781-795.

Brewer P.G., Spencer D.W. 1971. Colorimetric Determination of Manganese in Anoxic Waters. Limnology and Oceanography 16(1): 107-110.

Brouwers G., De Vrind J.P.M., Corstjens P.L.A.M., Cornelis P., Baysse C., De Vrind-De Jong E.W. 1999. *cumA*, a Gene Encoding a Multicopper Oxidase, is involved in Mn^{2+} Oxidation in *Pseudomonas putida GB-1*. Applied and Environmental Microbiology 65(4): 1762-1768.

Burdige D.J., Gieskes J.M. 1983. A Pore Water/Solid Phase Diagenetic Model for Manganese in Marine Sediments. American Journal of Science 283: 29-47.

Chapnick S.D., Moore W.S., Nealson K.H. 1982.Microbially Mediated Manganese oxidation in a Freshwater Lake. Limnology Oceanography 27(6): 1004-1014.

Coughlin R.W., Matsui I. 1976. Catalytic Oxidation of Aqueous Mn (II). Journal of Catalysis 41(1): 108-123.

DePalma S.R. 1993.Manganese Oxidation by *Pseudomonas putida.* Ph.D. Dissertation. Harvard University, Cambridge, Mass.

Diem D., Stumm W. 1984. Is Dissolved Mn^{2+} being Oxidized by O_2 in Absence of Mn-bacteria or Surface Catalysts? Geochemica et Cosmochimica Acta 48: 1571-1573.

Elderfield H., Greaves M.J. 1982. The Rare Earth Elements in Seawater. Nature 296: 214-219.

Froelich P.N., Klinkhammer G.P., Bender M.L., Luedtke N.A., Heath G.R., Cullen D., Dauphin P., Hammond D., Hartman B., Maynard V. 1979. Early Oxidation of Organic Matter in Pelagic Sediments of the Eastern Equatorial Atlantic: Suboxic Diagenesis. Geochemica et Cosmochimica Acta 43: 1075-1090.

Goto K., Komatsu T., Furukawa T. 1962. Rapid Colorimetric Determination of Manganese in Waters Containing Iron: A Modification of the Formaldoxime Method. Analytica Chimica Acta 27: 331-334.

Hakuta Y., Hayashi H., Arai K. 2003. Fine Particle Formation using Supercritical Fluids. Current Opinion in Solid State and Materials Science 7: 341-351.

Hem J.D., Lind C.J. 1983. Nonequilibrium Models for Predicting Forms of Precipitated Manganese Oxides. Geochemica et Cosmochimica Acta 47: 2037-2046.

Klump J.V., Martens C.S. 1981. Biogeochemical Cycling in an Organic Rich Coastal Marine Basin-II. Nutrient Sediment-Water Exchange Processes. Geochemica et Cosmochimica Acta 45: 101-121.

Kopp R.E., Kirschvink J.L., Hilburn I.A., Nash C.Z. 2005. The Paleoproterozoic Snowball Earth: A Climate Disaster Triggered by the Evolution of Oxygenic Photosynthesis. Proceedings of the National Academy of Sciences of the United States of America 102(32): 11131-11136.

Krumbein W.C., Sloss L.L.1963. Stratigraphy and Sedimentation. *W.H. Freeman, San Francisco.*

Learman D.R., Voelker B.M., Vazquez- Rodriguez A.I., Hansel C.M. 2011. Formation of Manganese Oxides by Bacterially Generated Superoxide. Nature Geoscience 4: 95-98.

Moffett J.W. 1990. Microbially Mediated Cerium Oxidation in Seawater. Nature 345: 421-423.

Moffett J.W. 1994. The Relationship between Cerium and Manganese Oxidation in the Marine Environment. Limnology Oceanography 39(6): 1309-1318.

Nealson K.H., Tebo B.M., Rosson R.A. 1988. Occurrence and Mechanisms of Microbial Oxidation of Manganese. Advances in Applied Microbiology ADAMAP 33: 279-318.

Stumm W., Morgan J. J. 1996. Aquatic chemistry: chemical equilibrium and rates in natural waters. *John Wiley, New York*.

Sunda W.G., Huntsman S.A., Harvey G.R. 1983.Photoreduction of Manganese Oxides in Seawater and its Geochemical and Biological Implications. Nature 301(20): 234-236.

Tebo B.M., Emerson S. 1986. Microbial Manganese(II) Oxidation in the Marine Environment: A Quantitative Study. Biogeochemistry 2: 149-161.

Tebo B.M., Clement B.G., Dick D.J. 2007. Biotransformations of Manganese Editor(s) Hurst C.J. Manual of environmental Microbiology 3rd edition 1223-1238.

Thamdrup B., Glud R. N., Hansen J.W. 1994. Manganese Oxidation and in situ Manganese Fluxes from a Coastal Sediment. Geochemica et Cosmochimica Acta 58(11): 2563-2570.

Wollast R., Billen G., Duinker J.C. 1979. Behavior of Manganese in the Rhine and Scheldt Estuaries: I. Physico-Chemical Aspects. Estuarine and Coastal Marine Science 9(2): 161-169.