

8-2020

Utilizing manganese and rhenium sediment concentrations to reconstruct past interglacial Southern Ocean circulation changes

Evan E. Rohde

Follow this and additional works at: https://aquila.usm.edu/honors_theses



Part of the [Climate Commons](#)

The University of Southern Mississippi

Utilizing manganese and rhenium sediment concentrations to reconstruct past interglacial
Southern Ocean circulation changes

by

Evan Earle Rohde

A Thesis
Submitted to the Honors College of
The University of Southern Mississippi
in Partial Fulfillment
of Honors Requirements

May 2020

Approved by:

Christopher Hayes, Ph.D., Thesis Adviser
Assistant Professor of Marine Science

Jerry Wiggert, Ph.D., Associate Director
School of Ocean Science and Engineering

Ellen Weinauer, Ph.D., Dean
Honors College

Abstract

The circulation in the Southern Ocean is a component of global nutrient, heat, and carbon cycles. Changes in any of these cycles can dramatically change ocean conditions around the world. Therefore, any changes that occurred to this circulation in the past is of scientific interest. We hypothesize that changes in the glacial cycle of the planet can affect this circulation. Specifically, we hypothesize that the strength of circulation in the Southern Ocean can be reduced by conditions during interglacial, or warm climate, time periods. It is proposed that during the interglacial period of Marine Isotope Stage (MIS) 11 (425 to 375 thousand years ago), there was a reduction to Southern Ocean circulation. This research seeks to assess these proposed circulation changes by chemically analyzing the trace metal concentrations of rhenium and manganese in sediments from the Ocean Drilling Program site 1094. These trace metal containing sediments are located in the Southern Ocean and were deposited during the MIS 11 interglacial. In this research the two trace metals, Re and Mn, are utilized as proxies for indirectly estimating oxygen delivery to the site which can be used to assess the strength of the ocean circulations. The assessment of Southern Ocean circulation allows for additional knowledge that can be used in characterizing past, present, and future ocean conditions.

Keywords: Trace Metals, Marine Isotope Stage 11, Southern Ocean, Ocean Circulation, Sediment Core

Dedication

This body of work is dedicated to Dr. Christopher Hayes and my fellows in the Hayes/Shiller Marine Geochemistry Group in the Department of Marine Science, without who this could not have been accomplished.

Acknowledgements

I would like to acknowledge the data contributions of Samuel Glasscock, Neil Redmond, and Dr. Samuel Jaccard. As well as the boundless patience, time, and funding contributed by Dr. Christopher Hayes. I would also like to acknowledge the contributions of the National Science Foundation grant to Dr. Hayes that made this research possible.

Table of Contents

Abstract	vi
List of Illustrations	viii
List of Abbreviations	iError! Bookmark not defined.
Chapter 1: Introduction	Error! Bookmark not defined.
Chapter 2: Literature Review	3
Trace Metal Analysis	3
Southern Ocean Characteristics	5
ODP Site 1094	9
Chapter 3: Methods	11
Sediment Acquisition	11
Sediment Prepration	11
ICPMS Analysis	12
Chapter 4: Data and Results	13
Detrital Removal Estimation	13
Concentration Changes Through Time	15
Chapter 5: Discussion	19
Chapter 6: Conclusion	21
References	Error! Bookmark not defined.

List of Figures

Figure 1: Southern Ocean Water Masses	6
Figure 2: Ocean Drilling Program Site 1094 Location Map.....	9
Figure 3: Rhenium Detrital Correction	13
Figure 4: Manganese Detrital Correction	14
Figure 5: Uranium Detrital Correction	14
Figure 6: Trace Metal Concentration Plot	17

List of Abbreviations

AABW	Antartic Bottom Water
AMOC	Atlantic Meridional Overturning Circulation
CDW	Circumpolar Deep Water
ICPMS	Inductively Coupled Plasma Mass Spectrometry
MIS	Marine Isotope Stage
NADW	North Atlantic Deep Water
ODP	Ocean Drilling Program
UCC	Upper Continental Crust

Chapter 1: Introduction

Analysis of ocean sediments can give an otherwise unknown look at the past conditions and events that occurred within the ocean. The dynamics of the world's oceans have changed throughout time. These changes occurred from different environmental influences and changes to global conditions. By understanding how ocean dynamics were altered by past changes in environmental conditions, the effects of new environmental changes on the ocean can be better predicted and quantified. One particularly dynamic area in the oceans of the world is the Southern Ocean, surrounding Antarctica. In this region, the world's deep waters are upwelled to the surface and the world's densest bottom water is formed by downwelling, playing a crucial role in air-sea carbon dioxide distribution and therefore global climate (Rintoul, 2018). The large circulation patterns of the Southern Ocean are not unchangeable and can be affected by large environmental changes. A specific event that could have altered these currents in the past is the melting of glaciers and large-scale reduction in ice coverage of the globe during interglacial time periods.

As conditions change in modern times and the world's ice reserves continue to melt, it is important to understand how this large input of fresh water and environmental change will affect the large-scale circulations in the Southern Ocean. By observing if and how these currents were affected and altered during large ice coverage changes and large freshwater inputs in the past, a better understanding of future possible effects can be ascertained. For instance, over the past 500,000 years there have been periodic ice ages, or glacial periods, every 100,000 years or so; in between these ice ages, there have been warm periods, or interglacial periods, similar to today's climate. One way to observe changes to these large-scale circulations is to observe changes in the sediment record during times of known large scale glacial change, specifically during interglacial

time periods. Changes in the strength of circulation patterns in the Southern Ocean would result in a change in the oxygen concentration in sediment pore waters. The pore water oxygen concentrations in turn affect trace metal oxidation states that are recorded in the sediments. Thus, the trace metals can be used as a proxy for past oxygenation and therefore past circulation. Manganese and rhenium are oxidized or reduced under different oxygen levels (Colodner et al., 1993). By observing changes in the concentrations of manganese and rhenium in ocean sediments from an area affected by deep ocean circulation, the changes in oxygen and corresponding changes in circulation strength can be assessed. One such area is the Ocean Drilling Program (ODP) Site 1094 . This site is directly in the path of deep ocean circulation currents in the Atlantic sector of the Southern Ocean and through the ODP, sediment cores from this area were acquired from Marine Isotope Stage (MIS) 11, which covers a prominent interglacial period. MIS 11 is an interglacial period that occurred from 375,000 to 425,000 years ago, where large ocean circulation change may have occurred. This period had a global average temperature approximately 2 degrees Celsius higher than today's and a global mean sea level 6 to 13 meters higher than present (Dutton et al., 2015). It can therefore be hypothesized that a large climatic change such as this would result in a complementary change in the circulations of the Southern Ocean. The goal of this research is to analyze the changes in manganese and rhenium concentration that occur in sediments that were deposited during MIS 11 to gain insight into any oxygen concentration changes during the same period, changes which could denote potential large-scale ocean circulation changes during the modern day time period as well.

Chapter 2: Literature Review

Trace Metal Analysis:

Trace metals in ocean sediments are present at concentrations of parts per billion to parts per million. Trace metals arrive in sediments mainly through two processes. For example, trace metals are added to the sediments through in situ precipitation from seawater, called the authigenic phase, or by deposition from the water column of mineral particles containing the trace elements substituted within mineral lattices, called the lithogenic phase (Morford & Emerson, 1999). In general, it is the authigenic phase of trace metals that is affected by oxygen levels through pore water chemistry and oxidation reduction reactions; the effects of oxygen concentration on various trace metals has been thoroughly investigated (Nameroff, Balistreri, & Murray, 2002). In this study, manganese (Mn) and rhenium (Re) will be utilized to analyze changes in oxygen. This will be accomplished by measuring their sediment concentration changes over time and comparing these fluctuations with the results from another trace metal, authigenic uranium (aU), which was analyzed in a previous study (Glasscock et al., 2020). Authigenic fractions of the measured metals in the present study will be estimated using the element Th, which is known to be only present in lithogenic material in the ocean, with a minimal authigenic phase.

In the case of Re, its authigenic phase forms under suboxic conditions, or conditions of reduced oxygen. Under oxygenated conditions, Re is relatively soluble and the only Re in sediments would be expected to be lithogenic (Morford & Emerson, 1999). The effect of low oxygen concentrations on Mn is the opposite. Authigenic manganese forms (as manganese oxides) under oxygenated conditions, whereas under suboxic conditions Mn is reduced and released back into seawater as dissolved ions (Hulth, Aller, & Gilbert, 1999; Mangini, Jung, &

Laukenmann, 2001). The concentration of aU is affected by oxygen concentration changes in a similar way as Re; when oxygen concentrations are lowered, aU is enriched in the sediments, precipitating out of the surrounding water (Mangini et al., 2001). The comparison of relative concentration changes in Mn and Re can be evaluated and areas of anticorrelation can suggest time periods of coherent oxygenation changes, potentially related to changes in deep water circulation in the Southern Ocean. The role that the anticorrelations play in the comparison of Re and Mn allows for more certainty in these concentration changes being explained by oxygen concentration changes because the oxygen level fluctuations effect the trace metal concentrations in opposite ways.

The amount of biological activity throughout MIS 11 is pertinent to this study because as decaying material falls through the water column it is consumed by organisms. These organisms are undergoing cellular respiration and therefore are utilizing oxygen from the water. A high abundance of these organisms could reduce the dissolved oxygen concentration enough to produce the same effects in the observed trace metal concentrations that a reduction in ocean circulation could produce (Loon, 1985). Therefore, times of high biologic activity must be characterized from the core to avoid data misintepretations. In this study, the barium to iron ratio (Ba/Fe) was used to estimate the amount of biological activity in the region throughout MIS 11. Biogenic barium (in the form of barite, a mineral of barium sulfite) is produced in the water column within microenvironments of sinking organic material (Dymond et al., 1992). The normalization to Fe allows for a reference of relatively stable input of lithogenic Fe to the sediments to qualitatively estimate the input of barium, and therefore organic matter, to the sediments. Biogenic Ba is well-preserved in oxic and suboxic sediments and is only subject to

loss in the sediments if they become sulfate-reducing. These types of chemical reactions are not known to have occurred at ODP Site 1094.

Consistent changes in the concentrations of three oxygen-sensitive elements strongly suggest changes in the levels of oxygen in the sediments and surrounding deep water. This study will observe the changes in oxygen through changes in trace metal concentrations in order to determine if oxygen concentration reductions occurred during MIS 11 and, if so, what phenomenon could explain such an alteration to physical oceanographic processes.

Southern Ocean Characteristics:

The Southern Ocean surrounds the isolated polar continent of Antarctica and, due to this isolation, possesses unique environmental and bathymetric conditions. The Southern Ocean is characterized by several large-scale ocean currents and water masses, distinctive ventilation and carbon sequestration dynamics, and influences on global ocean and atmospheric conditions (Hayes et al., 2014).

A major circulation feature of the Southern Ocean is the Antarctic Circumpolar Current (ACC). This current surrounds and isolates the Antarctic continent, inducing currents within the Southern Ocean that are among the strongest and swiftest in the world. This is due to the unobstructed flow around the South Pole by the ACC which is possible because of the lack of any large land bodies stretching north from the Antarctica continent to block this current. These water currents allow for the propagation of vast quantities of water in the form of several distinct water masses. Chief among these are the North Atlantic Deep Water (NADW), Circumpolar Deep Water (CDW), and Antarctic Bottom Water (AABW) masses. These water masses are responsible for the transport of warm water to the Southern Ocean and the export of nutrient- and

carbon- rich, cold water to the equator from the Southern Ocean. CDW is the mixture of NADW and the deep-water contributions from the Pacific and Indian Oceans, which up-well just south of the polar front in the Southern Ocean. NADW and AABW are downwelling water masses that provide oxygen to global deep water around the world (Hayes et al., 2014). The locations of these water masses can be observed in Figure 1, which refers to the location of the ODP 1094 site.

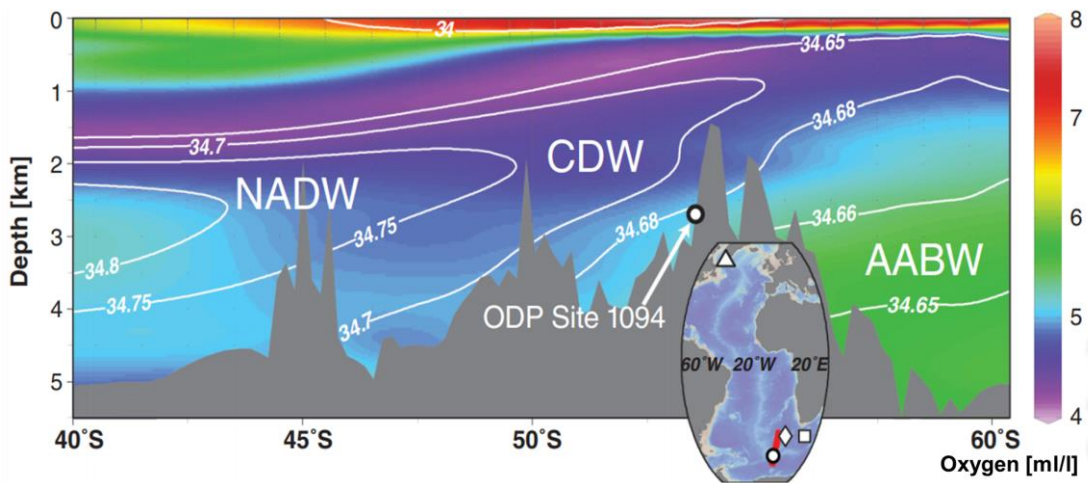


Figure 1: North Atlantic Deep Water, Circumpolar Deep Water, and Antarctic Bottom Water current impacts on ODP site 1094.

Oxygenated waters are important for the survival of any respiring organisms in deep water. Pockets of deoxygenated waters can result in large areas in the ocean that are uninhabitable for these organisms. Large areas of deoxygenated water can be the result of a lack of water mixing. A reduction in the formation of large water masses in the Southern Ocean can result in decreased mixing and stratification of waters, which become stagnant and prevent the movement of nutrient rich cold deep water from the ocean atmosphere interface into deep waters. These deep water masses are formed by the sinking of dense water at the surface of the Southern Ocean. The density of water is determined by two factors, temperature and salinity, with cold, salty water being more dense than warm, fresh water. Changes in temperature and salinity can

prevent surface waters from becoming dense enough to sink and mix through the water column.

This means that waters below the surface are inherently denser than surface waters if the two water masses are of the same salinity. An important factor that impacts the salinity and density of surface waters is the introduction of fresh water through glacial ice melt. The melting of continental ice from the Antarctic can dilute the surface ocean waters; this causes decreased density, which inhibits the formation of the AABW and in turn results in increased stratification.

The waters of the Southern Ocean are also part of the Atlantic Meridional Overturning Circulation (AMOC). The AMOC involves the formation of dense water in the far North Atlantic, which is the source of NADW, the southward return flow of this water mass at depth, and upwelling in the Southern Ocean, fueling in part a surface return flow north to close the Atlantic overturning circuit. Strong AMOC circulation may have led to enhanced upwelling of deep-water masses in the Southern Ocean in the past (Muglia, Skinner, & Schmittner, 2018). This means that old water masses which have been stored in the deep Southern Ocean can be reintroduced into atmospheric interactions, thus ventilating the deep water with oxygen (Klug et al., 2010). During glacial time periods the same deep-water masses, such as AABW and CDW, can directly cause increased carbon sequestration. Carbon, in the form of dissolved inorganic carbon, can be stored in these deep water masses while they are isolated from surface atmospheric interactions. The cold waters of the Southern Ocean are also an effective carbon sink. The cold waters allow for an increased amount of carbon dioxide absorption from the atmosphere and the AMOC pattern allows for the newly absorbed carbon to be drawn down into the deep areas of the Southern Ocean where it is stored (Marshall & Speer, 2012). In this manner, the Southern Ocean can effectively absorb atmospheric carbon dioxide and affect the

overall atmospheric carbon dioxide concentration. This is one of the mechanisms and processes in the Southern Ocean that allows for global atmospheric and oceanic regulation and alteration.

There are several ways the Southern Ocean is integrated into global conditions and cycles. The previously discussed carbon sequestration integrates the Southern Ocean into the world carbon cycle as a large carbon sink. The deep cold water of the Southern Ocean holds and deposits in the deep ocean on a timescale of hundreds to thousands of years. The AMOC pattern moves deep water (NADW) from the North Atlantic to the Southern Ocean where it upwells and the temperature of the water mass is decreased and the water sinks before it moves towards the equator once more as part of the AABW mass, which also carries nutrients northward to equatorial regions of the world. These nutrients support populations of organisms throughout the water column in the southern hemisphere. In many areas of the globe, surface waters can become stratified from deeper areas of the oceans, but in the Southern Ocean large scale vertical mixing allows for the linking of these layers and increases movement of nutrients, heat, and dissolved carbon throughout the ocean. These processes make understanding the interactions and changes in the Southern Ocean paramount to comprehending the effects of glacial cycle changes on circulation in the dynamic area.

ODP Site 1094:

The Ocean Drilling Program acquired sediment cores from Southern Ocean site ODP 1094 that cover the time period of MIS 11. This prominent interglacial period, which occurred between 375,000 to 425,000 years ago, is of interest because of potential changes in ocean circulation that could have occurred during global deglaciation. ODP 1094 is influenced by the large ocean currents and circulation patterns that occur in the Southern Ocean. These circulation patterns include CDW upwelling and AABW formation. This site has also been involved in studies pertaining to aU concentration changes during the same time period (Hayes et al., 2014) . The formation of AABW is partially the result of sinking dense water around Antarctica, as part of the global overturning circulation which can bring oxygenated water to the depths of the Southern Ocean. This oxygen rich water can then affect the concentration of various trace metals at ODP 1094. A reduction in deep water mass formation would cause a corresponding reduction in oxygen delivery to ODP 1094. Such an event could occur during an interglacial time period such as MIS stage 11. As observed by Hayes et al.,

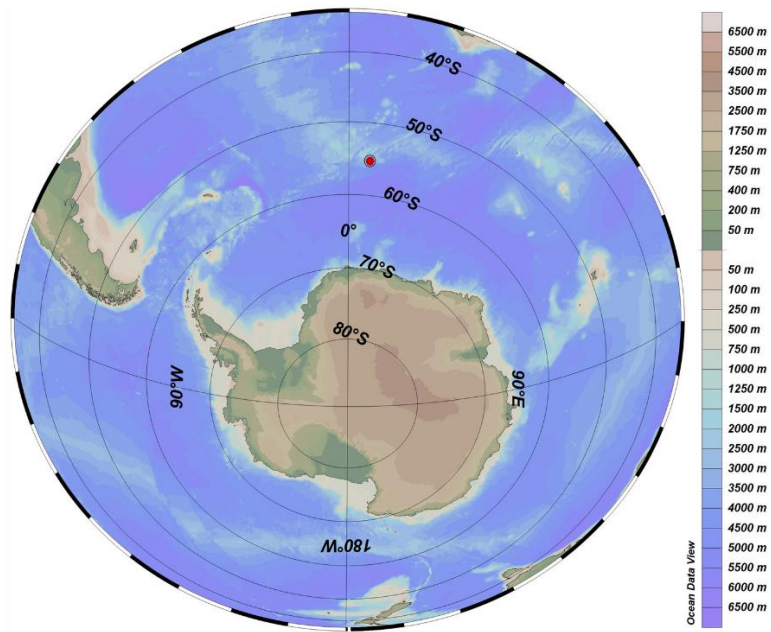


Figure 2: ODP Site 1094 location in the Southern Ocean.

(2014), ODP 1094 is situated at the intermingling of CDW and AABW and is therefore sensitive to the oxygen level changes due to changes in AABW circulation. We focused on MIS11 to determine additional proxies of oxygenation because Glasscock et al., (2020) performed a survey of authigenic uranium (enriched during low oxygen periods) for the past 500,000 years. MIS11 stood out (along with MIS5e, which had been previously studied) as a period with possible millennial-scale changes in deep ocean circulation during an interglacial period, relevant to possible changes in today's climate.

Chapter 3: Methods

Sediment Acquisition:

The sediment cores utilized in this research were acquired from the Bremen Core Repository. The cores were collected from the Southern Ocean during the Ocean Drilling Program at site 1094. This core has been dated by characterizing oxygen isotopes of using benthic foraminifera (Hasenfratz et al., 2019). The age model allowed for the sections of the core that cover MIS 11 to be selected for analysis in 10 cm coverage extents.

Sediment Preparation:

The sediments were prepared for inductively coupled plasma mass spectrometry (ICPMS) analysis by weighing 50 milligrams (mg) of homogenized sediment and adding 5 milliliter (ml) of 8 molar nitric acid . The sediment was then dried down at 300 degrees Fahrenheit using a hot plate. Next, 1 ml of 8 molar nitric acid was added along with 1 ml of hydrofluoric acid and then dried down again. Another round of 1 ml nitric acid was then added with an additional 1 ml of reagent grade hydrogen peroxide. The samples were then dried down a third time at 200 degrees Fahrenheit. The dried samples were then re-suspended in a 0.5 ml solution of 8 molar nitric acid by briefly reheating. Upon observation, if dark grains of particulate were present, another round of hydrofluoric acid was conducted. This was done by adding another 0.5 ml of hydrofluoric acid and repeating the dry down step. If white or translucent solids were present, then another 0.5 ml of hydrogen peroxide was added and the sample was dried down at 200 degrees Fahrenheit. These additional hydrogen peroxide and hydrofluoric acid steps were repeated until the sediment samples were observed to be sufficiently dissolved. Once the samples appeared to be dissolved in the 0.5 ml solution of 8 molar nitric

acid, they were dried down a final time at 300 degrees Fahrenheit and then suspended through brief heating in 2 ml of 2% nitric acid for ICPMS analysis.

ICPMS Analysis:

Samples were run in batches of 60-80 at a time on an Element XR (Thermo Scientific) high-resolution ICPMS, using a PC-3 (Elemental Scientific) spray chamber for sample introduction. The sample was first diluted to 1 ml using an internal Indium standard from an initial 50 microliter sample measurement. The samples were measured for U, Th, Re, and Mn. The U was measured in low resolution while the Re and Mn were measured in medium resolution with the Th being measured in both resolutions. The measurements were compared to external standard solutions of known concentrations (Zhou, 2005).

Chapter 4: Data and Results

Detrital Removal Estimation:

The estimated concentrations of the sediment samples were corrected for any percentage of the total measurement that was due to detrital dispositional influences. The concentrations of Re and Mn were corrected by utilizing the upper crustal abundance percent estimates calculated by Rudnick & Gao (2013). These corrections were conducted by comparing the measured trace metal concentrations to the measured Thorium concentration. The equation was as such, $aX = \text{measX} - \text{measTh}(\text{uccX}/\text{uccTh})$. The Upper Continental Crust (UCC) ratio for Re/Th was 1.9×10^{-5} g/g. The UCC for Mn/Th was 73.8 g/g. The UCC for U/Th was 0.16 g/g (Rudnick & Gao, 2013). These ratios were used as a correction factor for detrital trace metals of each type by utilizing the equation: $X(\text{authigenic}) = X(\text{measured}) - \text{Th}(\text{measured}) * (\text{Re}/\text{Th})$. This allows for a detrital correction estimate. In the case of Re the correction was <2.5% throughout all measurements and the correction of Mn was <20% with a <10% correction for U during the interglacial. These corrections are displayed in Figures 3 through 5

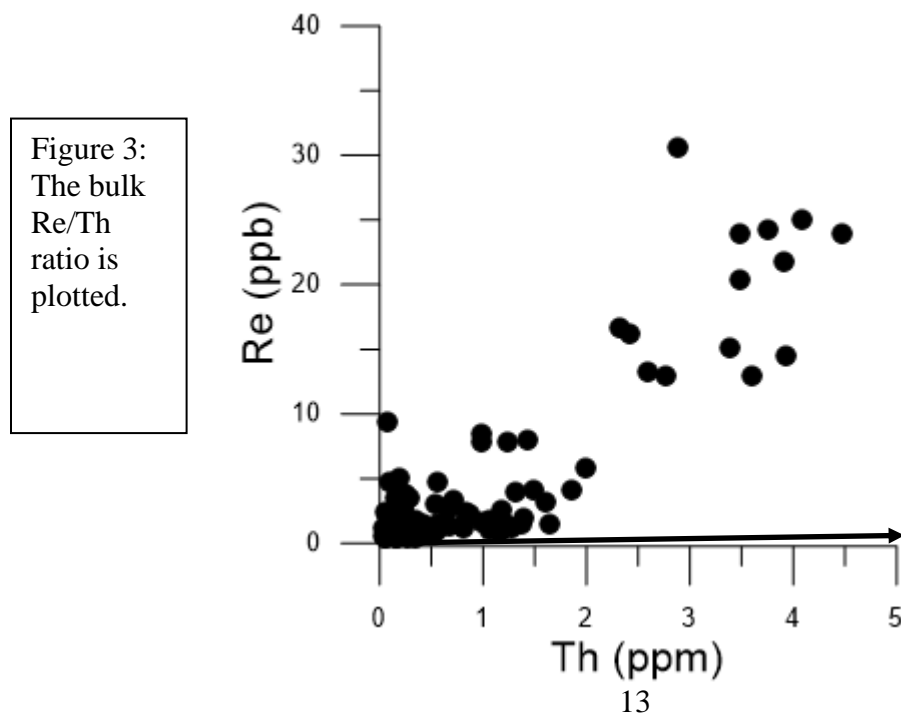


Figure 4:
The bulk
Mn/Th
ratio is
plotted.

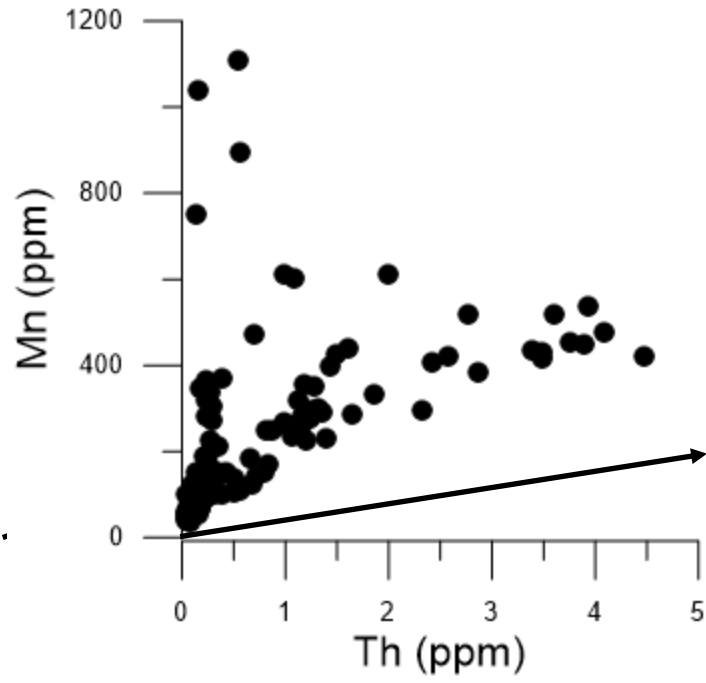
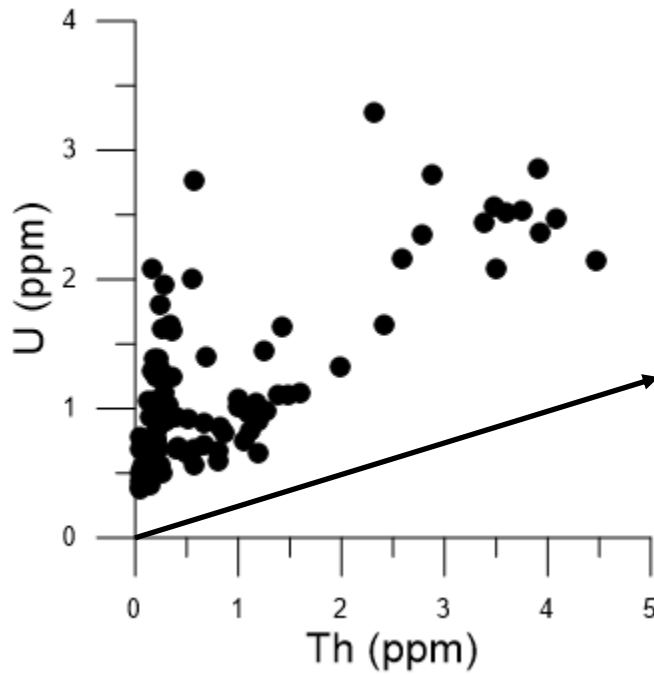


Figure 5:
The bulk
U/Th ratio
is plotted.



The detrital correction values each have their own inherent uncertainty due to how they were calculated. To be more exact, the UCC values utilized in the calculation were the most up

to date of the composition estimates; however, there are more than one reported value for each of the three elements. The variance in these reported values over time results in uncertainty in the calculated correction due to the alteration in the ratio dynamic between the trace metal values and the measured Th concentration. This uncertainty can be estimated by calculating the upper and lower ends of the ratio dynamic. The uncertainty on the lower end of the value, found by using the lowest reported trace metal value and the highest reported Th value, was so small as to be completely negligible compared to the proximity of the value that was utilized in the study. Additionally, the higher end uncertainties did not vary significantly when compared to the authigenic values that were being found via the correction. Out of the highest reported values for the three trace metals, all of the values were still well within an increase of two times the utilized value. For a correction of 2.5%, the new correction would be approximately double, 5%, which is still negligible in regard to the larger values of the calculated total measurements for the trace metal concentrations.

Concentration Changes Through Time:

The ICPMS measurements allowed for a thorough characterization of the changes in trace metal concentrations prior to, throughout, and after MIS 11. The authigenic values of Mn, Re, and U are displayed versus sediment age in Figure 3. This figure also shows the Ba/Fe concentration values to partially reconstruct biological productivity during MIS 11 (Jaccard, et al., 2013). The Ba/Fe values were utilized as a paleo-productivity proxy to allow for an examination of high productivity events throughout that stage. High productivity rate events were used to exclude changes in trace metal changes that could be attributed to respiration.

Each data set in the figure has a different unique trend. The Ba/Fe ratio data contains a maximum near the middle of the interglacial period and this peak covers approximately 435,000 to 395,000 years ago from start to finish. The aU concentration data begins at a maximum, with three significant peaks throughout the period at around 425,000, 410,000, and 395,000 years ago. The aRe concentration trend also begins with a maximum with scattered peaks throughout the period that culminate in another maximum at the end of MIS 11. The aMn concentrations throughout the MIS 11 period begin at a minimum and have two major peaks, at 425,000 and 400,000 years ago. After these two prominent peaks, intermittent peaks, almost cyclical in nature, appear three times, seemingly every 5,000 years, from 385,000 to 370,000 years ago.

There are four time periods of specific interest, highlighted in Figure 6. The first occurs approximately 435,000 years ago, where peaks in both aU and aMn are shown. Another period, located at approximately 420,000 years ago, shows a significant peak in the Ba/Fe data and aRe data. These two features are accompanied by noticeably lower aU and aMn measurements. A

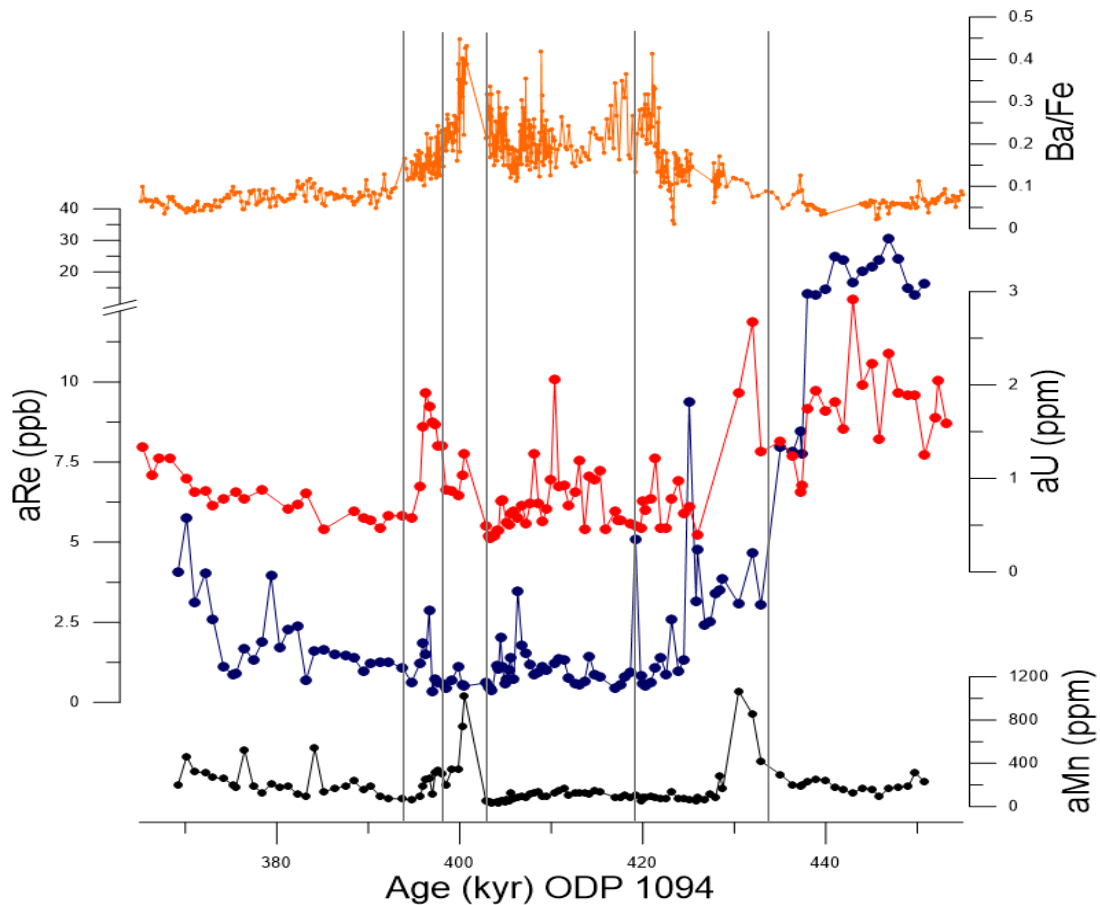


Figure 6: Authigenic Mn and Re concentrations are plotted along with aU (Glasscock et al.), another redox sensitive element, and Ba/Fe (Jaccard et al., 2013), a paleoproductivity proxy.

third period of interest occurs at around 405,000 years ago, where an increase to the Ba/Fe ratio is joined by the beginning of an aU maximum feature and an aMn peak. There is also a noteworthy reduction in aRe concentrations in between two aRe peak features. The fourth period of interest contains the most recent of these aRe peaks at approximately 395,000 years ago. This aRe peak has a concurrent peak in aU and reductions in aMn and Ba/Fe. It is at this point that the Ba/Fe reaches a gradual descent to a minimum. This behavior of the three trace metals is consistent with multi-millennial scale changes in bottom water oxygen, likely due to changes in AABW formation, as will be detailed in the discussion to follow.

Chapter 5: Discussion

In order to draw meaningful and significant conclusions from the collected data, the various trace metal concentration trends must be compared to one another. This allows for the analysis of anti-correlations between the metals that are enriched in concentration by the presence of oxygen, aMn and aU, and the element that is reduced by the presence of oxygen, aRe. Beginning at the oldest portion of the data set, it can be observed that there are characteristics consistent with glacial periods. As this section of the core is from the glacial period prior to MIS 11 (or MIS 12), this observation is congruent with previous thought about the glacial stages (Sigman, Hain, & Haug, 2010). The low productivity of glacial periods is represented by the low values during this period throughout the Ba/Fe record. The peaks in aU and aRe and anticorrelated minimum values of the aMn record suggest reduced oxygen was reaching the deep ocean sediments during this time due to sluggish ocean circulation. This can be attributed to a poorly ventilated Southern Ocean during the MIS 12 glacial period. Observing a reversal in the features of this trend as the core measurements move forward in time through the MIS 11 interglacial period would suggest a reduction in ocean currents (Wagner & Hendy, 2017). The previously mentioned areas of interest demonstrate this reversal perfectly. The peaks in aRe at 425,000 and 420,000 years ago are coupled with an overall reduction in aMn, which suggest the reduction of oxygen delivery to the deep ocean. This conclusion is also suggested by observing a similar pattern in the trace metal data trends during MIS 11 at approximately 395,000 years ago, when peaks are exhibited in both aRe and aU with minimums in aMn. The low productivity presented by the Ba/Fe record also suggest that this reduction was not due to biologic activity.

Given that the two prominent pathways for oxygen reduction in the deep ocean are biologic activity and ocean circulation, the ruling out of biologic activity as a cause suggests that the possible observed oxygen reduction event was due to a reduction in deep ocean ventilation. This reduction of deep ocean ventilation has been due to either decreased deep water mass formation or a significant alteration to Southern Ocean currents. The possible explanation that this was the result of large current deviations throughout the period is justifiable. The variation that can be observed at ODP 1094 over the course of MIS 11 suggests that the circulation and oceanographic changes did not occur as a single large event. This site is influenced at various times throughout the interglacial MIS 11 period; this suggests that there was a weakening and strengthening of circulation occurring at Site ODP 1094. This could be explained by a reduction in the ventilation of the deep ocean through the deep-water formation reduction, specifically the AABW mass. As Glasscock et al., (2020) pointed out, the apparent reduction in ventilation that we observe late in MIS11 did not occur during a significant period of sea level rise. Thus, the influence of freshwater from the Antarctic melt interfering with AABW formation, as was inferred for another recent interglacial period, MIS5e, is not a likely candidate for causing this event. Instead, a possible northerly shift in or weakening of the Southern hemisphere westerly winds could have reduced AABW ventilation. This expands our knowledge of possible scenarios for Southern Ocean circulation variability during warm climate periods.

Chapter 6: Conclusion

The results of this research suggest that the prominent warm climate period, late in MIS 11, was characterized by a possible reduction in sediment oxygen concentration, suggestive of a deep ocean ventilation reduction. Interglacial periods could be periods of great change in the Southern Ocean. Large changes to this region would suggest large impacts to the connected, related oceans of the world and the cycles within them. Biological, chemical, and physical planetary cycles could all be affected by such a large-scale alteration to the ocean currents of this region. Further research is necessary to fully understand how ocean interactions were altered during past interglacial periods. For instance, this study focused on the Atlantic sector of the Southern Ocean, whereas investigation of the dynamics in the Pacific or Indian sectors could provide more insight into the physical cause of circulation changes. Finally, one thing is for certain, insight into the large changes suggested by the results of this research could be a factor that calls for increased thought into how this planet could be effected by future warm climate periods and large scale global changes. The large scale global changes from diverted currents in the Antarctic Ocean could completely change ocean dynamics and human industry interactions with the ocean around the world. It is for this reason that these dynamics need to be researched and characterized, so that human populations and industrialization can work efficiently and in harmony with the world's oceans.

References

- Colodner, D., Sachs, J., Ravizza, G., Turekian, K., Edmond, J., & Boyle, E. (1993). The geochemical cycle of rhenium: a reconnaissance. *Earth and Planetary Science Letters*, 117(1–2), 205–221. [https://doi.org/10.1016/0012-821X\(93\)90127-U](https://doi.org/10.1016/0012-821X(93)90127-U)
- Dutton, A., Carlson, A. E., Long, A. J., Milne, G. A., Clark, P. U., DeConto, R., ... Raymo, M. E. (2015). Sea-level rise due to polar ice-sheet mass loss during past warm periods. *Science*, 349(6244). <https://doi.org/10.1126/science.aaa4019>
- Dymond, J., Suess, E., & Lyle, M. (1992). Abstract . We used sediment traps to define the higher barium contents in the intermediate and combined our particle flux data with existing water linkages to ocean productivity and the degree of. *Paleoceanography*, 7(2), 163–181.
- Hasenfratz, A. P., Jaccard, S. L., Martínez-García, A., Sigman, D. M., Hodell, D. A., Vance, D., ... Haug, G. H. (2019). The residence time of Southern Ocean surface waters and the 100,000-year ice age cycle. *Science*, 363(6431), 1080–1084. <https://doi.org/10.1126/science.aat7067>
- Hayes, C. T., Martínez-García, A., Hasenfratz, A. P., Jaccard, S. L., Hodell, D. A., Sigman, D. M., ... Anderson, R. F. (2014). A stagnation event in the deep south atlantic during the last interglacial period. *Science*, 346(6216), 1514–1517. <https://doi.org/10.1126/science.1256620>
- Hulth, S., Aller, R. C., & Gilbert, F. (1999). Coupled anoxic nitrification/manganese reduction in marine sediments. *Geochimica et Cosmochimica Acta*, 63(1), 49–66. [https://doi.org/10.1016/S0016-7037\(98\)00285-3](https://doi.org/10.1016/S0016-7037(98)00285-3)
- Jaccard, S.L., Hayes, C. T., Martínez-García, A., Hodell, D. A., Anderson, R. F., Sigman, D. M., & Haug, G. H. (2013). Two modes of change in Southern Ocean productivity over the past million years. *Science*, 339(6126). <https://doi.org/10.1126/science.1227545>
- Klug, A., Stark, A., Peters, K., Schnering, H. G., Umemoto, K., Yamaguchi, K., ... Pelzing, M. (2010). *Ventilation of the Deep Southern*. (May), 1147–1152.
- Loon, J. C. van. (1985). *Selected methods of trace metal analysis: biological and environmental samples*. Retrieved from <https://www.cabdirect.org/cabdirect/abstract/19861903135>
- Mangini, A., Jung, M., & Laukenmann, S. (2001). What do we learn from peaks of uranium and of manganese in deep sea sediments? *Marine Geology*, 177(1–2), 63–78. [https://doi.org/10.1016/S0025-3227\(01\)00124-4](https://doi.org/10.1016/S0025-3227(01)00124-4)
- Marshall, J., & Speer, K. (2012). Closure of the meridional overturning circulation through Southern Ocean upwelling. *Nature Geoscience*, 5(3), 171–180. <https://doi.org/10.1038/ngeo1391>

- Morford, J. L., & Emerson, S. (1999). The geochemistry of redox sensitive trace metals in sediments. *Geochimica et Cosmochimica Acta*. [https://doi.org/10.1016/S0016-7037\(99\)00126-X](https://doi.org/10.1016/S0016-7037(99)00126-X)
- Muglia, J., Skinner, L. C., & Schmittner, A. (2018). Weak overturning circulation and high Southern Ocean nutrient utilization maximized glacial ocean carbon. *Earth and Planetary Science Letters*, *496*, 47–56. <https://doi.org/10.1016/j.epsl.2018.05.038>
- Nameroff, T. J., Balistrieri, L. S., & Murray, J. W. (2002). Suboxic trace metal geochemistry in the eastern tropical North Pacific. *Geochimica et Cosmochimica Acta*, *66*(7), 1139–1158. [https://doi.org/10.1016/S0016-7037\(01\)00843-2](https://doi.org/10.1016/S0016-7037(01)00843-2)
- Rintoul, S. R. (2018). The global influence of localized dynamics in the Southern Ocean. *Nature*, *558*(7709), 209–218. <https://doi.org/10.1038/s41586-018-0182-3>
- Rudnick, R. L., & Gao, S. (2013). Composition of the Continental Crust. In *Treatise on Geochemistry: Second Edition* (2nd ed., Vol. 4). <https://doi.org/10.1016/B978-0-08-095975-7.00301-6>
- Sigman, D. M., Hain, M. P., & Haug, G. H. (2010). The polar ocean and glacial cycles in atmospheric CO₂ concentration. *Nature*, *466*(7302), 47–55. <https://doi.org/10.1038/nature09149>
- Wagner, M., & Hendy, I. L. (2017). Trace metal evidence for a poorly ventilated glacial Southern Ocean. *Quaternary Science Reviews*, *170*, 109–120. <https://doi.org/10.1016/j.quascirev.2017.06.014>
- Zhou, F. (2005). Electrochemistry combined on-line with atomic mass spectrometry and related techniques for trace-metal analysis and electrode-reaction studies. *TrAC - Trends in Analytical Chemistry*, *24*(3 SPEC. ISS.), 218–227. <https://doi.org/10.1016/j.trac.2004.11.015>