SEAWATER OSMIUM ISOTOPE RECORDS FROM PACIFIC ODP AND IODP SITES- REFINING THE PALEOGENE CURVE AND DATING RED CLAY SEQUENCES

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ABSTRACT

Seawater Osmium Isotope Records from Pacific ODP and IODP Sites- Refining the Paleogene Curve and Dating Red Clay Sequences. (May 2013)

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Reconstructing ancient ocean circulation patterns contributes to a better understanding of Earth's past climate conditions, as the two are known to be a strongly coupled system. Paleoceanographic reconstructions of the Late Cretaceous and early Cenozoic require enhanced geographic coverage, particularly in the Pacific, in order to better constrain meridional variations in environmental conditions. The challenge with the existing inventory of Pacific deep-sea cores is that they consist almost exclusively of pelagic clay with little existing age control. Recent work indicates that seawater Osmium (Os) isotope analyses provide useful age control for red clay sequences due to its relatively long residence time compared to oceanic mixing. The drawback to using seawater Os isotope stratigraphy to date Paleogene age sediments is that the compilation of existing data has some significant temporal gaps, notably between ~38 and 55 million years ago (Ma). To improve the temporal resolution of the seawater Os isotope curve, we present new data from Ocean Drilling Program (ODP) Site 865, which has excellent biostratigraphic age control over this time interval. Preliminary data indicate a seawater composition consistent with the apparent trend in the few existing data points. We also analyzed

the Os isotopic composition at Integrated Ocean Drilling Progam (IODP) Site U1370 to construct an age model for this predominantly pelagic clay section. The $^{187}Os/^{188}Os$ values generally increase from 0.312 at 64.46 meters below seafloor (mbsf), likely reflecting the Os isotope minimum recorded across the Cretaceous-Paleogene boundary, to 0.531 at 28.26 mbsf, likely correlating to the Eocene/Oligocene interval.

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NOMENCLATURE

Os: Osmium

Re: Rhenium

Fe-Mn: Ferromanganese (iron-manganese)

$CaCO_3$: Calcium carbonate

Ar: Argon

^{10}Be: Beryllium-10

^{230}Th: Thorium-230

Co: Cobalt

CCD: carbonate compensation depth

IODP: Integrated Ocean Drilling Program

ODP: Ocean Drilling Program

mbsf: meters below sea floor

Ma: Millions of years ago

Myr: Million years

K/Pg: Cretaceous-Paleogene

E/O: Eocene-Oligocene

HNO_3: Nitric acid

N (as in 2.2N HNO_3): normal (concentration)

ICP-MS: inductively-coupled plasma mass spectrometer

CHAPTER I

INTRODUCTION

Previous studies have shown that ocean circulation patterns are linked with past climate conditions and understanding ocean circulation has proven to provide a better understanding for the Earth's past climate (Thomas 2005). This knowledge is useful in interpreting current climate patterns and predicting future climate patterns. In order to understand ocean circulation patterns of the past, one first must reconstruct these circulations' ages to correlate them with past climates.

The presence of calcareous biogenic components in seawater sediments provides us with biostratigraphic age control, however in deeper and older areas of the ocean, such as the South Pacific, these biogenic components are very rare. This is because passed a certain depth (called the calcite compensation depth, or CCD) all of the calcareous components are dissolved (Zheng et al. 2012). These biogenic components dissolve passed this depth because these deeper, older waters have higher concentrations of dissolved CO_2. The dissolved CO_2 in the water reacts with and dissolves the $CaCO_3$ and hence preserves no calcite microfossils. The lack of calcite microfossils in these South Pacific waters poses a problem for determining the age of the sediments deposited here. These sediments are primarily red clays.

The constant hydrogenous Co-flux model is a common method of dating Fe-Mn crusts by applying it to estimate changes in growth rates in older sections of crust. This Co-model was developed by the ascertainment of crustal growth rates using the decay profiles of radioactive

^{10}Be and ^{230}Th; however, this model is only reliable for sediments that are younger than about 10 Ma, the limit of ^{10}Be (Klemm et al. 2005). Due to this limitation, there are many uncertainties with respect to the Co-model when used to date crusts over much longer periods of crust growth; therefore it is necessary to have a reliable method to date crusts older than 10 Ma (Klemm et al. 2005). Recent studies have shown that the reconstruction of the marine ^{187}Os/^{188}Os record is a valid tool for dating much older (~80 Ma) sediments, as well as red clay sediments (Ravizza 2007). Osmium has a relatively long seawater residence time compared to oceanic mixing, which indicates that the global seawater ^{187}Os/^{188}Os composition is basically homogenous (Peucker-Ehrenbrink et al. 2000). Homogeneity in the global seawater ^{187}Os/^{188}Os composition is necessary in order to have an effective dating mechanism of ancient ocean sediments. Work done in Klemm et al. 2005 has further constructed a seawater Os age model compiled using ^{187}Os/^{188}Os isotopic ratios from pelagic clay sediments of the central North Pacific, mealliferous carbonate sediments from the East Pacific Rise and the South East Pacific, and sediments from the Mediterranean Sea, the Southern Atlantic and the Equatorial Pacific, however the data has some significant hiatuses, notably between about 38-55 Ma. In this study, we analyze sediments from ODP Site 865, which has excellent biostratigraphic age control over that time interval, in order to improve the existing seawater Os isotope age model. Additionally, we use the same principles and methods to date red clay sediments in the South Pacific.

Study Sites

Two sediment cores, ODP Site 865 and IODP Site U1370, were analyzed in this study. Both of these cores are located in the Pacific Ocean. Site 865 (*Figure 1.*, on the following page) was cored during ODP Leg 143 in 1992 and is located at 18°26.41'N, 179°33.34'W in the equatorial

Pacific near Hawaii, at a water depth of 1518.4 meters. Site 865 is composed of $CaCO_3$-rich sediments and foraminiferal ooze (“Shipboard Scientific Party”, 1993).

Figure 1. ODP Leg 143

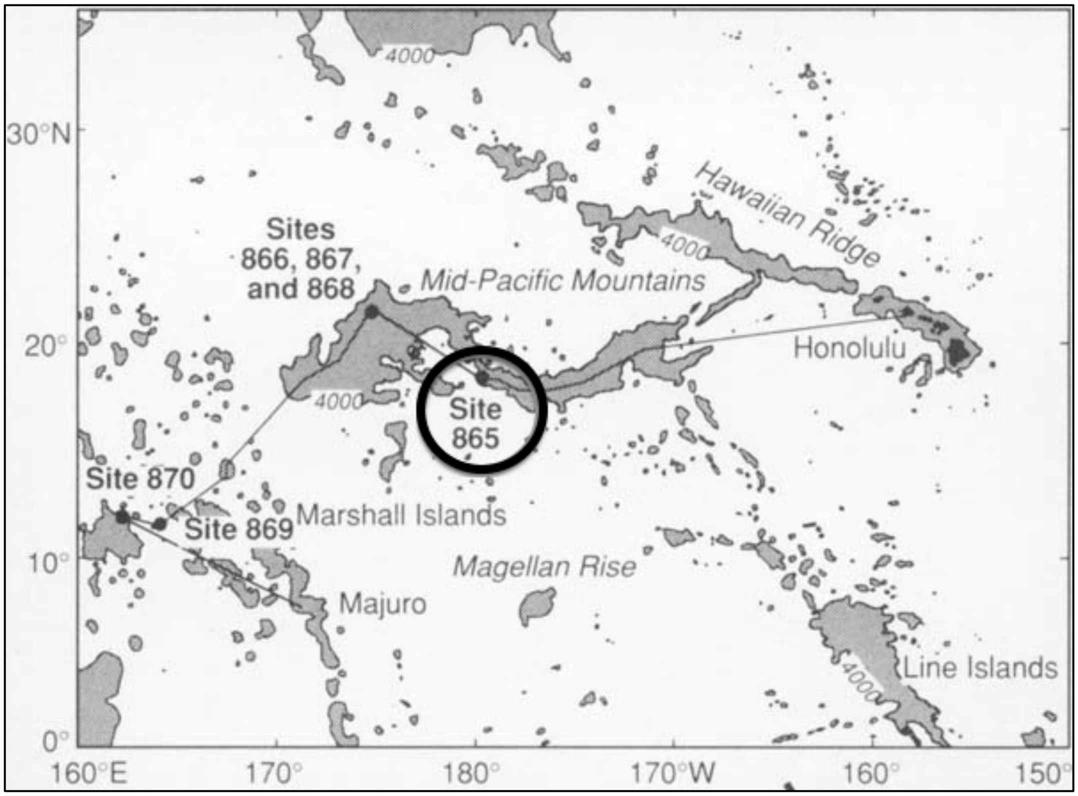

Figure 1. shows a map of ODP Leg 143 with the studied site, Site 865 circled. This Leg began in Honolulu and traveled west through the Mid-Pacific Mountains (From Winterer et al. 1995).

Site U1370 (*Figure 2.*, on the following page) was cored during IODP Expedition 329 in 2010 and is located at 41°51.43’S, 153°07.15’W in the South Pacific Gyre east of New Zealand, at a water depth of 5074 meters. Site U1370 is composed primarily of metalliferous pelagic clays (Expedition 329 Scientists, 2011).

Figure 2. IODP Expedition 329

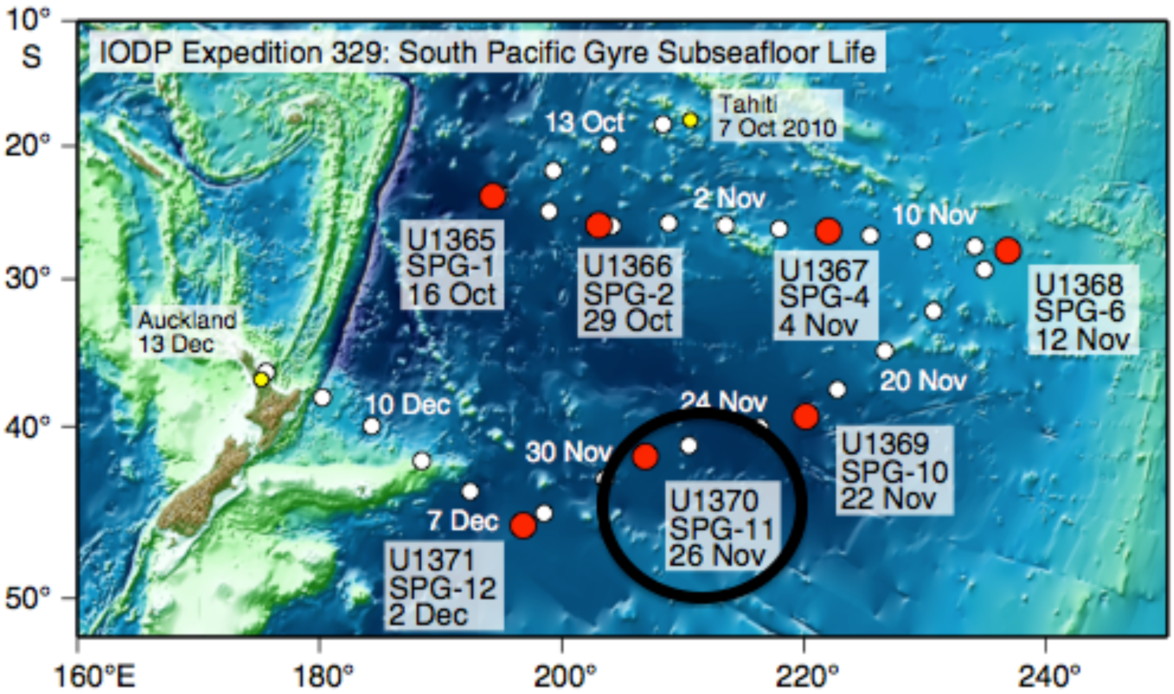

Figure 2. shows a map of IODP Expedition 329 with the studied site, Site U1370 circled. This Expedition began in Tahiti and traveled southwest, then southeast, and back southwest through the South Pacific Gyre to Auckland New Zealand (From Expedition 329 Scientists, 2011).

Purpose of this Study

In this study, we attempt to achieve favorable data that fills in the gap and eliminate the hiatuses.

In order to begin to fill in the gap in the Os age model, it is important to be able to replicate data from previous work. We intend to accomplish our goal by working with samples from Site 865, a site that has very good biostratigraphic age control, and compare it to the existing age model in order to begin to fill in the gap of the age model. Once, we have accomplished a successful replication of this data, we can then use the same method to confidently date sediments from Site U1370, comprised of pelagic clays, which have no other useful form of age control.

CHAPTER II

MATERIALS AND METHODS

Materials

We obtained our samples from the IODP Gulf Coast Core Repository and conducted our procedures and lab work in the Ken Williams ’45 Radiogenic Isotope Laboratory, both on the campus of Texas A&M University. Upon sample preparation, we collected our Os data by sparging OsO_4 into the ICP-MS.

Methods

Leaching techniques were used to extract hydrogenous Os from seawater sediments. The exact leaching solution and methods for sample prep and data collection are described below and adapted from Hassler et al. 2000.

Sample Prep

To begin sample preparations, we homogenized the sediment using a mortar and pestle and then weighed out about 1 to 4 grams (depending on the site and composition of the sediment- more mass for clays and less for $CaCO_4$ rich sediments) of the powdered sediment into a labeled, 125ml Erlenmeyer flask. Forty-eight milliliters of 2.2N HNO_3 and 0.6ml of 30% optima-grade H_2O_2 were then added to the flasks and the solution was heated on the hot plate (with the flask tightly capped) at 100-110°C for 1 hour. After 1 hour, the flasks were left to cool in a fume hood and once it was back to room temperature 0.6 more milliliters of 30% optima-grade H_2O_2 were added to the flasks (total solution in flask: ~49.2ml plus homogenized sediment). Once the 30% optima-grade H_2O_2 was added, the flasks were left to sit in the fume hood for 2 more hours and periodically was agitated throughout the 2 hours. After the 2 hours were up, the contents of the flasks were added into a labeled 50ml-centrifuge tube and spun down in the centrifuge until the liquid was completely clear and all of the sediment was at the bottom of each of the tubes. This was done over the course of 2 hours and the centrifuge speed was set to 3000rpm. The clear liquid was then transferred back into each sample's initial flask and ready to be oxidized for the ICP-MS.

Sparging OsO_4 into the ICP-MS

Before sparging the OsO_4 into the ICP-MS, the sample needed to be oxidized. This was done by adding 10ml of 14N (concentrated) HNO_3 to each of the flasks and placing them on the hot plate for 1.5 hours at 110°C. After the solution cooled to room temperature, we removed the caps from the flasks and exchanged them with Teflon transfer caps, which have two ports for Teflon tubing used to sparge the OsO_4 directly into the ICP torch. Argon sample gas is bubbled into the solution through one of the ports, while the other port is used to extract the Ar sample gas carrying volatile OsO_4 into the torch of the ICP-MS (Hassler et al. 2000).

CHAPTER III

RESULTS

I analyzed 27 samples at an approximate spacing of ~116 meters within the core at Site 865. The $^{187}Os/^{188}Os$ data from Site 865 (*Figure 3a*.) show a rather rapidly increasing and then slowly decreasing trend with depth. The data increase from 0.2477 at 19.1 mbsf to 0.5296 at 39.17 mbsf, and then slowly decrease over the next ~87 mbsf to a value of 0.2576. The data then increases back up to ~0.3 through the next ~7 mbsf. One sample was not plotted because the sample didn't run through the ICP-MS successfully.

I analyzed 8 samples at an approximate spacing of ~36 meters within the core at Site U1370. The $^{187}Os/^{188}Os$ data from Site U1370 (*Figure 3b*.) show an overall decreasing trend with depth. The data decrease from 0.5310 at 28.26 mbsf to 0.2616 at 59.78 mbsf and then increase up to 0.3115 at 64.46 mbsf. One sample was not plotted because the sample didn't run through the ICP-MS successfully.

It is important and necessary that more data be collected and analyzed in order to make more justified interpretations, however there were significantly fewer samples processed from Site U1370 because there were far fewer counts recorded by the ICP-MS on samples from this site. This is due to the lower abundance of Os in these sediments. Careful replications of the procedures possibly need to be done in order to gain more meaningful data in the future. The methods may also need to be revised to contribute a more effective means of sample prep in order to maximize the counts recorded.

Figure 3. ^{187}Os/^{188}Os with Depth

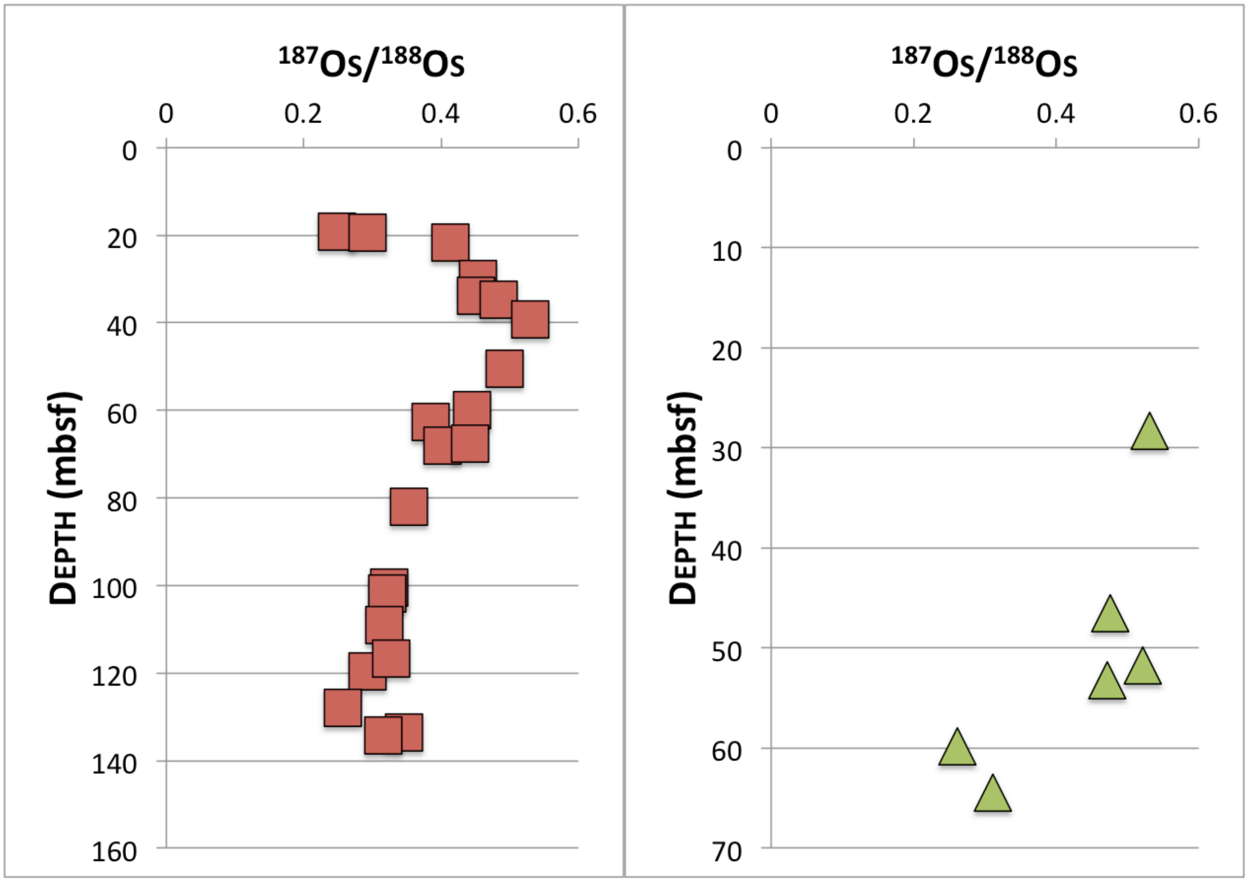

Figure 3a. (left) shows the ^{187}Os/^{188}Os plot with depth from Site 865 and *Figure 3b*. (right) shows the ^{187}Os/^{188}Os plot with depth from Site 1370. Note that the vertical axes differ on the two plots; the maximum depth at Site 865 is 134.32 mbsf and the maximum depth at Site U1370 is 64.46 mbsf.

CHAPTER IV

DISCUSSION

Continental weathering via river runoff and Aeolian dust are the dominant inputs to the seawater $^{187}Os/^{188}Os$ record. The $^{187}Os/^{188}Os$ ratios of rivers and Aeolian dust are ~1.4 and ~1.05, respectively, and the $^{187}Os/^{188}Os$ ratio of the world's oceans (currently) is ~1.06 (Peucker-Ehrenbrink et al. 2000). However, this number has increased throughout time as Os continental weathering inputs to the ocean increased. Shortly before the K/Pg boundary (~66Ma), the seawater $^{187}Os/^{188}Os$ record was at a value of ~0.5. In addition to continental weathering playing a significant role in the marine Os record, impact events such as the one at the K/Pg boundary and smaller ones at the E/O (~33Ma) boundary affected the seawater $^{187}Os/^{188}Os$ composition, almost resetting the record (Peucker-Ehrenbrink et al. 2000). An Os minimum of ~0.2 occurred at the K/Pg boundary and the value proceeded to increase, and then slightly drop again at the E/O boundary. Since this time, the seawater $^{187}Os/^{188}Os$ record has increased to the ~1.06 value that it is at present day.

Despite having run only one round of data analysis for each sample, there are some encouraging points to acknowledge. The results from Site 865 (*Figure 4.*) are generally consistent with the increasing trend in the age model from Klemm et al. 2005 suggesting that with further replication of results, we will be able to constrain the evolution of the seawater $^{187}Os/^{188}Os$ composition within the gaps of the existing age model. However, some of the data show slightly lower isotopic values than those in Klemm et al. 2005, which stresses the importance of replicating these results. Additionally, the use of a Re-Os spike during sample prep can help eliminate error and yield more accurate results.

The data from Site U1370 (*Figure 4.*) also provided encouraging results, in spite of limited data. The $^{187}Os/^{188}Os$ values generally increase from 0.312 at 66 Ma likely reflecting the Os isotope minimum recorded across the K/Pg boundary, to 0.531 at 35 Ma, likely correlating to the Eocene/Oligocene interval.

Figure 4. Site 865 and Site U1370 Ages with the Klemm et al. 2005 Age Model

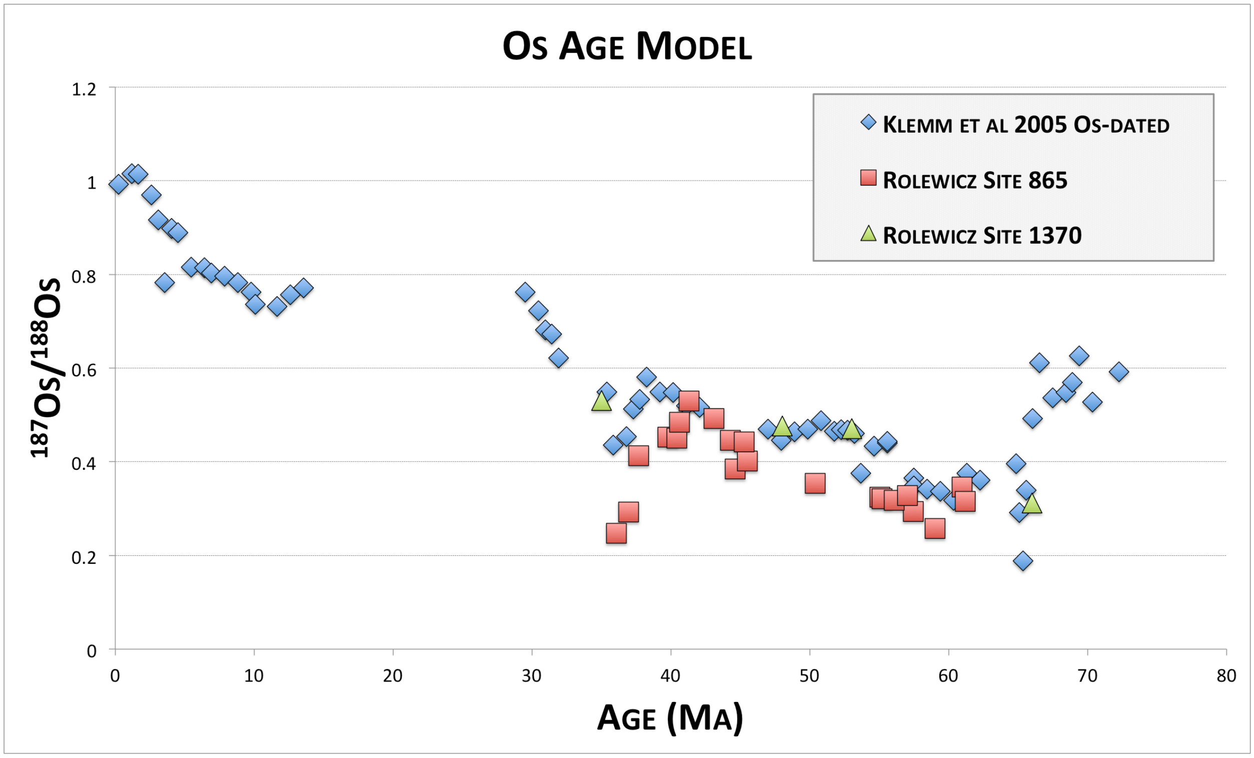

Figure 4. shows the experimental data from both Site 865 and Site U1370 with the Os age compilation from Klemm et al. 2005. The time frame of our data is from the K/T boundary (~66 Ma) to the E/O boundary (~33 Ma).

Because Os is one of the least abundant elements in seawater, a challenge of obtaining high Os counts is present. As shown by the difference in the number of samples successfully processed from each site, organic-rich sediments from Site 865 were easier to get Os counts from than the red clays from Site U1370. It is necessary that sample prep and processing is closely examined and tested in order to determine a way to maximize Os counts recorded on the ICP-MS. Improved methodology along with the introduction of a Re-Os spike will help to provide increased accuracy of future results.

CHAPTER V

CONCLUSION

Ocean circulation and climate patterns are a closely coupled system and understanding their relationship is important in understanding the Earth's past, present and future states. The reconstruction of the seawater Os-isotope record presented here provide a useful start to the further exploration of poorly age-constrained sediments of old, deep waters. Future work with Re-Os spikes, more samples and successful replications from both of these Sites is necessary in order to achieve the goals of this paper most accurately, however, the results provided here are encouraging.

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