

# Seawater and Detrital Marine Pb Isotopes as Monitors of Antarctic Weathering Following Ice Sheet Initiation

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Comparisons of seawater and detrital Pb isotopes from sites proximal to Antarctica are used to understand variations in continental weathering associated with the evolution of the East Antarctic Ice Sheet (EAIS) during the Oligocene to Miocene. Previous work suggests that similar values for the two Pb archives during Eocene warmth represent congruent chemical weathering of continental material, while distinct values for the two phases at the Eocene/Oligocene Transition represent increased incongruent chemical and mechanical weathering during initiation of the ice sheet. For this study, we expand beyond the initial glaciation at the Eocene/Oligocene Transition to determine whether less dramatic changes in ice volume and climate also produce variations in weathering that are recorded by seawater and detrital Pb isotopes. We collected Pb isotopic data from extractions of Fe-Mn oxide coatings of bulk decarbonated marine sediments, which are believed to record a seawater signal, and from complete dissolution of remaining detrital silicate fractions, which are believed to represent the composition of weathered bedrock. Samples were collected from Ocean Drilling Program Sites 744 and 748 on Kerguelen Plateau in the Indian sector of the Southern Ocean and Sites 689 and 690 on Maud Rise from the Atlantic sector. Our results illustrate that seawater Pb isotopes become more radiogenic relative to detrital values during enhanced chemical weathering of the warm Mid-Miocene Climatic Optimum, and subsequently trend toward less radiogenic values during the return to full glacial conditions.

## INTRODUCTION

The Antarctic cryosphere is a major component of the Earth's climate system, accounting for >90% of all modern ice. However, prior to the end of the Eocene (~34 Ma), Antarctica was not the ice-covered world that it is today. The Eocene/Oligocene transition (EOT) marked the onset of rapid glaciation on Antarctica, which is considered one of the most dramatic climate change events of the Cenozoic. Following the initial glaciation of the continent, the ice sheets persisted, waxed and waned, and were re-established due to variations in climate throughout the Oligocene and Miocene (Zachos et al., 2001). These major climate events may have had a significant influence on ocean chemistry and weathering. Over long time scales, silicate weathering plays a major role in the uptake of atmospheric CO<sub>2</sub>. Glacial erosion and ice dynamics mechanically reduce the underlying bedrock to rock flour that is easily weathered, and the subsequent chemical weathering reactions consume CO<sub>2</sub>. We have developed a record of continental weathering on Antarctica based on Pb isotopes that allows us to compare the impact of this process on the carbon cycle and on the chemistry of the ocean, which ultimately receives the dissolved ions generated by chemical weathering.

## *Chemical vs. Mechanical Weathering*

On long time scales, continental weathering of silicate material plays a major role in the carbon cycle. Sediments produced during mechanical breakdown of source rock during uplift or erosional events provide the rock flour necessary for Urey's reaction:  $\text{CaSiO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{SiO}_2$ . Thus, weathering of silicate rocks results in the transport of dissolved ions to seawater that are utilized during the precipitation of biogenic carbonate and silica that are deposited on the seafloor providing a "sink" to store carbon (Andersen, 1999). Congruent, or complete, chemical weathering of silicate material creates a weathering solution with the same chemical signature as the parent rock. In contrast, incongruent, or incomplete, chemical weathering produces a weathering solution with a distinct chemical signature relative to the parent rock or detritus.

## *U-Th-Pb Isotope Systematics*

Radiogenic isotope ratios reflect time-dependent decay processes and thus provide information on the age of a rock (Winter, 2001). The evolution of the U-Th-Pb system in a sedimentary rock provides a powerful tool for evaluating

style and intensity of weathering events, sediment provenance, and ocean circulation (Frank, 2002; Goldstein and Hemming, 2003).

Radioactive decay of  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$  yield three radiogenic isotopes of lead:  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ , respectively. In contrast,  $^{204}\text{Pb}$ , or common Pb, is a stable isotope of lead, and therefore is used as a reference when calculating isotopic ratios (Faure, 1977). U, Th, and Pb are all incompatible elements, meaning they preferentially concentrate in early stages of melt processes. As a result, these elements are generally more enriched in continental crust relative to bulk earth. Due to the heterogeneity of crustal rocks and the different decay rates of U and Th, parent rock compositions of weathered material reflect distinct isotopic ratios of Pb.

### ***Pb Isotopes as a Weathering Proxy***

Long-lived radiogenic isotopes of Pb dissolved in seawater are increasingly being used in geochemical studies to reconstruct paleocurrents in the ocean, determine sediment provenance, and study past continental weathering. Pb isotopes derived from authigenic Fe-Mn oxide coatings in deep-sea sediments are interpreted to preserve the isotopic signal of seawater at the time of deposition, while the remaining silicate detrital residues are considered to represent the composition of the material exposed to weathering.

Pb isotopes have the potential to record information on the style and intensity of weathering because they are fractionated during weathering of continental rocks. They also provide information about the type of material being weathered (silicate vs. carbonate) because unlike Pb, Th is largely excluded during carbonate precipitation. Previous studies have illustrated that incongruent weathering of silicate rocks preferentially releases the more labile, radiogenic Pb fraction (Erel et al., 1994; Harlavan et al., 1998; Jones et al., 2000). This phenomenon occurs because the crystalline structure of a mineral becomes damaged during radioactive decay, leaving radiogenic daughter isotopes loosely bound and susceptible to weathering. As a result, the Pb isotopic signature of the solution produced during incongruent chemical weathering tends to reflect a more radiogenic component when compared to the source rock (Frank, 2002; von Blanckenburg and Nagler, 2001). Basak (thesis, 2011) also pointed that the variations in  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  (daughter products of  $^{238}\text{U}$  and  $^{235}\text{U}$ ), unaccompanied by variations in  $^{208}\text{Pb}$  (daughter product of  $^{232}\text{Th}$ ), are likely to record inputs from weathering of carbonate. By studying variations in Pb isotopes preserved within the Fe-Mn oxides (seawater) and detrital fractions (parent bedrock), we can further understand how weathering of the Antarctic continent responded to ice sheet dynamics and climate change events.

The residence time of Pb in the oceans is ~50–200 yrs (Craig et al., 1973; Schaule and Patterson, 1981;

Henderson and Maier-Reimer, 2002), which is short relative to the mixing time of the oceans (~1500 yrs; Broecker and Peng, 1982); This characteristic of Pb allows us to study seawater isotopic signatures that record a combination of inter-basin advection and weathering (Abouchami and Goldstein, 1995), with the dominant signal being derived directly from local weathering inputs (van de Fleirdt et al., 2006). Therefore, variations in seawater Pb isotopes in this study are interpreted as being locally derived from Antarctic continental sources.

Previous studies of Pb isotopes preserved in seawater signals show that ice dynamics play a role in Pb input to the oceans via weathering processes. Foster and Vance (2006) concluded that glacial periods characterized by cold and dry conditions would ultimately reduce chemical weathering rates. During the subsequent deglaciation, retreating ice sheets expose previously ground up rock. The combination of freshly generated or exposed continental material with warming temperatures and melt water yields relatively radiogenic seawater Pb values as a result of increased chemical weathering. Kurzweil et al. (2010) observed a similar increase in seawater Pb records during the deglaciation from sites on the Laurentian Fan, consistent with conclusions from Foster and Vance (2006), but neither of these studies included examination of Pb isotopes of the detrital fraction to determine whether some seawater variations were related to changes in the composition of rocks exposed to weathering during glaciation. Basak (thesis, 2011) studied Pb records of both the seawater and detrital fractions during the EOT to evaluate weathering during the dramatic onset of continental glaciation on Antarctica. When combined, these archives provide information on both chemical and mechanical weathering processes before and after the initiation of a major ice sheet on the continent. Basak (thesis, 2011) concluded that congruent, chemical weathering dominated the warm Eocene and was followed by mechanical weathering and associated increased incongruent weathering as the continental ice developed.

This paper expands upon previous studies of Pb as a weathering proxy (von Blanckenburg and Nagler, 2001; Foster and Vance, 2006; Gutjahr et al., 2009; Kurzweil et al., 2010; Basak, 2011). Seawater and detrital residue Pb isotopes were analyzed in fifty-seven samples from Ocean Drilling Program (ODP) sites 689, 690, 744, and 748 located within the Southern Ocean proximal to Antarctica. The samples range in age from ~27–8 Ma (mid-Oligocene to late Miocene) and are taken at 0.5–1 m.y. intervals during a period following initial ice-growth at the EOT (~34 Ma). Temperatures remained cool and an ice sheet with a volume of approximately 80% of the modern East Antarctic ice sheet persisted through the early Oligocene (Pekar and Christie-Blick, 2008). The ice sheet approached modern volumes in the late Oligocene until a warming trend began ~26 Ma (Zachos et al., 2001), leading to melt back to ~60% of the current ice volume. This smaller

volume ice sheet continued through the mid-Miocene until temperatures peaked around 15–17 Ma and the ice sheet decreased to <50% of the modern volume (Pekar and Christie-Blick, 2008). This warm interval from 15–17 Ma is referred to as the Mid-Miocene Climatic Optimum (MMCO) and marks the warmest period since the Eocene (Flower and Kennett, 1994). It was followed by rapid cooling and re-establishment of a permanent, ~ modern volume ice on Antarctica (Shackleton and Kennett, 1975; Flower and Kennett, 1994; Zachos et al., 2001). We predict that more intense chemical weathering of fresh material exposed as a result of ice retreat during the deglacial event associated with MMCO warming will correlate with more radiogenic Pb seawater values. By reconstructing conditions on Antarctica during this interval of climate change, we can test this hypothesis.

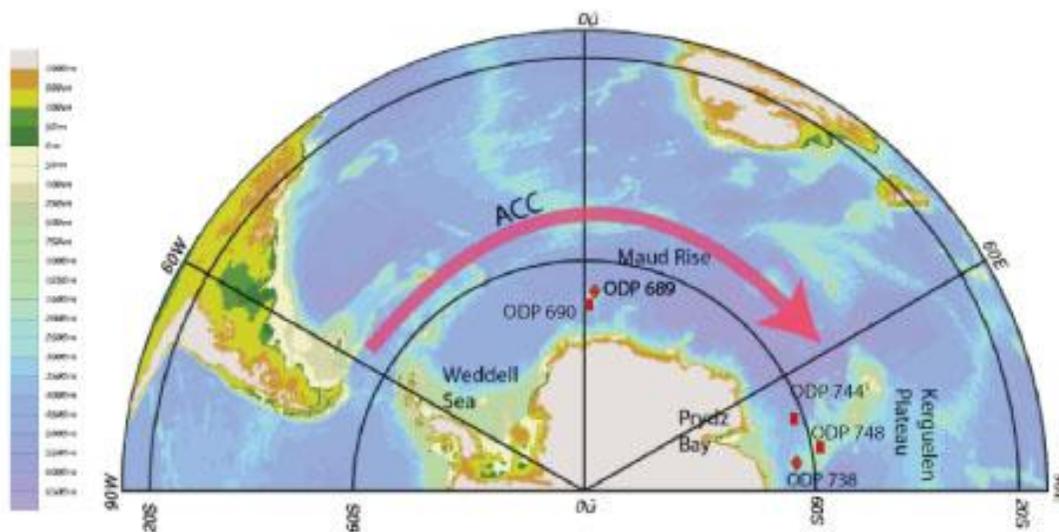
## METHOD

### *Ocean Drilling Program Sites*

The samples used in this study originate from Ocean Drilling Program (ODP) sites 689, 690, 744, and 748 (Fig.

1). Sites 689 (64°31'S, 03°06'E) and 690 (65°09.6'S, 01°12.3'E) are located on Maud Rise in the Atlantic sector of the Southern Ocean. Site 689 has a modern water depth of 2080 m. Site 690 has a modern water depth of 2914 m. This study used seventeen samples from site 689 that range from 8.0–18.0 Ma and were chosen at 0.5 m.y. intervals. Fifteen samples from site 690 were chosen at 0.5 m.y. intervals and span 8.0–17.0 Ma. Depositional hiatuses occur on Maud Rise in the late Oligocene (~19–23 Ma) and after 8 Ma (Barker et al., 1988).

Site 744 (61°34.6'S, 80°35.5'E) and Site 748 (58°26.45'S, 78°58.89'E) are located on Kerguelen Plateau in the Indian sector with modern water depths of 2300 m and 1290 m, respectively. This study uses twelve samples from site 748 that span 23.8–27.05 Ma, covering an interval from peak glaciation at 26.5 Ma into the onset of warming and melt back (Pekar and Christie-Blick, 2008). Thirteen samples from site 744 were chosen at 1 m.y. intervals between 9–21 Ma to span the transition into the MMCO and the subsequent re-establishment of a full ice sheet.



**Figure 1.** Ocean Drilling Program site locations in the Southern Ocean used in this study. Site 689 and 690 are located on Maud Rise in the Atlantic sector. Sites 744 and 748 are located on Kerguelen Plateau in the Indian sector (Basak thesis, 2011).

### *Sample Preparation*

Samples were prepared and analyzed following the methods outlined in Basak et al. (2011). Approximately 1–1.5 grams of bulk sediment was crushed and homogenized with an agate mortar and pestle. The bulk sediment was first decarbonated in three stages using 20 mL of a 2.7% optima glacial acetic acid buffered with Na acetate to a pH=5. Prior to use, the buffered acetic acid solution was batch cleaned with Chelex 100 cation exchange resin to

minimize the Pb blank. Samples were allowed to sit for 12–24 hours on an agitator and were degassed periodically. Following decarbonation, the solution was decanted and the remaining sample was rinsed three times in distilled 4x H<sub>2</sub>O and centrifuged to completely remove the acetic acid.

Each sample was then treated with 10 mL of 0.02 M hydroxylamine hydrochloride (HH) in 25% optima grade glacial acetic acid and placed on a rotator for 1.5 hours to reduce Fe-Mn oxide phases. After this time, the samples and HH solution were centrifuged and the supernatant was

divided into two 5 mL aliquots; one for isotopic analyses of seawater Pb and one for elemental analyses. This step was then repeated: 10 mL of HH were again added and samples were left on the rotator to react for 24 hours to ensure all remaining Fe-Mn oxides were removed. The remaining residue was again cleaned three times with 4x H<sub>2</sub>O to remove any remaining HH solution, and then the sample was dried down. Solid material remaining after this step is referred to as the detrital silicate fraction, which is interpreted to represent the carbonate-free terrigenous silicate fraction of the sediment.

Approximately 0.1 grams of the detrital silicates was powdered with a mortar and pestle and dissolved in a 3:1 ratio of optima grade HF:HNO<sub>3</sub> in a clean Teflon vial. The samples were allowed to react on a hot plate at >100°C for 48–72 hours while being periodically degassed. After 24 hours on the hot plate, the dissolving silicates were sonicated for ~10 minutes to facilitate breaking of silicate bonds. The samples were then dried and re-dissolved twice in 1 mL optima grade HNO<sub>3</sub> to ensure the breakdown of fluorides. Finally, 5 mL of 8N optima HNO<sub>3</sub> were added to the detrital fraction. A 1mL aliquot was taken for elemental analyses and the remaining 4 mL was dried and used for column chemistry.

### **Column Chemistry and Isotopic Analyses**

All sample preparation for elemental and isotopic work was conducted in a class 1000 clean lab in the Department of Geological Sciences at the University of Florida. Dried aliquots for isotope work were re-dissolved in 1N seastar HBr and passed through Dowex 1X-8 (100–200 mesh) resin (Manhes et al., 1978). The Pb fraction was collected in 20% Optima grade HNO<sub>3</sub> in clean Teflon vials.

A Tl normalization technique was used for Pb isotope analyses (Kamenov et al., 2004). Pb concentrates were re-dissolved in Tl-spiked 2% optima HNO<sub>3</sub> in preparation for isotopic analysis on a Nu-Plasma Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICPMS) at the University of Florida. Samples were adjusted for the appropriate dilution to obtain a 2–5 V beam on <sup>208</sup>Pb. Samples were aspirated through a Nu-Instruments desolvating nebulizer (DSN-100) into the plasma source. Long term NBS 981 values analyzed over several years are UF are <sup>206</sup>Pb/<sup>204</sup>Pb=16.937 (2σ=0.004), <sup>207</sup>Pb/<sup>204</sup>Pb=15.489 (2σ=0.003), and <sup>208</sup>Pb/<sup>204</sup>Pb=36.695 (2σ=0.008).

## **RESULTS**

No records are available for the depositional hiatus that occurs in the late Oligocene at Maud Rise. <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, and <sup>208</sup>Pb/<sup>204</sup>Pb seawater values in Sites 689 and 690 increase during the MMCO and then decrease in the subsequent cooling (Fig. 2). Detrital Pb values remain relatively unradiogenic during the MMCO with the

exception of <sup>207</sup>Pb/<sup>204</sup>Pb, which is more radiogenic than contemporaneous seawater values, but become less radiogenic after the MMCO. Site 748 samples from ~23–27 Ma record seawater <sup>206</sup>Pb/<sup>204</sup>Pb that is more radiogenic than detrital values, while detrital <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb values in are more radiogenic that seawater. Site 744 exhibits similar behavior as the Maud Rise over the interval from 20 to 8 Ma, but with less variation between the two archives.

## **DISCUSSION**

The Eocene/Oligocene transition (~34 Ma) is interpreted as a shift in weathering regime from dominantly congruent chemical weathering during the warm Eocene to incongruent mechanical and chemical weathering of freshly generated sediment during ice initiation (Basak thesis, 2011). The peak in seawater Pb isotopes for all three systems during the MMCO is consistent with prediction of increased incongruent chemical weathering during deglaciation (von Blanckenburg and Nagler, 2001; Foster and Vance, 2006; Gutjahr et al., 2009; Kurzweil et al., 2010). These data support the idea that preferential release of radiogenic Pb during weathering of newly exposed rock. During the glacial minima, the ice sheet may have retreated as much as several hundred kilometers inland (Pekar and Christie-Blick, 2008). This migration onshore would have exposed fresh moraine material to the agents of elevated chemical weathering during a warming period, thus resulting in the preferential release of the more radiogenic Pb component to seawater during early leaching (Erel et al., 1994; Harlavan et al., 1998; Foster and Vance, 2006; Kurzweil et al., 2010).

Following the MMCO, the global climates cooled rapidly and benthic oxygen isotopes increased ~1–1.13% from 16–12.5 Ma (Flower and Kennett, 1994). This trend towards cooler climates and the return to full glacial conditions suppressed chemical weathering rates, consistent with our pronounced change toward less radiogenic seawater Pb isotopes after the MMCO.

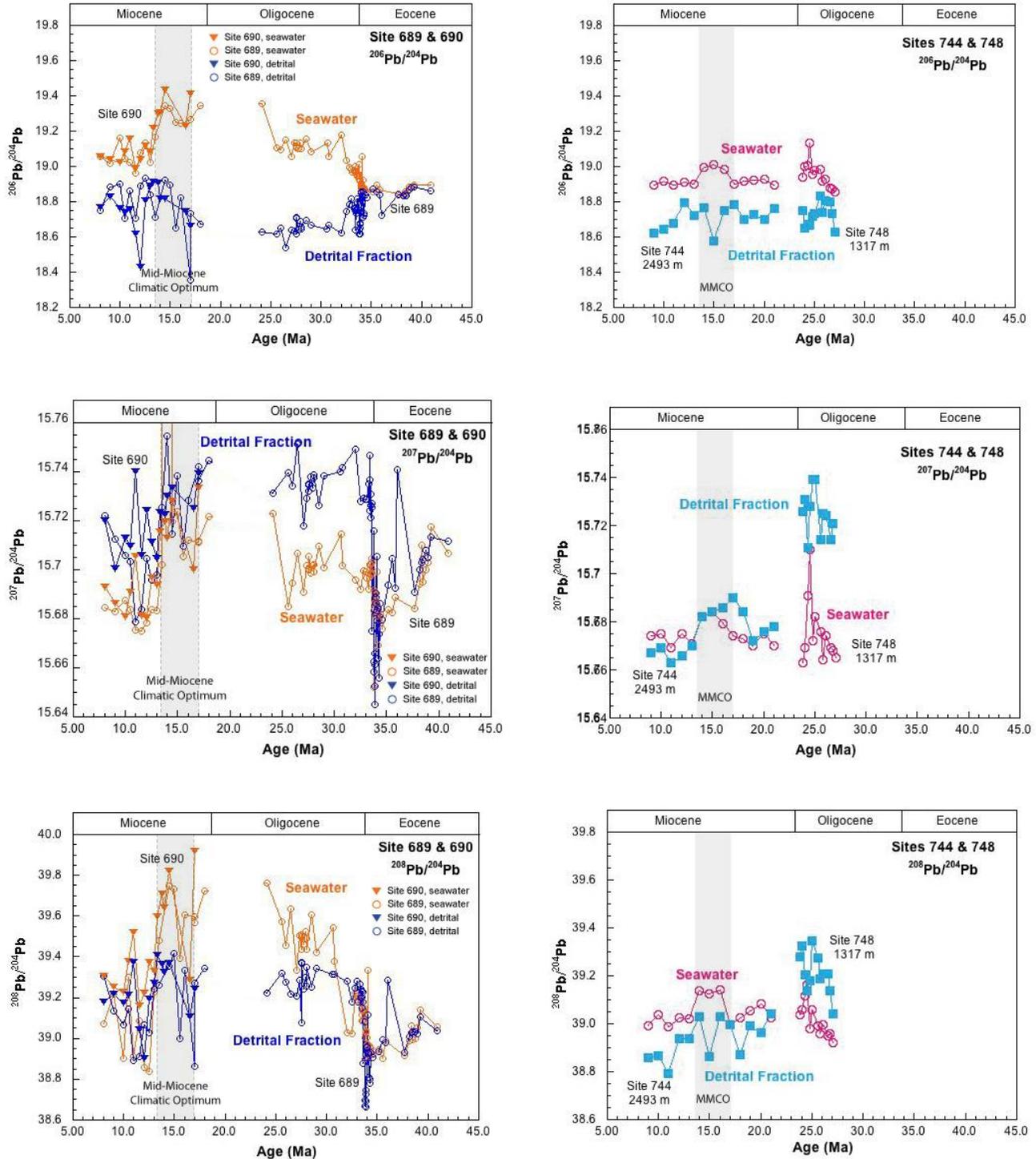
The shift in detrital Pb values observed in all sites implies a change in the composition of the rock exposed to mechanical weathered as the ice sheet waxed and waned. An ongoing investigation is designed to compare the isotopic composition of rock weathered during minimum and maximum ice sheet coverage to limited data on rock compositions on modern Antarctica.

Although less pronounced, Kerguelen data appear to follow the same trends as Maud Rise (Fig. 2). The variation in magnitude between seawater and detrital records at each site may be influenced by changes in source during weathering events or melt water runoff reorganization during deglacial periods (Kurzweil et al., 2010). Both Maud Rise and Kerguelen sites display <sup>207</sup>Pb/<sup>204</sup>Pb detrital values that are more radiogenic than, but similar to, the contemporaneous seawater component. A possible

explanation for this behavior is that the rocks exposed to weathering were younger than the Precambrian and therefore did not incorporate a lot of  $^{235}\text{U}$ , which had largely decayed away during the Archean.

Basak (thesis, 2011) attributed the difference in carbonate vs. silicate weathering to account for the lack in

variation of  $^{208}\text{Pb}/^{204}\text{Pb}$  at the EOT. The data during the Miocene do not exhibit this same trend, implying that the record is largely documenting silicate weathering. This is expected given that carbonates are more susceptible to weathering and are likely to have weathered out during the early stages of the ice sheet (Anderson, 2007).



**Figure 2.** Plots of  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios versus age (Ma) in seawater and detrital residues from ODP sites on Maud Rise and Kerguelen Plateau. Seawater values are from site 689 (orange open circles), site 690 (orange filled triangles), site 744 and 748 (magenta open circles). Detrital values are from site 689 (blue open circles), site 690 (blue filled circles), and site 744 and 48 (light blue filled squares). Eocene-Oligocene Pb data from site 689 was generated by Basak (thesis, 2011).

## CONCLUSION

In summary, Pb isotopes preserved in authigenic Fe-Mn oxide coatings represent seawater composition, while the contemporaneous detrital silicate fraction represents the mechanically weathered component. When combined, these Pb archives document changes in continental weathering style and intensity across an interval of climate change that is predicted to have profound consequences for weathering. Radiogenic seawater Pb isotopes documented during the warm MMCO indicate increased chemical

weathering. The covarying relationship between  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  imply that silicate weathering dominates the record. The relationship between seawater and detrital  $^{207}\text{Pb}/^{204}\text{Pb}$  indicates that sources may have been younger than the Precambrian and therefore did not contain incorporate a lot of  $^{235}\text{U}$ . Cooler climates following the MMCO led to re-establishment of ice on the continent and reduced chemical weathering rates as indicated by less radiogenic seawater Pb isotopes relative to detrital silicate values.

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