Reply to comments on "Constraints on ocean circulation at the Paleocene-Eocene Thermal Maximum from neodymium isotopes"

A.N. Abbott, B.A. Haley, A.K. Tripati, and M. Frank

Editor Comments to the Author:
Dear Authors,
Based on the two referee reports, I opt for reconsidering your submission after major revisions. Your contribution is certainly significant in terms of providing a new Nd isotopic data set and applying it to the PETM, but I ask you to revise your manuscript and carefully pay attention to the points brought up by the two referees, with respect to your methods and, in particular, your conclusion (referee #1, point 4) or hypothesis (referee #2, point 3).

Yours sincerely,

André Paul

We thank the reviewers and editor for their constructive feedback, which we have used to prepare the revised manuscript and have discussed in detail below. Please note that line numbers correspond to the clean version of the revised manuscript.

General Remarks
1) We have improved our method section to include more detailed descriptions of the reagents and the leaching procedure. The best practice for leaching sediments to obtain reliable bottom water εNd signatures is currently still debated (Wilson et al., 2013), however we used the standard leaching practice at the time of analysis (pre-Wilson, 2012), which has also been used in a series of other studies, including (Rutberg et al., 2000; Bayon et al., 2002, 2004), and this is now stated in lines (140-142). Sample limitations prevent re-leaching samples in response to the more recent work. While we present hydroxylamine leachate results, we collected both the buffered acetic acid and the hydroxylamine leaches (now stated in lines 150-154). Because the results from the acetic leaches that were analyzed for εNd were within error identical (lines 150-154) and we thus consider our leaches to reliably reflect bottom water signatures. The improvements to our methods section are further discussed in our response to reviewer 1, point 1 below.

2) In terms of conclusions, we now discuss the possibility of the observed differences in εNd being present in the absence of a topographic barrier in the manuscript (see lines 250-252). Our point with the original statement was that we are interpreting the global ocean subdivided into 3 basins with distinct εNd records, and this is now clearly stated (line 248). We have added additional text discussing circulation as a trigger for the carbon release. Specifically, we have added text discussing the excursion seen in the εNd from fish teeth in the Southern Ocean at the onset of the PETM, a time for which sediment samples were unavailable for the Southern Ocean sites. We note that the excursions in εNd for the Pacific and Southern Ocean are of similar magnitude (~2 *units). All of these εNd excursions precede the CIE (lines 213-217).*

We respond to specific reviewer remarks below. Please note that our responses to the reviewers have been updated to reflect additional changes made after the editor's remarks (including updated line numbers).

Anonymous Referee #1

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General comments In order to better constrain changes in thermohaline circulation across the PETM, this study provides 103 Nd isotopic compositions obtained from reductively leached decarbonated marine sediments. By combining new data with previously reported benthic foraminiferal 13C and "Nd values measured on fish teeth/debris as well as model simulations, the authors propose that a circulation changes in the Pacific Ocean was a trigger for carbon release. The large number of new Nd data has a potential to better understand the role of oceanic circulation during the PETM period. One of the essential contributions of this study is the application of leachate Nd isotopic ratios to reconstruct bottom water masses, which is not limited to the occurrence of fish teeth/debris. Consequently, the validation of the approach and usefulness of new data to constrain the ocean circulation are two major points. I, however, fond that these issues were not enough discussed in the present manuscript. Below I develop my suggestions and questions.

We thank this anonymous reviewer for helpful comments, which were used to revise the manuscript.

1. About faithfulness of leachate Nd isotopic compositions as a proxy of bottom water masses. The authors state that new "Nd values of leachates generally agree with fish teeth values. I rather observe the offsets up to 1 "-unit for sites 401, 527 and 690 in the early PETM (Figure 2). Indeed, comparison between leachates and fish teeth values is not always straightforward because of distinct temporal resolution. Furthermore, some recent studies pointed out the difficulty to extract bottom water "Nd values using reductive leaching if samples contain volcanogenic material (Elmore et al., 2011). Possible bias caused by decarbonation (Molina-Kescher et al., 2014; Wilson et al., 2012) are also suggested. Did the authors optimize the leaching method for their samples taking into account these studies? This is a critical point in particular for Pacific samples because Martin et al. (2010) reported "Nd comparison between fish teeth and leachate for site 690 in the South Atlantic but not for Pacific samples. More description about the leaching procedures is necessary including concentration and volume of leaching regents as well as leaching time. Also, "This may be. . .combination of the two" (P.2563, lines 20-23) is unclear and required to be further explained.

We recognize the reviewer's concerns about the leaching methods. While the best *practice for leaching sediments to obtain reliable bottom water εNd signatures is currently still debated (Wilson et al., 2013), we used the standard leaching practice at the time of analysis (pre-Wilson, 2012, lines 140-142), which has also been used in a series of other studies, including (Rutberg et al., 2000; Bayon et al., 2002, 2004). As no additional sediment was available, the leaching procedure could not be altered or repeated after the Molina-Kescher et al., 2014 or Wilson et al., 2012 methods, and this is now explicitly stated lines 162-164.*

We have improved our descriptions of the reagents and the leaching procedure to strengthen the methods section (lines 142-144), and we have no evidence for the presence of volcanogenic material in our sediments. We present hydroxylamine leachate results, but we collected both the buffered acetic acid and the hydroxylamine leaches (now stated in lines 150-154). Because the results from the acetic leaches that were analyzed for εNd were within error identical (lines 150-154) and we thus consider our leaches to reliably reflect bottom water signatures. This was recently supported by publications on Atlantic records by Khelifi and Frank (2014) in Climate of the Past and Böhm et al. (2015) in Nature, which clearly showed that in the absence of volcanogenic material reliable bottom water signatures are extracted by leaching with hydroxylamine. Specifically, the leach εNd signatures agree well with other methods, such as the extraction from coatings of planktonic foraminiferal shells. This is now stated in lines 154-156.

We now acknowledge in the edited text that there are potential uncertainties associated with leaching sediments that may have undergone late-stage diagenesis, although to our knowledge no concrete examples exist in the literature for the influence of late stage diagenesis on εNd signatures recorded in Cenozoic sediments. This is now stated in lines 156-160. Importantly, for these reasons, we do not base any of our interpretations on absolute εNd signatures of individual samples. Instead, we focus on the relative change in εNd between sites and over time at each site, and our interpretations are all based on these relative changes. Similarly we recognize that there may be offsets between leach and fish teeth data, which is why we only focus on the interpretation of relative trends in εNd signatures for both data sets (see also response to anonymous referee #2, point 1 for further explanation). This is now stated in lines 205-207.

2. Insufficient explanation about the link between proposed circulation scenarios (Figure 3) and the new Nd data. The authors describe “a fundamentally different circulation system than present during the PETM (section 3.3)” but this statement is not clearly shown by new Nd isotopic data. Considering uncertainty of extracted seawater Nd isotopic signals (difference between fish teeth/debris and leachates), it is not obvious which changes are significant. The scenarios shown in Figure 3 are ambiguous and incomplete. I suggest that the authors add "Nd values (and 13C values) to each step in Figure 3 to clarify the link between the hypothesis and the data. Also, it would be useful to indicate already published data in Figure 3 to improve the spatial coverage even if the previous data do not totally cover the study time interval. Another issue about the interpretation of "Nd records is a lack of alternative hypothesis. For instance, the distinct "Nd values in the Pacific ("Nd of -6 to -3.7) and the Southern Ocean ("Nd of -9.2) are interpreted as a sign of restricted water mass exchange between the two basins due to the

shallow seas between Asia and Australia. Nevertheless, the present- day mean "Nd values for the Southern Ocean, the equatorial Pacific and the North Pacific are -8.7, -3.9 and -3.8, respectively (Lacan et al., 2012). The difference of "Nd values of about 5 "-units between the Southern Ocean and the Pacific Ocean can be explained without any additional topographic barrier.

- *We have improved our link between the new εNd data and the circulation scenarios with the addition of the εNd values to Figure 3 as recommended below in the next comment.*
- *We have not included carbon isotope data nor existing published data in the interest of simplifying Figure 3. The fundamental shift we refer to is active versus absent deep-water formation in the North Pacific. Specifically, we propose that when the deep-water εNd signatures at site 1220 in the South Pacific became more positive (i.e. -3.4 to -4.0) there was deep-water formation in the North Pacific (Pre-PETM and during the PETM, temporarily "off" or minimal during the trigger event). These proposed on/off changes in North Pacific Deep Water formation agree well with the changes predicted by the model of Lunt et al. (2011). The periods of active deep-water formation in the North Pacific are shown in Figure 3 (arrows).*
- *Without a change in circulation, we would expect that the εNd signals would have remained constant over the entire record or showed a slow and predictable trend with any long-term changes (i.e., non-circulation) that may have occurred simultaneously (e.g. differing weathering inputs). We have modified the text to state this expectation (lines 243-246).*

3. The role of a circulation change in the Pacific as a trigger of carbon release. This is an important hypothesis but not enough discussed in the present manuscript. Even if consistency exists with some previous studies, only site 1220 record shows the corresponding "Nd variability and there is no discussion whether the observed variability is local/regional or basin-scale. I would suggest add a figure to discuss this point in more detail by comparing the site 1220 data with other reconstructed climate parameters.

We agree the new dataset might also be consistent with other alternative hypotheses. However, we present and discuss in detail the hypothesis we feel best explains our observations. We note that our data lend support to the modeling results of Lunt et al. 2011 (lines 60-63), which did not incorporate neodymium isotope evidence at all (see lines 79-81). We have added additional discussion to incorporate fish teeth neodymium isotope evidence into our discussion of circulation as a trigger for the carbon release, while recognizing the potential for offset between fish teeth data and our leachate data.

Figure 3 now includes εNd values to provide clear links between Figure 2 and Figure 3 and illustrate missing portions of the leach record. However, we emphasize again that the relative changes of εNd are more important than the absolute value of εNd for our reconstruction of the circulation patterns displayed in Figure 3.

We now acknowledge the observed differences in εNd can be present in the absence of a topographic barrier in the manuscript (see lines 250-252). The important point is that we are interpreting the global ocean having been subdivided into 3 basins with distinct εNd records, as now clearly stated (line 246-249).

Section 3 contains a number of statements that require more explanation (see my specific comments below). Since there exist already proxy reconstruction and modelling studies, synthesis of previous data and possible mechanism of inferred circulation changes would be appreciated.

Overall, it is necessary to clarify the original contribution of the new data. I believe that it will reinforce this work.

Minor or specific comments P. 2562, line 1, " Scher and Martin, 2006" would be deleted since the work uses fish teeth, not sediment leachates.

"Scher and Martin, 2006" removed

P. 2563, line 7, "Martin et al., 2012" would be deleted since the work uses fish teeth, not sediment leachates.

"2012" removed

P. 2564, lines 3-4, "convection occurred in both the North and South Pacific". It is not clear which data support this statement, which time interval is concerned. "Nd values of sites 1220 decreased just before and at the onset of PETM (Figure 2) but there is no data for site 1209 for the same time interval. The authors cite Thomas et al. (2014) for distinct overturning in the North and South Pacific but the paper discussed the Pacific trend for 70-30 Ma.

We have clarified that the time interval we were referring to is the PETM and we have removed the Thomas et al. (2014) citation.

P. 2564, lines 9-11, "While. . . (Fig. 2)". This sentence is unclear, in particular, "comparable changes".
We have clarified the sentence (lines 223-225); it now reads "While the change in the fish teeth ε_{Nd} *record is not a step-function, the observed magnitude and direction of change in leachate* ε_{Nd} *signatures is consistent with those changes reported for fish teeth* ε_{Nd} *signatures (Thomas et al., 2003) (Figure 2)."*

P. 2564, lines 4-5, about insignificant contribution of Tethyan deep-waters. More explanation is necessary for this point using the new data.

This sentence addressing the Tethyan deep-waters has been removed.

P. 2566, lines 8-9. Here the authors state that co-variation of "Nd values from the three sites in the southern hemisphere (213, 527 and 690) was enhanced during the PETM (Figure 1a). I notice that the co-variation continued after the PETM and extended to 55Ma. The co-variation is not specific for the PETM.

We have clarified the text to read that the covariation "was enhanced immediately before, during, and following the PETM"

P. 2566, lines 18-19, about "the contrast" between Southern Ocean and North Atlantic. The authors interpret that "the contrast" of "Nd values as a sign of little water mass exchange between these basins. But the "Nd values for the Southern Ocean is about -9.2 whereas the North Atlantic value is around -9.3 during the PETM. Consequently, the close values could be interpreted by the existence of water mass exchange.

We understand the confusion and have added clarification to the text. In short, we were referring the different trends in ε_{Nd} *observed between the two basins and not the absolute* ε_{Nd} *value.*

P. 2566, lines 26-27, "a corresponding sensitivity... variable deep-water masses". Please add more explanation.

The sentence was reworded for clarification to "The differences between the two North Atlantic ε_{Nd} *records can be readily explained by a weak North Atlantic deep-water overturning cell, resulting in higher sensitivity to local changes in Nd inputs or locally variable deep-water masses."*

P. 2567, line 7-9, about the difference of "Nd values between the North and South Atlantic. Please indicate reference(s) showing the difference of 2 "-units. According to Lacan et al. (2012), the mean values for the North and the South Atlantic are -11.5 and -10.5, respectively.

We have replaced the values with the reviewer's recommended values for the North and South Atlantic.

Figure 1. Add ticks of "Nd and 13C axis to all the three figures to improve the clarity.

These ticks have been added.

Figure 2. It is confusing that age axis, symbols and the order of oceanic basins are different between Figures 1 and 2.

We have changed the order of oceans to match the order of the oceans in Figure 2.

The axis values are different between Figure 1 and Figure 2 to provide more detail of the ε_{Nd} *values over the PETM in figure 1, while figure 2 is zoomed out to better place the sites in context with each other and the carbon record*

References

Elmore, A. C., Piotrowski, A. M., Wright, J. D., and Scrivner, A. E.: Testing the extraction of past seawater Nd isotopic composition from North Atlantic deep sea sediments and foraminifera, Geochem. Geophys. Geosyst., 12, Q09008, 2011.

Lacan, F., Tachikawa, K., and Jeandel, C.: Neodymium isotopic composition of the oceans: A compilation of seawater data, Chem. Geol., 300-301, 177-184, 2012.

Molina-Kescher, M., Frank, M., and Hathorne, E. C.: Nd and Sr isotope compositions of different phases of surface sediments in the South Pacific: Extraction of seawater signatures, boundary exchange, and detrital/dust provenance, Geochem. Geophys. Geosyst., 15, 3502-3520, 2014.

Wilson, D. J., Piotrowski, A. M., Galy, A., and McCave, I. N.: A boundary exchange influence on deglacial neodymium isotope records from the deep western Indian Ocean, Earth and Planetary Science Letters, 341-344, 35-47, 2012.

Anonymous Referee #2

This paper presents "Nd data measured on leachates of samples from 7 cores which span the Paleocene-Eocene Thermal Maximum and surrounding time periods. The paper uses this data to investigate the role that changes in ocean circulation played in the PETM. As such it addresses a question within the scope of this journal, and given the size of the new data set I believe this paper is appropriate for publication in Climate of the Past; however, there are a number of points which I think the authors should address in order to make their results and interpretations clearer for the reader.

We thank this reviewer for their helpful feedback.

Major comments include:

1. The comparison of the new leachate data presented in this study with published fish debris data from the same cores could be improved. It is unclear which depths (if any) have both fish debris and leachate data. If there are sufficient depths with values for both archives then a cross plot would seem the best way to compare leachate and fish debris data. If there is little data from the same depths then this won't be possible. In that case any apparent offset could be an artefact of sampling resolution, this may be the "higher-order variability" (p 2563 line 21) the authors refer to, but this could be elaborated upon. Although their results do not appear to show such a significant offset as has been reported by others (Elmore et al. 2011; Wilson et al. 2013), the authors should mention that decarbonated leachates have been shown to be susceptible to detrital contamination.

We recognize the offset between the fish teeth and the leachate data, but while the reason for the offset is not entirely clear the data are not contradictory. The fish teeth and sediments were generally collected from the same sites (213, 690, 527, and 401 are the same IODP sites for both fish teeth and leach samples), but the sediment core sections containing the fish teeth samples were not available for direct comparison (section data is not included in Thomas et al. 2003 or Stott et al. 1990). While there is some *uncertainty associated with the absolute εNd from both archival phases, we think that the common trends in the datasets are robust. Therefore, the discussion focuses on these trends (lines 205-207, see also anonymous reviewer 1 response 1).*

2. If the fish debris versus leachate question is dealt with separately using a cross plot then Figure 2 can focus more directly upon the paleoceanographic interpretation of the data. If the authors believe that both fish debris and leachates are predominantly a seawater signal then I suggest the two data sets could be made into composite records for each core in Figure 2 (but keeping the hollow/filled symbol key for leachates/fish debris suggested in minor comments below). At present the existing fish debris data is under-utilised and the variability in the data across the PETM is not fully captured by not connecting the two data sets. If the authors do not wish to connect the two data sets in case of a possible systematic offset between the two, a dashed line of the same colour connecting only the fish debris would be helpful.

We have tried to add a dashed line for the fish teeth data but the figure becomes even harder to read and therefore have chosen not to include lines connecting the fish teeth data points.

3. The connection between the data sets in Figures 1 and 2 and the circulation schemes presented in Figure 3 could then be made much more explicit by either colour scaling the core location dots in Figure 3 with the "Nd values for each time interval with a single scale bar on the side, or alternatively writing the "Nd value next to each core site. This would also help to clarify if there are time intervals where some cores have no data, for example site 213 prior to the PETM. At present the reader is made to work quite hard to establish how the authors arrived at the circulation schematics shown.

Thank you for the feedback on how to improve the clarity of the relationship between figures. We have altered figure 3 to include εNd values near the location of each core.

4. Although they argue in the conclusion that the Paleocene-Eocene ocean should not be compared to a conveyor-belt-like circulation regime (p2569 line 21), some consideration should be given to the modern circulation regime and the resultant "Nd values. In particular the fact that there is communication between the Atlantic, Southern and Pacific Oceans in the present day yet they display isotopically distinct values (Goldstein & Hemming 2003). Therefore, different "Nd values in different ocean basins alone cannot rule out water mass exchange between the basins.

We now acknowledge the observed differences in εNd can be present in the absence of a topographic barrier in the manuscript (see lines 250-252). The important point is that we are interpreting the global ocean subdivided into 3 basins with distinct εNd records, as now clearly stated (line 246-250).

Minor comments:

Although they are listed in Table 1, no mention of the paleodepths of each site is made in the text. It is worth explicitly stating that the sites were all estimated to have been at similar paleodepths which means they are not sampling water masses at different depths, especially for core sites within the same ocean basin.

We have added a sentence to the text pointing out the similarity of paleodepths (see lines 122-125).

p 2562 Section 2.3 Line 21. The authors could state that typical corrections made for this time period are small, approximately 0.5 " units, thus can be neglected as they have done (Thomas et al. 2003).

Following the advice of the reviewer, we have added a statement on the typical corrections for Nd isotopic compositions of PETM age (lines 176-178).

p 2563 section 3.2 line 11. Is site 1051B really in the eastern Atlantic? It appears to be western Atlantic in Figure 3.

We have corrected "eastern" to "western."

P 2568 lines 11-13 The authors argue that similar eNd shifts to those seen at site 1220 in the Pacific are not seen in the South Atlantic, however they have no leachate data from the corresponding time period (Figure 2). The only data in that time period is the published fish debris data which does potentially show a shift immediately prior to the PETM although it may not be coincident with the Pacific shift.

We have added text to discuss this point. See general response above. Specifically, we have noted that the Southern Ocean appears to have had an isotopic excursion of similar magnitude to that observed in the leachate data from the Pacific. We additionally note a smaller, less defined excursion is also visible in the Atlantic site 401 data. Without more constraints on the offset between the fish teeth and the leachates we are hesitant to speak to the relative timings of these shifts between basins, but in all cases the excursion in the neodymium isotope record precedes the CIE (see also response to question 1). Text added lines 212-217, 275-277, 299-302, and 320-322.

Table 1: It should be stated somewhere on the table that these are DSDP/ODP/IODP cores; although this is stated in the text, putting it at least in the table caption would make it clearer to the reader.

We have added 'IODP' to the table description.

Table 1: Rounding the coordinates to the nearest minute would be easier to read. Modern depths could also be rounded consistently (to the nearest metre).

We have taken the reviewer's advice. Specifically, we have rounded the coordinates as advised and we have rounded the modern depths to the nearest meter.

Figures 1 and Figure 2: Although the errors are stated in the text, average error bars should be included somewhere on all "Nd plots. This would make it easier for the reader to interpret whether any offsets between records from within the same ocean basins are significant.

We have added error bars to figures 1 & 2

Figures 1 and Figure 2: It would make it simpler to interpret these figures together if each core a had consistent colour/symbol between the two figures.

We have changed the colors to match figure 2 and figure 3 and we have added epsilon and carbon ticks to all panels on figure 2.

Figure 2: It would be easier to interpret the records if the same pattern of filled symbols for fish debris and hollow symbols of the same colour for leachates were adopted for each core as is done in Figure 1.

We have changed the symbols in Figure 2 to match figure 1 (specifically, solid for fish teeth, hollow for leachate).

Typographic errors p 2560 line 15 “. . .at the PETM, Specifically. . .” should presumably be: “. . .at the PETM. Specifically. . .”

Typographic error corrected

References:

Elmore, A.C. et al., 2011. Testing the extraction of past seawater Nd isotopic composition from North Atlantic deep sea sediments and foraminifera. Geochemistry Geophysics Geosystems, 12(9), p.Q09008.

Goldstein, S.L. & Hemming, S.R., 2003. Long-lived Isotopic Tracers in Paleoceanography and Ice Sheet Dynamics. In Treatise on Geochemistry. Elsevier Science Publish- ers B.V., pp. 453–489.

Thomas, D.J., Bralower, T.J. & Jones, C.E., 2003. Neodymium isotopic reconstruction of late Paleocene-early Eocene thermohaline circulation. Earth and Planetary Science Letters, 209(3-4), pp.309–322.

Wilson, D.J. et al., 2013. Reactivity of neodymium carriers in deep sea sediments: Implications for boundary exchange and paleoceanography. Geochimica et Cosmochim- ica Acta, 109, pp.197–221.

Constraints on ocean circulation at the Paleocene-Eocene Thermal Maximum from neodymium isotopes

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ABSTRACT

Global warming during the Paleocene Eocene Thermal Maximum (PETM) ~55 million years ago (Ma) coincided with a massive release of carbon to the ocean-atmosphere system, as indicated by carbon isotopic data. Previous studies have argued for a role for changing ocean circulation, possibly as a trigger or response to climatic changes. We use neodymium (Nd) isotopic data to reconstruct short high-resolution records of deep-water circulation across the PETM. These records are derived by reductively leaching sediments from seven globally distributed sites and comparing data with published data from fossil fish debris to reconstruct past deep ocean circulation across the PETM. The Nd data for the leachates are interpreted to be consistent with previous studies that have used fish teeth and benthic foraminiferal $\delta^{13}C$ to constrain regions of convection. There is some evidence from combining Nd isotope and $\delta^{13}C$ records that the three major ocean basins may not have had substantial exchanges of deep waters. If the isotopic data are interpreted within this framework, then the observed pattern may be explained if the strength of overturning in each basin varied distinctly over the PETM, resulting in differences in deep-water aging gradients between basins. Results are consistent with published interpretations from proxy data and model simulations that suggest modulation of overturning circulation had an important role for global recovery of the ocean-atmosphere system after the PETM.

1.0 Introduction

~~The PETM was the warmest time of the past 65 million years (myrs) representing a climatic extreme in which ocean temperatures increased globally by at least 4°C (Kennett and Stott, 1991; Sluijs et al., 2006; Tripati and Elderfield, 2004, 2005; Zachos et al., 2001, 2003, 2006) in response to the rapid release in less than 10,000 years (e.g. Farley and Eltgroth, 2003; murphy et al., 2010; Röhl et al., 2007) of a large amount of carbon from an isotopically light reservoir. Proposed sources for this carbon release include the dissociation of methane hydrates, volcanic exhalations, and changes in deep ocean circulation (e.g. Kennett and Stott, 1991; Bice and Marotzke, 2002; Dickens et al., 1995; Lunt et al., 2011, 2012; McInerney and Wing, 2011; Nunes and Norris, 2006; Sluijs et al., 2007; Tripati and Elderfield, 2005; Winguth et al., 2010; Zachos et al., 2001)~~. The PETM represents a time of profound global change with deep sea temperatures increasing 4-8°C (Katz et al., 1999; Kennett and Stott, 1991; Sluijs et al., 2006; Tripati and Elderfield, 2004, 2005; Zachos et al., 2001, 2003, 2006), widespread biological extinctions (e.g. Kennett and Stott, 1991), and ocean acidification marked by widespread carbonate dissolution occurring ~ 55 Ma (Dickens, 2000; Kump et al. 2009; Ridgwell and Schmidt, 2010; Zachos et al., 2005, 2008; Zeebe and Zachos, 2007). In general, the timing and global distribution of temperature records across the PETM are consistent with strong greenhouse forcing (Kennett and Stott, 1991; Tripati and Elderfield, 2004, 2005; Zachos et al., 2001, 2003; Sluijs et al., 2007) although the amount of carbon released, the type of carbon (Zeebe et al., 2009), and the possible role of other forcing agents (e.g., water vapor, aerosol loading, surface albedo feedbacks) is unclear (Bowen et al., 2004; Lunt et al., 2012). Changes in deep ocean circulation, orbital cycles, and volcanic exhalations are proposed causes of the initial warming (e.g., Kennett and Stott, 1991; Bice and Marotzke, 2002; Dickens et al., 1995; Lunt et al., 2011, 2012; McInerney and Wing, 2011 Nunes and Norris, 2006; Sluijs et al., 2007; Tripati and Elderfield, 2005; Winguth et al., 2010; Zachos et al., 2001). Climate simulations even suggest that the magnitude and pacing of the PETM and subsequent smaller events (ETM2 and ETM3) can be explained by orbitally induced changes in water temperature and circulation controlling the destabilization of methane hydrates (e.g. Lunt et al., 2010).

~~Perhaps the most~~ A striking characteristic of the PETM is a pronounced global negative stable carbon isotope ($\delta^{13}C$) excursion (CIE) (Kennett and Stott, 1991; Koch et al., 1992; Bowen et al., 2001; Nunes and Norris, 2006; McCarren et al., 2008; McInerney and Wing, 2011; Zachos et al., 2001). This isotopic excursion resulted from a rapid release (in less than 10,000 years) of carbon from an isotopically light reservoir, likely resulting from the warming climate (e.g., Farley and Eltgroth, 2003; Murphy et al., 2010; Röhl et al., 2007). Based on basinal gradients of available benthic $\delta^{13}C$ data (Nunes and Norris, 2006; Tripati and Elderfield, 2005), widespread carbonate dissolution (Dickens, 2000; Kump et al. 2009; Ridgwell and Schmidt, 2010; Zachos et al., 2005, 2008), inferred deep-sea carbonate ion gradients (Zeebe and Zachos, 2007), as well as numerical modeling studies (Bice and Marotzke, 2002; Lunt et al., 2012), it has been argued that a change in thermohaline circulation may have been associated with the PETM~~, and served as a trigger or amplifier of carbon release~~. Such studies have postulated circulation regimes fundamentally different than the modern ocean operating before and after the PETM (Kennett and Stott, 1991, Lunt et al., 2011). Specifically, studies have proposed the existence of Southern Ocean deep-water formation (Kennett and Stott, 1991) based on high-resolution carbon isotope records that are used to infer basinal deep-water aging gradients (Nunes and Norris, 2006; Tripati and Elderfield, 2005) and have suggested intermittent deep water formation in the North Pacific based on a fully coupled atmosphere-ocean general circulation model based on pCO2 simulations (Lunt et al., 2011). It is hypothesized that due to gradual changes in the temperature and hydrology of high-latitude surface waters, these southern-sourced waters were displaced during the PETM with the development of convection in the northern hemisphere (Alexander et al., 2015; Bice and Marotzke, 2002; Nunes and Norris, 2006; Tripati and Elderfield, 2005). The combination of warmer deep water and circulation changes may have served as a trigger or amplifier of the massive carbon release that resulted in the global CIE, possibly through the destabilization of methane hydrates (e.g. Bice and Marotzke, 2002; Lunt et al., 2011).

However, interpreting past benthic δ^{13}C records in benthic foraminifera of the PETM as ~~solely reflecting~~ a strict indicator of thermohaline circulation is complicated by possible contributions of fractionated carbon sources ~~(e.g. methane hydrates, burned terrestrial carbon, or volcanic sources)~~ (~~Higgens and Schrag, 2006;~~ Kurtz et al., 2003~~, Nunes and Norris, 2006; Storey et al., 2007; Svensen et al., 2004~~)~~or~~, changes in marine productivity (Paytan et al., 2007), ~~.~~ ~~Benthic δ^{13}C records can also be influenced by potential changes in contemporaneous surface ocean productivity and deeper~~ deep water carbon export (McCarren et al., 2008), ~~by~~ extinction and migration events of the biota, and potential signal loss through dissolution in highly corrosive bottom waters (Alexander et al., 2015; McCarren et al., 2008; Pagani et al., 2006; Zeebe and Zachos, 2007). In contrast, the geochemical cycling of Nd in the oceans allows Nd isotopes to be used as a quasi-conservative tracer of water mass distributions that is generally not affected by biogeochemical processes that can be used to reconstruct past ocean circulation (e.g., Frank, 2002; Goldstein et al., 2003; Thomas, 2004).

Published records of past seawater Nd isotope compositions (ε_{Nd}) extracted from fossil fish teeth serve as a quasi-conservative proxy for past deep-water mass distributions and mixing and do not show evidence for changes at the PETM. Specifically, the low-resolution ε_{Nd} data from fish teeth have been interpreted as possibly reflecting an uninterrupted contribution from a Southern Ocean deep-water source in multiple basins across the PETM (Thomas et al., 2003). This apparent disparity between proxy data may reflect the non-conservative nature of interpreting benthic foraminiferal $\delta^{13}C$, or could arise from the low-resolution nature of the published Nd isotope records.

To address whether there is Nd isotope evidence for changes in water mass distributions, we developed high-resolution records of the ε_{Nd} composition of Fe-Mn leachates from seven sites and compare these results to published ε_{Nd} data for fish teeth (Thomas et al., 2003) and benthic foraminiferal $\delta^{13}C$ (Nunes and Norris, 2006; Tripati and Elderfield, 2005; Zachos et al., 2001). The Nd isotope composition of Fe-Mn oxide leachates from core-top sediments has been used to accurately reconstruct bottom water values (Rutberg et al., 2000; Bayon et al., 2002; Gutjahr et al., 2007). This technique has also been applied to downcore sediments to study variations in bottom water circulation during the Pleistocene (Rutberg et al., 2000; Piotrowski et al., 2004, 2005, 2008). Measurements on older sediments ranging from Cenozoic (Martin et al., 2010) to Cretaceous (Martin et al., 2012) in age has shown that sequences from multiple localities can preserve a Nd isotope signal similar to fish teeth and can be used to develop much higher-resolution paleoceanographic records.

2. Materials and Methods

2.1 Sample and locality information

Details on the core locations, depths and paleo-depths are given in Table 1. Sites were located at similar water depths during the PETM, with paleodepths between 2400 and 3200 m in the Pacific, between 1900 and 2000 m in the North Atlantic, and between 1900 and 3400 m in the Southern and Indian Oceans (Table 1). Sources for the carbon isotope data referred to in this study is reported in this table. The age models used to plot all the data (including $\delta^{13}C$) are shown in Table 2, and are derived from the information given in the publications of the $\delta^{13}C$ data (Thomas et al., 2003; Nunes and Norris, 2006; Tripati and Elderfield, 2005). For completeness, we show in Table 2 the core depth-age curve fits that describe the age models for each core, where:

$$\text{Age (Myr)} = m(\text{Core Depth in mbsf}) + b.$$

Several segments are listed if sedimentation rates varied down core (the depth ranges of these segments are listed in Table 2). In all cases, simple linear sedimentation rates were used. These age models were also used to calculate the ages used here for the fish teeth/debris data (Thomas et al., 2003).

2.2 Sample preparation

Freeze-dried sediment samples were obtained from the Integrated Ocean Drilling Program (IODP). One to two grams dry weight of sediment was then rinsed with ultra-high purity (Milli-Q) water, and then processed following established sediment leaching protocols (e.g., Bayon et al., 2002, 2004; Haley et al., 2008a; Jacobsen and Wasserburg, 1979; Martin et al., 2010; Piotrowski et al., 2008; Rutberg et al., 2000; Scher and Martin, 2006). ~~This procedure basically involves the removal of carbonate phases using~~ Briefly, we thoroughly rinse the sediments with Milli-Q water, leach with buffered acetic acid~~, followed by thorough rinsing~~ for 2.5 hours and collect the leachate, then rinse thoroughly with Milli-Q water ~~and then the~~ again before the reduction of early diagenetic metal oxide coatings that carry the bottom water Nd isotope signatures with a dilute buffered hydroxylamine.HCl-acetic acid solution. This buffered hydroxylamine.HCl-acetic acid solution leaches the authigenic metal oxide coatings, which are then removed from the sediment and run through standard chromatographic procedures to extract a pure Nd solution for mass spectrometric analyses (AG 50W X12 resin for cation separation followed by di-2-ethylexyl-phosphate resin for rare earth element separation; see Gutjahr et al. 2007 for details). Many of the initial acetic leachates were run through the same chromatographic procedures for the same Nd analysis. ε_{Nd} of the first (buffered acetic) and second (hydroxylamine.HCl) leachates were dominantly within error of each other (0.5 ε_{Nd}), thus we consider our hydroxylamine.HCl leaches to reliably reflect bottom water signatures. The reliability of these signatures is further supported by recent publications demonstrating the validity of hydroxylamine.HCl leaches in the absence of volcanic material (e.g. Khélifi and Frank, 2014; Böhm et al., 2015). Still potential uncertainties are associated with leaching sediments that may have undergone late stage diagenesis, although to our knowledge no concrete examples exist in the literature for the influence of late stage diagenesis on the recorded εNd signature. For this reason we focus our interpretations on the relative changes in the Nd isotope signature rather than on absolute values. All sediments that could be sampled from the seven sites were analyzed and are presented here. No additional sediment was available to alter or repeat the leaching procedure after our original analysis (pre 2012) to account for new findings in leaching methods (Molina-Kescher et al., 2014; Wilson et al., 2012).

2.3 Sample analysis

Nd was analyzed on two instruments: a Triton Thermal-Ionization Mass Spectrometer at IFM-GEOMAR, using $^{146}Nd/^{144}Nd = 0.7219$ to correct for instrument fractionation, and a Nu Instruments multi-collector inductively coupled mass spectrometer at Oregon State University.

Nd isotopes are expressed in ε_{Nd} notation, defined as the deviation of measured ^{143}Nd/^{144}Nd ratios from a bulk Earth value of CHUR (chondritic uniform reservoir) in the 5th decimal place (Thomas et al., 2003). Long-term reproducibility of a Nd standard solution (SPEX source) gave a 2σ error of 0.5 ε_{Nd} units representing the total error of analyses and normalization, exactly as the samples. Analyses of the JNdi standard used for normalization had a lower 2σ error of 0.3 ε_{Nd} units. Nd isotope data are not corrected for decay of samarium given the limited temporal range of the data and the lack of constraints on sample Sm/Nd isotope ratios. Nd isotope corrections for the PETM are typically small (<0.5 ε_{Nd} units; Thomas et al. 2003) and therefore do not influence our interpretations.

3. Results and Discussion

We have applied a leaching technique (Gutjahr et al., 2007; Haley et al., 2008a; Haley et al., 2008b; Rutberg et al., 2000) that allows the extraction of past bottom water Nd isotope compositions from the Fe-Mn oxide component of marine sediments, expressed as ε_{Nd} units (Jacobsen and Wasserburg, 1979). Such data can provide high-resolution records of changes in past deep-water mass mixing and used to interpret changes in circulation (Martin et al., 2010, 2012; Piotrowski et al., 2004, 2005, 2008; Thomas et al., 2014). Below we compare results from leachates to data from fish teeth. We also compare results to carbon isotope data from the same cores. By combining high-resolution ε_{Nd} and benthic δ^{13}C records from the same locations it is possible to elucidate the causes and controls of δ^{13}C variations in the past deep oceans (Piotrowski et al., 2005). Our new isotopic Nd data are combined with existing δ^{13}C records and published Nd isotope data from fossil fish teeth of the Atlantic, Indian and Southern Oceans

(Thomas et al., 2003), in order to reconstruct global Nd isotope distributions across the PETM at a resolution comparable to the corresponding $\delta^{13}C$ data (Figure 1).

3.1 Comparison of neodymium isotope data obtained using different archives

Consistent with published results for a number of different sedimentary environments (Martin et al., 2012), we find evidence (Figure 1) for a general agreement between Nd isotopic data from sediment leaches and fish teeth (Thomas et al., 2003). There appears to be a small, possibly systematic offset at Site 401, and at 690B. This may be the result of higher-order variability at these locations, or the result of a temporal difference between the uptake or the retention of Nd in teeth and the ferromanganese coatings during sedimentation and diagenesis, or a combination of the two. In the first instance, model studies (Lunt et al., 2011; Winguth et al., 2010) have confirmed that locations near the Antarctic continent, such as at Site 690B, were sensitive to changes in climate conditions, and, as such, likely to have varied more substantially during the PETM (55.14-55.23 Ma for this study based on the CIE; Figure 2). Due to limited constraints of the offsets between fish teeth and leach records, we focus our interpretations on the relative trends in the ε_{Nd} signatures and their relation to the CIE.

3.2 Broad patterns in Nd isotope records

The broad patterns in these data support previous studies that have inferred convection occurred in the Southern Ocean, and that convection occurred in both the North and South Pacific during the PETM ~~(Thomas et al., 2014).~~ ~~The results are consistent with a relatively insignificant contribution of any Tethyan deep-waters.~~ The ε_{Nd} records cover the three major ocean basins (Figure ~~2~~1) and reveal distinct and basin-specific changes in deep circulation across the PETM. ~~The ε_{Nd} records for eastern North Atlantic Site 401 stabilize at ~ -9.3 during the PETM and then at ~-8.2 post-PETM. While the fish teeth ε_{Nd} record is not a step function, these are comparable changes to those reported from fish teet ε_{Nd} (Thomas et al., 2003) (Fig. 2). Deep waters at central (eastern) Atlantic Site 1051B, located near the proto-Caribbean, had a more positive ε_{Nd} (~-8) than site 401 prior to the PETM, but post-PETM ε_{Nd} from both sites converged. The record from Site 1051B exhibits similarities to post-PETM data from Site 401, which could reflect more intense mixing within the North Atlantic following the recovery (Fig. 1).~~ These data suggest that a change in ocean circulation may have triggered the carbon release associated with the PETM. Specifically, leachate ε_{Nd} records from Pacific Site 1220 show a negative excursion of ~2 units prior to the CIE while fish teeth ε_{Nd} records indicate a similarly sized excursion in the Southern Ocean.

Southern Sites 527 (subtropical South Atlantic) and 690 (Atlantic sector of the Southern Ocean) fluctuated (1 to 1.3 ε_{Nd} units) around a mean ε_{Nd} of ~ -9 throughout the record, with indications of a switch to in-phase co-variation during and after the PETM, also reflected by the evolution of Site 213 (Figure ~~2~~ 1). The ε_{Nd} records for eastern North Atlantic Site 401 stabilize at ~ -9.3 during the PETM and then at ~ -8.2 post-PETM, with the trend towards radiogenic values occurring at the end of the PETM. While the fish teeth ε_{Nd} record is not a step-function, the observed magnitude and direction of change in leachate ε_{Nd} signatures is consistent with those changes reported from fish teeth ε_{Nd} signatures (Thomas et al., 2003) (Figure 2). Deep waters at central (western) Atlantic Site 1051B, located near the proto-Caribbean, had a more positive ε_{Nd} (~-8) than Site 401 prior to the PETM, but post-PETM ε_{Nd} from both sites converged. The record from Site 1051B exhibits similarities to post-PETM data from Site 401, which could reflect more intense mixing within the North Atlantic following the recovery (Figure 2). Pacific sites 1209B and 1220B were more radiogenic than the other basins (ε_{Nd} from -6 to -2). With the exception of one data point (-2.1 ε_{Nd} at 55.02 Ma), the western Pacific (Site 1209B) had a remarkably constant ε_{Nd} signature of -3.7 pre- and post-PETM. In contrast, the eastern Pacific (Site 1220B) ε_{Nd} shows a short excursion from ~-4 to ~-5.5 ε_{Nd} at the onset of the PETM and remained near unradiogenic end member values post-PETM (ε_{Nd} = -5) (Figure 2).

3.3 A conceptual model to explain the records

The dissimilarities between the ε_{Nd} records confirm that the globally similar CIE dominantly reflects a change in source of oceanic carbon (Thomas et al., 2002). This change is not directly from a volcanic or extra-terrestrial source, as these would also be seen the ε_{Nd} records (Cramer and Kent, 2005). However, the ε_{Nd} data also clearly indicate that changes in water mass distributions and mixing were associated with the PETM and suggest a fundamentally different circulation system than present, with intermittent deep-water formation in the North Pacific, must have existed during the PETM if we interpret the ε_{Nd} record as strictly indicative of circulation. Without a change in circulation, we would expect that the εNd signals would remain constant over the entire record or show a slow and predictable trend with any changes other than circulation that may have occurred simultaneously (e.g. differing weathering inputs). Figure 3 illustrates our reconstruction of the evolution of global deep-water mass exchange during the PETM, based on the interpretation of the global ocean as three distinct deep-water basins ~~that only had restricted water mass exchange between them~~: the "Southern Ocean," the North

Atlantic and the Pacific. While in this model we hypothesize the basins only had restricted water mass exchange between them, we cannot eliminate the possibility of unrestricted exchange since similar scale inter-basinal differences in ε_{Nd} are observed in the modern ocean without this restriction.

This conceptual model, based on both $\delta^{13}C$ and ε_{Nd} data, supports changes in areas of convection that are consistent with simulations of the PETM with coupled climate models (Lunt et al., 2012, Thomas et al., 2014) and with a comprehensive climate model (Winguth et al., 2010). It is impossible to interpret from the Nd isotope data alone whether there was reduced or increased overturning associated with carbon release, as these data reflect water mass geometries and not rates of overturning. It is of note that model simulations support a weakening of the meridional overturning circulation with increased greenhouse gases, which might result in a water mass geometry similar to what is reconstructed. However, changes in the exchange between ocean basins will be dependent on several factors, including buoyancy-induced and wind-stress induced changes in overturning, as well as topography. Below we discuss whether there is evidence for changes in ventilation from basinal deep-water aging gradients, and what the nature of topographic barriers may ~~would~~ have been to produce the observed patterns in the data.

3.3.1. Southern records

An ε_{Nd} signature of -9.2 in the "Southern Ocean" most likely reflects an Antarctic margin source, similar to present day Antarctic-sourced intermediate waters (Stichel et al., 2012; Thomas et al., 2003). In agreement with previous inferences from $\delta^{13}C$ data (Tripati and Elderfield, 2005; Zeebe and Zachos, 2007), such a deep-water source can readily explain the post-PETM similarity of the ε_{Nd} records from both the Southern Atlantic (Site 527) and Indian Ocean (Site 213) with the Atlantic sector of the Southern Ocean (Site 690) (Figure 3). There are indications that the co-variation of ε_{Nd} at Sites 213, 527, and 690 was enhanced immediately before, during, and following the PETM, which could be consistent with intensification of Southern Ocean-sourced ventilation (Figure ~~1~~ 2a). Furthermore, ε_{Nd} signatures from fish teeth from site 690 and 527 suggest rapid changes in circulation leading into and during the early part of the PETM (Figure 1). The previously proposed formation of low-latitude Tethyan deep-water (e.g., Cope and Winguth, 2011; Huber and Sloan, 2001), or slower overturning circulation (Winguth et al., 2010) are unlikely to have generated such range and similarity in evolution of ε_{Nd} signatures at these three sites. Furthermore, numerical simulations indicate strong overturning circulation with multiple deep convection sites provide the best match to the ε_{Nd} record (Thomas et al., 2014).

3.3.2. Atlantic Ocean records

The contrast in ε_{Nd} trends between the Southern Ocean ε_{Nd} records and those of the North Atlantic (Figure 2) indicates that there was little exchange between these basins. The young Mid-Atlantic Ridge (MAR) between Africa and South America most likely represented an efficient barrier for north-south intermediate and deep-water exchange (Bice and Marotzke, 2002). This hypothesis differs from previous interpretations of overturning circulation in the Atlantic (Bice and Marotzke, 2002; Nunes and Norriz, 2006; Thomas et al., 2003), but confirms recent modeling results (Winguth et al., 2010). The differences between the two North Atlantic ε_{Nd} records ~~are most simply~~ can be readily explained by a weak North Atlantic deep-water overturning cell, ~~with a~~ corresponding resulting in higher sensitivity to local changes in Nd inputs or locally variable deep-water masses. Assuming weak, low-latitude, halothermally-driven downwelling in the North Atlantic basin, we would expect Site 401 to show a different ε_{Nd} evolution compared to Site 1051B, which is indeed documented in Figure ~~1~~ 2. The contrasting North Atlantic ε_{Nd} records (Figure 2c) also support model predictions (Winguth et al., 2010) that the North Atlantic was well-stratified until after the PETM, which is reflected by the convergence of the Nd isotope records indicating more efficient vertical mixing. This stratification was potentially interrupted briefly near the onset of the PETM. Specifically, ε_{Nd} signatures from fish teeth from site 401 indicate the Atlantic may have experienced rapid circulation changes early in the PETM (Figure 1) with ε_{Nd} briefly shifting from ~ -9 to ~-10. A caveat is that while it is possible that bathymetric barrier impeded exchange within the Atlantic, the isotopic composition of modern North Atlantic Deep Water increases by about 1 ε_{Nd} units from the North (-11.5 ε_{Nd}) to South Atlantic (-10.5 ε_{Nd}; Lacan et al., 2012), which is ~~larger than~~ a similar magnitude as the offset observed in these data (< 1 ε_{Nd} unit).

3.3.3. Pacific Ocean records

The distinct ε_{Nd} records of the Pacific point to restricted Pacific intermediate water mass exchange with the "Southern Ocean" (Figure 3). In this case, a possible barrier preventing substantial exchange between the Southern Ocean and Pacific Ocean might have been the shallow seas between southern Asia and Australia (Bice and Marotzke, 2002). Within the Pacific Ocean, times of convergent ε_{Nd} can be explained by a weakened southern Pacific ventilation which would allow northern Pacific water to influence both sites. With intensified

Southern Ocean sourced ventilation, Pacific Site 1220B ε_{Nd} would have diverged from the signatures of the northern source (Bice and Marotzke, 2002).

It follows that a Pacific circulation pattern, consistent with both $\delta^{13}C$ and ε_{Nd} data, must involve distinct southern- and northern-Pacific sources of deep waters, as predicted in previous studies (Lunt et al., 2011; Thomas, 2004; Thomas et al., 2008; Winguth et al., 2010). A sudden shift in the ε_{Nd} record at site 1220 immediately prior to the PETM may reflect the sudden onset of deep-water formation in the North Pacific (Figure 3). The initial change in ε_{Nd} from ~ -4 to ~ -6 at Site 1220B is recorded ~~The ε_{Nd} record at site 1220B are~~ stratigraphically below the negative carbon isotope excursion, consistent with the hypothesis that circulation changes triggered PETM carbon release. ~~This observation~~ Alternatively, the more negative ε_{Nd} at the beginning of the PETM may reflect a dramatic change in ventilation from a southern source that occurred just prior to the PETM. ~~Alternatively, this site~~ Also possible, the ε_{Nd} record at site 1220 may record significant changes in deep-ocean redox conditions due to its abyssal location in the tropical Pacific and the well-documented changes in dissolved oxygenation at the onset of the PETM. In that case, this Nd isotope shift might simply reflect the progression of a redox front in sediments. Unfortunately, no additional samples are available from site 1220B to further investigate these trends.

However several factors suggest this Nd isotope shift reflects changes in bottom water sourcing and not changes in the position of a sediment redox front. First, a ventilation change in the deep Pacific is in agreement with interpretations of carbon isotope data that support a reversal or large change in deep-water aging gradients between basins (Tripati and Elderfield, 2005). Secondly, carbonate geochemical data exist which suggest a reversal or dramatic change in deep ocean carbonate saturation gradients between basins, consistent with a circulation change (Zeebe and Zachos, 2007). Thirdly, substantially larger redox changes are observed in PETM sequences from other basins (i.e., the South Atlantic; Chun et al., 2010) that do not exhibit similar corresponding shifts in records of ε_{Nd}. Fourthly, similar types of changes are observed during Cretaceous ocean anoxic events (Martin et al., 2012) where there also is no clear-cut evidence for redox fronts driving the sediment leachate ε_{Nd} record. Finally, core photographs show that transitions in sediment redox at Site 1220B are not directly coincident with the ε_{Nd} change.

Thus we conclude these Nd isotope data are consistent with proxy data (Nunes and Norris, 2006; Tripati and Elderfield, 2005; Zeebe and Zachos, 2007) and models (Bice and Marotske, 2002; Lunt et al, 2011) and reflect a circulation change at the PETM. These data may record a Pacific circulation 'trigger' for carbon release. Some simulations indicate that at the PETM, a change in state of a Southern Pacific deep-water source could contribute to hydrate destabilization, which these data may reflect. Such changes in Southern Ocean water mass characteristics could ultimately have arisen from a gradual forcing such as volcanic outgassing (Kennett and Stott, 1991; Bice and Marotske, 2002; Lunt et al., 2011; Tripati and Elderfield, 2005).

CONCLUSIONS

Our study provides new neodymium isotope data from Fe-Mn leachates constraining changes in ocean circulation associated with the PETM. The novelty of these Nd isotope data reflect advances in our ability to extract such data from pelagic sediments, which has opened new avenues of paleoceanographic research. Using Nd isotopes, a proxy independent of carbon cycle processes, we unravel oceanographic changes during the PETM and are able to isolate competing factors controlling the carbon-isotope record during the PETM. In general, we find these data are similar to results from fish teeth (a more widely used proxy), and discuss the combined high-resolution records for seven sites.

The high-resolution combined Nd isotope records provide further evidence for changes in thermohaline circulation associated with the PETM, as previously inferred from basinal carbon isotope gradients (Nunes and Norris, 2006; Tripati and Elderfield, 2005) and constraints on deep-water carbonate ion concentrations (Zeebe and Zachos, 2007). In addition, these new records provide additional constraints on the timing and the nature of changes in circulation. The records are consistent with variations in bottom water mass mixing in each basin associated with the PETM, with water mass distributions implying intermediate and deep-water circulation changes. We find that changes in deep ocean circulation ~~appear to reflect processes in distinct basins of the Paleocene-Eocene oceans, and as such, may be oversimplified if interpreted in terms of a modern "global conveyor-belt-like" thermohaline circulation~~ occurred during the Paleocene-Eocene, and that these circulation changes likely preceded the carbon release, based on ε_{Nd} shifts observed stratigraphically below the carbon isotope excursion. ~~Data from the Pacific exhibit a shift just prior to the carbon isotope excursion, which could indicated that circulation changes preceded the carbon release.~~ Together with modeling results (Bice and Marotzke, 2002; Lunt et al., 2011, 2012; Winguth et al., 2010) and Mg/Ca-based bottom water temperature estimates (Tripati and Elderfield, 2005), Nd isotope data provide further evidence for thermohaline changes that may have served as a "trigger" of carbon release.

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Figure Captions:

Figure 1: Sediment leach ε_{Nd} and available fish teeth ε_{Nd} data from 55.1 to 55.4 Ma for all three ocean basins. Sediment ε_{Nd} values are connected with a dotted line and fish teeth data are represented by unconnected dots. The green shaded area represents the PETM as marked by the carbon isotope excursion from each core. These data sources are generally consistent, although higher-order differences, likely intrinsic to the natures of the archival sources, are present.

Figure 2: Nd and C isotope data (ε_{Nd} and δ^{13}C) across the PETM from the Southern Ocean (a), Pacific Ocean (b), and Atlantic Basins (c). The sediment leach ε_{Nd} are shown with circles and solid lines; the fish teeth/debris ε_{Nd} from Thomas et al. (2003) are shown as dots. All data are presented on directly comparable scales for both ε_{Nd} and δ^{13}C. The sample ages are based on the δ^{13}C age models. In (b) the age model of Site 1209B has been slightly adjusted (second x axis) such that the δ^{13}C excursion coincides with the age of the PETM in the other cores. The shaded vertical bar indicates the timing of the PETM as defined by the CIE in the cores.

Figure 3: A conceptual model of the intermediate/deep-water mixing changes across the PETM as inferred from ε_{Nd} records of intermediate/deep-water mass geometries. Arrow boldness reflects overturning circulation that could produce water mass geometries. Dashed arrows represent weak overturning. *Italicized numbers* indicate the interpreted ε_{Nd} from each site for the time period. The arrow directions reflect our interpretation of the general direction of flow, and are not meant to be viewed as precise flow-paths. The paleogeographic distribution of the continents is from Ocean Drilling Stratigraphic Network (ODSN).

List of tables