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

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.

G. Dickens

This manuscript is interesting. I leave detailed commentary to the formal referees.

We thank Dr. Dickens for his helpful feedback.

However, should the manuscript be published, I strongly encourage the authors to rewrite the Introduction. It currently does not give a good and sensible view of the PETM in which to frame their work.

– Page 2558: Lines 21-26 – The opening sentence perpetuates two misconceptions that permeate the literature and, as such, this sentence should be changed. First, it is by no means clear that the PETM was the warmest time of the Cenozoic. This is because intervals of EECO (←--3 to 6 Myr after the PETM) may have been warmer. Ba sically, the PETM occurred during a time of warming heading into EECO, and the time slice of true maximum global warmth is not certain. Second, there is ZERO evidence that the warming was the response to a rapid release of 13C-depleted carbon. This is because all evidence presented to date suggests the opposite: the carbon release, at least that manifested by the d13C excursion, responded to the warming. In fact, even the present submission suggests this possibility in the next paragraph and at the end. Carbon input associated with warming and a feedback to such warming – yes; carbon input causing the warming – no.

We agree that rewording the introduction will clarify the description of the PETM in context with the climatic variability of the rest of the Cenozoic, and will also increase the readability of the manuscript and fit better with the arguments presented throughout the paper. Therefore, we have rewritten the introduction as you have recommended (lines 46-51; 60-63).

– Page 2558/9: Lines 26-5 – This sentence makes little sense as written. Neither volcanic emissions nor a change in ocean circulation can directly explain the global negative CIE across the PETM for reasons of mass balance and carbonate chemistry, as known for over 20 years. Both these possibilities may be the trigger for another carbon source, such as seafloor methane, peat or permafrost, but they cannot be the root cause of the event, at least without clear elaboration. Things become more problematic, at least in terms of writing, because it is only in the next paragraph that part of reason for invoking a massive input of carbon during the PETM arises (i.e., the prominent d13C excursion). The other key part of the rationale, which is missing, is that the PETM is marked by prominent, though importantly variable, carbonate dissolution on the seafloor of all ocean basins.

We have added text and references describing the occurrence of carbonate dissolution on the seafloor of all major ocean basins (lines 49-50).

– Page 2558/9: Lines 28-4 – Lines 28-3: As above, this sentence also makes little sense. This is because volcanic emissions per se do not provide a “highly fractionated carbon source”, and because only one of the references (Kurtz et al., 2003) is applicable to concepts presented.

We have corrected these sentences (lines 89-94).

Good and bad introductions to the PETM have been presented numerous times over the last 20 years. I suppose I am now on a crusade to make sure mostly good introductions appear. Basically, the authors should set the key aspects of the PETM correctly, and present their findings, which are interesting, within this framework. They will see that such a change actually enhances and eases the discussion.

Anonymous Referee #1

Received and published: 12 August 2015

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 their 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 agree with 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), 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). 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, with lines 142-144. 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 Climates of the Past and Böhm et al. (2015) in Nature, which clearly showed that in the absence of volcanogenic material reliable bottom water signatures can be extracted using hydroxylamine.HCl leaches. Specifically, the leach εNd signatures agree well with other methods, such as the extraction from coatings of planktonic foraminiferal shells (e.g. Böhm et al., 2015). 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 the recorded εNd signature. 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 205-206.

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 the on-and-off deep-water formation in the North Pacific. Specifically, we propose that when site 1220 in the South Pacific becomes less negative (i.e. -3.4 to -4.0) there is 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 on periods of 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 remain constant over the entire record or show 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 239-242).

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 lends support to the modeling results of Lunt et al. 2011 (lines 60-63), a modeling approach that did not incorporate neodymium isotope evidence at all (see lines 79-81).

Figure 3 now includes an εNd value 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 246-248). The important point is that we are interpreting the global ocean subdivided into 3 basins with distinct εNd records, as now clearly stated (line 244).

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 citation for Thomas et al. (2014). Lines 210-211.

P. 2564, lines 9-11, "While. . . (Fig. 2)". This sentence is unclear, in particular, "comparable changes".

We have clarified the sentence; 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} is consistent with those changes reported from fish teeth ε_{Nd} (Thomas et al., 2003) (Figure 2)." Lines 214-216.

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" on Lines 269 and 270 in revised manuscript.

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. Line 279 in revised manuscript.

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." Lines 285-288 in revised manuscript.

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. Lines 295 and 296 in revised manuscript.

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

Ticks added on all three figures.

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 complementary trends in the comparison of datasets are robust. Therefore, the discussion focuses on these trends (lines 205-206, 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 on the fish teeth data.

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 246-248). The important point is that we are interpreting the global ocean subdivided into 3 basins with distinct εNd records, as now clearly stated (line 244).

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).

At the advice of the reviewer, we have added a statement on the typical corrections for the PETM (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.

"eastern" corrected to "western" on Line 217 in revised manuscript.

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 understand the reviewer's concern, but without more constraints on the offset between the fish teeth and the leachates we are hesitant to interpret the fish teeth data as filling in a gap where sediment samples were unavailable (see also response to question 1).

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.

'IODP' added to 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 coordinates are rounded as advised, *and modern depths rounded to 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.

Error bars were added 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.

Colors have been changed to match figure 2 and figure 3. Epsilon and carbon ticks have been added 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.

Symbols in Figure 2 have been changed to match figure 1 (solid for fish teeth, hollow for leachate)

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

This typographic error has been 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.

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