

“Evolution of ^{231}Pa and ^{230}Th in overflow waters of the North Atlantic”
by Feifei Deng et al.

Response to referees

We would like to thank all referees for their time reading the manuscript and giving constructive suggestions to improve the paper. We are pleased that all three referees appreciate the dataset and broadly welcome publication of this paper.

Four issues were raised by more than one reviewer. Before we respond to the points raised in individual reviews, we address these four issues.

1. Disagreement between the various referees about the key nature of findings led to a change in the introduction section, and the conclusion section accordingly.

It is interesting that referee comments varied from those that said our work confirmed the use of $^{231}\text{Pa}/^{230}\text{Th}$ as a paleoproxy, to those that thought we have proved the proxy does not work. It is clearly important to more clearly state how the proxy might be interpreted, and whether such interpretation is justified following our work. So we have clarified in the introduction section that there are two conceptual models that form the foundation of the interpretation of sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ ratios in terms of past rates of deep water circulation.

Model 1 relies on a net export of ^{231}Pa out of the Atlantic due to the residence time ^{231}Pa being longer than ^{230}Th (an approach adopted by studies such as McManus et al., 2014, and Bradtmiller et al., 2014).

Model 2 is based on the systematic evolution of $^{231}\text{Pa}/^{230}\text{Th}$ with water mass age, which has seen its application in Negre et al. (2010).

Our study provides an opportunity to assess the validity of these models. In the conclusion section, we made clear that our result supports the Model 1 interpretation that there is a northward export of ^{231}Pa out of the Atlantic, but raises questions about model 2 because there is no simple relationship between $^{231}\text{Pa}/^{230}\text{Th}$ and water mass age.

2. Reviewers questioned the reliability of CFC ages, especially for older waters, and asked for more details about how these ages were calculated.

We have clarified that CFC-based ages were calculated with Transit Time Distribution (TTD) method, and were different from the CFC concentration/tracer ages based on the atmospheric history of CFC.

Briefly, we computed CFC-based ages combining CFC concentrations and water mass composition obtained from extended Optimum Multi-Parameter (eOMP) analysis. First, TTD mean ages for each source water type (SWT) were calculated from CFC concentrations and eOMP analysis from OVIDE cruise 2012. These mean ages for each SWT were then combined with water mass composition obtained from

eOMP analysis for GEOVIDE 2014 to give an age for water at depths where water mass compositions are available. This approach assumes that the mixing of the ages (not the CFC concentrations) is linear, and decides that the aging of water is due to variations in water mass composition, rather than the increase of spreading time of the water. In further considering and discussing this calculation we have relied heavily on input from Reiner Steinfeldt and we have therefore added him as an author to the manuscript.

3. Reviewers questioned why ^{231}Pa and ^{230}Th concentrations given by the model did not reflect quoted preformed values at zero water age.

We have considered the modelling work carefully. On reflection, we consider our introduction of a surface term to the model to be incorrect and have consequently removed it during revision, to rely on the model exactly as originally presented in Moran et al. (1997).

4. Reviewers suggested the use of SI units adopted in GEOTRACES data product.

We have changed the units in the data table and throughout the text using $\mu\text{Bq/kg}$ for ^{231}Pa and ^{230}Th , and pmol/kg for ^{232}Th .

Below, we respond to the referees point by point. Reviewers' comments are in blue, and our responses are in black.

Response to Anonymous Referee #3

Deng and coworkers have produced an important data set by analyzing samples collected on GEOTRACES Section GA01 (GEOVIDE) for ^{231}Pa and ^{230}Th . These results hold valuable implications for the use of these radionuclides as tracers of North Atlantic deep water ventilation, and its variability through time (via the analysis of $^{231}\text{Pa}/^{230}\text{Th}$ ratios, henceforth “Pa/Th”, archived in marine sediments). However, there are some major issues that should be addressed before I can recommend that the manuscript be published, as detailed in the following.

Major Comments:

Clarify and emphasize the principal take home message. The concluding sentence of the manuscript states “and continues to support the use of sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ measurements at a basin scale to constrain overturning circulation.” This statement is based on the calculated southward export of dissolved Pa being substantially greater than the southward transport of Th. However, as clearly stated in the manuscript, there is no observable relationship between dissolved Pa/Th ratio and water mass age. This observation is in direct contradiction to the principles underlying the use of sedimentary Pa/Th ratios to reconstruct past variability of the ventilation of deep water in the North Atlantic Ocean, where it is assumed that dissolved Pa/Th ratios will increase monotonically with age after water mass formation due to the longer residence time of Pa compared to Th. How can the authors conclude that their results support the use of sedimentary Pa/Th ratios to constrain overturning circulation when there is no relationship between dissolved Pa/Th ratio and water mass age?

This issue becomes even more important if one considers the evolution over time of dissolved Pa/Th ratios down the length of the western Atlantic Ocean. Although the authors do not present Pa/Th ratios for the mid-latitude North Atlantic or at 40S along with the dissolved ^{230}Th and ^{213}Pa data in Figure 3, eyeballing the dissolved ^{230}Th and ^{231}Pa profiles for these regions suggests very little change in the dissolved Pa/Th ratio from north to south, from GEOVIDE near the formation region to GA10 at 40S. If a more rigorous analysis of the data reveals this to be true, i.e., that there is no change with water mass age in the dissolved Pa/Th ratio down the entire length of the Atlantic Ocean, then I do not see how Pa/Th ratios can be related to ventilation rate, either in the modern ocean or to reconstruct climate-related changes in ventilation rate in the past.

The manuscript would have much greater impact if this point were discussed at length, incorporating data from the entire Atlantic Ocean.

Author's response:

We have taken on board the reviewer's comments here. As explained in point 1 of our opening comments above, we have now clarified that there are two conceptual models that form the foundation of the interpretation of $^{231}\text{Pa}/^{230}\text{Th}$. This has significantly helped us to make clear the take-home messages in the conclusion section.

The development and application of CFC ages are unclear. The description in the Supplementary material (page 8) is helpful, but some of the output is not meaningful. CFC ages are not valid for time periods older than the initial introduction of CFCs into the environment in the middle of the 20th century. My colleagues who are experts in the use of CFC ages generally decline to interpret apparent ages greater than about 40 to 50 years due to the uncertainties inherent in interpreting CFC ages in water masses last exposed to the atmosphere during the earliest days when CFCs were tagging water masses. Therefore, I do not understand how Mediterranean Water can be assigned an age of 91 ± 8 years, or NEADW can be assigned an age of 989 ± 48 years (Table S2). Unless there is something not explained in the paper that allows CFC ages this old to be computed, the old ages should be removed from the paper. Accordingly, Figure 6a can be removed, leaving only Figure 6b in the paper.

Related to Figure 6, it is very confusing that the two panels have different longitude scales, but the scale for Figure 6a is not shown. If there is a reason to retain Figure 6a, then include the longitude scale and note that Figure 6b incorporates only the western half (approximately) of Figure 6a.

Author's response:

We have corrected the missing longitude mistake.

Thank you for suggesting clarification for the calculation of CFC-based ages. We have included more detailed information describing how CFC-based ages were calculated and uncertainties associated with it, as explained as point 2 on page 1 in this RtR.

The calculation and interpretation of scavenging (rates and percentages) relies strongly on the estimated CFC ages (Figures 7 through 9). Given this important sensitivity to estimated age, I recommend that the authors include a discussion of the uncertainty in the CFC ages, and how that may affect their interpretation.

Author's response:

Thank you for the suggestion. We have included the uncertainty of the CFC ages and how they affect our interpretation in the revised manuscript.

As discussed on page 6 of the manuscript, the initial (preformed) concentrations of dissolved ^{230}Th and ^{231}Pa at the time the water masses formed are unknown, so the authors assume that the preformed concentrations are either equal to average concentrations in surface waters sampled along the GEOVIDE transect or that preformed concentrations are zero. Unfortunately, until data are available for the Nordic Seas and the Labrador Sea during times of winter convection, these may be the only options available for the type of analysis described here. Nevertheless, it would be helpful if the authors provided additional discussion of the sensitivity of their derived products (e.g., fraction scavenged for each isotope) to the values assumed for the preformed concentration.

Author's response:

Thank you for this comment. We have added the discussion of how preformed values (i.e., two scenarios, preformed=0 and preformed =average) affect the calculation of the derived products in this section as suggested.

In this context, it would also be helpful to discuss the possibility that each water mass has a different preformed concentration, and how this might affect the interpretation of the data presented in Figure 8. Implicit in the presentation of the data presented in Figure 8 is the assumption that all water masses have the same preformed concentrations. What if this is not the case? How would that alter the interpretation of the data?

Author's response:

Thank you for your comment. This is a good point, and we have made clear that our results are based on the assumption of the same preformed value for different water masses, and addressed the influence of this assumption based on our discussion of how preformed values affect the results.

There seems to be a problem with the model curves shown in Figure 9, where the solid lines depict model results for the case where average surface water concentrations determined for samples collected on the GEOVIDE cruise were used in place of the preformed concentrations. If that were the case, then why do the projected model concentrations at zero age (solid lines) intersect the Y axis at concentrations about double the values reported for average surface concentrations on page 6 (0.108 dpm/1000 L for ^{230}Th and 0.089 dpm/1000 L for ^{231}Pa)? If I understand the model correctly, then the concentrations at zero age should equal the assigned preformed concentrations. Is this not the case? Is the problem that the preformed concentrations are introduced twice in equation 6 (supplementary material)? Note that $C(\text{pre})$ and $C(\text{surface})$ are one and the same. Should both terms be in equation 6?

Author's response:

Thank you for pointing this out. We ran some tests with the model and realized that introducing the surface term in the model is the reason causing the ^{231}Pa and ^{230}Th concentration twice of the preformed values at zero age. Considering this weakness in the model, we removed the surface term in the model as explained as point 3 of our opening comments. The new model gives y intercepts at preformed values at $t=0$.

Summary of major comments: Given all of the uncertainties in CFC age and in initial (preformed) concentrations of Pa and Th, it seems that a stronger paper than the one under review would be produced by integrating the new data from GEOVIDE with other data from GEOTRACES cruises down the length of the Atlantic Ocean (GA02, GA03, GA10 and, perhaps, other sections with data in the GEOTRACES IDP2017, if there are any) to establish firmly whether or not the dissolved Pa/Th ratio in deep Atlantic water evolves over time as assumed in the application of sedimentary Pa/Th ratios to constrain past changes in the rate of ventilation of North Atlantic Deep Water.

Author's response:

We agree that it would be great to integrate all the ^{231}Pa and ^{230}Th data available from GEOTRACES in the Atlantic Ocean. We are thinking of putting together a paper with that aim. With the present manuscript paper, however, we would prefer to focus on the data from GEOVIDE and how this new addition of data can provide evidence to assess the conceptual models adopted for the interpretation of $^{231}\text{Pa}/^{230}\text{Th}$. However, we continue to include data from GA02 and GA03 to put our new GEOVIDE data in the broader context and to show horizontal gradient of ^{231}Pa and ^{230}Th in the Atlantic.

Minor comments:

The authors report their results using historical units (dpm/1000 L) but their results will be converted to SI units when included in the next GEOTRACES data product. All of the Th and Pa data currently in the IDP2017 are presented using SI units, so why not make this conversion before publishing the GEOVIDE data?

Author's response:

We have reported our data in SI units adopted in the GEOTRACES data product as suggested.

page 6 line 1 "Steinfeldt" is misspelled.

Author's response:

We have corrected the misspelling.

page 6, definition of "Ingrown component": Are U concentrations normalized to a constant salinity? To the salinity measured for each sample? Something else?

Author's response:

We used constant U activities for all the sample when calculating the "ingrown component", and calculated ^{238}U following the equation in Owens et al., 2017, assuming a salinity of 35 permil. U-235 and U-234 activity was then calculated assuming natural abundance ratio of $^{238}\text{U}/^{235}\text{U}=137.88$ and the $^{234}\text{U}/^{238}\text{U}$ activity ratio in seawater is ~ 1.15 .

page 7 line 16: "three times more ^{230}Th has been removed by scavenging" than "what?" Complete the description of the comparison being made.

Author's response:

We have added: '... more than it remains in the water...'

page 8 line 7: Change "run" to "ran"

Author's response:

We have made changes as suggested.

page 8 line 27: delete the "in" prior to "from DSOW"

Author's response:

We have made changes as suggested.

page 8 line 28, and elsewhere: Bottom scavenging of ^{230}Th was first noted by Bacon and Anderson (1982) and by Anderson et al. (1983; EPSL 66(1-3), 73-90, not the paper cited by Deng et al.) in their study of the eastern tropical Pacific. These early indications of bottom scavenging should be cited.

Author's response:

We have included the suggested reference.

page 9 line 12: What is the source of the average ^{230}Th and ^{231}Pa concentrations in the upper limb? The values given here are not those given on page 6 for GEOVIDE surface waters, so the source should be given.

Author's response:

Here, the boundary between upper and lower was defined by potential density at 32.15 kg/m^3 as described in the discussion manuscript on page 9 line 10. The average ^{230}Th and ^{231}Pa in the upper and lower limb are average concentrations of these nuclides in water with potential density $< 32.15 \text{ kg/m}^3$ and $> 32.15 \text{ kg/m}^3$, respectively.

page 10 line 7: Change "that" to "than" i

Author's response:

We have made changes as suggested.

Additional references (added by authors):

Bradtmiller, L. I., McManus, J. F. and Robinson, L. F.: $^{231}\text{Pa}/^{230}\text{Th}$ evidence for a weakened but persistent Atlantic meridional overturning circulation during Heinrich Stadial 1, Nat. Commun., 5, 5817 [online] Available from: <http://dx.doi.org/10.1038/ncomms6817>, 2014.

Negre, C., Zahn, R., Thomas, A. L., Masqué, P., Henderson, G. M., Martínez-Méndez, G., Hall, I. R. and Mas, J. L.: Reversed flow of Atlantic deep water during the Last Glacial Maximum, Nature, 468, 84 [online] Available from: <http://dx.doi.org/10.1038/nature09508>, 2010.