

“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 Reviewer #1: R. Francois (Referee)

This paper is an important contribution to the growing database describing the distribution of Th-230 and Pa-231 in the world ocean. I recommend publication after considering the comments and questions listed below:

Abstract; line 19-20: The reason for a weaker correlation between Pa-231 and water mass age is likely due to the much lower concentrations and rate of ingrowth of Pa compared to Th. It may be worth adding error bars to Fig. 8(a), (c), (e) to highlight this point.

Author's response:

We agree with the reviewer that the lower concentration and slower ingrowth rate of Pa might be the reason for a weaker correlation. We have added error bars to Fig. 8(a), (c), (e), and pointed out this likely reason in the text as suggested.

P 3; line 13: why was a ^{236}U spike added to the sample?

Author's response:

We add the spike because we sometimes recover U during chemical separation of Th and Pa. We have made that clear in the revised manuscript.

P4; Line 20 – 23; Fig. 3: If the purpose of this figure is to show that the concentrations measured on the GEOVIDE line are much lower than measured further “downstream”, I don’t think that the data from 40S are useful because they raise questions that are likely beyond the scope of this paper. The wording used in line 20 – 23 is incorrect since there is an apparent southward decrease instead of an increase between the North Atlantic and 40S. Hayes et al.’s data show a strong longitudinal gradient for both Th-230 and Pa-231. Were the averages calculated over the entire longitudinal GA03 section? Were the averages calculated for 40S comparable?

Author's response:

We agree that 40°S data raise points outside the scope of this manuscript. We have replaced Fig 3 with a figure that compares only published data from west of the Mid-Atlantic Ridge from GA01 (i.e. this study), GA03 (Hayes) and GA02 (South Atlantic). This approach more closely follows deep-waters as they age along their flow path, and shows an increase of concentration of both nuclides.

Fig. 5: ISOW is not indicated on this figure, even though it is one of the most prominent water mass. I would suggest replacing the salinity contour lines by the contour of the main water masses reported on Fig. 4, since the purpose of this figure is to relate these water masses to the distribution of the radionuclides.

Author's response:

We agree with the reviewer that plotting contours of the main water masses instead of salinity contours would be more useful and have modified figures accordingly.

Line 31; p5 and Fig. 6: It is not entirely clear to me how the CFC ages were determined for the GEOVIDE section. Water masses and CFC ages were determined in 2012 of the eastern side of the section. From these data, the CFC ages of the different water masses could be determined for 2012 and these ages were used to determine the CFC ages of all the samples collected in 2014 from their water mass constituents.

My first problem is how you could estimate the CFC age of the water masses west of Greenland. Surely, the age of ISOW and DSOW in this section of the transect must be older than in the eastern section since these water masses are farther removed from their site of formation.

My second problem is how can you distinguish ages between 100 and 800 years with CFCs considering that CFC manufacture only started 80 years ago?

Finally, and maybe more fundamentally, I question whether you can apply CFC-age to Th-230 and Pa-231. I am not an expert on this question but here are my concerns: Each (most?) of your samples consists of a mixture of different water masses. Even the red zones on Fig. 4, indicate up to 20% mixing. If you mix 2 water masses of different ages, the CFC age of the mixed sample will be biased toward the younger age because there is more CFCs in the younger end member (although CFC concentrations have quasi plateaued since 1990). On the other hand, for the same mixed sample, the Th-230 age will be biased towards the older end-member because it contains more Th-230. So, in a mixed sample, Th-230 had more time for in-growth than indicated by the CFC age. Because Pa-231 grows in slower than Th-230, this effect is less pronounced. Therefore, I believe that the ingrown Th and Pa calculated

with CFC ages using equations 4.1 and 4.2 must be taken as minima and more so for Th than for Pa.

Author's response:

Thank you for raising the question. We have included a clear description of how CFC ages are determined, as explained as point 2 on page 1 of this Response to Reviewer (RtR). This approach allows projection of water age west of Greenland where CFC measurements were not available.

We could understand the reviewer's concern about the ISOW and DSOW ages not showing an increase in the eastern section. The approach we adopted to calculate CFC ages determines that the aging of water is due to the change in water mass composition (i.e. the mixture of water masses), rather than the increase of water spreading time.

Unlike the CFC apparent age calculated based on pCFC and the atmospheric history of CFC, the TTD approach inherently solves the mixing bias problem and is not limited by the fact that atmospheric history of CFC only started in 1930s. However, our age model does work better in the young age range between 0-80 years, and we restrict our discussion within that age range.

We agree that there exists a bias due to mixing of waters of different ages for CFC concentration age calculated based on the atmospheric history of CFC. CFC-based ages in our paper however are computed with TTD method and take into account advection and diffusion in the mathematical framework it employs and therefore will not be biased due to mixing. As we combine TTD-derived CFC age for each SWT with water mass composition, the water mass mixing of the CFC ages is linear (unlike the CFC concentrations). This addresses the reviewer's concern that CFC ages are biased due to mixing from this perspective. There is also no bias for ^{230}Th as the mixing is linear.

Fig. 6: Adding water mass contour lines would be helpful

Author's response:

As above, we have added water mass contour lines.

Line 16; p6 "Preformed component" "...in the absence of measurement at the exact location of deep water formation: :".

While this statement is correct for the formation of DSOW and ISOW, I would say that station 69 is essentially at the location of LSW formation.

Author's response:

We cannot totally agree with the reviewer that station 69 is the location of LSW formation. Pickart et al. (2003) for instance suggested that Labrador Basin is not the only Basin of LSW formation, and that Irminger Basin is a second formation site. We agree though that the wording needs some correction to make it clear that the preformed value of ^{230}Th and ^{231}Pa is very uncertain.

“..we set the preformed value as the average of concentrations measured in waters <100m depth for this section..”

I think the authors need to elaborate on their rationale for doing this. It is not like deepwater is formed uniquely from water sinking from a depth < 100m. Deep water convection homogenizes the water column in the Labrador and Nordic seas, which then spreads laterally at depth. Therefore, the homogenized water column at the sites of deepwater formation could be the starting point providing preformed concentrations. If so, data from station 69, as well as earlier data from Moran et al indicate that preformed Th-230 should be about 0.3 dpm/1000l both for the Labrador and Nordic seas, instead of 0.1 dpm/1000l. Such value for the Nordic Sea (based on one profile from Moran et al., 1995) is of course problematic since it is higher than measured here in the IC basin. In addition, Moran's data from the Labrador Sea shows substantial inter-annual variability. I think the authors should be more nuanced in their choice of preformed values and consider how the uncertainties on this number could affect their conclusions.

Alternatively, the reasoning followed by the authors may be that cooling happens at the surface, and therefore that must be the starting point, and the higher Th concentrations found in the water below at the sites of deep water formation reflects the residence time of this surface water in the convection cell. If this is the case, that should be more explicit in the paper. I would also use the available data for surface water in the Labrador and Nordic Seas only, which are available from this study and Moran's.

Author's response:

1. We did not mean to give the impression that deep water is formed uniquely from water sinking from a depth <100m, nor that the values we selected for preformed values are necessarily correct. An important conclusion from our work is that the preformed values of ^{231}Pa and ^{230}Th make a significant and long-lasting difference to the evolution of the $^{231}\text{Pa}/^{230}\text{Th}$ ratio as waters then age. Our selection of a particular preformed values serves to illustrate this point, rather than being a statement about true preformed values. It is, of course, also possible that the various water masses have different preformed values, making the use of a single value for the whole section inappropriate if seeking a “correct” value. We have made this logic clearer during revision; that we are not implying we know the preformed values, but that whatever they are will make a substantial difference to deep-water $^{231}\text{Pa}/^{230}\text{Th}$.

Instead, as we pointed on page 6, the preformed concentrations of dissolved ^{230}Th and ^{231}Pa at the time the water masses formed are unknown. We can only 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, until data are available for the Nordic Seas and the Labrador Sea during times of winter convection. The reason for the choice of < 100 m is that we consider <100 m as the surface mixed layer, where Pa and Th is well mixed.

2. This is why we discussed the effect of preformed values on the evolution of Pa and Th with water age in section 4.3. We have also added how preformed values might affect our calculation of scavenged components.

Line 30; p6: as per discussion above, calculated potential total concentration should be viewed as minima (because CFC ages underestimate the Th and Pa “ages”)

Author's response:

We hope that our opening comments above clarify that there is no age bias in our CFC ages calculated with TTD approach.

Line 4; p7: “..is the net of nuclide added from above by [add: DESORPTION FROM] settling particles: : :”

Author's response:

Changes are made as suggested.

Line 8-9; p7: Considering that the CFC ages are younger than the Th ages, potential and scavenged Th-230 must be viewed as minima. Also, the underestimation of fraction scavenged is larger for Th than Pa.

Author's response:

We hope that our opening comments above clarify that there is no age bias in our CFC ages calculated with TTD approach.

Line 14; p7: I guess the authors deduce that about 75% of the Th-230 produced is scavenged because the slope of slope of observed Th-230 vs time is 25% of the rate of production, right? If so, it would be helpful to be explicit and to report the value of the slope in Fig. 8a.

Author's response:

This is how we deduce the number. We have added the linear fit equations, giving the slope, on the figure.

Wouldn't the intercept also provide an independent estimate of preformed? I am not sure what the intercept on scavenged Th-230 figure means.

Author's response:

We agree with the reviewer that the intercept does provide some estimate of the preformed, especially for Th with a very good linearity. However, we would expect that at $t=0$, there is no scavenging taking place, and the y intercept of the scavenged Th figure should be 0, while that of the observed Th figure should be preformed value. However, we have a positive y intercept in scavenged Th figure, and a negative y intercept in observed figure. We attribute this to a combination of a lack of ^{230}Th data in younger waters and the uncertainty associated with ^{230}Th measurement and calculation.

I would also reiterate here that 75% scavenging is a minimum, and it could be that scavenging is more underestimated in older water than younger ones, producing this apparent intercept. It is not clear to me why the same can't be attempted for Pa, at least for the observed values.

Author's response:

As above, we do not think there is an age bias in our CFC ages based on TTD approach. We therefore do not think a change is required here.

Line 15-14; p7: "This ratio is consistent with the average ^{230}Th for these waters, which requires that about three times more ^{230}Th has been removed by scavenging"

Line 18; p7: "the average [Pa] values indicate that about half of the ^{231}Pa remains in the water"

I can't follow the line of reasoning here. I think the authors need to be more explicit.

Author's response:

From Fig. 8 (a) and (c), we have:

Average of Th in these waters = $3.24 \mu\text{Bq/kg}$

and average of Pa in these waters = $1.51 \mu\text{Bq/kg}$

From Fig. 8 (b) and (d), we have:

Average of scavenged Th = 11.8

Average of scavenged Pa = 1.02

To maintain an average Th of $3.3 \mu\text{Bq/kg}$ in water requires $12.1 \mu\text{Bq/kg}$ to be scavenged, which is three times more Th to be removed by scavenging.

Similarly, to maintain an average of Pa $1.5 \mu\text{Bq/kg}$ in water requires $1.2 \mu\text{Bq/kg}$ to be scavenged. That is, half of the ^{231}Pa remains in water and half removed by scavenging.

P2; line 23: "... there is no simple relationship between increasing Pa/Th and age, as would be expected"

P7; Line 21; p7: "...The hypothesis that Pa/Th ratios increase as water mass ages..."

We should not expect seawater Pa/Th to simply increase with water mass age. If dissolved Th and Pa activities are initially low, Pa/Th in the water column (and underlying sediments) should initially decrease with age of water mass because Th grows faster than Pa. It's only once Th has regained levels closer to equilibrium with scavenging (and therefore grows more slowly) that Pa starts growing faster, resulting in increasing Pa/Th. This effect is clearly illustrated in the paper by Luo et al. (2010) (see Fig. 14 in the paper). Fig. 8e,f may show a hint of this initial decreasing trend.

(Luo et al also argued "Clearly, it is impossible to constrain the history of changes in the AMOC from the evolution of $^{231}\text{Pa}/^{230}\text{Th}$ at one site, as was attempted by McManus et al.; p 395; last sentence of first paragraph).

Author's response:

We agree with the reviewer that we should not expect seawater Pa/Th to simply increase with water mass age. The model results plotted on Fig. 8e,f indicate an expectation that Pa/Th ratios can either increase or decrease in the first 10 to 15 years, depending on the preformed values. Beyond this age, Pa/Th ratios increase with age before reaching equilibrium. We have made this clearer in the manuscript accordingly.

Section 4.3: I am puzzled by Fig 9. The intercepts don't seem to match with the

preformed values. The fit with the data is terrible. I am not sure what this section is telling us.

Author's response:

As in our opening comment 3: We thank the reviewer for pointing out this issue, which contributed to our reconsideration of the model and removal of the incorrect surface term. This change gives Y intercept matching the preformed values at $t=0$.

We are aware of the 'terrible' fit of the model with data, even in the new model with surface term removed. It however supports what we aim to convey in this section that preformed values can influence the evolution of Pa, Th and Pa/Th with water mass age. Without a better knowledge of preformed values, we cannot give a simple description of how Pa/Th evolve with water mass age, and the model cannot generate profiles that better fit observations.

Line 28; p7: wouldn't it be better to follow density rather than depth?

Author's response:

We followed depth as the model is a function of depth, reflecting that the scavenging of ^{230}Th and ^{231}Pa takes place with particles sinking with depth instead of density. This is also the way that ^{230}Th and ^{231}Pa data have traditionally been considered.

Line 4; p8: why did you choose station 1 and 13? Is it because they are the least ventilated and therefore these parameters could be estimated from a linear fit? If this is the case, that should be indicated. However, is it reasonable to apply scavenging parameters from a margin to open ocean stations?

Author's response:

We chose station 1 and 13 as their profiles are the closest to the equilibrium profile with linear increase with water depth. We however realized, as the reviewer pointed out, that Station 1 is close to the margin, on the continental slope, and therefore used station 13 only, an open ocean station, to optimize model parameters.

Fig. 9: How can Pa/Th (zero preformed) increase with age (c) if Th (a) grows faster than Pa (b)?

Author's response:

With zero preformed Pa/Th is expected to increase from first ventilation. Despite the fact that Pa approaches an equilibrium value more slowly than Th, the Pa concentration increases more than Th concentration, i.e., more of the Th produced by decay is removed by scavenging than for Pa, at each time step. So the Pa/Th ratio increases monotonically from $T=0$.

Section 4.4:

This discussion should take into account that scavenged Th and Pa are underestimated and proportionally more for Th than Pa. Since potential and scavenged are underestimated by exactly the same absolute amount, calculated scavenged/potential ratios should also be taken as minima.

Author's response:

As above, we do not think there is underestimation of scavenged Th and Pa due to bias in CFC ages and Th ages as a result of mixing.

P 9; line 20-22; I think it would be helpful for the reader to provide the details of this mass balance calculation. For instance, what volume for the North Atlantic did you use to calculate production?

Author's response:

As we followed the Deng et al. (2014) for the calculation and used the number for the volume of the North Atlantic in that paper, which is referred to in the discussion manuscript, we did not give details here. However, we understand the reviewer's point that it would be helpful for readers so we now repeat this information in the revised supplementary material.

It seems that the results from this mass balance corroborate that scavenged (and therefore potential) Th and Pa calculated from equation 4.3 are underestimated because of the use of CFC ages. I am a little surprised that so much Pa is scavenged in the North Atlantic. If 77% of the production is scavenged, then the average Pa/Th of N. Atlantic sediments should be ca.0.073, which is higher than measured in the central N. Atlantic basin. That means that boundary scavenging must be more significant than I thought.

Author's response:

The 96% scavenged relative to produced for Th and 77% for Pa obtained from the mass balance calculation represents a basin-scale average in the North Atlantic. The lower scavenged to produced values from equation 4.3. represent more localized results when water masses are young, and nuclide concentrations and scavenging correspondingly low.

Additional references (added by authors):

Bradtmilller, 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.

Pickart, R. S., Straneo, F. and Moore, G. W. K.: Is Labrador Sea Water formed in the Irminger basin?, Deep Sea Res. Part I Oceanogr. Res. Pap., 50(1), 23–52, doi:[https://doi.org/10.1016/S0967-0637\(02\)00134-6](https://doi.org/10.1016/S0967-0637(02)00134-6), 2003.