<u>"Evolution of 231Pa and 230Th in overflow waters of the North Atlantic"</u> 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.

<u>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.</u>

It is interesting that referee comments varied from those that said our work confirmed the use of ²³¹Pa/²³⁰Th 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 ²³¹Pa/²³⁰Th ratios in terms of past rates of deep water circulation.

Model 1 relies on a net export of ²³¹Pa out of the Atlantic due to the residence time ²³¹Pa being longer than ²³⁰Th (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 ²³¹Pa/²³⁰Th 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 ²³¹Pa out of the Atlantic, but raises questions about model 2 because there is no simple relationship between ²³¹Pa/²³⁰Th 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.

<u>3. Reviewers questioned why ²³¹Pa and ²³⁰Th concentrations given by the model did</u> 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 μ Bq/kg for ²³¹Pa and ²³⁰Th, and pmol/kg for ²³²Th.

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

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 236U 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 bothTh-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 is computed with TTD method and takes 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 ²³⁰Th 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 ²³⁰Th and ²³¹Pa 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 intern-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 231Pa and 230Th make a significant and long-lasting difference to the evolution of the 231Pa/230Th 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 231Pa/230Th.

Instead, as we pointed on page 6, the preformed concentrations of dissolved 230Th and 231Pa 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 ²³⁰Th data in younger waters and the uncertainty associated with ²³⁰Th 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 230Th for these waters, which requires that about three times more 230Th has been removed by scavenging" Line 18; p7:" : : :the average [Pa] values indicate that about half of the 231Pa 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= 3.24μ Bq/kg and average of Pa in these waters= 1.51μ Bq/kg From Fig. 8 (b) and (d), we have: Average of scavenged Th = 11.8Average of scavenged Pa = 1.02

To maintain an average Th of 3.3 μ Bq/kg in water requires 12.1 μ Bq/kg to be scavenged, which is three time more Th to be removed by scavenging. Similarly, to maintain an average of Pa 1.5 μ Bq/kg in water requires 1.2 μ Bq/kg to be scavenged. That is, half of the 231Pa 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 in 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 231Pa/230Th 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 ²³⁰Th and ²³¹Pa takes place with particles sinking with depth instead of density. This is also the way that 230Th and 231Pa 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.

Roger Francois

Anonymous Referee #2

Here Deng et al. provide a very nice and concise piece of science. They examine crucial assumptions made for the application of 231Pa/230Th as an AMOC proxy by providing an extensive new data set of water 231Pa and 230Th concentrations. This is hard won data and the authors deserve credit for their efforts. The new data extends the former GEOTRACES transects by Hayes15 and Deng14 towards the northern North Atlantic representing a definite reality-check for the assumptions made when using 231Pa/230Th as a proxy. These assumptions have been made based on the elegant approach of measuring a kinetic tracer with a constant and well-defined inputcfunction not involved in the carbon-cycle (Yu1996). While previous studies already proofed the consistence and capability of 231Pa/230Th as an AMOC proxy the novelty of this study is the systematic examination of the behaviour of 231Pa and 230Th in the northern North Atlantic in the water masses recently influenced by NADW formation with a new set of samples and by state-of-the art analytical methods. Therefore, this manuscript certainly deserves publication in Biogeosciences. Given the published results from the 231Pa/230Th proxy of the last decades I would have wondered if this study would have come to a different conclusion. But here Deng et al. make very good cases by confirming the prerequisites for using 231Pa/230Th as AMOC proxy. The only little weakness of the manuscript is the missed opportunity of setting the new findings into the context of the attempts of using 231Pa/230Th as a large scale AMOC proxy. There are several of papers dealing with a single 231Pa/230Th profile from on location, but the results of the few which deal with comprehensive compilation approaches could be better assessed and discussed here. Besides the already mentioned Yu et al. 1996, I think in particular of Bradtmiller et al. 2014, which use the large scale 231Pa deficit for analyzing the HS1 AMOC. It would be worth of shortly recapitulate their results in the light of the new results presented here. Besides the connection to observational paleo data I also miss the comparison to theoretical or model studies. The authors should in particular present a short comparison to the predictions made by Marchal et al. 2000 and the most recent attempt by Rempfer et al. 2017. Further, most of the features reported here have been anticipated by the simple box-model approach by Luo et al. 2010. They already found a very weak correlation of 231Pa/230Th with water mass age, highlighting a vertical gradient not a horizontal in the presence of an active AMOC (see specific points below).

Thank you for suggestions of references to be included. We agree, and have included them during a rewrite of the introduction.

page 3, line 2: recurring typo of "R/V Pourquoi Pas?"

Author's response:

"R/V Pourquoi Pas?" is the correct spelling for the name of the French research vessel which undertook sampling in this study.

page 3, line 15: please specify how many several months are Author's response:

We have specified that it is four to five half-lives of 233 Pa (t_{1/2}=26.98 days, Usman and MacMahon, 2000) after spike production.

page 3, line 19: what was the analytical yield (range)of the anion chromatography for Pa and Th?

Author's response:

Analytical yield ranges from approximately 41-91% for Th, and 30-52% for Pa.

page 3, line 25: what was the 232Th/231Pa in the Pa-samples? Was the correction for the 232ThH interference necessary, if yes, how big was the contribution to the Pa-signal?

Author's response:

232Th/231Pa in the Pa samples are at about 1800. 232ThH interference contributes 0.1% of 233Pa signal. From this perspective, it does not seem necessary to correct for ThH interference in our case. However, the Th signal in the Pa sample was not known before the Pa measurement and conducted in case Th was not very well separated from Pa.

page 5, line 14: ISOW is mentioned but not shown in Fig. 5.

Author's response:

Thank you for pointing out. We have labelled ISOW in Fig.5.

Supplement: please add a column specifying the errors to the given concentrations

Author's response:

We assume that the reviewer meant Table S1 in the supplement. In this table, it is the 232Th-corrected Pa and Th concentrations that are used for the discussion. We therefore have only given errors (2se) associated with these concentrations, and do not think it is necessary to report errors for the measured concentrations without correction.

Supplement page 7 line 7: I'm aware that this is of marginal importance given the final result, but maybe the authors could elaborate on the value 0.7 in (3) and (4). 0.7 seems a little bit high for an average, or at least unnecessarily high at the high end of the possible range according to Henderson and Anderson 2003 or Bourne et al. 2012. Further, is the detrital correction required for particles slipping through the 0.45 m filters? Is the added HCI capable of leaching of the 232Th (and 230Th and 231Pa) from these particles?

Author's response:

We agree with the reviewer. Henderson and Anderson (2003) suggested average of 238/232 activity ratio to be 0.6 ± 0.1 in the Atlantic, and 0.7 ± 0.1 in the Pacific Ocean. We therefore have adopted the value of 0.6 in the revised paper as ²³⁸U/²³²Th activity ratio to correct for the detrital contribution of ²³¹Pa to ²³⁰Th. Equation (3) and (4) were rewritten and the data were recalculated accordingly.

Detrital correction is to correct for the contribution from the partial dissolution of lithogenic minerals to ²³⁰Th pool in seawater, rather than in the sample after being collected. It is therefore necessary regardless of the filtration and the acidification.

Fig. 3,8,9: error bars are missing

Author's response:

We have added error bars to the measured data in these figures.

page 7, line 21: It is not surprising that 231Pa/230Th does not correlate with water mass age very much. This has been already predicted by Luo et al. 2010. Much more important is the vertical decrease within one circulating mater mass (e.g. Burckel et al. 2016). Thus, the sentence that "231Pa/230 ratios increase as water mass ages forms the foundation of using 231Pa/230Th in discrete cores" is not completely accurate.

Author's response:

Thank you for pointing this out. We found this comment very helpful to improve our paper. We agree with the reviewer on the relationship between ²³¹Pa/²³⁰Th and water mass age. We have clarified the two conceptual models forming the foundation of the interpretation of Pa/Th in terms of rates of deep water circulation (as explained in point 1 of our opening comments above).

page 10, line 13: typo. two times "demostrates".

Author's response: We have corrected the typo.

Fig. 6: I assume the x-axis has changed between (a) and (b), but they are both shown on the same longitudinal scale.

Author's response:

Thank you for pointing out this error. We have corrected the longitudinal scale for Fig.6 (a) in the revised manuscript.

Fig. 3: maybe it would be worth of showing 231Pa/230Th as well in an additional panel

Author's response:

We do not think it is not necessary as we focus on discussing the latitudinal gradient of ²³¹Pa and ²³⁰Th rather than ²³¹Pa/²³⁰Th at this stage.

(c). Fig. 8: please indicate water depth at the colour bar.

Author's response:

We have added to the colour bar the water depth (m).

References: Bourne, M., et al., 2012. Improved determination of marine sedimentation

rates using 230Thxs. Geochemistry Geophysics Geosystems 13.

Bradtmiller, L., et al.,2014. 231Pa/230Th evidence for a weakened but persistent Atlantic meridional overturning

circulation during Heinrich Stadial 1. Nature Communications 5.

Burckel, P., et al., 2016. Changes in the geometry and strength of the Atlantic Meridional Overturning

Circulation during the last glacial (20-50 ka). Climate of the Past 12.

Deng, F., et al., 2014. Controls on seawater 231Pa, 230Th and 232Th concentrations along the flow paths of deep waters in the Southwest Atlantic. Earth and Planetary Science Letters 390.

Hayes, C., et al., 2015. 230Th and 231Pa on GEOTRACES GA03, the U.S. GEOTRACES North Atlantic transect, and implications for modern and paleoceanographic chemical fluxes. Deep Sea Research Part II: Topical Studies in Oceanography 116.

Henderson, G., et al., 2003. The U-series toolbox for paleoceanography, Uranium Series Geochemistry. Reviews in Mineralogy and Geochemistry 128.

Luo, Y., et al., 2010. Sediment 231Pa/230Th as a recorder of the rate of the Atlantic meridional overturning

circulation: insights from a 2-D model. Ocean Science 6.

Marchal, O., et al., 2000. Ocean thermohaline circulation and sedimentary 231Pa/230Th ratio. Paleoceanography

15.

Rempfer, J., et al., 2017. New insights into cycling of 231Pa and 230Th in the Atlantic Ocean. Earth and Planetary Science Letters 468.

Yu, E., et al., 1996. Similar rates of modern and last-glacial ocean thermohaline circulation inferred from

radiochemical data. Nature 379.

Anonymous Referee #3

Deng and coworkers have produced an important data set by analyzing samples collected on GEOTRACES Section GA01 (GEOVIDE) for 231Pa and 230Th. 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 231Pa/230Th 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 231Pa/230Th 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 230Th and 213Pa data in Figure 3, eyeballing the dissolved 230Th

and 231Pa 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 ²³¹Pa/²³⁰Th. 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 as supplemental information in the revised manuscript.

As discussed on page 6 of the manuscript, the initial (preformed) concentrations of dissolved 230Th and 231Pa 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 suggested sensitivity analysis in the Supplemental Information.

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 230Th and 0.089 dpm/1000 L for 231Pa)? 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(pre) and C(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 ²³¹Pa and ²³⁰Th 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 ²³¹Pa and ²³⁰Th 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 ²³¹Pa/²³⁰Th. 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 ²³¹Pa and ²³⁰Th 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 ²³⁸U 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 ²³⁸U/²³⁵U=137.88 and the ²³⁴U/²³⁸U activity ratio in seawater is ~1.15.

page 7 line 16: "three times more 230Th 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 230Th 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 230Th and 231Pa 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/m³ as described in the discussion manuscript on page 9 line 10. The average ²³⁰Th and ²³¹Pa in the upper and lower limb are average concentrations of these nuclides in water with potential density < 32.15 kg/m³ and > 32.15 kg/m³, 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.: ²³¹Pa/²³⁰Th 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.

Owens, S. A., Buesseler, K. O. and Sims, K. W. W.: Re-evaluating the ²³⁸U-salinity relationship in seawater: Implications for the 238U–234Th disequilibrium method, Mar. Chem., 127(1), 31–39, doi:https://doi.org/10.1016/j.marchem.2011.07.005, 2011.

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, 2003.

Usman, K. and MacMahon, T. D.: Determination of the half-life of ²³³Pa, Appl. Radiat.

lsot., 52(3), 585–589, doi:https://doi.org/10.1016/S0969-8043(99)00214-6, 2000.

Evolution of ²³¹Pa and ²³⁰Th in overflow waters of the North Atlantic

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- 10 Abstract. Many paleoceanographic studies have sought to use the ²³¹Pa/²³⁰Th ratio as a proxy for deep ocean circulation rates in the North Atlantic. As yet, however, no study has fully assessed the concentration of, or controls on, ²³⁰Th and ²³¹Pa in waters immediately following ventilation at the start of Atlantic meridional overturning. To that end, full water-column ²³¹Pa and ²³⁰Th concentrations were measured along the GEOVIDE section, sampling a range of young North Atlantic deep waters. Th-230 and ²³¹Pa concentrations in the water column are lower than those observed further south in the Atlantic, ranging
- 15 between 0.06 and 12.01 μBq/kg, and between 0.37 and 4.80 μBq/kg, respectively. Both ²³⁰Th and ²³¹Pa profiles generally increase with water depth from surface to deep water, followed by decrease near the seafloor, with this feature most pronounced in the Labrador Sea (LA Sea) and Irminger Sea (IR Sea). Analyzing this dataset with Extended Optimum Multi-Parameter (eOMP) Analysis and CFC-based water mass age indicates that the low values of ²³⁰Th and ²³¹Pa in water near the seafloor of the LA Sea and IR Sea are related to the young waters present in those regions. This importance of water age is
- 20 confirmed for ²³⁰Th by a strong correlation between ²³⁰Th and water mass age (though this relationship with age is less clear, for ²³¹Pa and ²³¹Pa/²³⁰Th ratio). Scavenged ²³¹Pa and ²³⁰Th were estimated and compared to their potential concentrations in the water column due to ingrowth. This calculation indicates that more ²³⁰Th is scavenged (~80%) relative to ²³¹Pa (~40%), consistent with the relatively higher particle-reactivity of ²³⁰Th. Enhanced scavenging for both nuclides is demonstrated near the seafloor in young overflow waters. Calculation of meridional transport of ²³⁰Th and ²³¹Pa with this new GEOVIDE dataset
- 25 enables a complete budget for ²³⁰Th and ²³¹Pa for the North Atlantic. Results suggest that net transport southward of ²³⁰Th and ²³¹Pa across GEOVIDE is smaller than transport further south in the Atlantic, and indicates that the flux to sediment in the North Atlantic is equivalent to 96% of the production of ²³⁰Th, and 74% of the production for ²³¹Pa. This result confirms a significantly higher advective loss of ²³¹Pa to the south relative to ²³⁰Th and supports the use of ²³¹Pa/²³⁰Th to assess meridional transport at a basin scale.
- 30 Key words. GEOTRACES; water-column ²³⁰Th and ²³¹Pa; water mass ageing; scavenging; meridional transport.

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1 Introduction

Several paleoceanographic proxies have been proposed that rely on the 231 Pa/ 230 Th ratio in marine sediments, <u>one of which is</u> that 231 Pa/ 230 Th may record the rate of deep-water circulation, particularly in the North Atlantic.

- Both ²³¹Pa and ²³⁰Th are produced in seawater at a constant rate by decay of uranium, but have decay activities much lower
 than their parent uranium isotopes due to rapid removal by adsorption onto sinking marine particles. Both nuclides are also reversibly scavenged, leading to particularly low concentrations at the surface and increasing concentrations with depth (Nozaki et al., 1981). Advection of surface waters to depth transports water with low concentrations of ²³¹Pa and ²³⁰Th into the deep ocean, where their concentrations subsequently increase towards an equilibrium value at a rate dependant on the residence time of the nuclide. The longer residence time of ²³¹Pa relative to ²³⁰Th (~130 years versus ~20 years, Henderson)
- and Anderson, 2003) means that the equilibrium concentration of ²³¹Pa is closer to that expected from uranium decay, and that the time taken to reach this equilibrium is longer.
 This oceanic behaviour of ²³¹Pa and ²³⁰Th suggests that their measurement in marine sediments may reveal information about the past environment, with one common use being as a recorder of deep-water circulation, particularly in the North Atlantic (e.g. Gherardi et al., 2005, 2009; McManus et al., 2004; Roberts et al., 2014; Yu et al., 1996). The interpretation of sedimentary
- 15 ²³¹Pa/²³⁰Th ratios for such past ocean circulation is based on two end-member conceptual models: Basin-scale Advection: The longer residence time of ²³¹Pa than ²³⁰Th means that deep-water contains more ²³¹Pa than ²³⁰Th relative to production from decay. Advection of deep-waters out of the North Atlantic therefore removes more ²³¹Pa than ²³⁰Th, leaving sediments in the basin with a ²³¹Pa/²³⁰Th ratio below the production ratio. If deep-water ventilation ceased, ²³¹Pa removal from the North Atlantic also ceases, and sedimentary ²³¹Pa/²³⁰Th values reach their production ratio. This
- 20 approach was first proposed by Yu et al. (1996) who measured ²³¹Pa/²³⁰Th in Holocene and Last Glacial Maximum (LGM) sediments from many core-top samples from the Atlantic and Southern Ocean. They found similar Holocene and LGM values at a basin scale, suggesting broadly similar overturning during the two periods. Subsequent application to sediments from Heinrich Stadial 1, initially in a single core (McManus et al., 2004) and progressively a geographical range of cores (Bradtmiller et al., 2014), revealed reduced advection of ²³¹Pa out of the basin at that time, suggesting decreased overturning.
- 25 Water-mass Evolution: The longer residence time of ²³¹Pa means that, following ventilation, it takes longer for deep-water ²³¹Pa concentrations to reach equilibrium with respect to scavenging than is the case for ²³⁰Th. This leads to a systematic evolution of ²³¹Pa/²³⁰Th with age of the water. Sediments capture this ratio (with a fractionation due to different scavenging coefficients for the two nuclides), so capture information about the age of the water. Simple models suggest an increase of ²³¹Pa/²³⁰Th with age over about 400 years (e.g. several residence times of ²³¹Pa). This approach to interpreting sedimentary
- 30 ²³¹Pa/²³⁰Th allows for the possibility of calculating flow rates for a single water mass and from a single core rather than at a basin scale. It has been pursued by (Negre et al., 2010) to assess deep-water flow in both southerly and northerly directions by comparing sediments in the North and South Atlantic, and allowed these authors to apply a simple model (Thomas et al., 2007) to calculate flow rates.

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Recent water-column measurements of ²³¹Pa and ²³⁰Th on GEOTRACES cruises shed new light on the chemical behaviour and controls on these isotopes in seawater and provided evidence to assess the validity of the models underlying the use of sedimentary ²³¹Pa/²³⁰Th as a proxy for deep-water circulation. These measurements have indicated that there is considerably more net advection of ²³¹Pa than ²³⁰Th out of the North Atlantic (Deng et al., 2014), supporting the Basin-scale Advection

- 5 model for ²³¹Pa/²³⁰Th. But these measurements also suggest that there is no simple relationship between increasing ²³¹Pa/²³⁰Th and age of water, as would be expected for the Water-mass Evolution model (e.g. Deng et al., 2014). Studies using 2-D and 3-D ocean models (e.g. Marchal et al., 2010; Siddall et al., 2007) have also supported the use of sedimentary ²³¹Pa/²³⁰Th to constrain deep-water circulation at a basin scale, and suggested that the relationship between ²³¹Pa/²³⁰Th and water mass age is more complex than assumed in earlier studies (e.g. Luo et al., 2010).
- 10 Observations and model studies of ²³¹Pa and ²³⁰Th have also suggested that other controls complicate ²³¹Pa/²³⁰Th as a dynamic tracer of deep-water circulation, such as the effect of boundary scavenging at seafloor and ocean margins (e.g. Anderson et al., 1994; Deng et al., 2014; Rempfer et al., 2017) and the influence of particle flux and composition (e.g. Chase et al., 2002; Hayes et al., 2014; Siddall et al., 2005).

To fully assess the behaviour of ²³¹Pa/²³⁰Th, and its potential as a dynamic tracer of deep-water circulation, knowledge of the
 concentrations and variations of these isotopes as deep waters form and enter the deep Atlantic is required. Some measurements have placed initial constraints on ²³¹Pa and ²³⁰Th values in young North Atlantic deep waters (e.g. Moran et al., 1997, 2002; Rutgers van der Loeff and Berger, 1993), but there has not yet been a systematic study of the composition of waters in the far north Atlantic. The GEOVIDE cruise allowed waters to be collected for such a study, along a line where significant other data are available, both from that cruise and previous occupations of OVIDE. GEOVIDE provided an ideal

20 opportunity to understand ²³¹Pa and ²³⁰Th at the start of the ocean meridional overturning circulation, and to assess the hypotheses underlying the use of ²³¹Pa/²³⁰Th as a paleo-proxy for the rate of deep-water circulation.

2 Sampling strategies and Analytical methods

Seawater samples were collected during the GEOVIDE cruise aboard the R/V Pourquoi Pas? from 15 May to 30 June, 2014
 as part of GEOTRACES Section GA01. The cruise sampled four regions in the North Atlantic between 40°-60°N: Labrador Sea (LA Sea), Irminger Sea (IR Sea), Iceland Basin (IC Basin), and Western European Basin (WE Basin) (Fig. 1).
 Full-depth water-column ²³¹Pa and ²³⁰Th for this study were collected from 11 stations (Fig. 1). Sampling followed the procedure suggested by GEOTRACES intercalibration work (Anderson et al., 2012). Briefly, seawater samples of 5 Litres were directly filtered from Niskin bottles mounted on the Stainless Steel CTD Rosette through AcroPakTM capsules with

30 Supor[®] Membrane (0.45 μm pore size). Filtered seawater samples were collected into acid cleaned HDPE plastic bottles, and sealed with a screw cap and Parafilm to reduce evaporation and contamination. Samples were then double bagged for storage in boxes for transport back to the shore-based lab for analysis. Deleted: Both 231Pa and 230Th are generated continuously by decay of uranium in the water column and are rapidly removed, leading to very low concentrations at the surface and increasing concentrations with depth due to reversible scavenging (Nozaki et al., 1981). Advection of surface waters to depth transports the low concentrations into the deep ocean, where they subsequently increase due to scavenging from above at a rate dependant on the residence time of the nuclide. Because ²³¹Pa has a longer residence time than ²³⁰Th (~130 years versus ~20 years, Henderson and Anderson, 2003), the concentration of 231Pa increases more slowly and its resulting removal to the seafloor also increases more slowly. This behaviour means that, in basins such as the North Atlantic with vigorous formation and advection of deep-waters, less 231Pa is removed to the sediment than is produced in the water column. Sediments underlying the North Atlantic will therefore have a 231 Pa/230 Th below the production ratio, with lower ratios caused by stronger advection. The use of ²³¹Pa/²³⁰Th to constrain past North Atlantic overturning was first proposed by Yu et al. (1996) who measured ²³¹Pa/²³⁰Th in Holocene and Last Glacial Maximum (LGM) sediments from many cores from the Atlantic and Southern Ocean. They found similar Holocene and LGM values at a basin scale, suggesting broadly similar overturning during the two periods. Later studies have generally relied on a smaller number of cores (e.g. McManus et al 2004; Gherardi et al. 2009; Roberts et al. 2014), chosen from particular depths to sample important water masses. This approach relies on the systematic evolution of the 231 Pa/230 Th ratio in each water mass

Recent water-column measurements of ²³¹Pa and ²³⁰Th on GEOTRACES cruises have shed new light on the chemical controls on these isotopes in seawater. These have indicated that there is considerably more net advection of ²³¹Pa than ²³⁰Th out of the North Atlantic (Deng et al., 2014), supporting the basin-scale application of ²³¹Pa/J²⁶⁰Th as initially pursued (Yu et al. 1996). But these

measurements have also suggested that there is no simple relationship between increasing $^{231}\text{Pa}^{/230}\text{Th}$ and age of water, as would be expected if the $^{231}\text{Pa}^{/230}\text{Th}$ at single cores is to be interpreted as reflecting the rate of ventilation (e.g. Deng et al., 2014). \P

Deleted: One important constraint on understanding ²³¹Pa/²³⁰Th is to learn about the controls on these isotopes as deep waters form and enter the deep Atlantic. Some measurements have placed initial constraints on ²³¹Pa and ²³⁰Th values in young North Atlantic deep waters (e.g. Moran et al., 1997, 2002; Rutgers van der Loeff and Berger, 1993), but there has not yet been a systematic study of the composition of waters in the far north Atlantic. The GEOVIDE cruise allowed waters to be collected for such a study, along a line where significant other data are available, both from that cruise and previous occupations of OVIDE. GEOVIDE provided an ideal opportunity to understand ²³¹Pa and ²³⁰Th at the start of the ocean meridional overturning circulation. ¶

Once returned to the laboratory in Oxford, samples were weighed and then acidified with quartz distilled concentrated HCl to $pH \sim 1.7$, shaken and left for at least four days to ensure that Pa and Th was desorbed from the walls of the bottle. A mixed $^{229}Th^{-236}U$ spike and a ^{233}Pa spike were then added to each sample to allow measurement of Th, U (for another study), and Pa by isotope dilution MC-ICP-MS (Multi Collector-Inductively Coupled Plasma-Mass Spectrometry). The ^{233}Pa spike was

- 5 freshly made by milking from ²³⁷Np (following Regelous et al., 2004) and calibrated against a known ²³⁶U solution after complete decay of ²³³Pa to ²³³U, <u>i.e. four to five half-lives of ²³³Pa (tr2=26.98 days, Usman and MacMahon, 2000) after spike production (Robinson et al., 2004).</u> 50 mg of pure Fe as a chloride solution was also added to each water sample. Samples were left overnight to allow for spike equilibrium after which the pH was raised to ~8.5 using distilled NH₄OH to co-precipitate the actinides with insoluble Fe-oxyhydroxides. At least 48 hours were allowed for scavenging of the actinides onto Fe-
- 10 oxyhydroxides. The precipitate was centrifuged and rinsed, and Th, Pa and U were separated using anion exchange chromatography following Thomas et al., 2006.

After chemical separation, Pa and Th were measured on a Nu instrument MC-ICP-MS at the University of Oxford. Mass discrimination and ion-counter gain were assessed with the measurement of a U standard, CRM-145 U, before each sample measurement. Use of a U standard for this purpose minimises memory problems that might be caused by use of a Th or Pa

- 15 standard (Thomas et al., 2006). Measurements were also made 0.5 mass units either side of masses of interest to allow accurate correction for the effect of abundance sensitivity on small ²³¹Pa and ²³⁰Th beams, and a correction for a small ²³²ThH interference on the ²³³Pa beam is made from assessment of the hydride formation rate on a ²³²Th standard. Concentrations of ²³¹Pa, ²³⁰Th together with ²³²Th were obtained from the precise MC-ICP-MS measurement of ²³¹Pa,²³⁰Th/²²⁹Th, and ²³²Th/²²⁹Th ratios together with well-calibrated concentrations of ²³³Pa, and ²²⁹Th-²³⁶U spikes.
- 20 Chemistry blanks were assessed by conducting the complete chemical procedure on ~100 ml of Milli-Q water with each batch of samples. Based on six blank measurements, the average blanks for dissolved ²³¹Pa, ²³⁰Th and ²³²Th are 0.21±0.14 fg, 1.59±0.60 fg and 5.13±1.47 pg, respectively (uncertainties are 2 standard errors). Blank contributions account for 2-22%, 2-26%, and 0.2-16% of the dissolved ²³¹Pa, ²³⁰Th and ²³²Th respectively (with the higher values being for surface samples due to their low concentrations).

25 3 Results

Measured ²³⁰Th and ²³¹Pa concentrations were corrected for blanks, ingrowth from U in seawater since the time of <u>sample</u> collection, and detrital U-supported ²³⁰Th and ²³¹Pa concentrations. Measured and corrected concentrations of ²³⁰Th, ²³¹Pa, and ²³²Th, along with details of corrections, are provided in the Supplemental Information S1. Although analysis was conducted in terms of fg/kg, results are converted to <u>the S1 units adopted by GEOTRACES data product</u>, i.e., µBq/kg for ²³⁰Th and ²³¹Pa.

30 and pmol/kg for ²³²Th, This conversion uses half-lives for ²³¹Pa, ²³⁰Th and ²³²Th of 32,760 yr, 75,584 yr and 1.405×10¹⁰ yr, respectively (Robert et al., 1969; Cheng et al., 2013; Holden, 1990). Uncertainties were propagated, including the contribution from sample weighing, spike calibration, impurities in the spikes, blank corrections, and mass spectrometric measurement,

Deleted: (i.e. several months after spike production) (Robinson et al., 2004)

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and are reported as 2 standard errors (2 s.e.). Average total uncertainties for 231 Pa, 230 Th and 232 Th are $\pm 0.17 \mu$ Bq/kg, \pm

Th-230 concentrations in the water column range between <u>0.06 and 12.01 μ Bq/kg</u> and initially generally increase with water 5 depth from surface to deep water. Towards the seafloor, six of the eleven stations show a prominent decrease of ²³⁰Th, with this feature most pronounced in the LA and IR Seas.

Pa-231 concentrations in the water column range between <u>0.37 and 4.80 μ Bq/kg and also increase with water depth, but less</u> rapidly than ²³⁰Th. ²³¹Pa profiles also often exhibit a decrease near the seafloor at stations showing a ²³⁰Th decrease. Station 38 at the Reykjanes Ridge distinguishes itself from other ²³¹Pa profiles in that an increase in ²³¹Pa concentrations from low

10 concentrations at 1000 m is observed, continuing towards the bottom. Observed ²³⁰Th and ²³¹Pa values at GEOVIDE are lower than those observed in inter-calibrated GEOTRACES data from further south in the Atlantic. Figure 3 compares average depth profiles <u>for ²³⁰Th and ²³¹Pa in the west Atlantic, covering highlatitude Northwest Atlantic (from GEOVIDE, west of the Mid-Atlantic Ridge), mid-latitude Northwest Atlantic (GEOTRACES section GA03_w, Hayes et al., 2015) and Southwest Atlantic (GEOTRACES section GA02, Deng et al., 2014).</u>

15 A southward increase of both ²³⁰Th and ²³¹Pa concentrations is observed below 1000 m.

4 Discussion

30

Early studies of water-column ²³⁰Th and ²³¹Pa reported a linear increase of both nuclides with water depth <u>(e.g., Anderson et al., 1983b;</u> Nozaki et al., 1981), and introduced a reversible scavenging model with exchange of both nuclides between their dissolved and particulate phases. Later studies observed a deviation of ²³⁰Th and ²³¹Pa profiles from this reversible scavenging

- 20 model, with the expected increase with depth often inverting near the seafloor(e.g., Anderson et al., 1983a; Bacon and Anderson, 1982). This feature has been further investigated in more recent studies. Rutgers van der Loeff and Berger (1993) observed that ²³⁰Th concentrations decrease in the bottom water in the South Atlantic south of the Antarctic Polar Front and interpreted this as the influence of relatively young bottom water in the region. Okubo et al. (2012) also found decreasing ²³⁰Th values near the seafloor in the North Pacific and, in the absence of ventilation in the area, interpreted these as due to
- 25 bottom scavenging. Deng et al. (2014) observed low concentrations of both ²³⁰Th and ²³¹Pa in near-bottom water coinciding with the presence of the nepheloid layer, and interpreted the low values as a result of enhanced scavenging by resuspended particles in the nepheloid layer.

In this study, recently ventilated overflow waters are sampled at depth, particularly in the Labrador and Irminger Seas. Low values of ²³⁰Th and ²³¹Pa near the seafloor might be expected to relate to these young waters, but the effects of scavenging must also be considered.

4.1 Water mass distribution and influence

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Deleted: (e.g. Deleted: Anderson et al., 1983; The presence of multiple water masses sampled by the GEOVIDE Section allows the influence of water mass (and age) on ²³⁰Th and ²³¹Pa to be assessed. Extended Optimum Multi-Parameter (eOMP) Analysis (García-Ibáñez et al., 2018) for the GEOVIDE section maps the presence of 10 water-mass end-members in the section (Fig. 4), including three recently ventilated waters in the GEOVIDE section;

- 5 *i*. Labrador Sea Water (LSW), which is formed by deep convection (Talley and McCartney, 1982), is the dominant deep water along the section, extending from 1000 to 2500 m depth in the east and from surface to 3500 m in the west of the section. *ii.* Iceland–Scotland Overflow Water (ISOW), which is formed in the Norwegian Sea and subsequently entrains overlying warmer and more salty waters. This water mass initially flows along the eastern flank of the Reykjanes Ridge before spreading back northwards, after crossing the Charlie-Gibbs Fracture Zone, into the Irminger and Labrador Seas (Dickson and Brown,
- 10 1994; Saunders, 2001). A pronounced layer of this water mass is observed immediately below the LSW, and extends as deep as 4000 m west of 20°W.

iii. Denmark Strait Overflow Water (DSOW), which is formed after the Nordic Seas deep waters overflow and entrains Atlantic waters (SPMW and LSW) (Yashayaev and Dickson, 2008) with dense Greenland shelf water cascading down to the DSOW layer in the Irminger Sea (Falina et al., 2012; Olsson et al., 2005; Tanhua et al., 2005). This water occupies the deepest part of the IR and LA Seas.

In the east of the section, deep waters consist of the much older Lower North East Atlantic Deep Water (NEADW_L) which is formed with a significant southern component from the Antarctic Bottom Water. A number of other water masses are also observed at shallow depths, including Mediterranean Water, and various mode waters.

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Some control of water mass on ²³⁰Th and ²³¹Pa concentration is evident in nuclide section plots (Fig. 5), particularly relatively low ²³⁰Th and ²³¹Pa concentrations in DSOW and high values in the old NEADW. In other places, the impact of water mass is less apparent. The challenge with these nuclides is that they are not conservative tracers of water mass, but evolve significantly during transport and water aging. On the GEOVIDE Section we can analyse this evolution because the ages of the water-masses can be assessed from CFC data.

CFC measurements are not available from the GEOVIDE cruise itself. de la Paz et al. (2017), however, measured CFC

25 concentrations along the west of the same section (covering WE Basin, IC Basin, and IR Sea) in 2012 (OVIDE/CATARINA cruise). This allowed the computing of CFC-based age with the Transit Time Distribution (TTD) method. Using the water mass distribution along GEOVIDE given by García-Ibáñez et al. (2018) and the distribution for the same water masses in 2012 (García-Ibáñez et al., 2015), we derived CFC-based ages for GEOVIDE waters (Fig. 6; further details in Supplemental Information S2). Uncertainties (1 standard error) associated with CFC-based age calculated with this approach range between 30 11-40%.

CFC-based water-mass ages range from \approx 10 years, observed in DSOW at the bottom of the LA Sea, to \approx 800 years, observed for NEADW at the bottom of the WE Basin. Because this study focuses on understanding controls on 231 Pa and 230 Th in recently ventilated waters, we omit detailed consideration of the upper 1km in subsequent discussion, and restrict our analysis to water sampled west of 35°W of the section where young waters (< 50 years) dominate. A rescaled version of the CFC age

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4.2 Evolution of ²³⁰Th and ²³¹Pa with water age

5 The presence of recently ventilated deep-waters with constrained CFC ages allows analysis of the rates at which ²³⁰Th and ²³¹Pa concentrations increase during transport, and the rates of scavenging of these nuclides. To conduct this analysis, we define five components in the budget of ²³⁰Th and ²³¹Pa:

i. Preformed component: The ²³⁰Th or ²³¹Pa transported from the surface into the interior. For this analysis, in the absence of measurements for the exact location of deep-water formation <u>during winter convection</u>, we <u>assume the same preformed value</u>

10 for all water masses and set this as average of concentrations measured in surface waters <100 m depth along GEOVIDE section. This gives preformed concentrations of 1.66 μBq/kg for ²³⁰Th and 1.31 μBq/kg for ²³¹Pa. We recognise that true preformed values may differ from these values and between water masses, and discuss the implications of uncertainty in preformed values in the following section. Preformed ²³⁰Th and ²³¹Pa will decrease due to radioactive decay during transport. Although we take this decay into account in the following analysis, it is insignificant given the ages of waters involved and

15 the much longer half-lives of ²³⁰Th and ²³¹Pa.

ii. Ingrown component: The ingrown ²³⁰Th or ²³¹Pa from radioactive decay of U since the water was last in contact with the surface. This component increases as the water mass ages. The concentration of this component in a water mass of age t can be calculated as:

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 ${}^{231}Pa_{lngrown} = {}^{235}U \times (1 - e^{-\lambda_{231}t})$ (4.2)

 ${}^{230}Th_{lngrown} = {}^{234}U \times (1 - e^{-\lambda_{230}t})$ (4.1)

where ²³⁰Th_{Ingrown} and ²³¹Pa_{Ingrown} are the ²³⁰Th and ²³¹Pa ingrown from their U parents, respectively; ²³⁸U and ²³⁵U are activities of ²³⁴U, and ²³⁵U in seawater (45551.2 μ Bq/kg (2801.4 dpm/1000l) and 1823.8 μ Bq/kg (112.2 dpm/1000l), respectively, assuming a constant seawater ²³⁸U activity of 39609.8 μ Bq/kg (2436 dpm/1000l) at salinity 35 psu, and seawater ²³⁴U/²³⁸U activity ratio of 1.15 and natural ²³⁸/²³⁵U abundance ratio of 137.88); λ_{230} and λ_{231} are decay constants of ²³⁰Th and ²³¹Pa (9.17

 25×10^{-6} yr⁻¹ and 2.12×10^{-5} yr⁻¹, respectively).

iii. Potential Total component: The ²³⁰Th and ²³¹Pa expected in the water due to the combination of preformed and ingrown components, if there were no removal by scavenging.

iv. Observed component: The ²³⁰Th and ²³¹Pa observed in the water column, i.e. dissolved ²³⁰Th and ²³¹Pa measured in this study (after correction for detritus and ingrowth from U since sample collection).

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v. Scavenged component: The net ²³⁰Th or ²³¹Pa removed from the water since it left the surface due to scavenging. For each depth, this component is the net of nuclide added from above by <u>desorption from</u> settling particles, and the removal downwards by scavenging.

These components are related to each other as follows:

5 $Preformed + Ingrown = Potential Total^{230}Th(or^{231}Pa) = Observed + Scavenged$ (4.3)

The difference between the Potential Total and the Observed concentration of 230 Th (or 231 Pa), therefore provides a measure of the amount of nuclide scavenged since the water left the surface (Fig. 7).

We examine the evolution of both the observed and scavenged components of ²³⁰Th and ²³¹Pa with water mass age (Fig. 8). Both ²³⁰Th and ²³¹Pa show an increase in observed concentration with age of water, with the increase for ²³⁰Th much more

10 regular than for ²³¹Pa. This strong ²³⁰Th relationship, regardless of depth of the sample (Fig. 8a), indicates a primary control of water-mass age on the increase of ²³⁰Th in these younger waters.

For ²³⁰Th, the rate of increase with age (i.e. slope in Fig. 8a) indicates that about one quarter of the ²³⁰Th formed from U decay remains in the water, with the other three quarters being removed by scavenging. This ratio is consistent with the average ²³⁰Th for these waters, which requires that about three times more ²³⁰Th <u>than remains in water</u> has been removed by scavenging

15 (Fig. 8a, 8b). The scatter between ²³¹Pa and age (Fig. 8c) precludes the use of the slope to assess the relative proportion of scavenged ²³¹Pa, but the average values (Fig. 8c, 8d) indicate that about half of the ²³¹Pa remains in the water, while half is removed by scavenging. The relative behaviour of ²³⁰Th and ²³¹Pa is consistent with previous expectations, with a higher fraction of scavenging of ²³⁰Th than ²³¹Pa.

The hypothesis that ²³¹Pa/²³⁰Th ratios increase monotonically as water mass ages forms the foundation of the Water-mass

20 <u>Evolution model for interpretation of sedimentary ²³¹Pa/²³⁰Th in terms of the rate of deep water circulation.</u> For these young waters, however, there is no clear relationship between observed ²³¹Pa/²³⁰Th and age (Fig. 8e), nor between the ²³¹Pa/²³⁰Th value scavenged to the sediment and age (Fig. 8t), calling the Water-mass Evolution model into question.

4.3 The importance of Preformed ²³⁰Th and ²³¹Pa in young waters

To assess the controls on 230 Th, 231 Pa, and particularly the resulting 231 Pa/ 230 Th ratio, we apply a simple scavenging-mixing model following Moran et al. (1997). This model was first created to assess the evolution of 230 Th in a 1D water column as it

25 model following Moran et al. (1997). This model was first created to assess the evolution of ²³⁰Th in a 1D water column as it ages following ventilation. Here we adopt it by modelling the nuclide evolution with age for each depth, and by also modelling ²³¹Pa. This <u>assumes</u> that waters have remained at the same depth since ventilation which, though not correct in detail, still allows the model to provide insights about controls on these nuclides.

The model requires values for four parameters: particle settling speed (S), suspended particle concentration (SPM), and 30 distribution coefficients for ²³⁰Th (K_d^{Th}) and ²³¹Pa (K_d^{Pa}). We select these parameters to give a good fit to the ²³⁰Th and ²³¹Pa

observations at an open ocean station, Station 13, on the east of the section (i.e. a station sampling older waters, which are

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close to equilibrium) and use these values to interpret the younger waters to the west. Best fits to Station 13 suggested S = 800 m/yr; SPM = 25 $\mu g/l$; K_d^{Th} =1.1×10⁷ ml/g; and K_d^{Pa} = 1.4×10⁶ ml/g (the first three of these are close to those of Moran et al. 1997). A fuller description of the model is given in Supplemental Information S3.

We show two sets of output from the model, once with a preformed component (Cpre) equal to the nuclide concentrations

- 5 observed in the upper 100 m of the GEOVIDE section (as in 4.2 above), and once with the preformed component set to zero for both nuclides. For both cases, the modelled evolution of nuclide concentrations with age between 0-50 years at 2000 m and 3500 m water depths is plotted in Fig. 9, and compared to data. As expected, modeled ²³⁰Th and ²³¹Pa concentrations increase with age, with deeper waters having higher concentrations and ²³⁰Th increasing more rapidly initially (Fig. 9), but the preformed concentration is seen to be important in setting total nuclide concentration for several decades after ventilation.
- 10 The fit of the model to observations in young waters from GEOVIDE is improved in the model run with zero preformed nuclide, particularly for ²³⁰Th. This is surprising, given that surface-water ²³⁰Th and ²³¹Pa values are generally non-zero, and typically close to the value observed in the GEOVIDE surface waters. For ²³⁰Th in young deep waters, even the model with zero preformed nuclide overestimates the observed value, possibly indicating additional scavenging from these waters close to the seafloor.
- 15 The most striking effect of changing the assumed preformed values in the model is on ²³¹Pa/²³⁰Th (Fig. 9c). When preformed values are set at zero, ²³¹Pa/²³⁰Th ratios <u>always</u> increase as water age increases, but when set at the average surface value from GEOVIDE, ²³¹Pa/²³⁰Th ratios <u>initially decrease before increasing</u>. The impact of preformed concentrations has a long-lasting impact on water-column and scavenged ²³¹Pa/-Th, lasting for hundreds of years following ventilation (Supplementary Information Figure S2 (c), (d)). This indicates that knowledge of the nuclide concentration at the site of deep-water formation
- 20 is critical to understanding the early evolution of 231 Pa/ 230 Th in waters and their underlying sediments.

4.4 Scavenging of ²³⁰Th and ²³¹Pa

Knowledge of the CFC ages of the waters analysed on the GEOVIDE cruise allow an assessment of the scavenging rates of ²³⁰Th and ²³¹Pa. To do so, we compare the Scavenged component to the Potential Total component (as defined in Section 4.2). <u>An analysis of uncertainty of this assessment is given in Supplemental Information S4.</u> The percentage of the Scavenged component relative to the Potential Total component is higher for ²³⁰Th, at an average of 80%, than for ²³¹Pa at an average of

40% (Fig. 10), consistent with the relatively higher particle-reactivity of ²³⁰Th. For both nuclides, there is higher fraction of scavenging in samples from near the seafloor, particularly those in from DSOW in the deepest LA Sea. Bottom scavenging has been indicated in previous studies (e.g. Bacon and Anderson, 1982; Deng et al., 2014; Okubo et al., 2012), but this study indicates that this enhanced nuclide scavenging occurs even in the very young overflow waters at the start of the meridional circulation.

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4.5 Meridional transport of $^{230}\mathrm{Th}$ and $^{231}\mathrm{Pa}$ in the North Atlantic

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Previous calculations have indicated removal of ²³⁰Th and ²³¹Pa from the North Atlantic by meridional transport southward. Deng et al. (2014) calculated net southward transport of 6% of the ²³⁰Th and 33% of ²³¹Pa, relative to production of these nuclides in the water column. That calculation, however, did not provide a complete budget for ²³⁰Th and ²³¹Pa for the North Atlantic because observations at the time did not constrain input of these nuclides from the north. Data in this study allow this calculation, and therefore a more complete budget for the modern North Atlantic.

- García-Ibáñez et al. (2018) calculated volume transports for the Portugal to Greenland section of the GEOVIDE section by combining the water mass fractions from eOMP analysis with the absolute geostrophic velocity field calculated using inverse model constrained by Doppler current profiler velocity measurements (Zunino et al., 2017). They <u>separated northward flowing</u> upper, and southward flowing lower limbs of the AMOC at isopycnal σ_1 (potential density referenced to 1000 dbar) = 32.15
- 10 kg/m³, with +18.7 ± 2.4 Sv and -17.6 ± 3.0 Sv flow across the section above and below this value (positive value indicates northward transport). With average ²³⁰Th and ²³¹Pa concentrations in the upper limb ($\sigma_{L} < 32.15 \text{ kg/m^3}$) of 1.60 and 1.32 μ Bq/kg respectively, northward transport of ²³⁰Th is 3.07 × 10¹⁰ and of ²³¹Pa is 2.53 × 10¹⁰ μ Bq/s. Average ²³⁰Th and ²³¹Pa concentrations in the lower limb ($\sigma_{I} > 32.15 \text{ kg/m^3}$) are 3.44 and 2.07 μ Bq/kg, respectively, indicating transports of ²³⁰Th and ²³¹Pa are -6.22 × 10¹⁰ and -3.74 × 10¹⁰ μ Bq/s, respectively.
- 15 Net transport of ²³⁰Th and ²³¹Pa across GEOVIDE is therefore to the south, and supplies $3.15 \times 10^{10} \mu$ Bq/s ²³⁰Th and $1.21 \times 10^{10} \mu$ Bq/s ²³¹Pa to the North Atlantic (Fig. 11). This is a smaller net transport than further south in the Atlantic (Fig. 11), due to the lower ²³⁰Th and ²³¹Pa concentrations in the water column close of the site of deep-water formation. The budget for these nuclides for the North Atlantic consists of: production in the water column; addition by advection from the North; loss by advection to the South and removal to the sediment. The data from this study allows this budget to be fully
- 20 assessed, and indicates that the flux to the sediment is equivalent to 96% of the production of ²³⁰Th, and 74% of the production for ²³¹Pa (Supplemental Information Table S5). For both nuclides, these fluxes are higher than in previous calculations (Deng et al. 2014) which ignored advective fluxes from the North. There is, however, still a significantly higher advective loss of ²³¹Pa relative to ²³⁰Th. At a basin scale, therefore, ²³¹Pa/²³⁰Th in the sediment must be lower than the production ratio. This lower value is generated by the meridional transport of the North Atlantic, and likely to be sensitive to changes in this transport.
- 25 Use the Basin-scale Advection model to interpret sedimentary ²³¹Pa/²³⁰Th to assess meridional transport, as initially proposed by Yu et. al (1996), is therefore still supported by the full modern North Atlantic budget for these nuclides.

5 Conclusion

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Measurement of ²³⁰Th and ²³¹Pa in waters from GEOVIDE show some control of water mass on ²³⁰Th and ²³¹Pa concentrations, particularly low concentrations in DSOW and high values in the old NEADW. There is, however, no close mapping of nuclide concentration to water mass.

With the availability of CFC ages on this section, the evolution of ²³⁰Th and ²³¹Pa concentration with age is possible. A systematic increase of ²³⁰Th concentration is observed over the first 50 years following ventilation, and a similar though more

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scattered relationship seen for 231 Pa_vThere is no clear relationship between the 231 Pa/ 230 Th ratio and age for these young waters. The <u>long-term</u> evolution of 231 Pa/ 230 Th is found from a simple model to be highly dependent on the preformed concentrations for these nuclides. <u>These results complicate the interpretation of sedimentary 231 Pa/ 230 Th as a paleo-proxy for deep water circulation based on systematic evolution of water 231 Pa/ 230 Th with age, and point to the importance of a better knowledge of</u>

- 5 preformed ²³⁰Th and ²³¹Pa concentrations to improve interpretation. This analysis of the ²³⁰Th and ²³¹Pa concentration relative to the age of the water not only demonstrates the influence of water mass aging on ²³¹Pa and ²³⁰Th, but also points to the influence of scavenging. Scavenged ²³⁰Th is much more extensive that ²³¹Pa, as expected, and enhanced removal of both nuclides is seen immediately above the seafloor, particularly for young waters.
- Calculation of meridional transport of ²³⁰Th and ²³¹Pa indicates a southward net transport of both nuclides across the GEOVIDE section. This advection is smaller than that further south in the Atlantic as a result of lower ²³⁰Th and ²³¹Pa concentrations at GEOVIDE. Calculation of the flux across GEOVIDE allows a more complete budget for the North Atlantic to be constructed and demonstrates a significantly higher advective loss of ²³¹Pa to the south relative to ²³⁰Th, with 2<u>6</u>% of the ²³¹Pa produced advected southward (relative to only 4% for ²³⁰Th). This calculation, supports the interpretation of sedimentary ²³¹Pa/²³⁰Th measurements as a proxy for overturning circulation, when based on advective loss of ²³¹Pa at a basin scale.

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25 in this volume. We also thank Yves Plancherel for valuable insight during discussion of the results presented.

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Figure 1: Map showing GEOVIDE cruise track (black line) and station locations (black dots). <u>Colour bars indicate water depth.</u> Sampling locations for water-column ²³¹Pa and ²³⁰Th in this study are shown by coloured dots, with colours representing the ocean regions they are located in.

I





Figure 2: Vertical profiles of 230 Th (a-d) and 231 Pa (e-h) in the water column along the GEOVIDE section. Colours corresponds to the region (as in Fig. 1). LA = Labrador, IR = Irminger, IC = Iceland, WE = West European). Uncertainties represent 2 standard error (2 s.e.).





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Figure 4: Results of Extended Optimum MultiParameter (eOMP) analysis for the GEOVIDE section (García-Ibáñez et al., 2018). Colours reflect the fraction of water at each location assigned to the water mass shown in that panel: ENACW₁₆ and ENACW₁₂ = East North Atlantic Central Water of 16°C and 12°C; SPMWs, SPMW7, IrSPMW = Subpolar Mode Water of 8°C, 7°C and of the Irminger Sea; SAIW₆ and SAIW₄ = Subarctic Intermediate Water of 6°C and 4°C; MW = Mediterranean Water; PIW = Polar Intermediate Water; JSOW=Iceland–Scotland Overflow Water; LSW=Labrador Sea Water; DSOW: Denmark Strait Overflow Waters; and NEADW₁: Lower North East Atlantic Deep Water; ABR= Azores-Biscay Rise.

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Figure 5: Distribution of ²³⁰Th and ²³¹Pa along the GEOVIDE section. Water masses were indicated by contours (black: DSOW; blue: ISOW; white: LSW; red: NEADW.) based on 50% level percentage composition of source water types from eOMP analysis.





Figure 6: Water mass age based on CFC data along the GEOVIDE section. (a) Full water-column data for the entire section, showing waters from 10 to 800 years in age; (b) A rescaled version of (a) omitting the upper 1000m and the older waters west of 35°W to show age variation in recently ventilated deep-waters. <u>Water masses were indicated by contours (black: DSOW; blue: ISOW; white:</u> LSW; red: NEADW.) based on 50% level percentage composition of source water types from eOMP analysis.





Figure 7: Potential Total, Observed, and Scavenged components of ²³⁰Th and ²³¹Pa in waters >1000 m water depth and west of 35°W,

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Figure 8: Relationship between water mass age and the Observed and Scavenged components of ²³⁰Th, ²³¹Pa and ²³¹Pa/²³⁰Th (colour coded by water depth). Least square fitting statistics were also given, i.e. slope and correlation coefficient r of the least square line, mean value and number of the data points. Note the increase of observed concentrations for both nuclides with age. Comparison of average values indicates that about three quarters of ²³⁰Th produced by decay is scavenged, compared with about half of the ²³¹Pa_x.

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Figure 9: Results from a scavenging-mixing model of ²³⁰Th, ²³¹Pa, Dissolved ²³¹Pa/²³⁰Th and particulate ²³¹Pa/²³⁰Th compared to observations. Preformed concentration (C_{pre}) were set at 0 (dashed line) and at the average surface concentration (C_{surface average}) from GEOVIDE section (solid line), i.e. ²³⁰Th= 1.66 µBq/kg, ²³¹Pa= 1.31 µBq/kg. A version of this figure extending to older waters is available in the Supplemental Information.

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Deleted: Figure 9: Results from a scavenging-mixing model of ²³⁰Th, ²³¹Pa, and ²³¹Pa/²³⁰Th compared to observations. Preformed values were set at 0 (dashed line) and at the average surface values from GEOVIDE section (solid line), i.e. ²³⁰Th_{surface}=0.108 dpm/10001, ²³¹Pa_{surface}=0.089 dpm/10001.



Figure 10: Ratio of Scavenged component to Potential Total component for ²³⁰Th and ²³¹Pa, providing an assessment of the relative importance of scavenging for the two nuclides, and of the location of scavenging.







Figure 11: Fluxes of ²³⁰Th (blue arrow) and ²³¹Pa (yellow arrow) across the GEOVIDE section (blue solid line), 4.5°S (green solid line) and 45°S (red solid line). Also shown are production of ²³⁰Th (blue box) and ²³¹Pa (yellow box) in the North Atlantic (between GEOVIDE section and 4.5°S) and in the South Atlantic (between 4.5°S and 45°S), based on calculation in Deng et al. (2014). These fluxes indicate that 4% of the ²³⁰Th produced in the North Atlantic is exported southward by ocean circulation, and 2<u>5</u>% of the ²³¹Pa.

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Supplemental Information of

Evolution of ²³¹Pa and ²³⁰Th in overflow waters of the North Atlantic

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Feifei Deng et al.

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S1. Data of water-column ²³¹Pa, ²³⁰Th and ²³²Th concentrations, and ²³¹Pa/²³⁰Th ratios along GEOVIDE section and details of correction

Station	<u>Depth</u>	231Pa	231Pacorr	231Pacorr	$2se$ $\frac{230}{Th}$	230Th	230Thcorr	<u>2se</u>	232Th	232Th	<u>2se</u>	231Pa/230Th	<u>2se</u>
	<u>m</u>	<u>fg/kg</u>	fg/kg	<u>µBq/kg</u>	<u>fg/kg</u>	fg/kg	<u>µBq/kg</u>		pg/kg	pmol/kg			
1	<u>3445.3</u>	<u>2.270</u>	2.269	<u>3.96</u>	<u>0.17</u>								
40.33°N	<u>2955.3</u>	<u>2.465</u>	2.463	4.30	<u>0.22</u>								
10.04°W	<u>2465.8</u>	<u>1.988</u>	1.982	3.46	<u>0.22</u> <u>9.00</u>	<u>8.83</u>	<u>6.72</u>	<u>0.20</u>	<u>52.33</u>	0.2248	<u>0.0046</u>	0.516	<u>0.036</u>
	<u>1974.9</u>	<u>1.592</u>	1.588	2.77	<u>0.19</u> <u>5.64</u>	<u>5.50</u>	<u>4.18</u>	<u>0.17</u>	<u>43.47</u>	<u>0.1867</u>	<u>0.0036</u>	0.663	<u>0.053</u>
	<u>1385.3</u>	1.522	<u>1.517</u>	2.65	<u>0.23</u> <u>3.43</u>	<u>3.28</u>	<u>2.50</u>	<u>0.14</u>	<u>44.96</u>	<u>0.1931</u>	<u>0.0041</u>	<u>1.061</u>	<u>0.108</u>
	<u>1039.6</u>	<u>1.176</u>	<u>1.170</u>	2.04	<u>0.20</u> <u>3.48</u>	<u>3.29</u>	<u>2.50</u>	<u>0.20</u>	<u>59.80</u>	0.2568	<u>0.0049</u>	<u>0.818</u>	<u>0.105</u>
	<u>495.6</u>	<u>0.861</u>	0.853	1.49	<u>0.22</u> <u>3.67</u>	<u>3.43</u>	<u>2.61</u>	<u>0.16</u>	<u>72.77</u>	<u>0.3125</u>	0.0058	0.571	<u>0.090</u>
	<u>246.9</u>	<u>0.635</u>	0.624	1.09	<u>0.18</u> <u>2.79</u>	<u>2.47</u>	<u>1.88</u>	<u>0.14</u>	<u>99.60</u>	<u>0.4278</u>	<u>0.0098</u>	0.581	<u>0.104</u>
	<u>49.6</u>	<u>0.641</u>	<u>0.623</u>	<u>1.09</u>	<u>0.20</u> <u>2.84</u>	<u>2.29</u>	<u>1.74</u>	<u>0.18</u>	<u>171.16</u>	<u>0.7351</u>	<u>0.0133</u>	0.625	<u>0.132</u>
	<u>4.7</u>	<u>0.238</u>	<u>0.210</u>	<u>0.37</u>	<u>0.08</u> <u>3.93</u>	<u>3.11</u>	2.36	<u>0.09</u>	<u>255.90</u>	<u>1.0991</u>	<u>0.0186</u>	<u>0.155</u>	<u>0.033</u>
<u>13</u>	<u>5330.4</u>	2.093	1.880	<u>3.28</u>	<u>0.24</u> <u>8.69</u>	<u>8.62</u>	<u>6.56</u>	<u>6.56</u>	<u>22.79</u>	<u>0.0979</u>	<u>0.0017</u>	<u>0.501</u>	<u>0.039</u>
<u>41.38°N</u>	<u>5263.1</u>	<u>2.421</u>	<u>2.178</u>	<u>3.80</u>	<u>0.26</u> <u>12.66</u>	<u>12.55</u>	<u>9.55</u>	<u>9.55</u>	<u>33.12</u>	<u>0.1422</u>	<u>0.0022</u>	<u>0.398</u>	<u>0.028</u>
13.89°W	<u>5194.3</u>	2.751	<u>2.747</u>	<u>4.80</u>	<u>0.24</u> <u>15.80</u>	15.67	<u>11.92</u>	<u>11.92</u>	<u>39.61</u>	<u>0.1701</u>	<u>0.0033</u>	<u>0.403</u>	<u>0.023</u>
	<u>4903.9</u>	2.013	2.009	<u>3.51</u>	<u>0.15</u> <u>14.79</u>	14.68	<u>11.17</u>	<u>11.17</u>	<u>35.27</u>	<u>0.1515</u>	<u>0.0031</u>	<u>0.314</u>	<u>0.016</u>
	<u>4417.8</u>	<u>2.627</u>	<u>2.624</u>	<u>4.58</u>	<u>0.24 11.16</u>	<u>11.07</u>	<u>8.42</u>	<u>8.42</u>	<u>28.70</u>	<u>0.1233</u>	<u>0.0026</u>	<u>0.545</u>	<u>0.033</u>
	<u>3444</u>	<u>2.399</u>	<u>2.396</u>	<u>4.19</u>	<u>0.14</u> <u>8.15</u>	<u>8.08</u>	<u>6.14</u>	<u>6.14</u>	<u>22.33</u>	<u>0.0959</u>	0.0022	0.681	<u>0.031</u>
	<u>2464.7</u>	<u>1.569</u>	1.565	<u>2.73</u>	<u>0.26</u> <u>5.77</u>	<u>5.67</u>	<u>4.31</u>	<u>4.31</u>	<u>30.57</u>	<u>0.1313</u>	0.0028	0.634	<u>0.066</u>
	<u>1187.3</u>	<u>0.869</u>	0.865	<u>1.51</u>	<u>0.12</u> <u>3.24</u>	<u>3.12</u>	2.38	<u>2.38</u>	<u>37.16</u>	<u>0.1596</u>	0.0032	0.637	<u>0.065</u>
	<u>989.1</u>	<u>1.239</u>	1.234	2.16	<u>0.15</u> <u>4.16</u>	4.03	<u>3.06</u>	<u>3.06</u>	<u>41.38</u>	<u>0.1777</u>	0.0035	0.704	<u>0.063</u>
	<u>248.4</u>	<u>0.602</u>	<u>0.602</u>	<u>1.05</u>	<u>0.11</u>								
	<u>148.5</u>	<u>0.525</u>	0.525	0.92	<u>0.13</u>								
	<u>29.7</u>	<u>0.508</u>	<u>0.507</u>	<u>0.89</u>	<u>0.11</u> <u>0.44</u>	<u>0.43</u>	<u>0.32</u>	<u>0.15</u>	<u>5.60</u>	<u>0.0241</u>	<u>0.0015</u>	<u>2.736</u>	<u>1.315</u>
	<u>4.3</u>	<u>0.330</u>	0.330	0.58	<u>0.08</u> <u>0.28</u>	<u>0.26</u>	<u>0.19</u>	<u>0.14</u>	<u>6.70</u>	0.0288	<u>0.0014</u>	2.968	<u>2.154</u>

Table S1 Water-column ²³¹Pa, ²³⁰Th and ²³²Th concentrations, and ²³¹Pa/²³⁰Th ratios along GEOVIDE section

Station	Depth	²³¹ Pa	231Pa	²³¹ Pa _{corr}	<u>2se</u> 230Th	²³⁰ Th	²³⁰ Th _{corr}	<u>2se</u>	²³² Th	²³² Th	2se	231Pa/230Th	<u>2se</u>
	<u>m</u>	<u>fg/kg</u>	<u>fg/kg</u>	<u>µBq/kg</u>	<u>fg/kg</u>	<u>fg/kg</u>	µBq/kg		pg/kg	pmol/kg			
<u>21</u>	<u>4514.9</u>	2.605	2.603	4.55	<u>0.15</u> <u>6.09</u>	<u>6.03</u>	4.58	<u>0.19</u>	<u>20.99</u>	0.0902	0.0017	0.992	<u>0.052</u>
46.54°N	<u>4475</u>	<u>2.404</u>	<u>2.401</u>	<u>4.20</u>	<u>0.18</u> <u>6.21</u>	<u>6.13</u>	4.66	<u>0.28</u>	<u>25.11</u>	<u>0.1079</u>	0.0025	<u>0.900</u>	<u>0.066</u>
19.67°W	4426.3	<u>2.413</u>	<u>2.411</u>	<u>4.21</u>	<u>0.17</u> <u>5.76</u>	<u>5.70</u>	4.33	<u>0.14</u>	<u>19.57</u>	<u>0.0841</u>	<u>0.0017</u>	<u>0.972</u>	<u>0.051</u>
	<u>4279.6</u>	<u>2.497</u>	2.495	<u>4.36</u>	<u>0.18</u> <u>5.91</u>	<u>5.85</u>	4.45	<u>0.19</u>	<u>20.48</u>	<u>0.0880</u>	<u>0.0018</u>	<u>0.980</u>	<u>0.059</u>
	<u>3929.3</u>	<u>2.081</u>	<u>2.079</u>	<u>3.63</u>	<u>0.17</u> <u>5.47</u>	<u>5.41</u>	4.11	<u>0.16</u>	<u>20.11</u>	0.0864	<u>0.0016</u>	0.884	<u>0.053</u>
	<u>3443.3</u>	<u>1.930</u>	<u>1.928</u>	<u>3.37</u>	<u>0.20</u> <u>4.63</u>	<u>4.57</u>	<u>3.47</u>	<u>0.14</u>	<u>18.16</u>	<u>0.0780</u>	<u>0.0015</u>	<u>0.970</u>	<u>0.070</u>
	<u>2268.9</u>	<u>1.114</u>	<u>1.114</u>	<u>1.95</u>	<u>0.22</u> <u>5.16</u>	<u>5.06</u>	3.85	<u>0.17</u>	<u>30.49</u>	<u>0.1309</u>	0.0021	0.506	<u>0.060</u>
	<u>1482.7</u>	<u>0.995</u>	<u>0.993</u>	<u>1.73</u>	<u>0.12</u> <u>2.48</u>	<u>2.39</u>	1.82	<u>0.14</u>	<u>26.83</u>	<u>0.1152</u>	<u>0.0016</u>	0.953	<u>0.097</u>
	<u>788.4</u>	<u>0.873</u>	<u>0.871</u>	1.52	<u>0.14</u> <u>1.31</u>	1.23	<u>0.93</u>	<u>0.16</u>	25.41	<u>0.1092</u>	0.0018	1.628	<u>0.312</u>
	<u>445.5</u>	<u>0.679</u>	<u>0.676</u>	<u>1.18</u>	<u>0.14</u> <u>2.18</u>	2.05	1.56	<u>0.14</u>	<u>39.91</u>	<u>0.1714</u>	0.0023	0.756	<u>0.115</u>
	<u>246.9</u>	<u>0.595</u>	<u>0.592</u>	<u>1.03</u>	<u>0.11</u> <u>1.64</u>	<u>1.53</u>	<u>1.17</u>	<u>0.13</u>	<u>33.41</u>	<u>0.1435</u>	<u>0.0019</u>	<u>0.886</u>	<u>0.139</u>
	<u>98.1</u>	<u>0.607</u>	<u>0.603</u>	1.05	<u>0.14</u> <u>1.32</u>	1.23	<u>0.93</u>	<u>0.12</u>	<u>28.01</u>	0.1203	<u>0.0019</u>	1.129	<u>0.209</u>
	<u>13.9</u>	<u>0.536</u>	<u>0.532</u>	<u>0.93</u>	<u>0.15</u>				<u>10.81</u>	<u>0.0464</u>	<u>0.0015</u>		
	<u>3.7</u>	0.522	<u>0.519</u>	<u>0.91</u>	<u>0.14</u>				<u>7.95</u>	0.0342	<u>0.0014</u>		
<u>26</u>	<u>4116.3</u>	<u>1.162</u>	<u>1.158</u>	<u>2.02</u>	<u>0.18</u> <u>3.43</u>	<u>3.29</u>	2.50	<u>0.17</u>	<u>42.15</u>	<u>0.1810</u>	0.0035	<u>0.808</u>	<u>0.088</u>
50.28°N	<u>2758.5</u>	<u>0.813</u>	<u>0.807</u>	<u>1.41</u>	<u>0.15</u> <u>3.04</u>	<u>2.85</u>	<u>2.17</u>	<u>0.14</u>	<u>57.40</u>	0.2465	0.0047	0.650	<u>0.081</u>
22.60°W	1973.5	<u>0.745</u>	<u>0.739</u>	<u>1.29</u>	<u>0.13</u> <u>2.83</u>	2.65	2.01	<u>0.16</u>	<u>56.40</u>	<u>0.2422</u>	0.0045	0.642	<u>0.081</u>
	<u>989.1</u>	0.695	<u>0.695</u>	1.22	<u>0.11</u>								
	<u>296.7</u>	<u>0.503</u>	<u>0.503</u>	<u>0.88</u>	<u>0.10</u>								
	<u>74.4</u>	<u>0.408</u>	<u>0.407</u>	<u>0.71</u>	<u>0.12</u> <u>0.67</u>	<u>0.62</u>	<u>0.47</u>	<u>0.17</u>	<u>13.57</u>	<u>0.0583</u>	<u>0.0018</u>	<u>1.498</u>	<u>0.603</u>

Station	Depth 231Pa	²³¹ Pa	²³¹ Pa _{corr}	<u>2se</u> 230Th	230Th	²³⁰ Th _{corr}	<u>2se</u>	232Th	²³² Th	2se	231Pa/230Th	<u>2se</u>
	<u>m fg/kg</u>	<u>fg/kg</u>	<u>µBq/kg</u>	<u>fg/kg</u>	<u>fg/kg</u>	<u>µBq/kg</u>		pg/kg	pmol/kg			
<u>32</u>	<u>3218.7</u> 0.973	<u>0.968</u>	1.69	<u>0.15</u> <u>5.49</u>	5.35	4.07	<u>0.15</u>	<u>43.48</u>	0.1867	0.0023	0.416	<u>0.039</u>
55.51°N	<u>3218.5</u> 0.984	<u>0.982</u>	<u>1.72</u>	<u>0.12</u> <u>1.68</u>	<u>1.63</u>	1.24	<u>0.14</u>	<u>15.25</u>	<u>0.0655</u>	<u>0.0016</u>	1.387	<u>0.184</u>
<u>26.71°W</u>	<u>3049.9 1.131</u>	<u>1.129</u>	<u>1.97</u>	<u>0.11</u> <u>3.27</u>	<u>3.21</u>	2.44	<u>0.13</u>	<u>20.44</u>	<u>0.0878</u>	<u>0.0016</u>	0.809	<u>0.063</u>
	<u>2949.6</u> <u>1.076</u>	1.075	1.88	<u>0.17</u> <u>1.74</u>	<u>1.70</u>	1.29	<u>0.13</u>	<u>12.96</u>	<u>0.0557</u>	<u>0.0014</u>	<u>1.456</u>	<u>0.198</u>
	<u>2854.3</u> <u>1.004</u>	1.002	<u>1.75</u>	<u>0.20</u> <u>2.65</u>	2.60	<u>1.97</u>	<u>0.17</u>	<u>16.46</u>	<u>0.0707</u>	<u>0.0016</u>	0.887	<u>0.128</u>
	<u>2610.4 1.109</u>	<u>1.108</u>	<u>1.94</u>	<u>0.13</u> <u>1.82</u>	<u>1.78</u>	<u>1.35</u>	<u>0.14</u>	<u>12.01</u>	<u>0.0516</u>	<u>0.0016</u>	<u>1.429</u>	<u>0.179</u>
	<u>2218.8</u> <u>0.843</u>	0.842	<u>1.47</u>	<u>0.14</u> <u>1.30</u>	<u>1.26</u>	<u>0.96</u>	<u>0.13</u>	<u>11.46</u>	<u>0.0492</u>	0.0015	<u>1.533</u>	<u>0.261</u>
	<u>1676.9</u> <u>1.200</u>	<u>1.199</u>	<u>2.09</u>	<u>0.14</u> <u>0.87</u>	<u>0.84</u>	0.64	<u>0.12</u>	<u>9.00</u>	<u>0.0387</u>	<u>0.0014</u>	3.261	<u>0.661</u>
	<u>1185.5</u> <u>1.087</u>	1.082	1.89	<u>0.14</u> <u>3.58</u>	<u>3.45</u>	2.62	<u>0.15</u>	<u>40.46</u>	0.1738	0.0022	0.721	<u>0.066</u>
	<u>890.5</u> <u>0.872</u>	<u>0.869</u>	1.52	<u>0.14</u> <u>1.64</u>	<u>1.55</u>	1.18	<u>0.13</u>	<u>29.00</u>	<u>0.1246</u>	0.0018	1.289	<u>0.187</u>
	<u>445.3</u> <u>0.944</u>	<u>0.939</u>	<u>1.64</u>	<u>0.14</u> <u>2.91</u>	<u>2.76</u>	<u>2.10</u>	<u>0.15</u>	<u>46.20</u>	<u>0.1984</u>	0.0026	0.781	<u>0.086</u>
	<u>222.9</u> <u>0.568</u>	<u>0.564</u>	<u>0.99</u>	<u>0.12</u> <u>1.70</u>	<u>1.57</u>	1.20	<u>0.13</u>	<u>39.69</u>	<u>0.1705</u>	0.0022	0.824	<u>0.135</u>
	<u>98.9</u> <u>0.553</u>	<u>0.550</u>	<u>0.96</u>	<u>0.25</u> <u>6.65</u>	<u>6.56</u>	<u>4.99</u>	<u>0.16</u>	<u>27.70</u>	<u>0.1190</u>	0.0018	<u>0.193</u>	<u>0.050</u>
	<u>29.5</u> <u>0.613</u>	<u>0.610</u>	<u>1.07</u>	<u>0.27</u> <u>5.50</u>	<u>5.41</u>	4.12	<u>0.16</u>	<u>27.73</u>	<u>0.1191</u>	<u>0.0019</u>	0.259	<u>0.067</u>
	<u>5.8</u> <u>0.584</u>	0.583	1.02	<u>0.14</u>				<u>9.92</u>	<u>0.0426</u>	<u>0.0015</u>		
<u>38</u>	<u>1338.1 1.604</u>	<u>1.602</u>	<u>2.80</u>	<u>0.22</u> <u>1.62</u>	<u>1.57</u>	1.20	<u>0.15</u>	<u>16.07</u>	<u>0.0690</u>	0.0020	<u>2.341</u>	<u>0.338</u>
58.84°N	<u>1303.6 1.336</u>	<u>1.333</u>	<u>2.33</u>	<u>0.11</u> <u>3.34</u>	<u>3.25</u>	<u>2.47</u>	<u>0.20</u>	<u>29.18</u>	<u>0.1253</u>	0.0026	<u>0.943</u>	<u>0.087</u>
31.27°W	<u>1234.5</u> <u>1.088</u>	1.085	<u>1.90</u>	<u>0.11</u> <u>3.42</u>	<u>3.33</u>	2.53	<u>0.15</u>	<u>28.39</u>	<u>0.1219</u>	0.0026	<u>0.748</u>	<u>0.064</u>
	<u>1084</u> <u>0.863</u>	<u>0.860</u>	<u>1.50</u>	<u>0.10</u> <u>3.64</u>	3.54	<u>2.69</u>	<u>0.19</u>	<u>31.67</u>	<u>0.1360</u>	0.0027	0.558	<u>0.053</u>
	<u>494.2</u> <u>1.621</u>	<u>1.616</u>	<u>2.82</u>	<u>0.25</u> <u>3.16</u>	<u>3.03</u>	2.30	<u>0.16</u>	<u>39.87</u>	<u>0.1712</u>	0.0033	1.226	<u>0.137</u>
	<u>198.4</u> <u>1.258</u>	1.253	<u>2.19</u>	<u>0.12</u> <u>3.12</u>	<u>2.97</u>	2.26	<u>0.14</u>	<u>46.64</u>	0.2003	0.0037	<u>0.969</u>	<u>0.081</u>
	<u>108.7</u> <u>1.274</u>	1.269	<u>2.22</u>	<u>0.19</u> <u>2.78</u>	<u>2.65</u>	2.01	<u>0.14</u>	<u>42.89</u>	0.1842	0.0036	<u>1.102</u>	<u>0.121</u>
	<u>20.3</u> <u>0.836</u>	0.835	<u>1.46</u>	<u>0.13</u> <u>0.84</u>	<u>0.80</u>	<u>0.61</u>	<u>0.13</u>	<u>11.88</u>	0.0510	<u>0.0016</u>	2.389	<u>0.566</u>
	<u>5.3</u> <u>1.230</u>	<u>1.228</u>	<u>2.15</u>	<u>0.25</u> <u>0.80</u>	<u>0.76</u>	<u>0.58</u>	<u>0.15</u>	<u>11.59</u>	<u>0.0498</u>	<u>0.0016</u>	<u>3.719</u>	<u>1.055</u>

Station	Depth	²³¹ Pa	²³¹ Pa	²³¹ Pa _{corr}	<u>2se</u> 230Th	²³⁰ Th	²³⁰ Th _{corr}	<u>2se</u>	²³² Th	232Th	<u>2se</u>	231Pa/230Th	2se
	<u>m</u>	<u>fg/kg</u>	<u>fg/kg</u>	<u>µBq/kg</u>	<u>fg/kg</u>	<u>fg/kg</u>	µBq/kg		pg/kg	pmol/kg			
<u>44</u>	<u>2918.9</u>	<u>0.839</u>	0.837	<u>1.46</u>	<u>0.17</u> <u>2.40</u>	2.33	1.77	<u>0.13</u>	22.85	<u>0.0981</u>	0.0022	0.827	<u>0.112</u>
<u>59.62°N</u>	<u>2878.5</u>	<u>0.875</u>	<u>0.873</u>	<u>1.52</u>	<u>0.15</u> <u>2.50</u>	<u>2.42</u>	<u>1.84</u>	<u>0.14</u>	<u>24.44</u>	<u>0.1050</u>	0.0023	<u>0.829</u>	<u>0.102</u>
38.95°W	<u>2829</u>	<u>0.723</u>	<u>0.723</u>	<u>1.26</u>	<u>0.22</u>								
	2681.9	<u>0.651</u>	<u>0.649</u>	<u>1.13</u>	<u>0.24</u> <u>2.65</u>	<u>2.57</u>	<u>1.96</u>	<u>0.15</u>	<u>25.27</u>	<u>0.1085</u>	<u>0.0024</u>	0.580	<u>0.129</u>
	<u>2561</u>	<u>1.164</u>	<u>1.161</u>	2.03	<u>0.23</u> <u>4.87</u>	<u>4.78</u>	3.64	<u>0.17</u>	<u>26.47</u>	<u>0.1137</u>	0.0025	<u>0.557</u>	<u>0.069</u>
	<u>2216.6</u>	<u>0.910</u>	<u>0.906</u>	<u>1.58</u>	<u>0.26</u> <u>6.18</u>	<u>6.08</u>	4.63	<u>0.18</u>	<u>31.25</u>	<u>0.1342</u>	<u>0.0028</u>	<u>0.342</u>	<u>0.058</u>
	<u>1776</u>	<u>1.416</u>	<u>1.412</u>	<u>2.47</u>	<u>0.39</u> <u>5.87</u>	<u>5.75</u>	4.37	<u>0.15</u>	<u>39.66</u>	<u>0.1704</u>	0.0032	<u>0.564</u>	<u>0.090</u>
	<u>1382.5</u>	<u>1.186</u>	<u>1.182</u>	<u>2.07</u>	<u>0.27</u> <u>5.85</u>	<u>5.72</u>	4.35	<u>0.15</u>	<u>41.00</u>	<u>0.1761</u>	<u>0.0034</u>	<u>0.475</u>	<u>0.065</u>
	<u>1087.5</u>	<u>0.795</u>	<u>0.790</u>	<u>1.38</u>	<u>0.18</u> <u>3.83</u>	<u>3.70</u>	2.81	<u>0.15</u>	<u>40.73</u>	<u>0.1749</u>	<u>0.0033</u>	<u>0.491</u>	<u>0.071</u>
	<u>593.2</u>	<u>1.116</u>	<u>1.111</u>	<u>1.94</u>	<u>0.36</u> <u>4.28</u>	<u>4.13</u>	<u>3.14</u>	<u>0.16</u>	<u>46.81</u>	<u>0.2010</u>	0.0038	<u>0.618</u>	<u>0.118</u>
	<u>297.3</u>	<u>1.083</u>	<u>1.078</u>	<u>1.88</u>	<u>0.20</u> <u>4.10</u>	<u>3.97</u>	<u>3.02</u>	<u>0.22</u>	<u>42.29</u>	<u>0.1816</u>	<u>0.0036</u>	0.625	<u>0.081</u>
	<u>78.8</u>	<u>0.929</u>	<u>0.925</u>	1.62	<u>0.19</u> <u>3.44</u>	<u>3.31</u>	2.52	<u>0.14</u>	<u>39.69</u>	<u>0.1705</u>	<u>0.0033</u>	<u>0.641</u>	<u>0.082</u>
	<u>25.5</u>	<u>0.998</u>	<u>0.997</u>	<u>1.74</u>	<u>0.16</u> <u>1.37</u>	<u>1.32</u>	<u>1.00</u>	<u>0.15</u>	<u>16.50</u>	<u>0.0709</u>	<u>0.0019</u>	<u>1.737</u>	<u>0.297</u>
	<u>5.5</u>	<u>0.722</u>	<u>0.720</u>	<u>1.26</u>	<u>0.33</u> <u>1.31</u>	1.27	<u>0.96</u>	<u>0.12</u>	<u>14.99</u>	<u>0.0644</u>	<u>0.0018</u>	<u>1.307</u>	<u>0.380</u>
<u>60</u>	<u>1710.9</u>	<u>0.844</u>	<u>0.841</u>	<u>1.47</u>	<u>0.07</u> <u>3.77</u>	<u>3.67</u>	<u>2.79</u>	<u>0.16</u>	<u>31.42</u>	<u>0.1349</u>	<u>0.0031</u>	<u>0.526</u>	<u>0.039</u>
<u>59.80°N</u>	<u>1652.6</u>	<u>0.881</u>	<u>0.878</u>	<u>1.53</u>	<u>0.07</u> <u>4.03</u>	<u>3.92</u>	<u>2.98</u>	<u>0.16</u>	<u>33.28</u>	<u>0.1429</u>	<u>0.0032</u>	<u>0.514</u>	<u>0.036</u>
42.01°W	<u>1603.1</u>	<u>0.845</u>	<u>0.842</u>	<u>1.47</u>	<u>0.07</u> <u>4.10</u>	<u>3.99</u>	<u>3.04</u>	<u>0.24</u>	<u>33.74</u>	<u>0.1449</u>	<u>0.0032</u>	<u>0.485</u>	<u>0.045</u>
	1481.2	<u>0.813</u>	<u>0.809</u>	<u>1.41</u>	<u>0.07</u> <u>4.19</u>	4.08	<u>3.10</u>	<u>0.17</u>	<u>33.94</u>	<u>0.1458</u>	0.0032	<u>0.455</u>	<u>0.034</u>
	<u>989.7</u>	<u>1.087</u>	1.082	<u>1.89</u>	<u>0.08</u> <u>5.29</u>	<u>5.15</u>	<u>3.91</u>	<u>0.20</u>	<u>45.60</u>	<u>0.1958</u>	<u>0.0040</u>	<u>0.483</u>	<u>0.031</u>
	<u>495.5</u>	<u>0.911</u>	<u>0.906</u>	<u>1.58</u>	<u>0.16</u> <u>3.69</u>	<u>3.56</u>	<u>2.71</u>	<u>0.14</u>	<u>39.63</u>	<u>0.1702</u>	<u>0.0033</u>	<u>0.585</u>	<u>0.064</u>
	<u>247.9</u>	<u>0.851</u>	<u>0.847</u>	<u>1.48</u>	<u>0.23</u> <u>3.16</u>	<u>3.03</u>	2.30	<u>0.14</u>	<u>40.61</u>	<u>0.1744</u>	<u>0.0034</u>	<u>0.643</u>	<u>0.109</u>
	<u>99.1</u>	<u>0.826</u>	0.822	<u>1.44</u>	<u>0.20</u> <u>2.34</u>	<u>2.23</u>	<u>1.69</u>	<u>0.13</u>	<u>34.75</u>	<u>0.1492</u>	<u>0.0029</u>	0.849	<u>0.134</u>
	<u>19.5</u>	<u>0.887</u>	<u>0.885</u>	1.55	<u>0.32</u> <u>1.36</u>	<u>1.30</u>	<u>0.99</u>	<u>0.16</u>	<u>18.14</u>	<u>0.0779</u>	0.0020	1.561	<u>0.405</u>
	<u>3.7</u>	<u>0.829</u>	<u>0.827</u>	<u>1.44</u>	<u>0.24</u> <u>1.53</u>	<u>1.46</u>	<u>1.11</u>	<u>0.14</u>	<u>22.32</u>	<u>0.0959</u>	0.0023	<u>1.301</u>	<u>0.266</u>

Station	Depth	²³¹ Pa	²³¹ Pa	²³¹ Pa _{corr}	<u>2se</u> 230Th	²³⁰ Th	²³⁰ Th _{corr}	2se	232Th	²³² Th	2se	231Pa/230Th	2se
	<u>m</u>	<u>fg/kg</u>	<u>fg/kg</u>	<u>µBq/kg</u>	<u>fg/kg</u>	<u>fg/kg</u>	<u>µBq/kg</u>		pg/kg	pmol/kg			
<u>64</u>	2466.8	0.759	<u>0.756</u>	<u>1.32</u>	<u>0.19</u> <u>3.24</u>	3.16	<u>2.40</u>	<u>0.14</u>	<u>25.71</u>	0.1104	0.0025	0.551	<u>0.087</u>
<u>59.07°N</u>	<u>2423.6</u>	<u>0.828</u>	<u>0.825</u>	<u>1.44</u>	<u>0.20</u> <u>3.71</u>	<u>3.62</u>	<u>2.76</u>	<u>0.18</u>	<u>26.12</u>	<u>0.1122</u>	0.0027	0.523	<u>0.080</u>
46.08°W	<u>2374</u>	<u>0.958</u>	<u>0.955</u>	<u>1.67</u>	<u>0.19</u> <u>3.76</u>	<u>3.68</u>	<u>2.80</u>	<u>0.13</u>	<u>27.16</u>	<u>0.1166</u>	0.0025	<u>0.597</u>	<u>0.074</u>
	<u>2226.6</u>	<u>1.051</u>	<u>1.048</u>	<u>1.83</u>	<u>0.27</u> <u>5.33</u>	<u>5.24</u>	<u>3.99</u>	<u>0.15</u>	<u>29.28</u>	0.1257	0.0028	0.460	<u>0.070</u>
	1775.6	1.155	1.152	2.01	<u>0.20</u> <u>5.50</u>	<u>5.38</u>	4.10	<u>0.17</u>	<u>34.64</u>	0.1488	0.0038	0.491	<u>0.054</u>
	<u>890</u>	<u>1.112</u>	<u>1.106</u>	<u>1.93</u>	<u>0.19</u> <u>4.56</u>	<u>4.39</u>	<u>3.34</u>	<u>0.19</u>	<u>53.17</u>	<u>0.2283</u>	<u>0.0045</u>	<u>0.579</u>	<u>0.066</u>
	<u>395.2</u>	<u>0.898</u>	<u>0.894</u>	<u>1.56</u>	<u>0.17</u> <u>3.61</u>	<u>3.48</u>	2.65	<u>0.18</u>	<u>40.79</u>	<u>0.1752</u>	<u>0.0110</u>	0.590	<u>0.074</u>
	<u>247.4</u>	0.923	<u>0.918</u>	1.60	<u>0.26</u> <u>3.23</u>	<u>3.10</u>	2.36	<u>0.18</u>	<u>40.00</u>	<u>0.1718</u>	0.0038	0.680	<u>0.122</u>
	<u>99.2</u>	1.044	1.039	<u>1.81</u>	<u>0.23</u> <u>3.45</u>	<u>3.30</u>	2.51	<u>0.16</u>	<u>46.12</u>	<u>0.1981</u>	0.0041	0.723	<u>0.105</u>
	<u>29.5</u>	<u>0.963</u>	<u>0.960</u>	1.68	<u>0.28</u> <u>2.18</u>	2.08	1.58	<u>0.14</u>	<u>30.23</u>	<u>0.1298</u>	0.0029	1.060	<u>0.200</u>
	<u>5.1</u>	<u>0.768</u>	<u>0.766</u>	<u>1.34</u>	<u>0.21</u> <u>1.54</u>	<u>1.46</u>	<u>1.11</u>	<u>0.17</u>	<u>23.73</u>	<u>0.1019</u>	0.0024	<u>1.202</u>	<u>0.269</u>
<i>co</i>		0.404	0.400	0.50	0.10.1.04	1.00	1.42	0.01	10.00	0.0040	0.0005	0.401	
<u>69</u>	3676.5	0.404	0.402	0.70	0.10 1.94	1.88	<u>1.43</u>	0.21	<u>19.60</u>	0.0842	0.0025	0.491	0.099
55.84°N	3637.3	0.336	<u>0.334</u>	0.58	<u>0.12</u> <u>1.92</u>	1.86	<u>1.41</u>	<u>0.16</u>	<u>19.15</u>	0.0822	0.0023	<u>0.414</u>	0.098
<u>48.09°W</u>	<u>3589.5</u>	<u>0.438</u>	<u>0.436</u>	<u>0.76</u>	<u>0.11</u> <u>2.15</u>	<u>2.08</u>	<u>1.58</u>	<u>0.19</u>	<u>21.39</u>	<u>0.0919</u>	0.0024	0.482	<u>0.091</u>
	<u>3444.7</u>	<u>0.528</u>	<u>0.525</u>	<u>0.92</u>	<u>0.11</u> <u>3.58</u>	<u>3.49</u>	<u>2.65</u>	<u>0.19</u>	<u>27.76</u>	<u>0.1192</u>	0.0028	<u>0.346</u>	<u>0.048</u>
	<u>2951.8</u>	0.581	<u>0.578</u>	<u>1.01</u>	<u>0.11</u> <u>5.75</u>	<u>5.64</u>	4.29	0.23	<u>33.80</u>	<u>0.1452</u>	0.0032	0.235	0.029
	2462.6	<u>0.604</u>	<u>0.599</u>	<u>1.05</u>	<u>0.11</u> <u>6.44</u>	<u>6.31</u>	4.80	0.21	<u>39.48</u>	<u>0.1696</u>	0.0037	0.218	0.025
	2168.1	0.855	0.850	<u>1.49</u>	<u>0.12</u> <u>6.03</u>	<u>5.90</u>	<u>4.49</u>	<u>0.22</u>	<u>40.95</u>	<u>0.1759</u>	0.0039	<u>0.331</u>	<u>0.031</u>
	1481.3	<u>0.670</u>	<u>0.661</u>	<u>1.16</u>	<u>0.10</u> <u>4.98</u>	<u>4.73</u>	<u>3.60</u>	<u>0.20</u>	<u>79.22</u>	<u>0.3402</u>	0.0066	<u>0.321</u>	<u>0.033</u>
	<u>989</u>	<u>0.729</u>	<u>0.723</u>	<u>1.26</u>	<u>0.11</u> <u>4.53</u>	<u>4.35</u>	<u>3.31</u>	<u>0.21</u>	<u>57.18</u>	<u>0.2456</u>	0.0049	0.382	<u>0.041</u>
	<u>445.6</u>	<u>0.692</u>	<u>0.686</u>	<u>1.20</u>	<u>0.07</u> <u>4.23</u>	4.05	3.08	<u>0.23</u>	<u>55.48</u>	0.2383	<u>0.0047</u>	0.389	<u>0.037</u>
	<u>248.8</u>	<u>0.604</u>	<u>0.598</u>	<u>1.04</u>	<u>0.07</u> <u>4.06</u>	<u>3.87</u>	<u>2.95</u>	<u>0.18</u>	<u>59.43</u>	<u>0.2552</u>	0.0052	0.355	<u>0.033</u>
	<u>99.5</u>	<u>0.513</u>	<u>0.507</u>	<u>0.89</u>	<u>0.10</u> <u>3.58</u>	<u>3.40</u>	<u>2.58</u>	<u>0.22</u>	<u>56.06</u>	<u>0.2408</u>	<u>0.0049</u>	<u>0.343</u>	<u>0.047</u>
	<u>28.7</u>	<u>0.554</u>	<u>0.550</u>	<u>0.96</u>	<u>0.07</u> <u>1.50</u>	1.40	1.07	<u>0.24</u>	<u>30.11</u>	<u>0.1293</u>	0.0029	<u>0.903</u>	<u>0.210</u>
	<u>8.2</u>	<u>0.457</u>	<u>0.453</u>	<u>0.79</u>	<u>0.07</u> <u>1.42</u>	<u>1.31</u>	<u>0.99</u>	<u>0.17</u>	<u>34.28</u>	<u>0.1472</u>	<u>0.0031</u>	<u>0.797</u>	<u>0.153</u>

Station	Depth	²³¹ Pa	²³¹ Pa	²³¹ Pa _{corr}	<u>2se</u> 230Th	²³⁰ Th	²³⁰ Th _{corr}	<u>2se</u>	²³² Th	232Th	2se	231Pa/230Th	2se
	<u>m</u>	<u>fg/kg</u>	<u>fg/kg</u>	μBq/kg	<u>fg/kg</u>	<u>fg/kg</u>	<u>µBq/kg</u>		pg/kg	pmol/kg			
<u>77</u>	2487.5				4.02	<u>3.93</u>	<u>2.99</u>	<u>0.14</u>	<u>29.43</u>	<u>0.1264</u>	0.0026		
53°N	<u>2462.8</u>	<u>1.261</u>	1.258	<u>2.20</u>	<u>0.15</u> <u>4.07</u>	<u>3.97</u>	<u>3.02</u>	<u>0.14</u>	<u>30.06</u>	<u>0.1291</u>	<u>0.0026</u>	0.728	<u>0.059</u>
51.10°W	<u>2414.2</u>	<u>1.113</u>	<u>1.110</u>	<u>1.94</u>	<u>0.10</u> <u>4.09</u>	<u>4.00</u>	<u>3.04</u>	<u>0.15</u>	<u>29.56</u>	<u>0.1270</u>	<u>0.0026</u>	0.638	<u>0.044</u>
	<u>2268.5</u>	<u>0.989</u>	<u>0.985</u>	<u>1.72</u>	<u>0.12</u> <u>6.11</u>	<u>6.00</u>	4.56	<u>0.16</u>	<u>33.99</u>	<u>0.1460</u>	<u>0.0030</u>	0.377	<u>0.029</u>
	<u>2170.5</u>	<u>1.355</u>	<u>1.352</u>	<u>2.36</u>	<u>0.13</u> <u>5.32</u>	<u>5.22</u>	<u>3.97</u>	<u>0.17</u>	<u>30.77</u>	<u>0.1322</u>	0.0028	<u>0.595</u>	<u>0.041</u>
	<u>1678.1</u>	<u>1.267</u>	<u>1.263</u>	<u>2.21</u>	<u>0.13</u> <u>5.48</u>	<u>5.36</u>	4.08	<u>0.16</u>	<u>37.02</u>	<u>0.1590</u>	<u>0.0031</u>	0.541	<u>0.039</u>
	<u>1235.4</u>	<u>0.580</u>	<u>0.576</u>	<u>1.01</u>	<u>0.13</u> <u>5.36</u>	<u>5.22</u>	<u>3.97</u>	<u>0.18</u>	<u>44.75</u>	<u>0.1922</u>	<u>0.0037</u>	<u>0.253</u>	<u>0.035</u>
	<u>989.6</u>	<u>1.772</u>	<u>1.767</u>	<u>3.09</u>	<u>0.23</u> <u>4.96</u>	<u>4.79</u>	<u>3.64</u>	<u>0.17</u>	<u>53.23</u>	0.2286	<u>0.0041</u>	0.848	<u>0.073</u>
	<u>496.4</u>				4.33	4.15	<u>3.16</u>	<u>0.17</u>	<u>55.68</u>	0.2391	<u>0.0044</u>		
	<u>297.9</u>	<u>0.501</u>	<u>0.494</u>	<u>0.86</u>	<u>0.07</u> <u>4.71</u>	<u>4.50</u>	<u>3.42</u>	<u>0.23</u>	<u>64.41</u>	0.2766	0.0055	0.252	0.026
	<u>78.8</u>	<u>1.200</u>	<u>1.193</u>	2.08	<u>0.14</u> <u>3.50</u>	<u>3.29</u>	2.50	<u>0.20</u>	<u>65.47</u>	0.2812	0.0053	0.834	<u>0.086</u>
	<u>2.5</u>	<u>0.926</u>	<u>0.923</u>	1.61	<u>0.12</u> <u>1.34</u>	1.25	<u>0.95</u>	<u>0.17</u>	<u>28.01</u>	<u>0.1203</u>	<u>0.0026</u>	<u>1.699</u>	<u>0.332</u>

²³⁰Th and ²³¹Pa are dissolved ²³⁰Th and ²³¹Pa activities corrected for the ingrowth from seawater ²³⁴U and ²³⁵U, respectively, since the time of collection following equations:

$${}^{230}Th = {}^{230}Th_m - {}^{234}U \times (1 - \exp(-\lambda_{230Th} \times t)) \quad (1)$$

5

$$^{231}Pa = ^{231}Pa_m - ^{235}U \times (1 - \exp(-\lambda_{231Pa} \times t))$$

²³⁰Th and ²³¹Pa are further corrected for detrital, U-supported ²³⁰Th and ²³¹Pa concentrations as follows:

$$^{230}Th_{corr} = ^{230}Th_{m} - (0.6 \times ^{232}Th_{m}) (3)$$

$$^{231}Pa_{corr} = ^{231}Pa_{m} - 0.046 \times (0.6 \times ^{232}Th_{m}) (4)$$
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(2)

where ²³⁰Thm, ²³¹Pam and ²³²Thm are activities obtained from measurement; ²³⁵U and ²³⁴U are their average activities in seawater,
 1824 μBq/kg (112 dpm/1000l) and 45551μBq/kg (2801 dpm/1000l,) respectively, obtained from ²³⁸U activity of 39610 μBq/kg
 (2436 dpm/1000l) at salinity of 35 (Owens et al., 2011) and assuming natural ²³⁸U/²³⁵U abundance ratio of 137.88 and seawater
 ²³⁴U/²³⁸U activity ratio of 1.15; ⁴λ_{230Th} and <sup>λ_{231Pa} are decay constants of ²³⁰Th and ²³¹Pa; t is the time between sample collection and chemical separation of U from ²³¹Pa and ²³⁰Th. <u>0.6 is the average ²³⁸U/²³²Th activity ratio in detrial material in the Atlantic (Henderson and Anderson, 2003)</u> and 0.046 represents the ²³⁵U/²³⁸U activity in seawater (Anderson et al., 1990). Half-lives
</sup>

15 for ${}^{231}Pa$, ${}^{230}Th$ and ${}^{232}Th$ are 32,760 yr, 75,584 yr and 1.40×10^{10} yr (Robert et al., 1969; Cheng et al., 2013; Holden, 1990).

Deleted: ²³⁵U and ²³⁸U are their average activities in seawater, 118 dpm/1000l and 2436 dpm/1000l, respectively;

Deleted: 0.7 is the average ²³⁸U/²³²Th activity ratio in detrital material (Marcantonio et al., 2001)

Deleted: Activities of 231 Pa, 230 Th and 232 Th have been converted to dpm/1000l assuming the density of seawater ρ = 1.025g/cm³.

All errors are two standard errors including the contribution from sample weighing, spike calibration, ²³¹Pa, ²³⁰Th and ²³²Th in the respective ²³³Pa and ²³⁰Th spikes, blank correction, internal precision and related corrections of mass spectrometric measurement.

5 S2. CFC-based Age determination

CFC measurement are not available for the GEOVIDE cruise itself. However, with the availability of CFC measurements from OVIDE section in 2012 and water mass composition estimated using extended Optimum Multi-Parameter (eOMP) analysis for both OVIDE and GEOVIDE sections, CFC-based ages can be derived for GEOVIDE section.

1. CFC measurements were available along OVIDE section in 2012 (OVIDE/CATARINA cruise) (de la Paz et al., 2017).

- 10 This allows the computing of the mean age of water masses using transient time distribution (TTD) method. A more detailed description of TTD method is given in other studies (e.g. Steinfeldt et al., 2009; Waugh et al., 2003). It is important to note that this mean age (referred to as CFC-based age hereafter and in the manuscript) is different from the age calculated based on atmospheric history of CFC (referred to as CFC apparent age hereafter), and therefore is not limited by the time span of the presence of CFC in the atmosphere and inherently deals with age bias due to water mass mixing in CFC apparent age.
- 15 Combining CFC-based ages computed with the TTD method for each water sample with water mass composition estimated using eOMP analysis for OVIDE section in 2012 (García-Ibáñez et al., 2015), CFC-based age was calculated for each Source Water Type (SWT) defined in García-Ibáñez et al., 2015 by the equations,

$$\log [CFC-based age]^{j} = \sum_{i=1}^{12} SWT_{i}^{j} \times (log [CFC-based age]_{i}) + \varepsilon_{j} \ j = 1 \rightarrow 424 \ samples (5)$$
$$[CFC-Age]^{j} = anti \log [CFC-Age]^{j} (6)$$

- 20 where SWT^j is the fraction of SWT "i" to sample "j" (obtained through the eOMP analysis); [CFC-based age]^j is CFC-based age for each water sample computed with TTD method along OVIDE section 2012; and ɛ_j is the residual, representing the portion of CFC-based age that can not be modelled by mixing of SWTs, i.e. the difference between log [CFC-based age]^j and that obtained as the sum of the contributions by mixing of the individual SWT, [12] SWT^j_i × (log[CFC-based age]_i).
- 25 The output of log[CFC-based age]_i and its inversion ([CFC-age]_i) is given in Table S2. The squared correlation coefficient (r^2) and standard deviation of the residual, ε_i , are 0.94 and 0.12, respectively.

2. CFC-based age for GEOVIDE section was then calculated employing equation (5) with water mass composition estimated using eOMP analysis along GEOVIDE section (García-Ibáñez et al., 2018) and the output of CFC-based age for SWT (Table S2).

30

Deleted: CFC measurement are not available along the GEOVIDE line. However, Paz et al. (2017) determined the CFC-based age along the same line in 2012 (OVIDE/CATARINA cruise). We projected the CFC-based age along GEOVIDE line using the water mass distributions (Steinfeldt personal communication) along GEOVIDE line given by Garcia-Ibanez et al. (2018) and the distribution for the same water masses in 2012 (García-Ibáñez et al., 2015). The water mass analysis was applied already for different purposes related with the chemical characterization. This approach was successfully applied to dissolved-organic-carbon water mass definitions in the North Atlantic (Fontela et al., 2016) and for evaluating the impact of water mass mixing and remineralization on the N2O distribution in the North Atlantic (Paz et al., 2017). Previous studies have also applied the water mass analysis to determine the nutrient ratio utilization and organic matter mineralization (Pérez et al., 1994, Brea et al., 2004; Álvarez-Salgado et al., 2013). Cossa et al. (2018) characterized the HgTUNF concentration of each water mass using the water mass analysis shown here. The first step determined the CFCage for each Source Water Types (SWTs) defined in García-Ibáñez et al. (2015). They have used an extended Optimum Multi-Parameter (eOMP) analysis to quantifies the fractions of the different Source Water Types (SWTs) that contribute to a given water sample for OVIDE line done in 2012. The CFC-age for each SWT "i" (12 unknowns [CFC-age],) were estimated through an inversion of the

analysis (C) explore the system of 124 equations.¹ following systems of 424 equations.¹ log [CFC – Age]^j = $\sum_{i=1}^{12} SWT_i^j \times (\log[CFC - Age]_i) + \varepsilon_j \ j = 1 \rightarrow 424 \ samples$ (5)

where SWT^j are the fractions of SWT "i" to sample "j" (obtained through the cOMP analysis), [*CFC-agej*^j is the CFC-age for each sample measured in 2012, and ε_j the residual. The 424 ε_j of the inversion resented a null mean and a standard deviation of 0.12 ($R^2 = 0.94$). The output of the inversion ([CFC-age]) is given in Table S2. With this output, we use the same equation to compute the [CFC-age] of each water sample of GEOVIDE cruise, using the fractions of the each SVT obtained by Garcia-Ibañez et al. (2018) for GEOVIDE. Because of the low fractions of the SWT SAIW₄, its fraction has been added to SAIW₆.

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Table S2 Output of log(CFC-age) and the inversion [CFC-age]₁ (i.e. CFC-based age) for source water types (SWT)

	log(CFC-age)	CFC-age
ENACW ₁₆	1.05±0.20	11±5
ENACW ₁₂	1.11±0.03	13±1
SPMW ₈	1.69±0.04	49±5
SAIW	1.19±0.07	16±3
SPMW7	1.26±0.05	18±2
IrSPMW	0.98±0.03	10±1
LSW	1.54±0.02	35±1
MW	1.96±0.04	91±8
PIW	1.33±0.15	22±8
DSOW	1.22±0.07	17±3
ISOW	1.70±0.03	50±4
NEADWL	3.00±0.02	989±48
r ²	0.94	0.943
std(Resid)	0.12	41

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ENACW₁₆ and ENACW₁₂ = East North Atlantic Central Water of 16°C and 12°C; SPMW₈, SPMW₇, IrSPMW = Subpolar Mode Water of 8°C, 7°C and of the Irminger Sea; SAIW = Subarctic Intermediate Water; MW = Mediterranean Water; PIW = Polar Intermediate Water; ISOW=Iceland-Scotland Overflow Water; LSW=Labrador Sea Water; DSOW: Denmark Strait Overflow Water; and NEADW₁₂. Lower
 North East Atlantic Deep Water, r² and std (Resid) represents the squared correlation coefficient and standard deviation of the residual, e_x.

i.e. the difference between log [CFC-based age]^j and that obtained as the sum of the contributions by mixing of the individual SWT, $\sum_{i=1}^{12} SWT_i^j \times (log[CFC-based age]_i)$

S3. Scavenging-mixing model and parameterization

A more detailed description of the scavenging-mixing model used in this study is given in Moran et al. (1997). Briefly, the

- 10 model takes into account reversible scavenging of the nuclides and water mass mixing. It describes the evolution of nuclides through time of a one-dimensional system, an ocean water column. In the Atlantic, the system is assumed to start at time t=0 in the far North Atlantic and moves southward with time. Transport of material downward relative to the direction of water flow is permitted, to represent the effect of scavenging of radionuclides by sinking particles. Lateral exchange with water outside of the 1-D system is not permitted.
- 15 The equation to derive the dissolved concentration of each nuclide follows that of Moran et al., (1997). Dissolved concentration of the nuclide is given by,

$$c_d = \frac{c_{pre,t} + P - \tau_w}{(K_d SPM + 1)} \times \left[1 - \exp\left(-\frac{(K_d SPM + 1)}{SK_d \tau_w SPM} \times z\right)\right]$$
(7)

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where C_d is the dissolved concentration of the nuclide; P is the production rate of ²³⁰Th and ²³¹Pa, <u>0.42 µBq/kg/yr (2.57 × 10⁻² dpm/1000l/yr</u>), respectively; K_d is the distribution coefficient of the nuclide; λ is the decay constant of the nuclide; $C_{pre,t}$ is the preformed total concentration of ²³⁰Th (or ²³¹Pa); SPM is the

5 suspended particle concentration; and S is the particle settling speed, which represents the net effect of particle sinking, disaggregation and aggregation; T_w is water mass age; z is the water depth.

Initial parameterization was conducted using S=500-1000 m/yr, $K_d^{Th} = 1 \times 10^7$ ml/g, $K_d^{Pa} = 5 \times 10^5$ ml/g, SPM= 20-50 µg/l, for preformed concentrations set at 0 and surface average from GEOVIDE, i.e., $C_{pre}^{Th} = C_{surface \ average}^{Th} = 1.66 \mu$ Bq/kg, $C_{pre}^{Pa} = 1.66 \mu$ Bq/kg, $C_$

 $C_{surface\ average}^{Pa} = 1.31 \mu Bq/kg_With T_w$ known from CFC measurements for every depth where ²³⁰Th and ²³¹Pa was 10 measured along GEOVIDE section, water-column profiles of both nuclides were simulated for GEOVIDE station 13 and the parameters were adjusted for the best fit between the simulated and observed profiles (Fig. S1). This gives us the optimized parameters for the analysis in discussion section 4.3, which are listed in Table S3. Our optimized parameters are consistent with values reported by other studies (also listed in Table S3).

Adopting the optimized parameters and setting preformed component (C_{pre}) equal to the nuclide concentrations observed in the upper 100 m of the GEOVIDE section, the modelled evolution of nuclide concentrations with age between 0-500 years at

2000 m and 3500 m water depths, together with GEOVIDE data, is plotted in Figure S2.

15



GEVIDE station 1 GEVIDE station 1 GEVIDE station 1

Figure S1: Modelled (dashed black lines) profiles with preformed value set at 0 and surface average concentration from GEOVIDE, and observed (solid blue lines) profiles of and 13 from GEOVIDE section. The best fit was first sought for ²³⁰Th, which gives us the optimized parameters S, SPM and K_d^{Th} . These parameters were then adopted for the simulation of ²³¹Pa profiles, adjusting only K_d^{Pa} to obtain the best fit.

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and ²³¹ Pa are in most of cases not 0 at the surface (i.e. z=0). We
therefore introduce a surface term to reflect this observation and set
its value the same as the preformed concentration. Dissolved
concentration of the nuclide can be then derived with the equation:
• • • • • • • • • • • • • • • • • • •

$$_{d} = \frac{C_{pre+P} T_{w}}{(K_{d} SPM+1)} \times \left[1 - \exp\left(\frac{-z(K_{d} SPM+1)}{SK_{d} T_{w} SPM}\right)\right] + C_{surface} \quad (6)$$

Deleted: 2.57×10^{-2} dpm/1000l/yr and 2.37×10^{-3} dpm/1000l/yr

Deleted: C_{pre} is the preformed concentration of ²³⁰Th (or ²³¹Pa); C_{surface} is the concentration of ²³⁰Th and ²³¹Pa in surface water, set at a value the same as the preformed concentration for both nuclides;



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 Figure S2: Results from a scavenging-mixing model of ²³⁰Th, ²³¹Pa, Dissolved ²³¹Pa/²³⁰Th and Particulate ²³¹Pa/²³⁰Th compared to observations. Preformed concentration (C_{pre}) were set at 0 (dashed line) and at the average surface concentration ($C_{surface average}$) from GEOVIDE section (solid line), i.e. ²³⁰Th=1.66 µBq/kg, ²³¹Pa=1.31 µBq/kg.

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Deleted: Figure S1: Modelled (dashed black lines) profiles with preformed value set at 0 and surface average concentration from GEOVIDE, and observed (solid blue lines) profiles of station 1 and 13 from GEOVIDE section. The best fit was first sought for 239 Th, which gives us the optimized parameters S, SPM and K_{1}^{Ph} . These parameters were then adopted for the simulation of 231 Pa profiles, adjusting only K_{1}^{Pa} to obtain the best fit.⁶

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Table S3 Parameterization of the scavenging-mixing model

	This study	Literature
S (m/yr)	800	500-1000 (Moran et al., 1997)
SPM (µg/l)	25	30 (Labrador Sea, Brewer et al., 1976)
K_d^{Th} (ml/g)	1.1×10^{7}	1.1×10^7 (Moran et al., 1997)
K_d^{Pa} (ml/g)	1.4×10^{6}	2.2×105 (pure carbonate)~1.4×106 g/g (pure opal) (pseudo-Kd, Chase
		et al., 2002)

S4. Uncertainty analysis of the assessment of the scavenging of ²³⁰Th and ²³¹Pa

5 Both the uncertainty of the CFC-based ages and the fact that the preformed values of ²³⁰Th and ²³¹Pa are unknown contribute to the uncertainty of the scavenging of ²³⁰Th and ²³¹Pa. Here we analyze how these two factors influence the assessment of the scavenging of ²³⁰Th and ²³¹Pa.

1. CFC-based ages

Uncertainties (1 standard error) associated with CFC-based age range between 11-40%. This uncertainty leads to an average

- 10 uncertainty of 23% and 13% in potential total ²³⁰Th and ²³¹Pa respectively, corresponding to an average uncertainty of 30% in the scavenged component of ²³¹Pa.
 2. Preformed values
 As the exact values of preformed values are unknown, we analyse the sensitivity of the scavenging component to this factor.
 A two-fold increase in preformed values results in an increase by a factor of 1.2 and 1.6 in the total potential component of ²³⁰Th and ²³¹Pa, respectively, leading to an increase by a factor of 1.2 in the scavenged component of ²³⁰Th and of 2.6 in the
- scavenged component of ²³¹Pa. Clearly, the scavenged component of ²³¹Pa is more sensitive to the preformed component compared with the scavenged component of ²³⁰Th. This difference however becomes less significant when comparing the scavenging component to the potential total component, i.e. the ratio of scavenged/potential total, with an increase in the ratio of scavenged/potential total by a factor of 1.1 and 1.4 for ²³⁰Th and ²³¹Pa, respectively. This sensitivity analysis suggests that
 a better knowledge of preformed values will benefit the assessment of the scavenging of both nuclides.

S5. Meridional transport of ²³⁰Th and ²³¹Pa in the Atlantic

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	Table S4 Mass balance calculation of meridional transport of ²³⁰ Th and ²³¹ Pa in the Atlantic											
		<u>Net meridional</u> <u>transport</u> <u>× 10¹⁰ µBq/s</u>		Volume of seawater between two latitudes	$\frac{Production in}{water column} \times \frac{10^{10} \mu Bq/s}{\mu}$		$\frac{\text{in }}{\text{nn }} \frac{\text{Removal to}}{\text{sediment}}$ $\frac{\text{/s }}{\text{/s }} \times 10^{10} \mu \text{Bq/s}$		Removal/Production			
				$\times 10^{17} \mathrm{m}^3$					<u>%</u>			
		²³⁰ Th	²³¹ Pa		230Th	²³¹ Pa	230Th	²³¹ Pa	²³⁰ Th	²³¹ Pa		
<u>GEOV</u>	/IDE-4.5°S	<u>-7.76</u>	<u>-4.75</u>	<u>1.48</u>	<u>200.8</u>	<u>18.6</u>	<u>193.1</u>	<u>13.8</u>	<u>96.2</u>	<u>74.2</u>		
<u>4.5</u>	<u>°S-45°S</u>	<u>0.33</u>	<u>0.017</u>	<u>1.02</u>	<u>138.4</u>	<u>12.8</u>	<u>138.7</u>	<u>12.8</u>	<u>99.8</u>	<u>100.0</u>		

Positive value indicates northward transport; negative value indicates southward transport. Production rate of ²³⁰Th and ²³¹Pa in water column are 0.42 and 0.039 µBq/kg/yr, respectively.

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