# Does sedimentary $^{231}Pa/^{230}Th$ from the Bermuda Rise monitor past Atlantic Meridional Overturning Circulation?

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[1] Ocean circulation may have undergone reductions and reinvigorations in the past closely tied to regional climate changes. Measurements of $^{231}Pa/^{230}Th$ ratios in a sediment core from the Bermuda Rise have been interpreted as evidence that the Atlantic Meridional Overturning Circulation (AMOC) was weakened or completely eliminated during a period of catastrophic iceberg discharges (Heinrich-Event 1, H1). Here we present new data from the Bermuda Rise that show further $^{231}Pa/^{230}Th$ peaks during Heinrich-2 (H2) and Heinrich-3 (H3). Additionally, a tight correlation between diatom abundances (biogenic silica) and $^{231}Pa/^{230}Th$ is discovered in this core. Our results redirect the interpretation of $^{231}Pa/^{230}Th$ from the Bermuda Rise as a proxy for ocean circulation towards a proxy that reacts highly sensitive to changes of particle composition and water mass properties. **Citation:** Lippold, J., J. Grützner, D. Winter, Y. Lahaye, A. Mangini, and M. Christl (2009), Does sedimentary $^{231}Pa/^{230}Th$ from the Bermuda Rise monitor past Atlantic Meridional Overturning Circulation?, *Geophys. Res. Lett.*, *36*, L12601, doi:10.1029/2009GL038068.

## 1. Introduction

[2] $^{231}Pa$ (half-life: 32.5 kyr) and $^{230}Th$ (half-life: 75.4 kyr) are produced by alpha decay of natural $^{235}U$ and $^{234}U$ dissolved in the ocean. As U is spatially uniform distributed to a good approximation due to a very long residence time [*Mangini et al.*, 1979; *Henderson*, 2002] $^{231}Pa$ and $^{230}Th$ are expected to be constantly produced with an activity ratio of 0.093 throughout the Oceans [*Yu et al.*, 1996]. In contrast to uranium protactinium and thorium are very particle reactive. After production they are removed from the seawater by reversible scavenging on settling particles and incorporated into the sediments. The scavenging efficiency of $^{230}Th$ is generally higher, leading to a shorter residence time of $^{230}Th$ (5–40 yr) compared with $^{231}Pa$ (50–200 yr) [*Anderson et al.*, 1983]. Thus, in the modern Atlantic Ocean, $^{231}Pa$ would be preferentially transported to the Southern Ocean where biogenic opal acts as a sink for $^{231}Pa$ due to its high affinity to this element [*Asmus et al.*, 1999; *Chase et al.*, 2002]. The combination of southward advective transport with high scavenging rates in the Southern Ocean causes a deficit compared to the production ratio of $^{231}Pa$ in the Atlantic sediments and an excess of $^{231}Pa$ in Southern Ocean sediments. Several studies therefore suggested that $^{231}Pa/^{230}Th$ recorded in marine sediments could be used as a proxy for the strength of the Atlantic deep water circulation [*Yu et al.*, 1996; *Marchal et al.*, 2000; *McManus et al.*, 2004].

[3] However, the fractionation of $^{230}Th$ and $^{231}Pa$ in the ocean is a function of several additional parameters such as particle flux [*Anderson et al.*, 1983], particle composition [*Chase et al.*, 2002; *Geibert and Usbeck*, 2004] and particle size [*Kretschmer et al.*, 2008]. This behaviour also may depend on depth and oceanic region [*Scholten et al.*, 2008]. Most notably, the presence of biogenic opal (particulate silica) in oligotrophic regions has a substantial influence on sedimentary $^{231}Pa/^{230}Th$ [*Bradtmiller et al.*, 2007].

[4] The first high resolution $^{231}Pa/^{230}Th$ record from the Western North Atlantic (Bermuda Rise core GGC5) has been interpreted to directly reflect changes in AMOC [*McManus et al.*, 2004]. In particular, increased $^{231}Pa/^{230}Th$ during the Younger Dryas (YD) and H1 were used as an indicator for a weakened AMOC.

[5] Here we present new $^{231}Pa/^{230}Th$ data from the Bermuda Rise (ODP Leg 172 Site 1063, 33°41′N, 57°37′W, water depth 4584 m; cf. GGC5, 33°42′N, 57°33′W, 4550 m water depth), extending the Bermuda Rise $^{231}Pa/^{230}Th$ record back to the last 35 kyr. Additionally, a highly resolved profile of total diatom abundances (the main contributor to biogenic opal) was generated for this core to test the possible influence of biogenic opal on $^{231}Pa/^{230}Th$.

## 2. Methods

### 2.1. $^{231}Pa/^{230}Th$

[6] Isotope dilution was applied by spiking the sediment samples with $^{233}Pa$, $^{229}Th$, $^{236}U$ and $^{233}U$. The samples were dissolved and separated into Pa-, Th-, and U- fractions by adapted standard procedures [*Pichat*, 2004] followed by cleaning of each fraction (for detailed description of the method see Text S1 of the auxiliary materials).[1] The $^{233}Pa$ spike was milked from a $^{237}Np$ solution and cleaned as described by *Regelous et al.* [2004].

[7] Pa, U and Th isotopes were measured using a Finnigan Neptune multi collector ICP-MS. Configurations

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[1]Auxiliary materials are available in the HTML. doi:10.1029/2009GL038068.

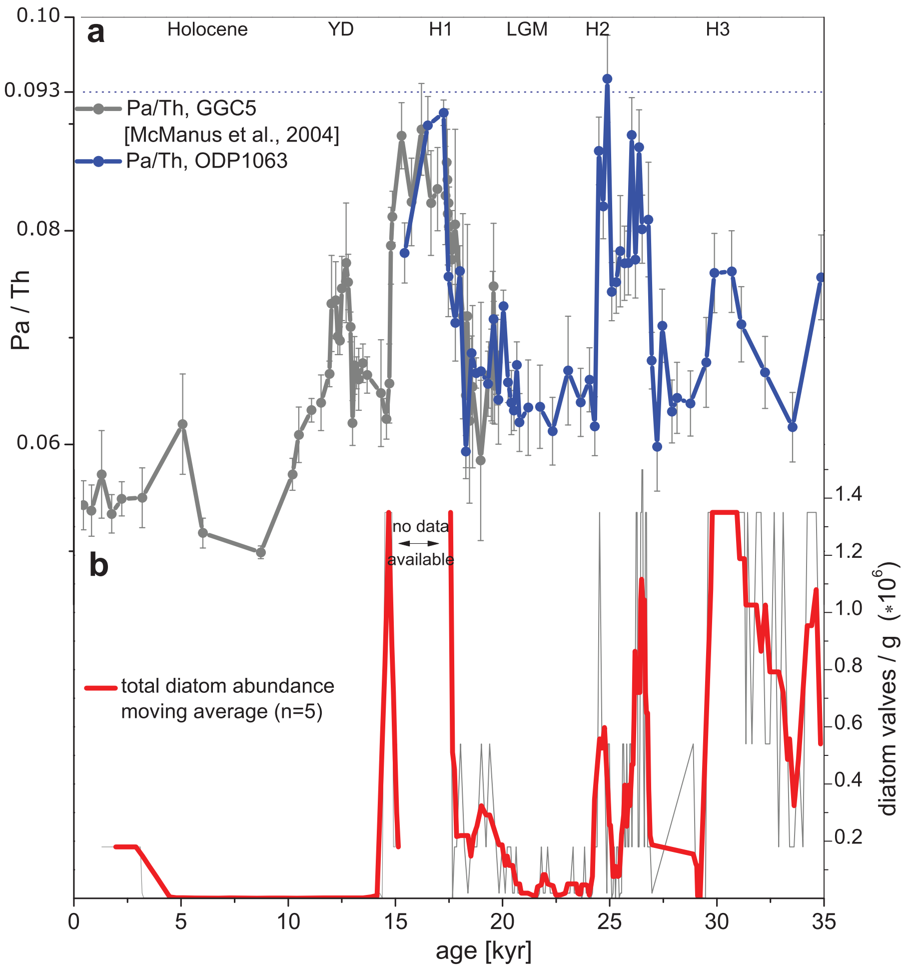


**Figure 1.** (a) $^{231}Pa/^{230}Th$ activity ratios from Bermuda Rise. Grey: Core GGC-5 [*McManus et al.*, 2004], blue: this study, ODP Site 1063. The dashed line indicates the production ratio of 0.093. (b) Total abundance of diatoms. Grey: original data, red: smoothed data.

and correction procedures broadly followed the suggestion of *Hoffmann et al.* [2007]. Reproducibility for full replicate analyses was always better than 6% ($2\sigma$) for the measured $^{231}Pa/^{230}Th$. Detrital corrections of the excess $^{231}Pa$ and $^{230}Th$ were obtained assuming a $^{238}U/^{232}Th$ activity ratio of 0.5 deduced from the minima in the $^{238}U/^{232}Th$ profile measured down to 300 kyr at the same core.

### 2.2. Diatom Abundance

[8] Sediment slides made from Hole D of ODP Site 1063 were used to estimate diatom abundance and to generate biostratigraphic data. No chemical processing was performed on the sediment prior to slide preparation. Diatom abundance was derived by classification of 1.5 g sediment respectively into seven distinct categories of occurrence. These categories are the common ones used for initial description of ODP core material with the addition of an extra category for very abundant diatom occurrence. These categories are as follows: Very Abundant, Abundant, Common, Few, Rare, Scarce and Barren (diatoms are not present in the sediment). As these categories define overall diatom abundance in the sediment they have been converted to the total number of diatom valves per g sediment by extrapolating the numbers from the examined microscopic field of view [*Winter*, 2001]. Diatom abundances were estimated for the time interval from 35 to 3 kyr, with a gap between 16 and 18 kyr, resulting from the unsampled Core 1H core catcher.

### 2.3. Age Model

[9] The age model we use for ODP Site 1063 is an improvement of an astronomical tuned timescale [*Grützner et al.*, 2002], which was based on high resolution $CaCO_3$ data derived from XRF core scanning. This new carbonate record for ODP Site 1063 shows a high similarity to the $CaCO_3$ content in the nearby (distance <150 m) piston core GPC 5 [*Keigwin and Jones*, 1994]. Thus, a detailed correlation of the two $CaCO_3$ curves (see Text S2) was used to transfer the radiocarbon-based age model of GPC 5 to ODP Site 1063. The 21 radiocarbon dates reported by *Keigwin and Jones* [1994] for the last 36 kyr have been converted to calendar ages as described by *Fairbanks et al.* [2005].

## 3. Results and Discussion

[10] Our $^{231}Pa/^{230}Th$ data (Figure 1a: blue curve) from ODP Site 1063 are broadly consistent with the record from

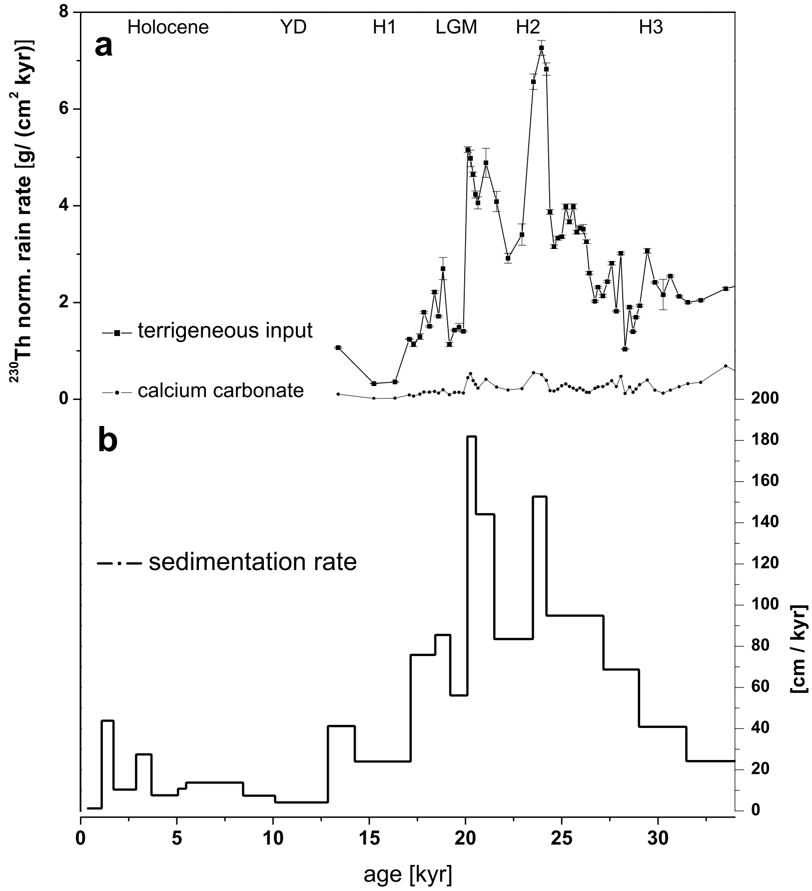


**Figure 2.** (a) $^{230}$Th-normalized vertical accumulation rate of calcium carbonate and terrigenous material (based on XRF data) at ODP Site 1063. (b) Sedimentation rate of ODP Site 1063.

the nearby core GGC5 (Figure 1a: grey curve). The new data reveal further distinct peaks around the H2 and H3 Event, indicating that $^{231}$Pa/$^{230}$Th peaks are a recurrent phenomenon.

[11] $^{230}$Th-normalised vertical mass accumulation rates (Figure 2a) do not show enhanced vertical particle flux during Heinrich Events (in consistency with earlier results, [*McManus et al.*, 2004]). Therefore, the $^{231}$Pa/$^{230}$Th peaks

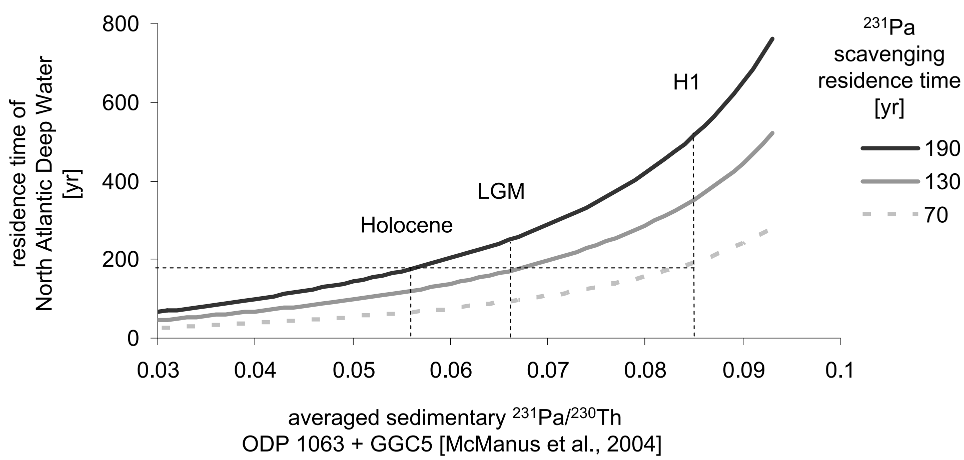


**Figure 3.** Time averaged $^{231}$Pa/$^{230}$Th ratios from the Bermuda Rise (combined data set from this study (ODP Site 1063) and from *McManus et al.* [2004] (GGC5) for three different intervals: Holocene, $^{231}$Pa/$^{230}$Th = 0.056 (n = 11, 1$\sigma$ = 0.004, 8–0 kyr); H1, $^{231}$Pa/$^{230}$Th = 0.086 (n = 7, 1$\sigma$ = 0.004, 17–15 kyr); LGM, $^{231}$Pa/$^{230}$Th = 0.067 (n = 15, 1$\sigma$ = 0.004, 23–19 kyr). Applying a one-box model of the Atlantic Ocean [*Yu et al.*, 1996] the residence time of NADW can be deduced from sedimentary $^{231}$Pa/$^{230}$Th. The curves below show this dependency for three different scavenging residence times of $^{231}$Pa. Increased ratios during LGM or H1 can be explained either by a longer NADW residence time or by a enhanced scavenging of $^{231}$Pa due to biogenic opal, or by a combination of these two effects.

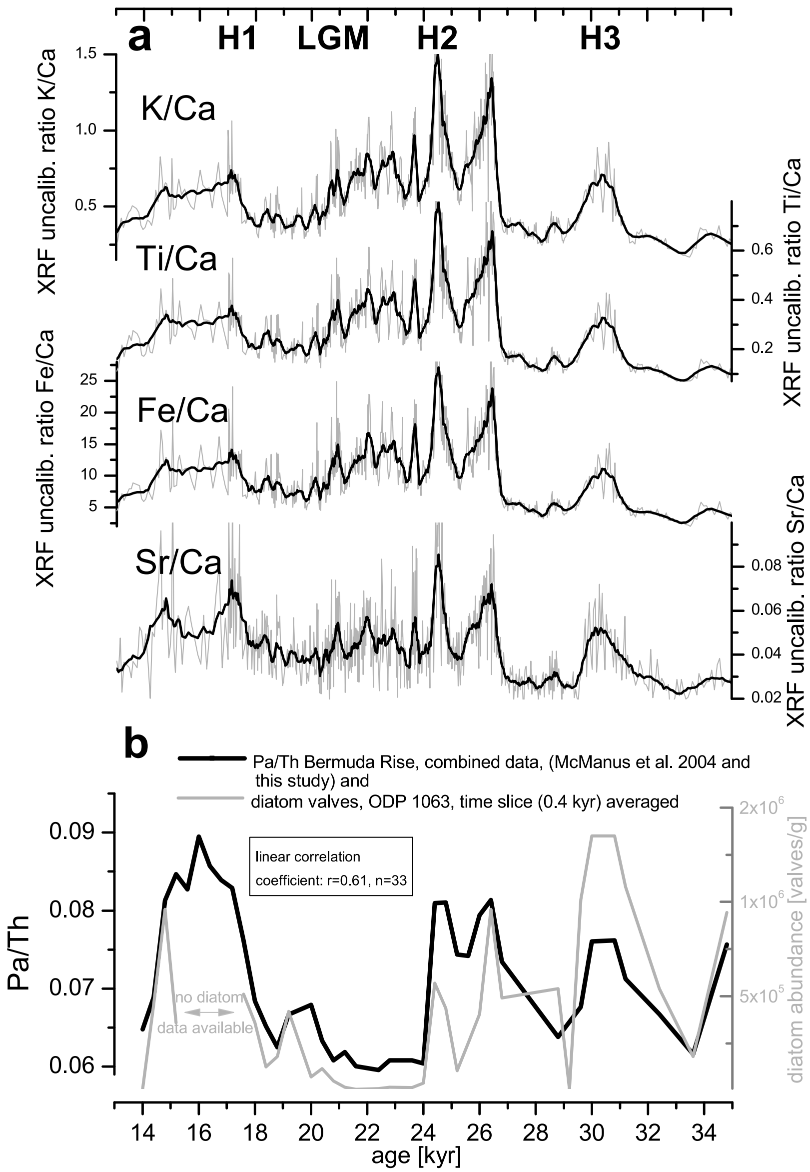


**Figure 4.** (a) Ratio of different indicators of detrital input to Ca obtained by XRF scanning of ODP Site 1063. XRF data from ODP Site 1063 is available only before 13 kyr. (b) The variations shown here are also recorded in the $^{231}Pa/^{230}Th$ ratios and in the diatom abundances, especially during H2 and H3.

at the Bermuda Rise are most likely not caused by temporary increased vertical mass flux that would cause enhanced scavenging of $^{231}Pa$.

[12] Our high resolution record of total diatom abundance correlates well with $^{231}Pa/^{230}Th$ between 35 kyr and 14 kyr BP, especially during the Heinrich Events (Figure 1b, red curve). This high correlation (r = 0.61, n = 33, see also Figure 4b) indicates the well-known affinity of Pa to biogenic opal [*Chase et al.*, 2002; *Geibert and Usbeck*, 2004; *Keigwin and Boyle*, 2008]. The time interval 35–14 kyr is also characterized by increased sedimentation rates (>20 cm/kyr, Figure 2b). These continuously high average sedimentation rates may have led to good opal preservation in the sediments at ODP Site 1063. It is therefore likely that the biogenic opal preserved in the sediment mirrors past opal flux in the water column [*DeMaster et al.*, 1996]. In contrast, opal dissolution at the sediment water interface probably was more important during the past 14 kyr when sedimentation rates where significantly lower, leading to low diatom abundance and a poor correlation with the $^{231}Pa/^{230}Th$ ratio (Figure 1) [*Brzezinski and Nelson*, 1995; *Sayles et al.*, 1996]. Hence, the lack of diatoms while $^{231}Pa/^{230}Th$ ratios are increased during the YD may be a consequence of insufficient opal preservation. Likewise, moderate diatom abundances over the last 5 kyr (when sedimentation showed slightly higher rates again) may not be a consequence of increased diatom productivity, instead the diatoms in these sediments have not yet been significantly influenced by post-depositional opal dissolution [*Raup*, 1979].

[13] We notice that only the $^{231}Pa/^{230}Th$ peak during H3 meets the duration and the timing of the Heinrich Events as recorded by layers of ice rafted debris (IRD) in the North Atlantic [*Hemming*, 2004]. While the $^{231}Pa/^{230}Th$ from the

Bermuda Rise outlasts the actual IRD depositions during H1 by several thousand years, H2 is characterized by a first $^{231}Pa/^{230}Th$ peak clearly preceding the actual Heinrich Event.

[14] As biogenic opal reduces the fractionation between $^{231}Pa$ and $^{230}Th$ in the water column, increased $^{231}Pa/^{230}Th$ can not solely be interpreted as an indicator of the past AMOC. The residence time of $^{231}Pa$ in the Atlantic Ocean can be considered as a combination of two separate residence times due to particle scavenging ($\tau_{scav}$) and water advection ($\tau_{adv}$). In the simple one-box model of *Yu et al.* [1996] the residence time of North Atlantic Deep Water (NADW) is equal to $\tau_{adv}$, which can be quantified from the $^{231}Pa$ deficit in the sediment. Assuming a constant value of $\tau_{scav}$ the sedimentary $^{231}Pa/^{230}Th$ would monitor $\tau_{adv}$ and hence the strength of the AMOC. However, a strong increase of the opal fraction in the vertical particle flux significantly would reduce $\tau_{scav}$ for $^{231}Pa$ [*Geibert and Usbeck*, 2004; *Bradtmiller et al.*, 2007]. Therefore, $^{231}Pa/^{230}Th$ mirrors variations of $\tau_{adv}$ or $\tau_{scav}$ or a combination of both (Figure 3). Consequently, time averaged $^{231}Pa/^{230}Th$ data from the Bermuda Rise (ODP Site 1063 and GGC5) around H1 (17–15 kyr) and the Last Glacial Maximum (LGM, 23–19 kyr) might also be interpreted in terms of shorter scavenging residence times of $^{231}Pa$ with a constant NADW residence time (similar to the Holocene (8–0 kyr)).

[15] On the other hand an increase of diatom abundance may reflect a change of the silica concentration in the ocean water [*Keigwin and Boyle*, 2008]. One striking feature of the $^{231}Pa/^{230}Th$ profile from ODP Site 1063 is a drop in $^{231}Pa/^{230}Th$ occurring at about the middle of the H2 associated peak, which is tightly traced by the diatom abundance. This pattern is also observed in the ratio of lithogenic elements to calcium (Figure 4a) during Heinrich Events 1 to 3 which could arise from changing terrigenous dilution and/or variable calcite dissolution [*Dunbar*, 2001]. In this case it is likely that elemental ratios were primarily controlled by changing dissolution of calcium carbonate because both, the sedimentation rates and the terrigenous fluxes (Figure 2) show a different pattern during H2. Dissolution of calcium carbonate is, for example, intensified by the presence of more corrosive southern sourced water masses [*Broeker and Peng*, 1982]. Accordingly, a northward penetration of carbonate-corrosive and silica-rich southern water masses may be responsible for the increase in diatom abundance and for the high $^{231}Pa/^{230}Th$ during Heinrich Events. Recent studies also show evidence for the dominance of southern water masses at abyssal depths in the Atlantic Ocean during the last glacial termination [*Rickaby and Elderfield*, 2005; *Gutjahr et al.*, 2008].

## 4. Conclusion

[16] Both the impact of biogenic opal and the reduction of the AMOC may result in increased sedimentary $^{231}Pa/^{230}Th$. In the absence of independent information from the sediments it is not possible to disentangle these two effects. Therefore, our observations question the interpretation of $^{231}Pa/^{230}Th$ in terms of ocean circulation alone. Possibly northward advances of silica-rich waters [*Keigwin and Boyle*, 2008] during Heinrich Events, may have led to enhanced opal production causing increased diatom abundances in the sediments at the Bermuda Rise. This process alone would cause high sedimentary $^{231}Pa/^{230}Th$ ratios. However, advances of southern water masses cannot occur without a significant reduction of AMOC. To disentangle the influence of Ocean circulation, chemical composition and water mass properties on the sedimentary $^{231}Pa/^{230}Th$ ratio further studies are needed that correctly reflect the sensitivity of $^{231}Pa$ to these various parameters.

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