New insights into cycling of $^{231}$Pa and $^{230}$Th in the Atlantic Ocean

Johannes Rempfer $^{a,b,*}$, Thomas F. Stocker $^{a,b}$, Fortunat Joos $^{a,b}$, Jörg Lippold $^{c,b}$, Samuel L. Jaccard $^{c,b}$

$^a$ Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, 3012 Bern, Switzerland
$^b$ Oeschger Centre for Climate Change Research, University of Bern, 3012 Bern, Switzerland
$^c$ Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland

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A B S T R A C T

We use the Bern3D model of intermediate complexity to examine the marine cycle of isotopes $^{231}$Pa and $^{230}$Th and the relationship between the particle-bound ratio $P_{\beta}/T_{\beta}$ and changes in the formation of the North Atlantic Deep Water (NADW). Model parameters describing reversible scavenging of isotopes by organic particles, opal, calcite and resuspended sediments were systematically varied and alternative sink parameterisations explored. It proves difficult to simultaneously achieve a good agreement with observations of dissolved and particle-associated concentrations of $^{231}$Pa and $^{230}$Th ($P_{\beta}, T_{\beta}, P_{\beta}, T_{\beta}$) as well as the particle-bound ratio $P_{\beta}/T_{\beta}$ within the classical concept of reversible scavenging alone. Agreement between simulated and observed $P_{\beta}, T_{\beta}$ and estimates of mean ocean residence times is improved by taking into account simplified representations of additional sinks at the sea floor (bottom scavenging) and at continental boundaries (boundary scavenging). We also find improved agreement between model and data by increasing lateral advection, in particular for $P_{\beta}$. These results point to the importance of sink processes that act in addition to reversible scavenging to shape the steady state distribution of $^{231}$Pa and, to a lesser degree, of $^{230}$Th.

In transient experiments in which the strength of the Atlantic meridional overturning circulation (AMOC) is periodically turned on and off, we find a strong statistical relationship between variations in AMOC strength and $P_{\beta}/T_{\beta}$ at great depths in the Northwest Atlantic region. These conclusions are robust across the range of sink parameterisations, that are consistent with estimates in the mean ocean residence time of $^{231}$Pa and $^{230}$Th. Our results indicate that the relationship between $P_{\beta}/T_{\beta}$ and AMOC-strength may not be fundamentally affected by uncertainties in sink processes, at least on the large spatial and temporal scale considered here, and support the idea that changes in $P_{\beta}/T_{\beta}$ in sediments of the Northwest Atlantic are indicative of changes in AMOC strength. Taking into account our simplified approach, our results indicate that the relationship between $P_{\beta}/T_{\beta}$ and AMOC-strength in the deep Northwest Atlantic is not affected by boundary scavenging or bottom scavenging. Our results thus support the idea that changes in $P_{\beta}/T_{\beta}$ in sediments of the Northwest Atlantic are indicative of changes in AMOC strength.

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1. Introduction

The purpose of this study is to improve the understanding of the cycling of $^{230}$Th and $^{231}$Pa in the Atlantic Ocean. We present results from sensitivity experiments with our model where we apply idealised representations of sediment resuspensions by bottom currents (nepheloid layers) and preferential removal of radionuclides at continental margins (boundary scavenging), as well as a stronger AMOC. Agreement between observed and simulated profiles of dissolved ($P_{AD}, T_{AD}$) and particle-bound ($P_{PA}, T_{PA}$) activities as well as of the dissolved and particle-bound $^{231}$Pa to $^{230}$Th ratios ($^{231}$Pa$/^{230}$Th$_{PA}, ^{231}$Pa$/^{230}$Th$_{PA}$) in the Atlantic, is evaluated by statistical means (Taylor, 2001). Furthermore, we examine the relationship between $P_{PA}/T_{PA}$ and AMOC-strength in transient experiments where AMOC is periodically turned on and off. As a considerable progress over previous studies, the coupling of a bio-geochemical model allows us to consistently simulate effects of changes in the export of biogenic particles, in response to changes in ocean circulation and the nutrient balance of the surface ocean (e.g., Plattner et al., 2001; Schmittner, 2005).

Due to the long residence time of uranium in seawater (>100 kyr), radionuclides $^{231}$Pa ($t_{1/2} = 32.5$ kyr) and $^{230}$Th ($t_{1/2} = 70$ kyr),...
75.2 kyr) are uniformly produced within the water column by decay of 235U and 234U, respectively, 231Pa and 230Th are subject to adsorption to and desorption from particle surfaces and are readily removed from the water column by settling particles (reversible scavenging) (Bacon and Anderson, 1982). As 230Th is strongly particle reactive, its residence time in seawater, $\tau_{230}$Th, is only a few decades. $\tau_{230}$Pa almost linearly increases with depth due to the process of reversible scavenging. 231Pa is relatively less particle reactive and has a longer residence time ($\tau_{231}$Pa $\approx$ 100–200 yr) (Bacon and Anderson, 1982; Anderson et al., 1983b; Yu et al., 1996; Moran et al., 2002). Depth profiles of $P_{\text{ad}}$ deviate from linearity, and show little increase below depths of 1–2 km (Moran et al., 2002). Such depth evolution cannot be explained by reversible scavenging alone (Nozaki and Nakajima, 1985) and has been associated with various processes of lateral mixing towards regions of high particle flux (boundary scavenging) (Anderson et al., 1983a; Moran et al., 2002; Roy-Barman, 2009; Christi et al., 2010), bottom scavenging by resuspended sediments, i.e., nepheloid layers (Deng et al., 2014; Hayes et al., 2015b), and lateral export by water masses (Luo et al., 2010).

The ratio of particulate 231Pa and particulate 230Th ($P_{\text{ad}}/T_{\text{ad}}$) has been proposed to reflect the rate of the meridional overturning circulation (MOC) (Yu et al., 1996; McManus et al., 2004; Gherardi et al., 2009).

An important characteristic of the cycling of 231Pa and 230Th is their differential affinity to sinking particles, resulting in preferential scavenging of 230Th relative to 231Pa (Walter et al., 1997; Chase et al., 2002; Kretschmer et al., 2011). The different affinity of 231Pa and 230Th to type particle i is reflected by the so-called fractionation factor, $f_i(\text{Th}/\text{Pa})$ (Anderson et al., 1983b; Henderson et al., 1999)

$$ f_i(\text{Th}/\text{Pa}) = \frac{(\text{Th}/\text{Pa})_{p,i} - \rho/(A_{\text{p},i} \cdot C_i)}{(\text{Th}/\text{Pa})_{d}} = K_{i}^{\text{Th}} - K_{i}^{\text{Pa}} = f_i, \quad (1) $$

where $K_i$ is $A_{\text{p},i} \cdot \rho/(A_{\text{p},i} \cdot C_i)$, with $A_{\text{p},i}$ dissolved activity of isotope j, j density of seawater, $A_{\text{p},i}$ particle-bound activity, and $C_i$ concentration of particle type i. Substantial variations of fractionation factors with latitude and depth from about 1–40 have been observed which mainly reflect the variable composition of particle types (Walter et al., 1997; Moran et al., 2002; Scholten et al., 2005; Hayes et al., 2015b).

A number of studies using models of different complexity, have been performed to gain better understanding of the marine cycle of Pa and Th (Siddall et al., 2005; Dutay et al., 2009; Roy-Barman, 2009) and the effect of AMOC-strength on the distribution of Pa/Thp at the seafloor (Marchal et al., 2000; Siddall et al., 2007; Luo et al., 2010). Some of these models rely on a simplified approach in terms of model geometry or ocean dynamics (Marchal et al., 2000; Luo et al., 2010), or they lack a dynamic coupling of biogenic particle fluxes to circulation and nutrient availability (Siddall et al., 2005, 2007). Moreover, some models suffer from weaknesses in the realistic simulation of $\tau_{230}$ Pa, and in particular Pa (Siddall et al., 2005; Dutay et al., 2009).

2. Methods

We use the Bern3D ocean model of intermediate complexity (Müller et al., 2006), coupled to an energy-moisture balance model (Ritz et al., 2011). The resolution of the ocean model is 36 x 36 grid cells in the horizontal, equidistant in longitude and in the sine of latitude. Spacing of the 32 depth layers is logarithmic, increasing with depth from 39 m at the surface to 397 m in the deepest layer. The ocean model contains a biogeochemical module which calculates export production of biogenic particles such as calcite (CaCO$_3$), opal, and particulate organic carbon (POC) from prognostic equations (Fig. A1). Annual export production from the euphotic zone is comparable to available estimates (Tschumi et al., 2008; Remper, 2011). Biological productivity (i.e., production of POC) in the euphotic zone (uppermost 75 m) is controlled by temperature, light, phosphate and iron and follows the parameterisation of Doney et al. (2006) (Tschumi et al., 2008, Parekh et al., 2008). Remineralisation and redissolution of POC, opal and CaCO$_3$ in the water column below 75 m takes place instantaneously and follows prescribed profiles (e.g. based on Martin, 1990) as outlined in Remper et al. (2011), their equations 2, 3a, 3b). 231Pa and 230Th are included into the Bern3D model following Bacon and Anderson (1982), Marchal et al. (2000) and Siddall et al. (2005). For the calculation of adsorption constants we follow two different approaches: For the 2d-approach (Marchal et al., 2000) we assume no remineralisation and redissolution of biogenic particles with depth. For the 3d-approach (Siddall et al., 2005) we take into account remineralisation and redissolution of POC, opal and calcite below the euphotic zone (see section 3 for details on the experimental set-up). We assume the 3d-approach to be more realistic as it includes differential particle dissolution and remineralisation. Besides, it is consistent with the simulation of Nd isotopes within the Bern3D model (Remper et al., 2011).

The main source of 231Pa and 230Th in the ocean is radioactive ingrowth from uranium decay, which is homogeneously distributed throughout the ocean. Sinks of 231Pa and 230Th are radioactive decay and removal from the water column by settling particles, 231Pa and 230Th are adsorbed onto particle surfaces and are released back to the water column by remineralisation and dissolution of particles at depth. The physical process of adsorption onto and desorption from particle surfaces is called reversible scavenging and is known to play an important role in the marine cycle of a number of isotopes (Bacon and Anderson, 1982; Marchal et al., 2000; Siddall et al., 2005; Oka et al., 2009; Remper et al., 2011).

The conservation equations of dissolved and particle-bound 231Pa and 230Th activities are:

$$ \frac{\delta A_{j}^{d}}{\delta t} = T(A_{j}^{d}) + \beta j + k_{j}^{d} \cdot A_{j}^{d} - (k_{j}^{d} + \lambda j) \cdot A_{j}^{d} \quad (2) $$

$$ \frac{\delta A_{j}^{p}}{\delta t} = T(A_{j}^{p}) - \frac{\delta(W_{s} \cdot A_{j}^{p})}{\delta z} - (k_{j}^{d} + \lambda j) \cdot A_{j}^{p} + k_{j}^{1} \cdot A_{j}^{d}, \quad (3) $$

where $A_{j}^{d}$ corresponds to the dissolved activity (dpm m$^{-3}$ yr$^{-1}$) and $A_{j}^{p}$ to the particle-bound activity (dpm m$^{-3}$ yr$^{-1}$) of isotopes 231Pa and 230Th, as denoted by the index j (see Table 1 for a list of symbols, abbreviations and values). T is the transport operator accounting for advection, diffusion and convection, as simulated by the Bern3D model (Müller et al., 2006). $k_{j}^{1}$ denotes the uniform desorption constants taken as 2.4 yr$^{-1}$ for both isotopes, $k_{j}^{d}$ denotes adsorption constants (yr$^{-1}$), $\beta j$ is the production of 231Pa and 230Th from U-decay (dpm m$^{-3}$ yr$^{-1}$), $\lambda j$ is the constant for radioactive decay (yr$^{-1}$), and $W_{s}$ is the particle settling velocity taken as globally uniform (1000 m yr$^{-1}$).

Adsorption rate constants are calculated for every grid cell and each isotope j:

$$ k_{j}^{d}(\theta, \phi, z) = \sum_{i=1}^{M} \sigma_{j}^{i} \cdot F_{j}(\theta, \phi, z). \quad (4) $$

where $F_{j}$ denotes the flux (mol m$^{-2}$ yr$^{-1}$) of particle type i (POC, opal, CaCO$_3$, resuspended lithogenic material – litho) for the given grid cell at longitude ($\theta$), latitude ($\phi$) and depth (z). $\sigma_{j}^{i}$ defines the scavenging efficiency (m$^2$ mol$^{-1}$) for each particle type i for 231Pa.
and $^{230}\text{Th}$. The relationship between flux $F$ and concentration $C$ is given by $M_i = \frac{C}{w_i}$, where $M_i$ is the molar mass (g mol$^{-1}$).

Following Marchal et al. (2000) values of scavenging efficiency $\sigma_i$, which are required for the calculation of adsorption constants (equation (4)), are defined as indicated in equations (5a)–(6b). These particle-specific adsorption constants, are derived from a reference scavenging efficiency, $\sigma_0$ (m$^2$ mol$^{-1}$), and are used for model tuning (Tables A1, A2), viz.,

$$\sigma_{\text{POC}} = \sigma_0 \cdot f_{\text{POC}}$$

(5a)

$$\sigma_{\text{Ca}} = \sigma_0 \cdot f_{\text{Ca}}$$

(5b)

$$\sigma_{\text{Ca,op}} = \sigma_0 \cdot f_{\text{Ca}} \cdot \eta_{\text{Ca,op}} = \sigma_{\text{Ca}} \cdot \eta_{\text{Ca,op}}$$

(5c)

$$\sigma_{\text{liitho}} = \sigma_0 \cdot f_{\text{liitho}}$$

(5d)

$$\sigma_{\text{POC,ca,liitho}} = \sigma_0 \cdot 1$$

(6a)

$$\sigma_{\text{op}} = \sigma_0 \cdot f_{\text{Ca}} \cdot \eta_{\text{Ca,op}} \cdot f_{\text{op}}^{-1} = \frac{\sigma_{\text{po}}}{f_{\text{op}}}$$

(6b)

Fractionation factors $f_i$ describe the fractionation of $^{231}\text{Pa}$ and $^{230}\text{Th}$ by a certain particle type $i$ (equation (1)), $\eta_{\text{Ca,op}}$ describes the relative affinity of $^{231}\text{Pa}$ to opal compared to CaCO$_3$. $\sigma_{\text{Ca,op}}$ is the scavenging efficiency on CaCO$_3$ (Table A1).

We assume that $^{230}\text{Th}$ adsorbs equally on POC, CaCO$_3$ and litho (equation (6a)). We note that some uncertainty is associated with the exact value of desorption and adsorption rates. Our values are similar to that of previous studies by Marchal et al. (2000) and Luo et al. (2010).

Regarding the fractionation of $^{231}\text{Pa}$ and $^{230}\text{Th}$ by individual particle types we rely on observations (see Table A1 for a compilation of values). However, less information is available on the relative affinity of $^{231}\text{Pa}$ or $^{230}\text{Th}$ to different particle types (as indicated e.g., by $\eta_{\text{Ca,op}}$ (Walter et al., 1997; Chase et al., 2002; Scholten et al., 2005). In modelling approaches these scaling constants are generally used as tuning parameters and it is therefore not surprising that differences emerge between studies (Marchal et al., 2000; Siddall et al., 2005; Dutay et al., 2009).

It has been suggested that bottom scavenging in nepheloid layers acts as an additional sink for $^{231}\text{Pa}$ and $^{230}\text{Th}$ at the seafloor and is shaping profiles of $^{234}\text{Pa}$ and $^{238}\text{Th}$ (Anderson et al., 1983b; Thomas et al., 2006; Okubo et al., 2012; Deng et al., 2014; Hayes et al., 2015b). Our model is too coarse for a dynamical simulation of processes which lead to the formation of nepheloid layers (Biscaye and Eittreim, 1977). Therefore, and consistent with recent observations (Lam et al., 2015, 40 to 1650 µg/L) we assume a globally uniform concentration of resuspended lithogenic material (litho) in grid cells which are adjacent to sediment of 60 µg/L. The thickness of the nepheloid layer depends on the thickness of the corresponding bottom grid cell which increases with depth from 39 m at the surface to 397 m in the deepest layer. Besides and in agreement with Deng et al. (2014) we assume that nepheloid layers preferentially remove $^{231}\text{Pa}$ relative to $^{230}\text{Th}$ (factor of 10).

At ocean margins Pa has been reported to be removed from the water column more efficiently than in the open ocean (Anderson et al., 1983a). In order to examine the effect of boundary scavenging of Pa in particular on Pa$_d$ we scale export production (and thus adsorption coefficients) in grid cells at continental boundaries by a factor 2, within the model describing the cycle of Pa. Thus, this scaling does not affect the cycling of nutrients, oxygen, and carbon within the model.

We are aware that our approaches for taking into account bottom scavenging and boundary scavenging are simplifications. This is consistent with the aim of this study to present sensitivity experiments based on idealised simulations to identify the first-order processes controlling the marine cycling of $^{231}\text{Pa}$ and $^{230}\text{Th}$.

### Table 1

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Variable</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$j$</td>
<td>Index for $^{231}\text{Pa}$, $^{230}\text{Th}$</td>
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<td></td>
</tr>
<tr>
<td>$A_j$</td>
<td>Dissolved activity</td>
<td>dpmm$^{-1}$</td>
<td>yr$^{-1}$</td>
</tr>
<tr>
<td>$A_j^g$</td>
<td>Particle-associated activity</td>
<td>dpmm$^{-1}$</td>
<td>yr$^{-1}$</td>
</tr>
<tr>
<td>$i$</td>
<td>Index for particle type</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_i$</td>
<td>Particle flux</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v$</td>
<td>Globally uniform settling velocity</td>
<td>1000</td>
<td>m yr$^{-1}$</td>
</tr>
<tr>
<td>$\beta_{\text{Pu}}$</td>
<td>Production of $^{231}\text{Pa}$ from U-decay</td>
<td>2.33·10$^{-3}$</td>
<td>dpmm$^{-1}$ yr$^{-1}$</td>
</tr>
<tr>
<td>$\lambda_{\text{Pu}}$</td>
<td>Production of $^{230}\text{Th}$ from U-decay</td>
<td>2.52·10$^{-2}$</td>
<td>dpmm$^{-1}$ yr$^{-1}$</td>
</tr>
<tr>
<td>$\lambda_{\text{Pu}}$</td>
<td>Decay constant $^{231}\text{Pa}$</td>
<td>2.13·10$^{-3}$</td>
<td>yr$^{-1}$</td>
</tr>
<tr>
<td>$\lambda_{\text{Th}}$</td>
<td>Decay constant $^{230}\text{Th}$</td>
<td>9.22·10$^{-6}$</td>
<td>yr$^{-1}$</td>
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<tr>
<td>$k_{\text{sol}}$</td>
<td>Desorption constant $^{231}\text{Pa}$, $^{230}\text{Th}$</td>
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<td>yr$^{-1}$</td>
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<tr>
<td>$k_{\text{ads}}$</td>
<td>Adsorption constant $^{231}\text{Pa}$, $^{230}\text{Th}$</td>
<td>Eq. (4)</td>
<td>yr$^{-1}$</td>
</tr>
<tr>
<td>$f_i$</td>
<td>Fractionation factor, particle type $i$</td>
<td>Table A1</td>
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<tr>
<td>$\eta_{\text{Ca,op}}$</td>
<td>Relative affinity factor, $^{231}\text{Pa}$ on CaCO$_3$, opal</td>
<td>Table A1</td>
<td></td>
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<tr>
<td>$\sigma_0$</td>
<td>Reference scavenging efficiency</td>
<td>Table A1</td>
<td>m$^2$ mol$^{-1}$</td>
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<tr>
<td>$\sigma_i$</td>
<td>Scavenging efficiency of $i$ by particle type $j$</td>
<td>Eq. (5c)–(6a)</td>
<td>m$^2$ mol$^{-1}$</td>
</tr>
</tbody>
</table>

3. Overview of experiments and evaluation of model performance

The Bern3D model is a climate model of intermediate complexity suitable for long-term paleoclimatic and large ensemble studies. Parameters are tuned such that atmospheric and surface ocean temperature, sea surface salinity, sea ice cover, Atlantic and Pacific zonal mean temperature, salinity, and radiocarbon are simulated in reasonable agreement with observations (Ritz et al., 2011). Compared to other models and available estimates (13 to 23 Sv, Talley et al., 2003; Srokosz and Bryden, 2015), simulated AMOC strength ($\approx$14 Sv) is at the lower end of the estimated range. In this study we aim to investigate processes which are important for the simulation of Pa and Th in agreement with observations. In particular regarding Pa one important process is advection (e.g., Marchal et al., 2000; Luo et al., 2010). We therefore examine an alternative steady-state where AMOC strength is increased to $\approx$18 Sv (Fig. A3a) by increasing the Atlantic-to-Pacific freshwater-flux (see Table A2 for further details). The AMOC strength can only be increased to a certain degree by increasing the Atlantic-to-Pacific freshwater-flux. The model becomes numerically unstable for very large freshwater fluxes.

Based on the control 3d-approach (parameter set Re3d, Table A2) we aim to improve agreement between simulated and observed values of Pau, Thd, Pa/d, Thd and Pa/d/Thd by taking into account additional sinks (1) at the sea floor, i.e., bottom scavenging of Pa and Th in a simplified representation of nepheloid.
layers (Re3d_Bt) and (2) at the ocean margins, i.e., boundary scavenging of Pa in a simplified representation of increased particle flux at ocean margins (Re3d_Bd). We also consider the case (3) where bottom scavenging and boundary scavenging are combined (Re3d_BtBd) and (4) show results from a transient experiment with stronger overturning circulation (Re3d_BtBd_Fw). Finally (5), we present results from an experiment which is similar to Re3d_BtBd_Fw but which is based on the 2d-approach (Re2d_BtBd_Fw) of Marchal et al. (2000). In the second part of the study we examine the effect of changes in AMOC-strength on \( \text{Pa}_p/\text{Th}_p \) in the Northwest Atlantic, by applying periodic freshwater perturbations (±0.3 Sv, similar to Rempfer et al., 2012) to the North Atlantic (45 to 70°N). We focus on the deep Northwest Atlantic as the discussion on the role of variations in AMOC during past climate changes has also largely focused on this region (e.g., McManus et al., 2004; Ritz et al., 2013; Böhm et al., 2015). Beyond that, \( \text{Pa}_p/\text{Th}_p \) in the deep Northwest Atlantic was reported to be sensitive to AMOC variations (Luo et al., 2010) and the Bern3D model is able to simulate large-scale features of the AMOC (Ritz et al., 2011; Rempfer et al., 2011). We note that our experiments and analyses, aimed to investigate changes in the deep Northwest Atlantic, do not allow to conclude on the relationship between overturning circulation and \( \text{Pa}_p/\text{Th}_p \) in other regions.

An adequate value of \( \sigma_0 \) is determined by minimising the deviation (i.e., the root mean squared error, \( \text{RMSE} = \sqrt{\frac{1}{N-1} \sum_{k=1}^{N} (\text{sim}_k - \text{obs}_k)^2} \)) divided by the standard deviation of observations \( \sigma_{\text{obs}} \) between simulated (\( \text{sim}_k \)) and observed (\( \text{obs}_k \)) values of \( \text{Pa}_d, \text{Th}_d, \text{Pa}_p, \text{Th}_p \) and \( \text{Pa}_p/\text{Th}_p \) (k is an index over all observations N). Furthermore, agreement between observed and

**Fig. 1.** Root mean squared error (RMSE) of simulated from observed values, divided by standard deviation of observed values \( (\sigma_{\text{obs}}) \) for \( \text{Pa}_d, \text{Th}_d \) (right y-axis, note the log-scale), \( \text{Pa}_p, \text{Th}_p, \text{Pa}_p/\text{Th}_p \) and \( \text{Pa}_p/\text{Th}_p \) (left y-axis) for experiments where reference scavenging efficiency, \( \sigma_0 \), was increased from 0.2 to 1.9. Except for \( \sigma_0 \) the parameter sets equal Re3d respectively (see Table A2 for further details).

**Fig. 2.** Simulated \( \text{Pa}_d, \text{Th}_d \) and \( \text{Pa}_p/\text{Th}_p \) (indicated on top of the figure) along GEOTRACES transect GA03 (Hayes et al., 2015b) (the course of the track is indicated in Fig. A4) as obtained from experiments Re3d, Re3d_Bd, Re3d_BtBd (indicated at the right side of the figure). Available observations from the water column (\( \text{Pa}_d, \text{Th}_d \)) and sediment surfaces (\( \text{Pa}_p/\text{Th}_p \)) are superimposed using the same colorscale. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
simulated values is evaluated by means of correlation coefficient, root mean squared error and relative standard deviation which are summarised in a Taylor-plot (Taylor, 2001).

Observational data have been compiled using data from the references listed in Table A3, yielding a stack of 537 Thd, 111 Thp, 362 Pa(d), 45 Pa(p) and 52 core-top Pa(p)/Thp data points (the distribution of observations of Pa(d), Thd, Pa(p)/Thp on the Bern3D model grid is indicated in Fig. A3). As no thorough intercalibration has been carried out in studies preceding the GEOTRACES project, data quality may differ between studies. The evaluation of such an effect, however, is beyond the scope of this manuscript. Therefore, and due to the relatively small number of available observations, we assume all published data to be valid. Information on particle-affinity (Walter et al., 1997; Chase et al., 2002; Kretschmer et al., 2011), fractionation factors (Walter et al., 1997; Moran et al., 2002; Hayes et al., 2015b), and residence times (Bacon and Anderson, 1982; Anderson et al., 1983b; Yu et al., 1996; Moran et al., 2002) is used for the evaluation of the different models on a qualitative basis.

4. The modern-day marine cycle of 231Pa and 230Th

The model value for the efficiency of reversible scavenging ($\sigma_0$, equation (4)) for model setup Re3d is determined from observations. $\sigma_0$ is varied over a large range (Fig. 1), while keeping all other parameters constant. Results are compared with observations of Pa(d), Thp, Pa(d), Thd and Pa(p)/Thp. For Pa(p)/Thp a distinct minimum of RMSE is observed around 1.0 (Fig. 1). For Thd, Thp, Pa(d) and Pa(p) RMSE is decreasing slowly with increasing $\sigma_0$. Hence, for the following simulations we choose $\sigma_0 = 1.0$ as it represents a reasonable compromise with regard to RMSE for Pa(d), Thd and Pa(p)/Thp.

Modelled Pa(d), Thd concentrations are substantially overestimated in the deep Atlantic when applying parameter set Re3d (Figs. 2, 3 and blue solid line in Fig. 4a, b). Similarly, variability and absolute values of Pa(d)/Thd are overestimated by the model throughout the water column (Fig. 4c). In contrast, simulated Atlantic Pa(p)/Thp is in reasonable agreement with observations (Fig. 4d). The agreement with observations is quantified in Fig. 5 (blue markers with solid border line). Unrealistically large Thd and Pa(p) values result in high global mean residence times $\tau_{Pa}$ (310 yr) and $\tau_{Th}$ (42 yr) which are at the upper end of the estimated ranges for 231Pa (100–200 yr) and 230Th (a few decades) (Bacon and Anderson, 1982; Anderson et al., 1983b; Yu et al., 1996; Moran et al., 2002). Note, in this manuscript residence times are obtained from steady-state as ratios of the total inventories (i.e., particulate and dissolved) and the globally integrated radioactive ingrowth of 231Pa and 230Th.

The effect of associated near-bottom scavenging on profiles of Pa(d) and Thd is investigated next. We apply a globally uniform concentration of resuspended particles of 60 µg/L to grid cells which are adjacent to sediment (suffix _bt in experiment label, Table A2). We assume that particle-bound Pa and Th are in equilibrium with dissolved concentrations and that the settling speed of
resuspended particles equals \( w_c \) (see Table 1). Furthermore, we assume that \(^{230}\)Th is scavenged 10 times more efficiently than \(^{231}\)Pa (\( f_{sb} = 10 \), Tables A1, A2).

Taking into account bottom scavenging in \(_{bt}\) improves the agreement between simulated and observed \( P_{ad} \) and \( \text{Th}_d \) (Figs. 2, 3 and green solid lines, Fig. 4a, b). \( \tau_{Pa} \) and \( \tau_{Th} \) are reduced to 220 and 28 yr and are in better agreement with available observational estimates. Note that even stronger bottom scavenging, which may help for obtaining more realistic \( P_{ad} \), leads to stronger and unrealistic depletion of \( \text{Th}_d \) at the seafloor (not shown). From this and based on the results shown in Figs. 2, 3, and 4a, b we conclude that bottom scavenging may provide an explanation for certain characteristics in profiles of \( P_{ad} \) and \( \text{Th}_d \) but that additional processes affect the vertical distributions in particular of \( P_{ad} \).

Although not well-quantified, the concept of boundary scavenging is assumed to play an important role for the removal of adsorption-prone elements with residence times greater than about 100 yr (Anderson et al., 1983a; Yu et al., 1996; Roy-Barman, 2009). The Bern3D model does not allow an explicit simulation of processes like lithogenic input and nutrient input via rivers or submarine groundwater discharge, which may lead to increased particle flux at ocean boundaries (Siddall et al., 2005). We take into account boundary scavenging by scaling particle fluxes (and thus adsorption constants) of POC, opal, CaCO\(_3\) and resuspended lithogenic material (litho) in grid cells which are adjacent to continents by a factor of 2. Additional simulations were performed using scaling factors of 4 and 10 (not shown). Overall, the effect of boundary scavenging on \( P_{ad} \) and \( P_{ad}/\text{Th}_d \) appears less important than the effect of bottom scavenging. Note that the factor of 2 may rather be interpreted as an additional tuning factor and, again due to the coarse resolution of our model, can barely be compared to observations at specific locations. Margins were reported to be preferential sinks for Pa (Anderson et al., 1983a; Lippold et al., 2012; Hayes et al., 2015a). In our simplified approach we assume that boundary scavenging affects only Pa.

Overall, boundary scavenging leads to smaller values of \( P_{ad} \) in \(_{bd}\) (Figs. 2, 3, and solid red line in Fig. 4b) which is also reflected in smaller \( \tau_{Pa} \) (280 yr). As boundary scavenging does not affect Th in our model, \( \text{Th}_d \) and \( \tau_{Th} \) of \(_{bd}\) are equal to Re3d (Fig. 4a).

For illustrative purposes we combine bottom scavenging and boundary scavenging in parameter set Re3d_BtBd (turquoise solid line in Fig. 4, turquoise markers with solid border line in Fig. 5), which leads to better overall agreement between observed and simulated \( P_{ad} \). Simulated \( \tau_{Pa} \) and \( \tau_{Th} \) (220 and 28 yr) are consistent with available observations (Bacon and Anderson, 1982; Anderson et al., 1983b; Yu et al., 1996). However, despite reasonable agreement between simulated and observed \( P_{ad} \) at depths shallower than 2.5 km, simulated \( P_{ad} \) exceeds observations at greater depths.

Summing up results of parameter sets Re3d_Bt, Re3d_Bd and Re3d_BtBd we find that \( P_{ad}/\text{Th}_d \) and in particular \( P_{ad}/\text{Th}_d \) are only slightly affected by boundary and/or bottom scavenging (solid green, red and turquoise lines in Fig. 4c, d). However, agreement between simulated and observed \( P_{ad}/\text{Th}_d \) is slightly reduced for Re3d_BtBd compared to Re3d (Fig. 5). Due to the simplified representation of bottom and boundary scavenging in our approach, we prefer not to put too much emphasis on these small changes. Detailed experiments with more sophisticated models are needed in this regard.
Lateral export affects the distribution of Pa. Figs. 4 and 5 (dashed lines and transparent markers with dashed border lines) indicate the effect of an even stronger AMOC on Pa_d/Th_d, Pa_d/Th_d and Pa_d/Th_d for parameter sets Re3d_BtBd and Pa_d/Th_d (Table A2). We find improved agreement between simulated and observed Pa_d and Th_d (Figs. 4a, b, 5). It becomes clear that stronger overturning affects Pa_d and Th_d in a way similar to boundary scavenging and bottom scavenging. Thus, in Re3d_BtBd_FwOn and compared to Re3d_BtBd a smaller magnitude of additional sinks is required to obtain similar agreement with observations for Pa_d and Th_d.

Following the 2d-approach of Marchal et al. (2000), we find that the overall sink for Pa and Th is more pronounced due to larger adsorption constants at depth and therefore that less additional scavenging at ocean boundaries and/or at the seafloor is required to obtain reasonable agreement with observations (Fig. 4).

Fig. 6. Atlantic (from 34°S–71°N, excluding the Southern Ocean) profile of simulated Pa_d/Th_d for AMOC on (as indicated by the additional suffix FwOn, solid lines) and off-states (indicated by the suffix FwOff, dashed lines). Simulated values are taken from grid cells where observations are available. If more than one observation is available at one depth, the weighted mean is shown. Gaps in the profiles are due to missing observations at certain depths. AMOC is periodically turned off and on by applying positive and negative freshwater perturbations (±0.3 Sv, similar to Rempfer et al. (2012)) to the North Atlantic (45° to 70°N). Values are averaged over 1 kyr as indicated by grey bars in Fig. 7. Further details on the experimental set up are given in Table A2. Basin mean of available observations from sediment surfaces are indicated by black dots (see Table A3, for references).

4.1. Comparison with previous studies and further implications

Simulated Pa_d and Th_d exceeded observed values in previous studies by Siddall et al. (2005) and Dutay et al. (2009) as well. In contrast, Pa_d and Th_d were simulated in agreement with observations by Marchal et al. (2000).

Apart from the magnitude of the additional boundary scavenging as mentioned above, one explanation for the reasonable agreement in the study of Marchal et al. (2000) is the strong AMOC (≈24 Sv), compared to studies of Siddall et al. (2005) (≈14 Sv) and Dutay et al. (2009) (≈17.5 Sv). Another explanation is the larger affinity (larger σ_0) of 231Pa and 230Th to particle surfaces, in particular to opal (Table A1). We tested the effect of larger σ_0 (Fig. 1). On the one hand, we find better overall agreement between simulated and observed Pa_d and Th_d. On the other hand, agreement is less pronounced for Pa_d/Th_d (in particular in the Equatorial Pacific, the South Atlantic and the Southern Ocean, not shown). One reason that Pa_d/Th_d e.g., in the Equatorial Pacific or the South Atlantic is not affected by the more pronounced particle affinity in the study of Marchal et al. (2000) is that export production of opal was represented in a simplified manner.

No opal export outside the Southern Ocean was taken into account by Marchal et al. (2000) and no opal export outside the Southern Ocean, the North Pacific and the Arctic was considered by Siddall et al. (2005, their Fig. 1). In contrast, in our study, where particle export production is calculated from prognostic equations, export production of opal is simulated not only in the Southern Ocean opal belt and the North Pacific, but also in the Equatorial Pacific, the South Atlantic off Africa and in the North Atlantic (Fig. A1). The simulated patterns and globally integrated magnitudes of export production are consistent with estimates presented by Sarmiento and Gruber (2006).

5. Pa_d/Th_d during AMOC on/off-states

In this section we examine differences between spatially and temporally averaged profiles of Pa_d/Th_d during AMOC-on-
states and AMOC-off-states in the Northwest Atlantic, an important oceanic region for reconstructions of past changes in AMOC strength (e.g., McManus et al., 2004; Ritz et al., 2013; Böhm et al., 2015) (Fig. 6). Time periods for which averages of $P_{230}$/$Th_{400}$ and AMOC-strength are calculated span 1 kyr and are indicated by grey bars in Fig. 7. Average AMOC-strength during on-state approximates 24 Sv, average AMOC-strength during off-state is close to 0 Sv (Fig. A2b, c). Although these time slices do not represent a real steady-state, quasi steady-state may be assumed for $231$Pa and $230$Th due to the long periodicity of the freshwater-forcing and the relatively short mean residence times of $231$Pa and $230$Th.

During on-states and at depths greater than about 1 km, $P_{230}$/$Th_{400}$ linearly decreases from 0.10–0.12 to 0.04–0.06 dependent on the parameter set (indicated by solid lines in Fig. 6). In contrast during off-states the decrease in $P_{230}$/$Th_{400}$ with depth is less pronounced (from 0.09–0.10 to 0.07–0.08, indicated by dashed lines in Fig. 6).

A linear decrease in $P_{230}$/$Th_{400}$ with depth has been observed at different locations (Walter et al., 2000). At first, this decrease was ascribed to changes in particle composition (Scholten et al., 2008). Subsequent studies however argued that it reflects lateral export of Pa from the Atlantic to the Southern Ocean by NADW (Gherardi et al., 2009; Luo et al., 2010; Lippold et al., 2011, 2012).

Our results indicate that overturning-strength largely affects the depth-evolution of $P_{230}$/$Th_{400}$ and thus support the reasoning of Luo et al. (2010) and Lippold et al. (2011). It is important to note however, that $P_{230}$/$Th_{400}$ does not simply reach the production ratio in case of halted AMOC (which agrees with Luo et al., 2010). Instead, during AMOC-off-states, $P_{230}$/$Th_{400}$ is greater than the production-ratio at depths shallower than about 2–3 km and is smaller at greater depths. This may be due to the fact that circulation is not halted completely, e.g., wind-driven circulation (Fig. A2c) and that lateral transport (diffusion) in particular of Pa into regions of higher export productivity remains effective during a slowdown of the AMOC (Roberts et al., 2014).

6. $P_{230}$/$Th_{400}$ in transient perturbation simulations

Similar to Rempfer et al. (2012) we examine the effect of transient changes in AMOC-strength on spatially-averaged $P_{230}$/$Th_{400}$ in the Northwest Atlantic for different parameter sets (Re3d, Re3d_Btbd, Re2d_Btbd, Fig. 7). Therefore, we apply periodic freshwater perturbations ($\pm0.3$ Sv) of durations of $T_{FW} = 10$ kyr to the North Atlantic, which results in a periodic collapse and resumption of the AMOC (Fig. 7a). Maximum AMOC-strength, $\psi_{AMOC}$, varies from about 0–26 Sv. These end-member experiments are highly idealised and thus not directly comparable to past changes in ocean circulation. Instead we aim to examine effects of changes in overturning strength on $P_{230}$/$Th_{400}$ and compare these effects to those of the above mentioned processes.

Spatially-averaged deep ocean $P_{230}$/$Th_{400}$ in the Northwest Atlantic shows large temporal variations which appear to be closely related to variations in $\psi_{AMOC}$ (Fig. 7b, c). Largest values of $P_{230}$/$Th_{400}$ ($\approx0.07$) occur during AMOC-off-state, smallest values ($\approx0.03$) occur during AMOC-on-state. As discussed above, $P_{230}$/$Th_{400}$ exceeds the production ratio of 0.093 during AMOC-off-state at depths above 2–3 km and reaches values slightly smaller than 0.093 below.

Temporal patterns and absolute changes in $P_{230}$/$Th_{400}$ are very similar for individual parameter sets despite substantial differences in mean residence times of $231$Pa and $230$Th (Fig. 7b). This indicates that processes such as reversible scavenging, boundary scavenging and bottom scavenging do not substantially disturb the relationship between overturning strength and $P_{230}$/$Th_{400}$ at least on the larger spatial and temporal scales considered in these experiments.

Although the relationship between $P_{230}$/$Th_{400}$ in the Northwest Atlantic and $\psi_{AMOC}$ is close, it is not 1:1 (Fig. 7c). This may partly be due to the fact that $\psi_{AMOC}$ reflects overturning strength within the 3-dimensional Atlantic basin and cannot be expected to capture spatial heterogeneity in $P_{230}$/$Th_{400}$ at any specific site. In addition, we find differences in the relationship between $P_{230}$/$Th_{400}$ and $\psi_{AMOC}$ for decreasing and increasing $\psi_{AMOC}$: the relationship between decreasing AMOC-strength (and increasing $P_{230}$/$Th_{400}$) is about linear. In contrast, $P_{230}$/$Th_{400}$ shows a step like decrease from 0.07 to 0.03 (between 15 and 20 Sv, grey arrows indicate the direction of cycling in Fig. 7c) for increasing AMOC-strength.

We spatially extended our analysis of the relationship between $P_{230}$/$Th_{400}$ and $\psi_{AMOC}$ for parameter set Re3d_Btbd to GEO-TRACES transect GA03. Correlation coefficients indicate a more pronounced relationship at greater depths (Fig. 8a). Similarly, changes in $P_{230}$/$Th_{400}$ per unit change in $\psi_{AMOC}$ are larger at greater depths (Fig. 8b). We therefore suggest not to simply use the regression slopes as shown in Fig. 8b for the interpretation of reconstructed changes of $P_{230}$/$Th_{400}$ from sediment cores. Instead, spatial patterns in Fig. 8a, b indicate that our model simulates the classical relationship between $P_{230}$/$Th_{400}$ and $\psi_{AMOC}$ (negative correlation) pri-
mainly in the North Atlantic at depths below 2 km. In more northern latitudes and depths above 2 km the correlation is positive, i.e., increasing \( {P}_{p}/\text{Th}_p \) ratios indicate increasing \( \psi_{\text{AMOC}} \). We stress that this spatially dependent behaviour of the paleoceanographic tracer of AMOC variations should be investigated in more detail using a better resolved ocean-tracer model.

7. Summary, conclusions and outlook

Our major findings are: (i) Given the available observational data sets, no single model can be defined, which yields maximum agreement for each of \( P_{A_{d}} \), \( P_{A_{p}} \), \( \text{Th}_{d} \), \( \text{Th}_{p} \) and \( P_{A_{p}}/\text{Th}_p \) based on the classical concept of reversible scavenging of \( ^{231}\text{Pa} \) and \( ^{230}\text{Th} \) by particles in the water column alone.

(ii) Taking into account additional sinks at the seafloor and at ocean margins (simplified representations of bottom and boundary scavenging) yields improved agreement with observations in particular for Atlantic \( P_{A_{d}} \), \( \text{Th}_{d} \), \( P_{A_{p}}/\text{Th}_p \) and to a smaller extent for \( P_{A_{p}}/\text{Th}_p \). This indicates that additional sinks such as nepheloid layers and boundary scavenging are important sinks of \( ^{231}\text{Pa} \) and \( ^{230}\text{Th} \) and that lateral export of \( ^{231}\text{Pa} \) is particularly important for the particle profiles of \( P_{A_{d}} \).

(iii) Atlantic profiles of \( P_{A_{p}}/\text{Th}_p \) decrease with depth in all parameter sets during AMOC-on and off-states. The rate of the decrease depends on the parameter set and is reduced during AMOC-off-states but does not approach zero in any parameter set at great depths (below \( \approx 3000 \text{ m} \). Even during AMOC-off states \( P_{A_{p}}/\text{Th}_p \) does not simply approach the production ratio. Lateral export of \( ^{231}\text{Pa} \) into regions of high particle flux, such as at continental boundaries, may remove Pa from the open ocean despite halted overturning.

(iv) Marked variations in \( P_{A_{p}}/\text{Th}_p \) are observed at great depths in the Northwest Atlantic in experiments in which ocean circulation is turned on and off in a transient way. This relationship is robust across parameter sets examined in this study and is not much affected by changes in the marine cycle of \( ^{231}\text{Pa} \) and \( ^{230}\text{Th} \), for instance mean residence times.

Although our approach is a step forward compared to previous studies we are aware that it is still based on strong simplifications which do not allow accurate representations of real world processes: only three particle types and one particle size class are considered in the present version of the carbon cycle model; dissolution profiles and settling speed are globally uniform; nepheloid layers and boundary scavenging as well as fractionation of \( ^{231}\text{Pa} \) and \( ^{230}\text{Th} \) by different particle types are represented in a simplified manner. These simplifications on the one hand are due to the missing understanding of processes and on the other hand are due to the coarse resolution of our model. Nonetheless, on larger regional scales our results yield meaningful insights. However, a better understanding of the effects of these processes is required for a reasonable simulation of smaller-scale patterns in particular of \( P_{A_{d}} \). This will also lead to increased confidence on \( P_{A_{p}}/\text{Th}_p \)-based reconstructions of past changes in AMOC.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2017.03.027.

References


