The $^{231}$Pa/$^{230}$Th ratio as a proxy for past changes in opal fluxes in the Indian sector of the Southern Ocean

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Abstract

Published scavenging models generally assume that the $^{231}$Pa/$^{230}$Th ratios of surface sediments are primarily determined by the mass flux of particles. In this study we compare the $^{230}$Th normalized vertical fluxes of both total sediments and opal to the $^{231}$Pa/$^{230}$Th ratios measured from six sediment cores sampled across the Antarctic Circumpolar Current (ACC). We observe a better correlation between the $^{231}$Pa/$^{230}$Th ratios and the vertical opal fluxes corrected for dissolution than with total sediment vertical fluxes. This observation indicates that opal may explain the enhanced scavenging of $^{231}$Pa. This result is consistent with the studies of Loeff and Berger [Deep-Sea Res. 40 (2) (1993) 339], Kumar et al. [Nature 378 (1995) 675] and Walter et al. [Earth Planet. Sci. Lett. 149 (1997) 85] who speculated that opal may explain enhanced scavenging of $^{231}$Pa. Finally, our results suggest that the $^{231}$Pa/$^{230}$Th ratio is a reliable indicator of opal mass flux and can be used, taking some precautions, as a proxy for opal paleoproductivity in the Indian sector of the Southern Ocean.

Keywords: $^{231}$Pa/$^{230}$Th ratio; Opal flux; Southern Ocean

1. Introduction

One of the most exciting discoveries of the 1980s with implications for the global carbon cycle was that the carbon dioxide content of the last glacial age atmosphere was about one-third lower than typical Holocene values (180 vs. 280 ppm). This evidence is contained in the air trapped within polar ice (Barnola et al., 1987). The Southern Ocean is considered to play a key role in the glacial lowering of atmospheric CO$_2$. Investigators have attempted to link the biologic productivity of Southern Ocean with variations in atmospheric CO$_2$ content as recorded in ice cores (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Martin, 1990), however, estimates of past changes in Southern Ocean productivity are still

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uncertain. The use of different productivity proxies (for example opal and organic carbon accumulation rate) to estimate the productivity of the Southern Ocean has yielded ambiguous results and therefore other productivity proxies have been used in order to avoid these complications.

Primary productivity generally controls the mass flux of particles through the oceanic water column (Deuser et al., 1981). In this paper we focus on the $^{231}$Pa/$^{230}$Th ratio a tracer that has been proposed to respond to changing particle flux. The Protactinium-$^{231}$ ($t_{1/2} = 32,500$ years) and thorium-$^{230}$ ($t_{1/2} = 75,200$ years) are produced in sea water by radioactive decay of dissolved $^{235}$U and $^{234}$U. The isotopic composition of U in seawater is spatially uniform (Ku et al., 1977), and provides a uniformly distributed source of $^{231}$Pa and $^{230}$Th with a constant initial Pa/Th activity ratio of 0.093. $^{231}$Pa and $^{230}$Th are removed from sea water by scavenging to particulate matter and their mean oceanic residence times, with respect to scavenging to the sea floor, are 10–40 and 50–100 years, respectively (Anderson et al., 1983a). This difference in particle reactivity of Pa and Th is responsible for a fractionation of the two radionuclides in the water column. Due to its short residence time over most of the ocean, the flux of $^{230}$Th to the sediment is assumed to equal its local production rate in the water column, whereas the longer oceanic residence time for $^{231}$Pa allows this nuclide to be transported over basin-wide distances prior to being scavenged. Consequently, fluxes of particulate $^{231}$Pa scavenged from the water column vary as a function of particle flux (scavenging intensity) (Taguchi et al., 1989; Lao et al., 1992), so the particulate $^{231}$Pa/$^{230}$Th ratio generally increases with increasing particle flux. The $^{231}$Pa/$^{230}$Th ratios in surface sediments in upwelling regions at ocean margins usually exceed the production ratio of 0.093 (boundary scavenging), while the $^{231}$Pa/$^{230}$Th ratio of particulates usually decreases with decreasing particle flux (e.g. in the central gyres) and the ratio is lower than the production ratio of 0.093 (for reviews of this process, see Anderson et al., 1983a,b). Based on this apparently well established relationship between $^{231}$Pa/$^{230}$Th ratio and mass flux, the $^{231}$Pa/$^{230}$Th ratio has been used to assess past changes in oceanic productivity of dated sediment cores (Kumar et al., 1993; Lao et al., 1992; Francois et al., 1993a,b). In this model, variations in the $^{231}$Pa/$^{230}$Th ratio through time were simply explained by changes in ocean productivity.

However, this model does not seem to be valid throughout the oceans. Recent study has revealed that hydrology may also control the scavenging of $^{231}$Pa. Yu et al. (1996) found a lack of boundary scavenging in the Atlantic Ocean due to the short mean residence time of deep water (80–100 years) in comparison to the mean residence time of $^{231}$Pa. Moreover, in the South Atlantic, south of the Polar Front, Walter et al. (1997) and Rutgers van der Loeff and Berger (1993) showed enhanced scavenging of $^{231}$Pa relative to $^{230}$Th in the water column of an area with a low particle flux. This observation was probably due to a change in the chemical composition of particulate matter, and not by a high mass flux. The authors speculated that the southward increase in opal content in the particulate matter could explain the enhanced scavenging of $^{231}$Pa to the south.

The objective of the present study is to determine whether the $^{231}$Pa/$^{230}$Th ratio is a reliable tracer for the mass flux of particles in the Indian sector of Southern Ocean. In this study, we compare the $^{230}$Th normalized vertical fluxes of both total sediments and opal (corrected for dissolution) to the $^{231}$Pa/$^{230}$Th ratios in four sediment cores that were sampled across the Subantarctic Front (SAF) and Polar Front (PF). To test the $^{231}$Pa/$^{230}$Th ratio tracer, we selected an area where vertical opal flux has varied quantitatively and spatially during the last 40 kyeas.

2. Material and methods

2.1. Core material

Six gravity cores taken along a transect across the Antarctic Polar Front and Subtropical Front from 54°S to 43°S were analyzed in this study (Table 1; Fig. 1). All cores were recovered as part of the “APSARA” program in 1984 and 1988, and during the “PACIMA” program in 1994. In choosing which cores to analyse, it was important that all frontal zones of the Antarctic Circumpolar Current were sampled. The selected cores hence consisted of two cores (MD 84-552, MD 88-773) located
within the Antarctic Zone, three cores (MD 88-769, MD 88-770 and MD 94-104) located in the Polar Frontal Zone and one core (MD 94-102) located in the Subantarctic Zone of the Southwest Indian Ocean. The core MD 88-773 was previously studied by François et al. (1992). An additional advantage of using these cores was that the results of our study could be calibrated with a good sedimentological, micropaleontological and stratigraphical data base produced at the Laboratoire des Sciences du Climat et de l’Environnement (LSCE, Gif/Yvette) and Département de Géologie et d’Océanographie (DGO, Bordeaux).

The gravity cores were sampled continuously with a resolution of 5–25 cm between samples depending on macroscopical changes in lithology and the previously determined stratigraphy.

2.2. Analytical methods

– U and Th isotopes were measured by alpha spectrometry after separation on anion exchange columns and deposition onto aluminum foil. Analytical precision for $^{230}$Th as determined from the uncertainty due to counting statistics was 5%. Samples were only occasionally run in duplicate and analytical precision was lower or equal to the uncertainty due to counting statistics. Analytical precision for $^{238}$U was 6% as determined from the uncertainty due to counting statistics.

– $^{231}$Pa activity was measured by alpha spectrometry through its short half-lived granddaughter $^{227}$Th (Mangini and Sonntag, 1977). Radioactive equilibrium is assumed between both nuclides because ingrowth of the intermediate $^{227}$Ac ($T_{1/2}=22$ years) is assumed to be achieved after about 100 years, a short time compared with the time scale over which sedimentary processes operate. In the alpha spectrum of thorium, four isotopes are measured: $^{232}$Th, $^{230}$Th, $^{228}$Th and $^{227}$Th. Energies of

<table>
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<th>Longitude (E)</th>
<th>Depth</th>
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</tr>
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<td>MD 88-770</td>
<td>46°0</td>
<td>90°3</td>
<td>3290</td>
</tr>
<tr>
<td>MD 88-773</td>
<td>52°5</td>
<td>109°5</td>
<td>2460</td>
</tr>
<tr>
<td>MD 84-552</td>
<td>54°6</td>
<td>73°5</td>
<td>1780</td>
</tr>
</tbody>
</table>

Fig. 1. Location of the gravity cores from the transect across the ACC.
the main alpha rays of $^{227}$Th are between 5.680 and 6.036 keV where several decay products of $^{228}$Th interfere, mainly $^{212}$Bi and $^{220}$Rn but also a $^{227}$Th daughter, $^{223}$Ra. The contribution of the three daughter nuclides to the $^{227}$Th peak can be determined exactly by an ingrowth calculation from the time of chemical separation, i.e. the Th deposition on the counting plate. In the present study this correction does not exceed 30% of the $^{227}$Th alpha peak. Uncertainty due to counting statistics is < 20%.

– The relative amount of biogenic silica in the sediments was obtained using the chemical dissolution method described by Mortlock and Froelich (1989) for carbonate-free sediments (Bareille et al., 1990).

2.3. Unsupported $^{230}$Th (excess $^{230}$Th)

2.3.1. Theory

Thorium-230 is produced at a rate $2.63 \times 10^{-5}$ dpm cm$^{-3}$ kyear$^{-1}$ in the oceanic water column from the radioactive decay of $^{234}$U dissolved in seawater. Because of the long (4 $\times$ 10$^5$ years) residence time of U in the ocean, its concentration in seawater shows no significant geographical variations (Ku et al., 1977). Since Th is strongly adsorbed by marine particulate matter, its residence time in the water column is short (<40 years, Moore and Sackett, 1964), and the rate of $^{230}$Th delivery to the sediments is equal to the rate of production; i.e., practically none of the $^{230}$Th is lost by decay in the water column. Measurements using deep-sea sediment traps (Anderson et al., 1983b) have confirmed that the production and vertical flux of $^{230}$Th carried by settling particles are nearly in balance. Thorium-230-normalized flux calculations are based on the assumption that the flux of $^{230}$Th to the seafloor is constant and equal to the rate of production (Bacon, 1984; Suman and Bacon, 1989; Francois et al., 1990). Excess $^{230}$Th activity in settling particulates is then inversely related to total mass flux. Hence, excess $^{230}$Th activities in the sediment (corrected for decay and ingrowth: cf. 2.3.2) can be used as a reference against which the flux of other sedimentary components can be established:

$$F_i = \beta Z f_i / ^{230}\text{Th}_{ex}$$  \hspace{1cm} (1)

where $F_i$ is the $^{230}$Th-normalized rain rate of the sedimentary component $i$; $\beta$ is the constant production rate of $^{230}$Th in the water column ($2.63 \times 10^{-5}$ dpm cm$^{-3}$ kyear$^{-1}$); $Z$ is the water depth; $f_i$ is the percentage of the sedimentary component $i$; $^{230}$Th$^o_{ex}$ is the activity of decay- and ingrowth-corrected excess $^{230}$Th in the sediment.

Although this approach permits the evaluation of fluxes in regions where sediment focusing leads to inhomogeneous patterns of sediment accumulation (Dezileau et al., 2000), it is limited by the fact that dissolution of labile biogenic phases also influences the ratio ($f_i / ^{230}$Th$^o_{ex}$) preserved in the sediments (Yang et al., 1986). For this reason the calculated fluxes are referred to here as “preserved fluxes”. However, it is possible to reconstruct the real vertical flux of the component $i$ (at the sediment–water interface) if we can quantify the dissolution of the biogenic component.

2.3.2. Calculating age-corrected excess $^{230}$Th activity at the time of deposition

There are two prerequisites for utilization of $^{230}$Th data to determine accumulation fluxes. First, the measured concentrations of $^{230}$Th have to be corrected both for detrital and authigenic contributions produced from decay of $^{234}$U in the sediment in order to calculate the amount of $^{230}$Th originating from scavenging in the oceanic water column (excess concentrations). Second, an independent time scale for the core is necessary to calculate the corresponding value at the time of deposition ($^{230}$Th$^o_{ex}$) for each measured $^{230}$Th$^o_{ex}$ content.

2.3.2.1. Evaluation of detrital and authigenic $^{238}$U activities. The total uranium-238 measured in the samples consists of two components: uranium present in detrital minerals ($^{238}$Ud) and bio-authigenic uranium ($^{238}$U ba) derived from seawater.

Detrital uranium ($^{238}$U$_d$) is estimated as:

$$^{238}\text{U}_d = (^{238}\text{U} / ^{232}\text{Th})_d (^{232}\text{Th})_s$$  \hspace{1cm} (2)

where ($^{238}\text{U} / ^{232}\text{Th})_d$ is the detrital U/Th ratio and ($^{232}\text{Th})_s$ is the measured content of $^{232}$Th in the
sediment samples. $^{232}$Th is considered to be present exclusively in detrital minerals.

The bio-authigenic uranium ($^{238}$U ba) contents of the samples were then calculated using the relation:

$$^{238}\text{U}_{\text{ba}} = \frac{^{238} \text{U}_T}{^{238} \text{U}_d}$$  \(\text{(3)}\)

where $^{238}\text{U}_T$ is the measured total uranium content.

In core MD 94-102, the good correlation of $^{232}$Th with $^{238}$U$_T$ ($r^2 = 0.8$) suggests that bio-authigenic uranium is not present. The detrital ($^{238}$U/$^{232}$Th)$_d$ ratio of 0.58 from this core is applied to the calculations for all cores in the study area.

In order to calculate the activities of detrital and bio-authigenic uranium, Francois et al. (1993) assumed a ($^{238}$U/$^{232}$Th)$_d$ activity ratio of the detrital sediment phase in the range of 0.5 to 1. Our U/Th ratio is within the range used in this and other previous studies.

2.3.2.2. Age corrected excess $^{230}$Th activity. The following equations are applied to calculate the age-corrected excess $^{230}$Th activity (noted $^{230}$Th$_{\text{ex}}$):

$$^{230}\text{Th}_{\text{ex}} = ^{230} \text{Th}_{\text{meas}} - (^{232}\text{Th} \times 0.58)$$

$$- \left( \frac{^{238}\text{U}_{\text{auth}}}{(1 - e^{-\lambda^{234}t}) + \lambda^{230}} \right) \left( 1 - e^{-\lambda^{234}t} \right)$$

$$\times ((^{234}\text{U}/^{238}\text{U} - 1)), \text{ with}$$  \(\text{(4)}\)

$$^{238}\text{U}_{\text{auth.}} = ^{238} \text{U}_{\text{meas}} - (^{232}\text{Th} \times 0.58)$$  \(\text{(5)}\)

($^{232}$Th $\times 0.58$) represents the estimate of the mean activity of detrital $^{238}$U in dpm g$^{-1}$; $\lambda^{230}$ and $\lambda^{234}$ are the corresponding decay constants of the $^{230}$Th and $^{234}$U in a year; $(^{234}\text{U}/^{238}\text{U})$ refers to the initial activity ratio of $^{234}$U and $^{238}$U at the time of sediment deposition; and $t$ is the age in years estimated from the previously determined stratigraphy.

The $^{238}$U$_{\text{auth.}}$ term represents the equilibrium activity of $^{230}$Th produced from authigenic uranium, assuming uranium precipitation occurred at the time of sediment deposition.

After the stratigraphy is established, the excess activities of the radionuclides are decay-corrected to the time of deposition of the sediment ($^{230}$Th$_{\text{ex}}$) according to the following equation:

$$^{230}\text{Th}_x = ^{230} \text{Th}_x \times e^{\lambda t}$$  \(\text{(6)}\)

2.4. Dissolution approach

In the modern environment, it is possible to calculate how much biogenic silica is dissolved at the sediment–water interface. However, this approach, based on dissolved silica profiles in pore water, cannot be applied to past sediment–water interface levels. Indeed, no reliable methods are presently available by which such an estimate can be achieved. Shemesh et al. (1989) artificially dissolved diatom assemblages from the Antarctic sediment–water interface by chemical leaching. This approach was used to artificially reproduce observed diatom assemblages from both Holocene and glacial level. The study concluded that dissolution transforms initial diatom assemblages to a diatom assemblage dominated by robust species at the final stage of dissolution, resulting in erroneous paleotemperature estimates derived from transfer functions. Pichon et al. (1992a) employed the same approach as Shemesh et al. (1989) in order to test whether dissolution can increase the uncertainty in temperature estimates based on transfer functions.

For this work, samples consisting of diatoms characteristic of each Antarctic biozonation were dissolved using the protocol of Shemesh et al. (1989). Samples were selected if they displayed two characteristics: first those samples judged to have a better preservation, based on smear slide observations such as minimum broken valves, high number of different species; second, those samples from high sedimentation sites. The rate of sedimentation is important as rapid sedimentation limits the dissolution of diatoms as they are rapidly buried, and hence experience only a short time in contact with undersaturated dissolved silica in pore-water. Samples taken from the Indian sector of the Permanently Open Ocean Zone (POOZ) and the Seasonal Ice Zone (SIZ) met the sample criteria for the dissolution experiment quite well. However, samples from the Subantarctic Zone (SAZ) were not a high sedimentation site. The two other samples used for the dissolution experiment, selected from
the Atlantic sector, were also visually quite well preserved and taken from high sedimentation zones.

Dissolved silicate concentrations were analyzed at different time during the dissolution experiment to see how much silica was removed from solid to solution as diatom assemblages changed. Modified diatom assemblages were included in the modern reference diatom data base of the transfer function of Pichon et al. (1992a) because they are a known source of variability related to dissolution. This data base contains the results from 124 Holocene core tops from the whole Southern Ocean plus 42 artificially dissolved samples. The first phase of the transfer function gave a new loading factor F4. This factor based on diatom assemblages is exclusively related to the amount of silica removed at each step of the chemical dissolution. Pichon et al. (1992a) then defined an empirical relationship between the value F4 and the percent of silica dissolved. The accuracy is around 20%.

Estimations made by Pichon et al. (1992a) and Bareille (1991) are not completely different from estimations made by other workers using dissolved silica profiles measured from modern sediment–water interfaces (Van Bennekom and Berger, 1988; DeMaster et al., 1991; Rabouille et al., 1997).

However, this approach can be criticized because the 100% preservation from Pichon et al. (1992a,b) refers more to the less dissolved samples in the transfer function rather than to the time at which diatom assemblages (and hence opal) reached the sediment–water interface.

Because dissolution experiments start with surface sediment that has already suffered dissolution of opal, the 100% preservation result given by the loading factor F4 is probably related to 100 − T%. The factor T is the percent opal dissolved to reach diatom assemblage equivalent to the less dissolved samples in the transfer function from diatom assemblages arriving at the sediment–water interface or deep traps. In their study of sediment traps, Gersonde and Wefer (1987) found that differences in the relative abundance of diatom species between traps and surface sediments result from the disappearance of the less silicified diatom valves leading to the enrichment of strongly silicified valves. Most of these changes seem to occur in the upper part of the water column (Gersonde and Wefer, 1987) because the diatom associations found on the surface sediment more closely resemble those of the deeper traps than the diatom assemblages in surrounding surface water. Anyway, the percent dissolution from Pichon et al. (1992a) corresponds to X (%) = TF (%) × [100 − T (%)]/100 when related to 100% preservation corresponding to the trap used by Pondaven et al. (2000).

The factor T can be estimated by comparing sediment trap data (Pondaven et al., 2000), the 230Th normalized accumulation rates of opal and the opal dissolution estimates of Pichon et al. (1992a), according to the following equations:

\[ T(\%) = D(\%) - X(\%) \]

with D equal to the percent dissolution calculated by Pondaven et al. (2000) by comparing the opal rain rates from sediment trap and the 230Th normalized accumulation rates of opal in the POOZ.

Replacing X(%) by TF(%) × [100 − T(%)]/100 in Eq. (1) gives:

\[ T = \left[D - \frac{TF}{100}\right]/\left[1 - \frac{TF}{100}\right] \]

Taking D = 58% from Pondaven et al. (2000) and TF = 51% from Table 2 for core MD 84-552, this gives an estimate of 14% for T and X = 44%.

It can then be postulated that the percent dissolution obtained by the empirical relationship of Pichon et al. (1992a) is a minimum. Furthermore, because T seems to be rather low, we postulate that the percent dissolution given by the empirical relationship from Pichon et al. (1992a) refers to 100% preservation at the sediment–water interface. This minimizes the underestimation of the percent dissolution from the transfer function. There is actually no other approach to estimate opal dissolution in past sediment.

Using the above reasoning allows to estimate the intensity of dissolution for each sediment level where diatom assemblages were determined and treated within the transfer function. So, using F4 and the empirical relationship determined by Bareille (1991) and Pichon et al. (1992a), we estimated opal dissolution for both Holocene and glacial intervals preserved in cores MD 88-770, MD 88-
Baseline stratigraphic age interpretation was focused on the determination of isotopic stage and substage boundaries using oxygen-isotope stratigraphy. Oxygen isotopic ratios were measured at the Laboratoire des Sciences du Climat et de l’Environnement (Gif-sur-Yvette) on planktonic foraminifera (*Neogloboquadrina pachyderma s.*), and on benthic foraminifera (*δ¹⁸O-values are reported to the Pee Dee Belemnites standard*).

The chronologies for the paleoceanographic records from cores MD 94-102, MD 88-769, and MD 88-770 were determined by Bareille (1991), Pichon et al. (1992b), Labeyrie et al. (1996) and Lemoine (1998) according to the following method.

First, accelerator mass spectrometry (AMS) ¹⁴C dating of *N. pachyderma s.* was used to generate a preliminary time scale spanning the last 30 kyears. Dating followed the standard procedures at the LSCE (gif-sur-Yvette) with sampling limited to peaks in relative abundance of the considered species in order to minimize the effect of bioturbation. AMS ¹⁴C ages were corrected by 480 years, the adopted mean reservoir age (Bard et al., 1990), in order to obtain corrected ages.

Second, the benthic foraminiferal *δ¹⁸O record was graphically correlated with the benthic record of equatorial Pacific core V19-30 (Shackleton and Pisias, 1985), using the Analyseries software developed at CFR (D. Paillard et al., CFR internal report, 1993).

For two of the cores, MD 94-104 and MD 84-552, we have no absolute age constraints. The proposed age scale for these cores was developed as follows: The core MD 84-552 was correlated graphically to core MD 84-551, which is located in the same area and has age constraints from both *δ¹⁸O* benthic records and AMS ¹⁴C ages (Labracherie et al., 1989).

The same procedure has been applied to cores MD 84-552, MD 88-769, MD 94-102 and MD 94-104 (Table 2).

### Table 2
Vertical, preserved opal vertical flux, vertical opal flux and Pa/Th data

<table>
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<tr>
<th>Cores</th>
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<th>Vertical flux (g cm⁻² ka⁻¹)</th>
<th>Preserved opal vertical flux (g cm⁻² ka⁻¹)</th>
<th>Dissolution (%)</th>
<th>Vertical opal flux (g cm⁻² ka⁻¹)</th>
<th>Pa/Th</th>
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<td></td>
<td>2</td>
<td>1.60 ± 0.10</td>
<td>1.10 ± 0.07</td>
<td>55</td>
<td>2.44 ± 0.24</td>
<td>0.20 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.25 ± 0.08</td>
<td>1.00 ± 0.06</td>
<td>59</td>
<td>2.44 ± 0.24</td>
<td>0.20 ± 0.03</td>
</tr>
</tbody>
</table>

“Stage” refers to marine isotope stage. “Vertical flux” refers to ²³⁰Th normalized total mass accumulation rate. “Preserved opal flux” is the opal accumulation rate evaluated by the ²³⁰Th normalization method. “Dissolution” is estimated using the diatom transfer function of Pichon et al. (1992a). “Vertical Opal flux” is estimated by dividing preserved opal flux by (1% dissolution). “Pa/Th” is the ²³¹Pa/²³⁰Th x ¹⁰⁰ ratio, i.e. ²³¹Pa and ²³⁰Th values are corrected for decay and for authigenic and detrital contributions.
used for core MD 94-104, which was correlated with core MD 88-769. The results are displayed on an age/depth plot for all the cores (Fig. 2).

4. Results and discussion

4.1. Total preserved rain rates

Application of Eq. (1) to \(^{230}\text{Th}_{\text{ex}}\) data reveals relatively low and constant preserved rain rates for the four northern cores with values recorded between 0.8 and 1.5 g cm\(^{-2}\) kyear\(^{-1}\) throughout the investigated period of time (Fig. 3). In core MD 84-552, which is located on the Kerguelen Plateau, preserved rain rates during the Holocene are represented by values of up to 3 g cm\(^{-2}\) kyear\(^{-1}\) while lower values are evident during glacial periods.

4.2. Preserved opal rain rates

4.2.1. Subantarctic zone

The low opal fluxes recorded throughout the investigated time period (40 kyears) in the northern core MD 94-102 are presumably due to low production of siliceous organisms in the overlying surface waters (Fig. 3).

4.2.2. Polar frontal zone

In cores MD 88-769, MD 94-104 and MD 88-770, even when low opal fluxes are recorded throughout the Holocene, relatively high opal fluxes are recorded during the glacial stages, presumably indicating higher production of siliceous organisms at this time (Fig. 3). The glacial rain rates for these cores (0.3 to 0.7 g cm\(^{-2}\) kyear\(^{-1}\)) are about a factor of 3 to 4 higher than the Holocene rates (0.09 to 0.15 g cm\(^{-2}\) kyear\(^{-1}\)). Estimates of opal dissolution from the diatom transfer function of Pichon et al. (1992a) did not reveal any clear difference in opal dissolution between glacial and warm periods and dissolution rates seem to be constant at a value of around 20% throughout the last 40 kyears recorded by the cores.

4.2.3. Antarctic zone

The pattern of biogenic opal rain rate in the southernmost core (MD 88-552) is very similar to the total sediment rain rate pattern, which is no surprise as the sediment consists of up to 65% biogenic opal. High rain rates between 0.6 and 2.6 g cm\(^{-2}\) kyear\(^{-1}\) are determined for the isotopic stage 1 (Fig. 3). During the glacial stages, low amounts of biogenic opal (0.4 g cm\(^{-2}\) kyear\(^{-1}\)) accumulated during the periods when dense sea ice cover likely covered the core location. Low opal
fluxes recorded during glacial stages also reflect higher opal dissolution due to lower sediment accumulation rates. Estimates of opal dissolution from the diatom transfer function of Pichon et al. (1992a) reveal an increase in opal dissolution from 51% in Holocene to 75% in isotopic stages 2 and 3.
4.3. $^{231}\text{Pa}_{\text{ex}}^{\circ}/^{230}\text{Th}_{\text{ex}}^{\circ}$

During the Holocene, the $^{231}\text{Pa}_{\text{ex}}^{\circ}/^{230}\text{Th}_{\text{ex}}^{\circ}$ ratio is below the production rate ratio (0.093) north of the Subantarctic Front (SF) (Fig. 3). It approaches 0.093 towards the Polar Front (PF), coinciding with a gradual increase in preserved opal rain rates (Fig. 3). South of the PF, the ratio is invariably higher than the production rate ratio. During the glacial period, the ratio is higher in cores MD 88-769, MD 88-770 and MD 94-104 and lower in core MD 84-552. These observations appear to record the northward shift of the Frontal system and the opal belt.

4.4. $^{231}\text{Pa}_{\text{ex}}^{\circ}/^{230}\text{Th}_{\text{ex}}^{\circ}$ documents past changes in opal export fluxes

In order to determine whether $^{231}\text{Pa}$ exhibits a stronger affinity for scavenging by biogenic opal than by other particulate phases, we compare six sediment cores sampled across the SF and PF in terms of the following:

1. $^{230}\text{Th}$ normalized total sediment preserved fluxes to the $^{231}\text{Pa}/^{230}\text{Th}$ ratios (average values for each isotopic stage) and,
2. $^{230}\text{Th}$ normalized preserved opal fluxes to the $^{231}\text{Pa}/^{230}\text{Th}$ ratios (average values for each isotopic stage).

A plot of the $^{231}\text{Pa}_{\text{ex}}^{\circ}/^{230}\text{Th}_{\text{ex}}^{\circ}$ ratios vs. total preserved sediment rain rates does not suggest a correlation between the two (Fig. 4). If we plot the $^{231}\text{Pa}_{\text{ex}}^{\circ}/^{230}\text{Th}_{\text{ex}}^{\circ}$ ratios vs. preserved biogenic opal rain rates, we can identify a correlation (Fig. 5, $r^2 = 0.76$), suggesting that $^{231}\text{Pa}$ exhibits a stronger affinity for scavenging by biogenic opal than by other particulate phases.

Kumar et al. (1993) suggested that unlike $^{230}\text{Th}$ normalized fluxes, the $^{231}\text{Pa}_{\text{ex}}^{\circ}/^{230}\text{Th}_{\text{ex}}^{\circ}$ ratio is not affected by dissolution on the sea floor. If this suggestion is true, we would observe a better correlation between $^{231}\text{Pa}_{\text{ex}}^{\circ}/^{230}\text{Th}_{\text{ex}}^{\circ}$ ratio and biogenic opal rain rates corrected for dissolution than with the preserved opal rain rates.

If we plot the $^{231}\text{Pa}_{\text{ex}}^{\circ}/^{230}\text{Th}_{\text{ex}}^{\circ}$ ratios vs. opal rain rates (i.e. corrected for dissolution), we can observe that the correlation is better (Fig. 6, $r^2 = 0.9$) as predicted by Kumar et al. (1993).

As a result, the increase in Pa/Th with opal rain rates corrected from dissolution can be expressed according to this linear regression:

$$\text{Pa/Th} = (0.05 \times O_{\text{FC}}) + 0.09$$  \hspace{1cm} (9)

with $O_{\text{FC}}$ representing the minimum opal rain rates, i.e. the rain rate corrected for estimated percentage opal dissolution according to the method of Pichon et al. (1992a).

This correlation is rather surprising if we consider that a certain number of processes, not previously
mentioned, can affect the Pa/Th ratio. There are two principal processes:

(1) Changes in Pa exported from the Atlantic to the Antarctic Circumpolar Current (ACC) via inflow of North Atlantic Deep Water (NADW) between glacial and interglacial times.

Recently, Chase et al. (2002) have shown that the supply of dissolved Pa in the Pacific sector of the Southern Ocean by advected deep water is just as great in the Atlantic, despite the absence of a Pacific equivalent of NADW. The reason for this is that large-scale meridional overturning circulation transports a volume of water much greater than that attributable to NADW alone (i.e., in terms of mass transport, NADW exported from the Atlantic represents only 20% of the total southward flow of deep water into the Southern Ocean). Most of the meridional overturning flow is driven by processes in the Southern Ocean that are independent of the flow of NADW. The reason for this is that large-scale meridional overturning circulation transports a volume of water much greater than that attributable to NADW alone (i.e., in terms of mass transport, NADW exported from the Atlantic represents only 20% of the total southward flow of deep water into the Southern Ocean). Most of the meridional overturning flow is driven by processes in the Southern Ocean that are independent of the flow of NADW. Consequently, climate-related changes in formation of NADW will have had an insignificant effect on the advective supply of dissolved Pa to the Southern Ocean. In that case, changes in Pa exported from the Atlantic to the ACC do not alter the linear regression between the $^{231}\text{Pa}_{\text{ex}}/^{230}\text{Th}_{\text{ex}}$ ratios and opal rain rates in the Indian sector of the Southern Ocean.


There are different studies (Rutgers van der Loeff and Berger, 1993; Kumar et al., 1995; Walter et al., 1997; Chase et al., in press) which have also suggested that the affinity of particles for Pa increases with the increasing opal content. However, Chase et al. (2002) have also recently shown that opal is less effective in scavenging Th than are other particle phases (i.e., detrital phase for example). So, it is possible that the linear regression is useful only in circumstances where opal fluxes are much greater than the fluxes of detrital particles (which is the case in this work). For example, the algorithm may fail to predict opal fluxes in areas that have high fluxes of lithogenic material. This possibility needs to be tested by further work.

Finally, unlike $^{230}\text{Th}$ concentration in sediments and $^{230}\text{Th}$ normalized sediment fluxes, the ratio $^{231}\text{Pa}_{\text{ex}}/^{230}\text{Th}_{\text{ex}}$ is not affected by dissolution on the sea floor. Hence, the ratio documents past changes in opal export fluxes rather than the preserved opal rain rates. So, as already suggested, we can demonstrate that $^{231}\text{Pa}$ exhibits a stronger affinity for scavenging by biogenic opal and this preference may contribute to high $^{231}\text{Pa}/^{230}\text{Th}$ ratios in the southernmost cores (MD 84-552 and MD 88-773) and to the low $^{231}\text{Pa}/^{230}\text{Th}$ ratios in the northernmost core, where opal accumulation rates and concentrations remain relatively low throughout the record.

If this observation is confirmed and taking some precautions, the $^{231}\text{Pa}_{\text{ex}}/^{230}\text{Th}_{\text{ex}}$ ratio may be used to quantify silica fluxes and, thus, to constrain how sedimentation has been reduced by biogenic dissolution in sediments over time in the Indian sector of the Southern Ocean.

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