

The influence of particle composition and particle flux on scavenging of Th, Pa and Be in the ocean

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Abstract

We have examined the relative affinity of Th, Pa and Be for sorption from seawater onto particles of variable composition (opal, carbonate, lithogenic particles and organic carbon). Nuclide concentrations in particles collected from time-series sediment traps were normalized by the dissolved nuclide concentration in the overlying water column in order to compute partition coefficients under conditions spanning a wide range of particle flux and particle composition. Our results suggest that the affinity of particles for Pa and Be increases with their increasing opal content and decreasing carbonate content, while the affinity of particles for Th increases with increasing carbonate content, and decreases with increasing opal content. We find no correlation between the aluminosilicate content of particles and their affinity for scavenging of any of these elements. Extrapolating to a pure CaCO_3 end member, the partition coefficient for Th ($9.0 \times 10^6 \text{ g g}^{-1}$) is ~ 40 times greater than for Pa, and roughly 100 times greater than for Be, whereas for a pure opal end member, the partition coefficient for Th ($3.9 \times 10^5 \text{ g g}^{-1}$) is slightly less than that for Pa and Be. Partition coefficients decrease with increasing particle flux in open-ocean settings, but not in an ocean-margin region. This kinetic effect reflects the increasing contribution of unaltered surface material reaching the sediment traps as particle flux increases. The degree of fractionation between Pa and Th and between Be and Th depends on the opal:carbonate rain ratio. These results challenge the use of sedimentary $^{231}\text{Pa}/^{230}\text{Th}$ and $^{10}\text{Be}/^{230}\text{Th}$ ratios as simple proxies of particle flux. However, the strong dependence of nuclide scavenging on the opal:carbonate rain ratio may provide a needed tool for reconstructing past changes in planktonic community composition.

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1. Introduction

Like many trace elements, dissolved Th, Pa and Be are removed from the oceans by particulate scavenging and subsequent burial in sediments [1,2]. Among these three elements, Th is the most reactive, with a residence time in the ocean

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of 10–50 yr with respect to removal to the sediments [3]. Thorium-230 (half-life 7.5×10^4 yr) is removed from solution so effectively that its rain to the seafloor is largely independent of particle flux, and approximately equal to its (known) rate of production by decay of ^{234}U in the overlying water column [4,5]. Protactinium-231 (half-life 3.2×10^4 yr), a product of ^{235}U decay, and ^{10}Be (half-life 1.5×10^6 yr), a cosmogenically produced radionuclide, are less particle-reactive than Th, and have oceanic residence times with respect to scavenging of 50–100 yr [3] and 500–1000 yr [6], respectively. In contrast to ^{230}Th , in regions of low particle flux, the rain of ^{231}Pa to the seafloor is often less than its integrated production rate by decay of ^{235}U in the overlying water column. Similarly, the rain of ^{10}Be in regions of low particle flux is less than the global average production rate of ^{10}Be .

If scavenging is independent of particle composition, then the probability for scavenging depends on the particle surface area available for uptake and exchange of dissolved species. In general, then, one expects the removal of reactive elements to be greatest in regions of high particle flux, such as ocean margins. Indeed, ^{231}Pa [7], ^{10}Be [6], and, to a lesser degree, ^{230}Th [7] are all scavenged preferentially at ocean margins, a process that has been called ‘boundary scavenging’ [8]. The extent to which an element’s fate in the ocean is influenced by boundary scavenging depends on the relative magnitude of its residence time with respect to scavenging ($\tau(\text{scav})$) and the mixing time for lateral transport, which can be thought of as a water residence time ($\tau(\text{mix})$) [9]. Highly particle-reactive metals with low solubility are rapidly removed from solution, such that $\tau(\text{scav}) \ll \tau(\text{mix})$ and downward vertical flux dominates over lateral transport. As $\tau(\text{scav})$ increases for less particle-reactive elements, $\tau(\text{scav})$ approaches $\tau(\text{mix})$, lateral transport becomes a significant term in the mass budget of an element and the downward flux of a scavenged element becomes proportional to particle flux. To the extent that the downward flux of Th is insensitive to particle flux, and the downward fluxes of Pa and Be are proportional to particle flux, the ratios of adsorbed Pa/Th and Be/Th preserved in ocean

sediments can serve as indicators of past particle flux [6,10,11].

In reality, different oceanic particle types almost certainly differ in their ability to scavenge reactive elements from seawater, so that scavenging should depend both on particle flux and on particle composition. The focus of this study is the extent to which particle composition affects the scavenging of, and fractionation between, Th, Pa and Be. A variety of methods have been used previously to study the effect of particle composition on nuclide scavenging. These include laboratory studies with idealized particulate phases (e.g. [12]), observations of geographic variability in solid–solution partitioning of nuclides [7,13], correlation between nuclide concentrations and carrier phases in sediments [14–16], and finally, sediment-trap studies where nuclide fluxes are observed as a function of particle composition [15,17–21]. There are complications with each of these approaches. The laboratory studies may not be applicable to real marine particles in a seawater solution [22]; studies of sediment composition may be biased by post-depositional dissolution of biogenic components; sediment-trap studies may be biased by not covering the full range of oceanic particle compositions, or by not accounting for differences in the local pool of dissolved nuclides, from which nuclides are scavenged. Strategies that involve physical separation or chemical dissolution (selective leaching) of particles to determine the specific association of radionuclides risk biasing due to redistribution of particle-reactive nuclides from one phase to another.

The approach taken here is to combine measurements of nuclide concentrations in particles collected by time-series sediment traps with measurements of nuclide concentrations in the water above the sediment traps to obtain ‘bulk partition coefficients’ – K_{ds} – as a function of particle composition. Recent US-JGOFS (Joint Global Ocean Flux Study) sediment-trap deployments in the Southern Ocean [23] and the equatorial Pacific (EqPac) [24] provide predominantly opal-rich and carbonate-rich end members, respectively. We combine these data with K_{d} values calculated from the literature, in order to cover a wide range of particle compositions.

2. Methods

2.1. Sample collection

Sediment-trap material was collected in the equatorial Pacific along 140°W, between 9°N and 12°S in 1991–93, and in the Southern Ocean along 170°W between 65°S and 53°S in 1996–98, as part of the US JGOFS EqPac and AESOPS (Antarctic Environment and Southern Ocean Process Study) programs, respectively. In November–December 1992 for EqPac and February–April 1998 for AESOPS, water-column samples were taken for the analysis of total (dissolved+particulate) nuclide concentration. Sediment-trap material from the Mid Atlantic Bight was collected in 1984 from the SEEP-I transect south of Cape Cod [25]. These data are combined with water-column profiles of ^{230}Th and ^{231}Pa (R. Francois, unpublished data) and ^{10}Be [26] from the same region to calculate K_d s, as described below.

2.2. Radionuclide data

In order to obtain sufficient sediment-trap material for radionuclide analyses some individual sample cups had to be combined into composite samples. Thorium-232, ^{230}Th and ^{231}Pa concentrations in AESOPS trap samples were measured by isotope-dilution inductively coupled plasma mass spectrometry and for ^{10}Be by accelerator mass spectrometry [36]. U-series and ^{10}Be concentrations in EqPac trap samples were measured by isotope-dilution alpha spectrometry and accelerator mass spectrometry, respectively [17]. Analysis of seawater samples for ^{232}Th , ^{230}Th and ^{231}Pa was by thermal ionization mass spectrometry and for ^{10}Be by accelerator mass spectrometry [40,53]. All particulate ^{231}Pa and ^{230}Th concentrations reported here are ‘excess’ concentrations (e.g. $^{231}\text{Pa}_{\text{ex}}$ and $^{230}\text{Th}_{\text{ex}}$), and have been corrected for the presence of ^{231}Pa and ^{230}Th supported by detrital U. Details are provided in [36].

2.3. Particle composition

Sample composition (%organic carbon, %opal and %carbonate) and mass flux data for AE-

SOPS, EqPac and SEEP traps were taken from [23–25], respectively. For composite samples the measured weights of each contributing sample aliquot (the entire (1/10)th split) were used to derive a composite composition. Honjo et al. [23] measured opal by analyzing Si and Al by ICP-ES after sample digestion and then subtracting a detrital contribution, proportional to Al, from the total Si to get biogenic Si. Because of concerns about the mass balance of components being significantly less than 100% in some AESOPS trap samples, we re-analyzed a subset of these samples (including both individual and composite samples) for opal by the method of Mortlock and Froelich [27]. These results were indistinguishable from those reported by Honjo et al. [23]. For the AESOPS samples, lithogenic content was estimated from measurements of ^{232}Th , assuming a purely detrital source for ^{232}Th [28] and an average ^{232}Th content of 10 ppm in detrital material [29]. For the EqPac samples, the percentage of lithogenic material was estimated by assuming a Ti content of 0.4%, typical of average crustal material [29]. For the SEEP traps, lithogenic content was estimated as $100 - (\%opal + \%carbonate + 2 \times \%organic\ carbon)$.

2.4. Calculation of partition coefficients from sediment-trap data

Partition coefficients (K_d) describe the equilibrium partitioning of a species between the dissolved and the particulate phase. Field-based estimates of K_d are usually derived from the ratio of particulate nuclides, per g of filtered particles, to dissolved nuclides, per g of seawater (e.g. [30–32]). Here we define a ‘pseudo- K_d ’ as the ratio of nuclides per g of trapped particles to total nuclides (dissolved+particulate) per g of seawater in the water through which the particles sank (see also [20]). Because the residence time of dissolved nuclides is of the order of tens of years or more, their concentration does not vary seasonally (at least below the surface mixed layer), so it is valid to combine time-series data from sediment traps with water-column measurements made at a single point in time.

For each sediment-trap sample, the partition

Table 1

Correlation coefficients (r) for the relationships between $\log K_d(K)$, where $K = \text{Th, Pa or Be}$, and particle composition (Fig. 1), not including the SEEP samples

	Opal	Carbonate	Lithogenics	Organic carbon
Thorium	-0.77	0.81	0.39	n.s.
Protactinium	0.67	-0.63	n.s.	-0.49
Beryllium	0.85	-0.86	n.s.	-0.34

n.s. = not significant ($P < 0.005$).

coefficient for nuclide i , $K_d(i)$, was calculated as $[i]_{\text{trap}}/[i]_{\text{water}}$, where $[i]_{\text{trap}}$ is the activity of nuclide i per g of trapped particles and $[i]_{\text{water}}$ (dpm g^{-1}) is the average activity of nuclide i throughout the water column 1000 m above the depth of the sediment trap. A 1000 m depth interval was selected because modeling work has suggested that the exchange between large sinking particles and the small suspended particles presumed to be in equilibrium with respect to ^{230}Th scavenging, occurs over a depth of about 1000 m [33]. The validity of this assumption is examined in more detail in section 4.2. Profiles of total ^{230}Th , ^{231}Pa and ^{10}Be were used to calculate average water-column concentrations, using simple trapezoidal integration. Although we have used the total concentration of nuclides in the water (dissolved+particulate) to calculate K_d , previous work has shown that the concentrations of particulate Th and Pa are in general less than 10% of their dissolved concentrations (e.g. [30,34,35]).

The sediment-trap and water-column nuclide concentrations, sediment-trap particle composition, and the derived K_d s are available in electronic form (see Appendix 1 in the **Background Data Set**¹). A note on data sources: the AESOPS data are presented in Chase et al. [36], the EqPac data have not been previously published, the SEEP sediment-trap ^{230}Th , ^{232}Th and ^{231}Pa data are from Anderson et al. [37], and the SEEP sediment-trap ^{10}Be data have not been previously published. The SEEP-region water-column ^{230}Th and ^{231}Pa data are from 31°50'N/64°10'W and 36°17'N/68°44'W (R. Francois, unpublished data, 2001), and the SEEP-region dissolved ^{10}Be

data at 41°32'N/63°37'W and 34°1.0'N/63°0.0'W are from Ku et al. [26].

3. Results

The use of a pseudo- K_d , defined above, is a convenient way to evaluate the influence of particle composition on nuclide scavenging. The K_d s calculated in this way have the same units as conventional K_d s (g g^{-1}), and absolute values that are consistent with conventional K_d s. From our compilation of K_d s (Appendix 1 in the **Background Data Set**¹), we calculate an average $K_d(\text{Th})$ of $4.8 \times 10^6 \text{ g g}^{-1}$, an average $K_d(\text{Pa})$ of $5.7 \times 10^5 \text{ g g}^{-1}$ and an average $K_d(\text{Be})$ of $3.4 \times 10^5 \text{ g g}^{-1}$. Typical values of $K_d(\text{Th})$ estimated by filtration range from 10^4 to 10^7 g g^{-1} [31], with $K_d(\text{Pa})$ being about an order of magnitude lower, at least in the open ocean [3].

The nuclide partition coefficients show distinct trends with respect to particle composition. At the EqPac and AESOPS sites, which are dominated by biogenic particles (%opal+carbonate \cong 100%) both $K_d(\text{Pa})$ and $K_d(\text{Be})$ increase with increasing opal content and decreasing carbonate content of particles, while $K_d(\text{Th})$ increases with increasing carbonate and decreasing opal content of particles (Fig. 1A). The samples from the Mid Atlantic Bight (MAB) have a lithogenic content much larger than at other sites, and in general the K_d s for these samples show different trends than EqPac and AESOPS with respect to %opal and %carbonate. Excluding the sites from the MAB, strong and statistically significant correlations are found between $\log(K_d)$ and opal and carbonate content, for all nuclides, whereas weak or statistically insignificant correlations are found between $\log(K_d)$ and lithogenic and organic carbon con-

¹ <http://www.elsevier.com/locate/epsl>.

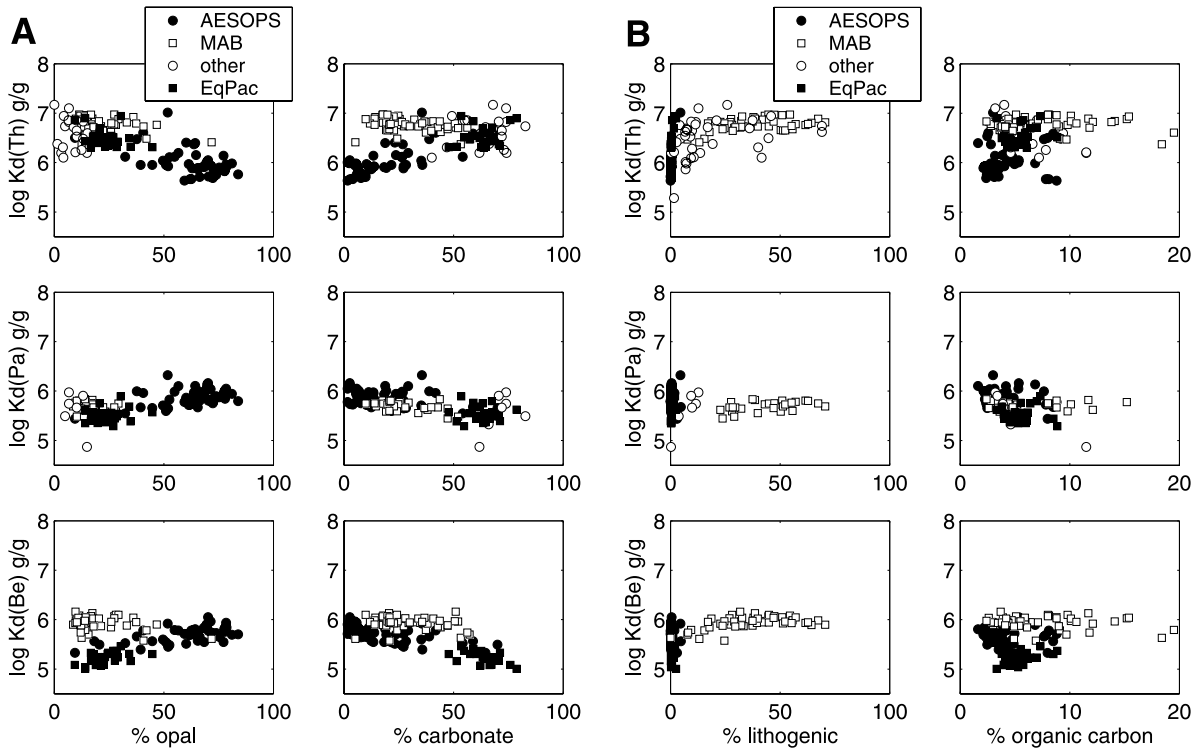


Fig. 1. (A) Partition coefficients (K_d) for Th, Pa and Be as a function of opal and carbonate content of particulate matter. Note the logarithmic scale for the y axis. Data are from the SW Pacific sector of the Southern Ocean (AESOPS), the equatorial Pacific (EqPac), the Mid Atlantic Bight (MAB; calculated from the Pa and Th trap data of [37] and previously unpublished ^{10}Be trap data (Appendix 1 in the **Background Data Set**¹) together with dissolved ^{10}Be data from [26] and unpublished dissolved ^{231}Pa and ^{230}Th data from R. Francois) and ‘other’ data calculated from the sediment-trap studies of Anderson et al. [7], Anderson et al. [3], and Scholten et al. [18] as well as the K_d data reported by Guo et al. [52] based on filtration. Data from open-ocean environments (AESOPS and EqPac) are plotted in solid symbols. (B) Same as A, only partition coefficients (K_d) for Th, Pa and Be are plotted as a function of the lithogenic and organic carbon content of particulate matter. Where %lithogenic was not reported it was estimated by assuming either a ^{232}Th content of 10 ppm, a Ti content of 0.4%, or an Al content of 8%, typical of average crustal material [29]. For the MAB, lithogenic content was estimated as $100 - (\%opal + \%carbonate + 2 \times \%organic\ carbon)$. The data in this figure are available on-line in tabular form (see Appendix 1 in the **Background Data Set**¹).

tent (Table 1). If only data from traps deeper than 3000 m (26 samples) are considered, the correlations between %opal and both $K_d(\text{Pa})$ and $K_d(\text{Th})$ are significantly lower (0.47 and 0.54 for Th and Pa, respectively), whereas the correlation between %opal and $K_d(\text{Be})$ is almost the same in the deep samples (0.85) as it is in the complete data set.

A fractionation factor, F , can be defined as the ratio of K_d values for two different nuclides, and describes the fractionation between nuclides during scavenging [3,7]. The fractionation factor, $F(\text{Th}/\text{Pa})$ ($=K_d(\text{Th})/K_d(\text{Pa})$), together with the

dissolved Pa/Th ratio, determines the Pa/Th ratio of particles that reach the sediments and form the paleo-record. Our data show clearly that the fractionation of Th relative to Pa ($F(\text{Th}/\text{Pa})$) and relative to Be ($F(\text{Th}/\text{Be})$) varies with particle composition (Fig. 2). Specifically, the lack of a relationship between F and %lithogenic and %POC suggests the fractionation between Pa (or Be) and Th depends primarily on the balance between the biogenic components opal and carbonate, rather than on the absolute contribution of biogenic versus lithogenic fluxes. When the bio-

Table 2

Correlation coefficients (r) for the relationships between $K_d(K)$, where $K = \text{Th, Pa or Be}$, and either %opal (C) or log particle flux (F), not including the SEEP samples

	Th	Pa	Be
$r_{_KC}$	-0.77	0.67	0.85
$r_{_KF}$	-0.76	0.34	0.59
$r_{_KC(F)^a}$	-0.49	0.66	0.76
$r_{_KF(C)^b}$	-0.45	-0.30	-0.08

Partial correlation coefficients are also presented, where $KF(C)$ is the partial correlation coefficient between K_d and flux, holding %opal constant and $KC(F)$ is the partial correlation coefficient between K_d and %opal, holding flux constant. All regressions are significant at $P < 0.005$, except the partial correlation coefficient between $K_d(\text{Be})$ and F , holding C constant – $r_{_KF(C)}$ – which is not significantly different from zero. The sample size is between 73 and 77.

^a The partial correlation coefficient between K_d and %opal (C), holding flux (F) constant.

^b The partial correlation coefficient between K_d and flux (F), holding %opal (C) constant.

genic component is dominated by carbonate, scavenging strongly favors Th ($F \cong 10$) as found in the oligotrophic gyres [3]. Where the particle flux is dominated by opal, as in the Southern Ocean, sinking particles essentially do not fractionate between Th, Pa and Be (i.e. $F(\text{Th}/\text{Pa})$ and $F(\text{Th}/\text{Be})$ both $\cong 1$). This is due not only to the strong affinity of opal for Pa (Fig. 1; [13]) and for Be (Fig. 1), but also, to the weaker affinity of opal for Th, relative to other particle types (Fig. 1).

4. Discussion

4.1. Effect of particle composition on nuclide partition coefficients

The results provide clear evidence that opal, carbonate and lithogenics are all important scavengers, and each nuclide (Th, Pa and Be) has a different suite of K_d s for each phase. The EqPac and AESOPS sites form a convenient two-end-member system, where lithogenic material is unimportant. Results from these sites support the suggestion that Pa [13,14,21] and Be [14,17] are more effectively scavenged by opal than by carbonate. From the EqPac and AESOPS data we

extrapolate K_d s for Th, Pa and Be with respect to pure opal of 3.9×10^5 , 1.4×10^6 and 1.1×10^6 , respectively, and K_d s for Th, Pa and Be with respect to pure carbonate of 9.0×10^6 , 2.2×10^5 and 9.1×10^4 , respectively. Extrapolating to a pure lithogenic end member is more tenuous, primarily because most of the samples with high lithogenic contents are from the MAB, where total particle fluxes are very high and where sediment remobilization is significant [37]. However, some trends are evident. The samples from the MAB clearly do not support the claim [16,19] that Be is scavenged primarily by clays; Be has a high affinity for both opal and lithogenics, and a low affinity for carbonate (Fig. 1). Pa appears to be scavenged equally (poorly) by lithogenics and carbonate, and Th appears to be scavenged equally (strongly) by lithogenics and carbonate.

The compiled results offer no support for the suggestion (e.g. [15]) that lithogenic phases are the primary agents responsible for scavenging of Th and Pa from seawater, even in regions of minimum lithogenic flux. Specifically, Luo and Ku [13] concluded that lithogenic phases have a $K_d(\text{Th})$ that is 490 times greater than that of biogenic particles, and a $K_d(\text{Pa})$ that is 45 times greater than that of biogenic particles. Results in Fig. 1B show these conclusions to be incorrect. The partition coefficient for Th would show a much greater sensitivity to the lithogenic content of particles than is observed if the $K_d(\text{Th})$ of lithogenic particles were truly 490 times larger than the K_d values of biogenic phases. Rather, given the insensitivity of $K_d(\text{Th})$ to the lithogenic content of particles (Fig. 1B), the large $K_d(\text{Th})$ values observed for samples high in CaCO_3 but low in lithogenic content (Fig. 1) indicate that CaCO_3 has an affinity for Th at least as large as that of lithogenic phases. Similarly, the largest $K_d(\text{Pa})$ values observed in our compilation are from samples that have the maximum opal content, but low lithogenic contents, whereas samples with maximum lithogenic contents and low opal contents have intermediate values of $K_d(\text{Pa})$. These results indicate that opal has a larger $K_d(\text{Pa})$ than do lithogenic phases.

Luo and Ku [15] concluded, in addition, that neither opal nor CaCO_3 impose a significant frac-

tionation between Th and Pa during scavenging. Our compiled results show this to be incorrect as well. Extrapolating EqPac and AESOPS results in Fig. 1 to pure end-member compositions indicates that scavenging by CaCO_3 strongly favors uptake of Th over Pa [$K_d(\text{Th})/K_d(\text{Pa}) \sim 42$], whereas scavenging by opal imparts a smaller fractionation, and in the opposite sense [$K_d(\text{Th})/K_d(\text{Pa}) \sim 0.3$]. Indeed, the relative proportion of opal and carbonate in sinking particles is far more important than the lithogenic content of particles in determining the fractionation between Th and Pa, as well as between Th and Be (Fig. 2).

A careful examination of the experimental approach used by Luo and Ku [15] reveals an artifact that created an apparent association of Th with lithogenic phases. Their approach separated particles by size and density. The fine-grained size fraction, to which most of the ^{230}Th was adsorbed, contained most, if not all, of the lithogenic phases as well. The coarsest size fraction, dominated by calcareous foraminifera, held relatively little ^{230}Th because of its smaller surface area to mass ratio. Consequently, the ^{230}Th content of sediments appeared to show a positive correlation with lithogenic content, and a negative correlation with CaCO_3 content, due to the fact that particle size was not independent of particle composition

in their study. Because our results (Fig. 1) were obtained without physical or chemical fractionation of particles, they provide more reliable relationships between partition coefficients and particle composition than those reported by Luo and Ku [15]. With the more reliable methods used here, we see that biogenic particles scavenge Th, Pa and Be at least as efficiently as do lithogenic phases. Furthermore, opal and CaCO_3 lie at the opposite ends of the spectrum with respect to fractionation between Th and Pa, with CaCO_3 exhibiting the maximum fractionation and opal virtually none.

The surface chemical properties of the various particle phases leading to the observed trends are unknown, but the trends are robust in that they are internally consistent throughout diverse oceanic environments (Atlantic, equatorial Pacific, Southern Ocean). This suggests that the empirical relationships reflect the intrinsic surface properties of the major particle phases, and that chemical properties of inorganic (biogenic) phases regulate scavenging in the ocean. This result is surprising in light of growing evidence that organic phases are the primary scavengers for many reactive elements in the ocean [22,38,39]. However, most of the evidence for scavenging by organic phases comes from surface waters, and it may be that

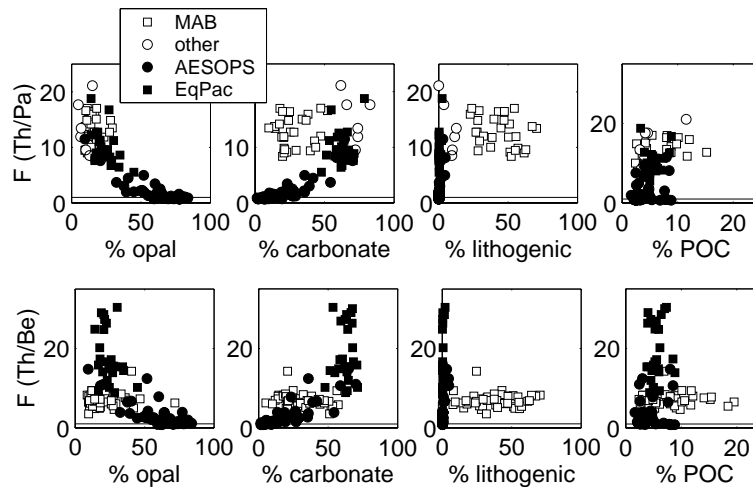


Fig. 2. Fractionation factor ($F = K_d/K_d$) as a function of particle composition from a compilation of sediment-trap studies (for references see Appendix 1 in the **Background Data Set**¹). Data from open-ocean environments (AESOPS and EqPac) are plotted in solid symbols. The $F=1$ line, indicating no fractionation between Th and Pa or between Th and Be, is drawn in each panel. An expanded x axis scale (0–25%) is used in the POC panel.

scavenging by organic phases is less important below the biologically active surface layer. Laboratory studies have shown that, above pH 5–6, Th does not sorb appreciably to silica [12], but similar data are not available for sorption of Pa and Be to opal. We are not aware of any laboratory studies reporting the sorption of these nuclides to CaCO_3 in seawater. It is conceivable that the correlations we observe between nuclide partition coefficients and the inorganic biogenic phases opal and carbonate arise because these phases are associated with different organic coatings, and it is these (tightly associated) organic coatings that are in fact responsible for scavenging. However, we are unaware of any evidence to support that possibility.

4.2. The role of particle flux

The use of sediment traps to infer partition coefficients as a function of particle composition has the disadvantage that the results may be influenced by particle flux, in addition to particle com-

position. Indeed, we find some correlation between particle flux and partition coefficients in the sediment-trap data set (Fig. 3). In theory, K_d should be independent of particle flux, but the ‘pseudo- K_d ’ calculated from sediment-trap data may be sensitive to particle flux, if, for example, as mass flux increases, particles collected by sediment traps are increasingly less completely equilibrated with the dissolved and suspended nuclides in the 1000 m above the sediment trap. Particle flux and particle composition are in general not independent variables, because high-flux regions tend to be dominated by diatoms (opal) [40]. Because both particle flux and particle composition may in theory affect K_d , it becomes difficult to separate the two influences in the empirical data.

Further statistical analyses can shed some light on this problem. First we consider only the EqPac and AESOPS data, which show the strongest relationships between particle flux and K_d and between %opal and K_d . Following this we will address the lack of a relationship between K_d and particle flux at the MAB site. Within the AESOPS

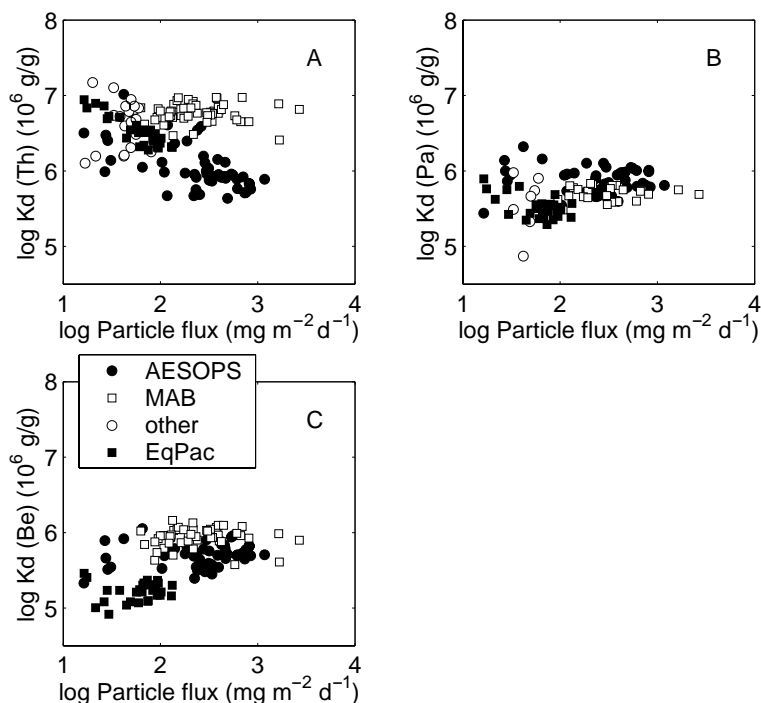


Fig. 3. Relationships between particle flux and K_d for Th (A), Pa (B) and Be (C) from the AESOPS, EqPac and MAB and other sediment-trap studies. See Fig. 1 for sources of ‘other’ data.

and EqPac data we find a significant positive correlation ($r^2 = 0.52$; $P < 0.005$) between %opal and (log) particle flux, which is consistent with the view that diatoms are prominent among phytoplankton taxa in regions of high particle flux [40]. For Th, the negative correlation between K_d and particle flux is just as strong as between K_d and %opal (Table 2), whereas for Pa, and especially for Be, the relationship between K_d and particle flux is much weaker than between K_d and %opal (Table 2). If particle flux was the dominant influence on K_d , and if the apparent particle-composition effect (e.g. Fig. 1) were entirely due to the correlation between particle composition and particle flux, then for each nuclide the correlation between K_d and particle flux should be equal to the correlation between K_d and particle composition. Because this is not observed, we conclude that K_d is affected by both particle flux and particle composition. Partial correlation coefficients, which describe the correlation between two variables while holding all other variables constant [41], help elucidate the nature of the composition and flux effects on K_d . The partial correlation coefficients indicate that the importance of the flux effect decreases as $\text{Th} > \text{Pa} > \text{Be}$, while the importance of the composition effect decreases in the opposite sense, as $\text{Be} > \text{Pa} > \text{Th}$ (Table 2). Indeed, Be is unaffected by the flux effect, while the strong negative correlation between $K_d(\text{Th})$ and %opal (Fig. 1A, Table 2) is driven at least in part by a strong negative correlation between $K_d(\text{Th})$ and particle flux.

Within the combined data from EqPac and AE-SOPS we find for Th, Pa and Be that, as particle flux increases, the apparent K_d decreases. For Pa and Be, this tendency is offset by the fact that during periods of high flux, particle composition is dominated by opal, while the opposite is true for Th.

The trend of decreasing K_d s with increasing particle flux may be understood if, during periods of high flux, unaltered material from the surface makes up a large proportion of the material caught by the sediment traps. This surface material has low nuclide concentrations, because it is formed at the surface, where dissolved nuclide concentrations are low, and does not have suffi-

cient time to acquire nuclides through adsorption during its transit to the sediment trap. The fact that average sinking rates increase with particle flux [42] also contributes to this effect.

Results from the MAB differ from those described above in that K_d values do not exhibit a measurable dependence on particle flux (Fig. 3). We believe this is due to the fact that particle flux to the MAB sediment traps varies primarily as a consequence of lateral transport of particles [25], rather than as a result of variable biological productivity and export of biogenic particles from surface waters. Laterally transported particles, in contrast to surface-derived particles, may well have been suspended in the water column for a period of time long enough to have achieved adsorption–desorption equilibrium with surrounding seawater. In that case, K_d is expected to be insensitive to particle flux because an increase in the flux of particles collected by sediment traps reflects an increase in the collection of particles that have reached a similar degree of adsorption–desorption equilibrium with the surrounding water mass.

More detailed study of the upper water column, including sampling of both sinking and suspended particles, and greater temporal coverage of dissolved nuclide concentrations, should help resolve this issue.

4.3. Implications

4.3.1. ^{230}Th as a constant-flux proxy

An important application of ^{230}Th in marine science is its use as a constant-flux proxy (CFP). The flux of ^{230}Th to the seafloor has been found to be largely independent of particle flux, and roughly equal to its known rate of production by U-decay in the overlying water column [4,5]. The fact that the flux of ^{230}Th is constant and known makes it a valuable reference for estimating the accumulation rates of other sedimentary components in the face of post-depositional sediment focusing or winnowing [43,44].

Thorium has typically been assumed to be scavenged equally by all particle types [5,13] and an important question to resolve is whether composition-dependent scavenging of Th affects the util-

ity of ^{230}Th as a CFP. For example, if ^{230}Th is scavenged below its production rate when and where opal dominates the particulate flux, then rain rates calculated by normalizing to ^{230}Th concentrations may be systematically over-estimated in regions and at times when the particle flux is dominated by opal.

Sediment traps deployed for at least 1 year can be used to compare the flux of ^{230}Th at a given location (F) to its integrated rate of production (P) by in situ U decay in the water column above the trap. For a perfect CFP, $F=P$ everywhere. Sarin et al. [45] report that $F/P(\text{Th}) \cong 1$ in a deep (~ 2300 m) sediment trap in the Bay of Bengal, where the total particle flux of $\sim 100 \text{ mg m}^{-2} \text{ day}^{-1}$ was dominated by CaCO_3 . Similarly, $F/P \cong 1$ in the high-flux, carbonate-dominated regime of the Arabian Sea [4]. These two examples suggest that even in the worst-case scenario of high particle flux dominated by carbonate (high $K_d(\text{Th})$), the flux of ^{230}Th is not significantly greater than its production rate. This places limits on the possible deficit of ^{230}Th flux in opal-dominated regions, since on average in the oceans the flux of ^{230}Th must equal its production rate. Indeed, $F/P(\text{Th})$ was close to 1 ($=0.7$) at an AE-SOPS sediment trap at 66°S , which collected a relatively low particle flux ($74 \text{ mg m}^{-2} \text{ yr}^{-1}$) composed of 2% CaCO_3 and $< 1\%$ lithogenics (the rest presumably being opal and organic matter) [36].

The fact that diatoms (low $K_d(\text{Th})$) tend to dominate in regions with high productivity [46] and high export [40], while carbonate producers (high $K_d(\text{Th})$) tend to dominate in low-flux regions, may help the performance of ^{230}Th as a CFP. The high particle flux, and hence high scavenging rates, characteristic of diatom-dominated regions will tend to balance the tendency for ^{230}Th to be scavenged by particles with a relatively low K_d in these regions.

4.3.2. Boundary scavenging

According to classical boundary scavenging theory (e.g. [47]) the high Pa/Th ratios characteristic of ocean margin sediments (at least in the Pacific) can be explained on the basis of the longer average scavenging residence time of dissolved

Pa, relative to Th, and the greater particle fluxes of coastal regions, compared to the ocean gyres. According to this view, scavenging at ocean margins is so intense that, in addition to removing all nuclides produced in situ by U decay (at a production ratio (Pa/Th) of 0.093), it also removes nuclides advected from the ocean gyres (at a typical dissolved Pa/Th ratio of 0.3–0.6 [3]). Similar arguments apply to ^{10}Be [6,48].

Scavenging rates at ocean margins are certainly high, as can be inferred from the fact that dissolved nuclides are depleted in the water column, relative to the ocean gyres [7]. However, ocean margins also have relatively high diatom productivity and therefore an opal-rich particle rain. Biogenic opal production rates in coastal regions are up to 12 times the global mean, whereas biogenic opal production rates in the oligotrophic gyres are as much as four times below the global mean [46]. The fact that coastal regions tend to be dominated by diatoms (low $F(\text{Th}/\text{Pa})$), while ocean gyres tend to be dominated by carbonate-forming organisms (high $F(\text{Th}/\text{Pa})$) may well contribute to the high Pa/Th ratios found in margin sediments. That is, the preferential removal of Th from open-ocean waters (particulate Pa/Th < 0.093), and the corresponding enrichment of these waters in dissolved Pa (dissolved Pa/Th ~ 0.3 – 0.6 [3]), may be due in part to the small contribution of diatoms to the productivity of the oligotrophic gyres [46]. Similarly, the high Pa/Th ratios of margin sediments could in part reflect the minimal fractionation between Pa and Th during scavenging by the opal-rich particles characteristic of coastal regions, in addition to the overall higher particle flux. In summary, the tendency for marine particles to be dominated by CaCO_3 in open-ocean regions and by opal in ocean-margin regions reinforces the pattern of boundary scavenging generated by the differential residence times of these nuclides.

4.3.3. Nuclide ratios as proxies for particle flux

Based on spatial patterns observed in the modern ocean, where sedimentary Pa/Th and Be/Th ratios increase with increasing particle flux, these nuclide ratios have been proposed as proxies for reconstructing past changes in export production

[6,10,11]. Given the evidence presented above, showing that fractionation between nuclides during scavenging depends on particle composition, the relationship between particulate nuclide ratios and particle flux needs to be reexamined.

Yu et al. [49] have presented particulate Pa/Th data from a large number of sediment traps covering a wide range of oceanic environments. We have combined these data with annual average Pa/Th ratios from the equatorial Pacific and AE-SOPS traps [36] to further evaluate the relationship between the particulate Pa/Th ratio reaching the sediment and mass flux (Fig. 4A and Appendix 2 in the **Background Data Set**¹). Because of possible seasonal variability in Pa/Th ratios [50], we include only sediment-trap records that cover at least a full annual cycle. An analogous, but much smaller global data set for particulate Be/Th ratios in sediment-trap material is also presented (Fig. 4B).

In the global data set, we find weak, but statistically significant relationships between particulate Pa/Th and annual average particle flux ($r^2 = 0.18$;

Fig. 4A) and between particulate Be/Th and annual average particle flux ($r^2 = 0.31$; Fig. 4B). Given the large range of locations, trap depths, and studies that went into creating these ‘calibration plots’ we are not surprised to see such variability. Much of the variability about the mean regressions in Fig. 4 can be explained by particle composition (Fig. 5A,C), with trap depth also contributing (Fig. 5B,D). The effect of trap depth on Be/Th ratios is expected to be particularly important, because ^{10}Be is supplied to the sea surface. It seems that particle composition is at least as important as particle flux in determining the mean Pa/Th ratio of sinking material in a wide range of oceanic environments. The application of Pa/Th and Be/Th ratios as particle flux proxies independent of particle composition needs to be reconsidered in light of these results. Empirically, the opal:CaCO₃ rain ratio explains much of the variability in the ocean-wide data set for particulate Pa/Th and Be/Th ratios (Fig. 6). These nuclide ratios – particularly Pa/Th, which is least affected by lithogenic content – may prove to be

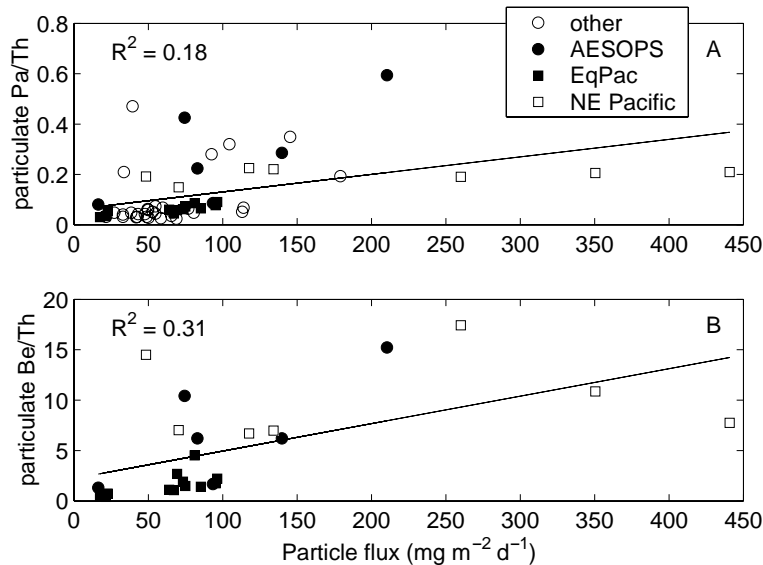


Fig. 4. (A) $^{231}\text{Pa}/^{230}\text{Th}$ ratio (activity ratio) and (B) $^{10}\text{Be}/^{230}\text{Th}$ (10^8 at/dpm) of trapped particles as a function of particle flux for sediment traps deployed for at least 1 year. ‘Other’ samples are year-long records taken from published compilations [4,18]. Data have not been corrected for potential biases in trapping efficiency. North East (NE) Pacific data are from Lao et al. [17], and those Be/Th ratios have been corrected (reduced by 40%) to account for a ^9Be spike calibration error (R.F. Anderson, unpublished). The regression line in A is: $\text{Pa/Th} = 0.0007 \times (\text{particle flux}) + 0.061$ ($r^2 = 0.18$). The regression line in B is $\text{Be/Th} = 0.0272 \times (\text{particle flux}) + 2.224$ ($r^2 = 0.31$). The data used to produce this figure are available in tabular form (see Appendix 2 in the **Background Data Set**¹).

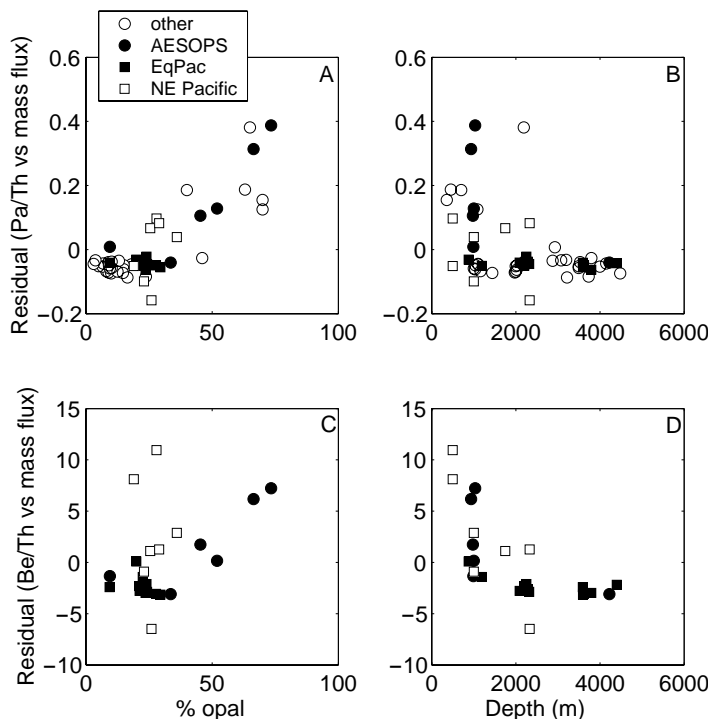


Fig. 5. The residuals (distance from linear regression line) of the relationship between particle flux and particulate $^{231}\text{Pa}/^{230}\text{Th}$ and $^{10}\text{Be}/^{230}\text{Th}$ ratio (Fig. 4) are plotted as a function of the opal content (A,C) of the particulate flux and against the depth of the sediment trap (B,D).

better suited as a tool for reconstructing the opal:carbonate ratio of particles raining to the seafloor, prior to dissolution, than as a tool for reconstructing particle flux. Such a proxy would be of value in reconstructing past changes in the

relative abundance of calcareous versus silicious phytoplankton, with implications for understanding the role of upper ocean ecology in affecting the partitioning of CO_2 between the ocean and the atmosphere [51].

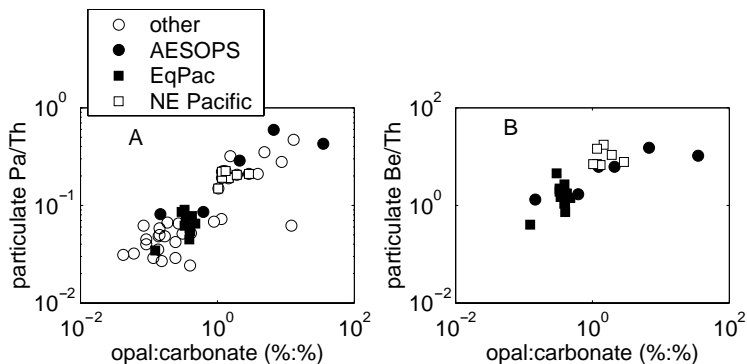


Fig. 6. A log–log plot of the annual average $^{231}\text{Pa}/^{230}\text{Th}$ ratio (activity ratio) (A) and $^{10}\text{Be}/^{230}\text{Th}$ ratio (10^8 at/dpm) (B) of sediment-trap material as a function of the ratio of opal to carbonate (wt%) of sinking particles. North East (NE) Pacific data are from [17] and those Be/Th ratios have been corrected (reduced by 40%) to account for a ^9Be spike calibration error. See the caption for Fig. 1 for sources of ‘other’ data.

5. Conclusions

We find that Th is scavenged strongly by carbonate and lithogenic material and weakly by opal, Pa is scavenged strongly by opal and weakly by carbonate and lithogenics, and Be is scavenged strongly by opal and lithogenics, but weakly by carbonate. The full spectrum of fractionation factors ($F(\text{Th}/\text{Pa})$), from <1 to >15 , is found in samples with very low lithogenic content and can be explained solely by the relative contribution of the biogenic phases, carbonate and opal. Partition coefficients calculated using sediment-trap samples decrease with increasing particle flux, because of the varying contribution of unaltered surface-derived material.

Empirical evidence indicates that the utility of ^{230}Th as a constant-flux proxy is not compromised by the dependence of Th scavenging on particle composition. The tendency for opal content of particles to increase with increasing particle flux creates a situation where $K_d(\text{Th})$ decreases as particle flux increases, coincidentally favoring a situation where $F(\text{Th}) \cong P(\text{Th})$ everywhere, despite the sensitivity of $K_d(\text{Th})$ to particle composition.

Composition-dependent scavenging of Th, Pa and Be, together with the resulting fractionation among these tracers, has important implications for the use of Pa/Th and Be/Th as paleo-flux proxies. These nuclide ratios may prove better suited to constraining the composition of the particle rain, an important parameter in reconstructing climate-related changes in the composition of the planktonic community.

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