



Controversy over the relationship between major components of sediment-trap materials and the bulk distribution coefficients of ^{230}Th , ^{231}Pa , and ^{10}Be

Yuan-Hui Li*

Department of Oceanography, University of Hawaii, Honolulu, HI 96822, USA

Received 16 August 2004; received in revised form 2 February 2005; accepted 15 February 2005

Available online 29 March 2005

Editor: E. Boyle

Abstract

A four-end-member mixing model is introduced to estimate the distribution coefficients of ^{230}Th , ^{231}Pa , and ^{10}Be for pure end members (lithogenic clays, organic carbon, carbonates, and opal) in sediment-trap materials from three oceanic regions. Four pure end members contribute differently to the fractionation of nuclides in three regions. Contribution of organic matter to the bulk distribution coefficients cannot be ignored.

© 2005 Elsevier B.V. All rights reserved.

Keywords: distribution coefficients; fractionation; nonlinear regression; mixing model; sediment-trap materials

1. Introduction

Chase et al. [1] estimated the bulk distribution coefficients ($K_d = X/C$) of ^{230}Th , ^{231}Pa , and ^{10}Be , using nuclide concentrations in sediment-trap materials (X) and the total nuclide concentrations in the nearby water column (C) from different regions (mainly from the Equatorial Pacific, Southern Ocean, Middle Atlantic Bight, and others). For the sediment-trap materials, they also provided the

percentage contents of four major end-member components (lithogenic clays, organic carbon, carbonates, and opal). From the plots of K_d as a function of opal and carbonate contents of sediment-trap materials, they estimated the K_d for the pure opal and carbonate end members. Luo and Ku [2,3] introduced a three-end-member mixing model to obtain the K_d for the three end members (pure opal, carbonate, and lithogenic clay) from different regions, using the same data set given by Chase et al. [1]. The controversy centers on whether the $K_d(\text{Th})$ for the lithogenic clay end member is as high as 230×10^6 g/g [2,3], or as low as 10×10^6 g/

* Tel.: +1 808 956 6297; fax: +1 808 956 7112.

E-mail address: yhli@soest.hawaii.edu.

g [1], or varies with regions [4], and what is the relative importance of opal, carbonate, and lithogenic clay end members toward the observed K_d . For example, Chase et al. [1] suggested that the degree of fractionation or unequal K_d among Th, Pa, and Be is closely related to opal-to-carbonate ratio in sediment-trap materials, while Luo and Ku [2] emphasized the importance of opal-to-lithogenic clay ratio. They, however, all assumed that the contribution of organic matter to K_d is negligible. As will be shown later, this assumption is not always applicable.

In order to treat the same data set more objectively, a four-end-member mixing model is introduced here:

$$100 \cdot K_d = \sum_{i=1}^4 k_i f_i = k_1 f_1 + k_2 f_2 + k_3 f_3 + k_4 f_4 \quad (1a)$$

$$100 = \sum_{i=1}^4 f_i = f_1 + f_2 + f_3 + f_4 \quad (1b)$$

Here, K_d =the observed bulk distribution coefficient of a given nuclide, k_i =the hypothetical distribution coefficient for pure end member i , f_i =percent content

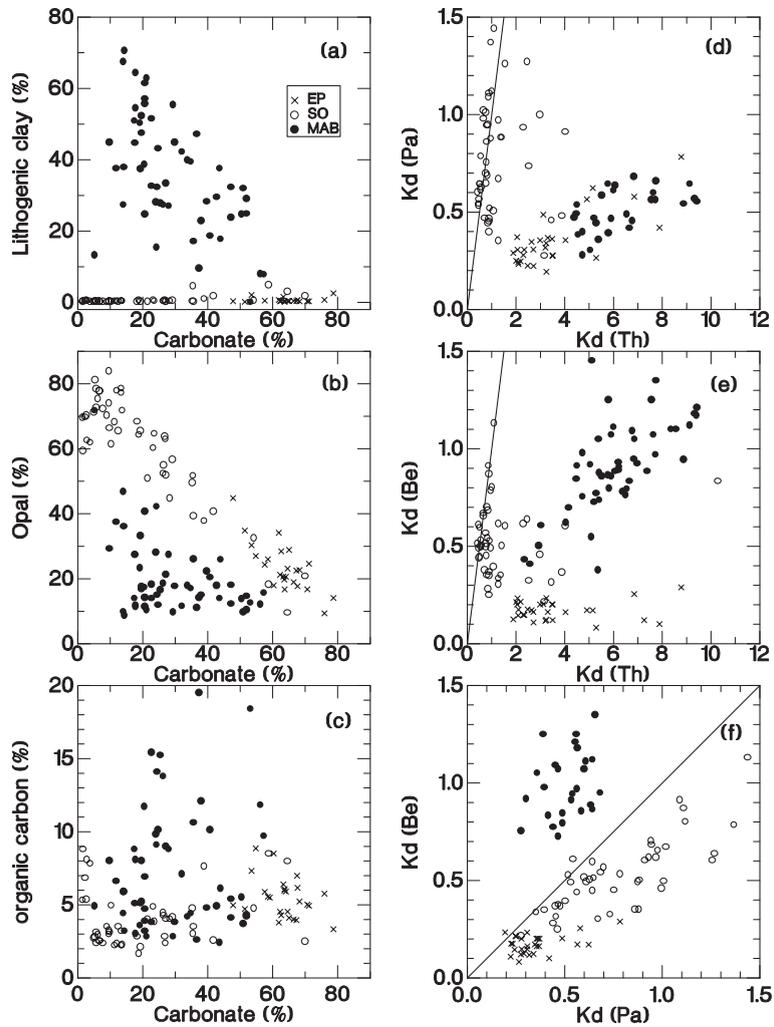


Fig. 1. Percent concentration of carbonate in sediment-trap materials vs. (a) lithogenic clay, (b) opal, and (c) organic carbon from the equatorial Pacific (EP), Southern Ocean (SO), and Middle Atlantic Bight (MAB) regions. Diagrams (d–f) are the xy plots of observed distribution coefficients (K_d) of ^{230}Th , ^{231}Pa , and ^{10}Be in units of 10^6 g/g. Solid lines are the equation $y=x$.

of pure end member i in sediment-trap materials, $i = 1$ (lithogenic clays), 2 (organic carbon), 3 (carbonates), and 4 (opal).

Since f_i and K_d are all known for a set of given samples from a chosen region, the unknown k_i can be estimated simultaneously by the nonlinear regression analysis using Eq. (1a). Since a negative k_i has no physical meaning, all k_i are constrained to be equal to or greater than zero ($k_i \geq 0$), and their initial values are all set to 10^6 g/g for the nonlinear regression. The only assumption is that all k_i are positive constants for the chosen region. A nonlinear regression program in the Statistical Package for the Social Sciences (SPSS) was adopted here.

2. Results and discussion

For clarity, only samples from the Equatorial Pacific (EP), Southern Ocean (SO), and Middle Atlantic Bight (MAB) regions in the Appendix 1 of Chase et al. [1] are selected for the nonlinear regression analysis. Sediment-trap materials from EP and SO regions are very low in lithogenic clay content (mostly less than 0.6%), and high in carbonate for EP and high in opal for SO (Fig. 1a and b). In contrast, sediment-trap materials from MAB contain significant amounts of all end members (lithogenic clays, carbonate, opal, and organic carbon; Fig. 1a–c). The magnitudes of the observed K_d values for Th, Pa, and Be have the following general trends: $K_d(\text{Th}) \gg K_d(\text{Pa}) > K_d(\text{Be})$ for EP; $K_d(\text{Th}) \geq K_d(\text{Pa}) \geq K_d(\text{Be})$ for SO; and $K_d(\text{Th}) \gg K_d(\text{Pa}) < K_d(\text{Be})$ for MAB (Fig. 1d–f). Because the f_i and K_d data from three chosen regions are distinctively different, they were treated separately first, then together to discern the difference and similarity. If samples have any missing values for f_i and K_d , the computer program will automatically exclude those samples. Since $\sum f_i$ are not equal to 100% in the original appendix table [1], all f_i are first replaced by $100 \cdot f_i / \sum f_i$ before the nonlinear regression analysis.

The k_i values obtained from the nonlinear regression on the data from each separate region are summarized in Table 1a as functions of regions, nuclides, and end members. Whenever the number of cases is small (20–21 cases for EP, and 28 cases for Pa in MAB), the uncertainties of estimated k_i can be large (Table 1a).

Table 1a

Model-predicted distribution coefficients (k_i ; in units of 10^6 g/g) of ^{230}Th , ^{231}Pa , and ^{10}Be for four end members of sediment-trap materials from the Equatorial Pacific (EP), Southern Ocean (SO), and Middle Atlantic Bight (MAB) regions

Z	Region	Case	k_i (10^6 g/g)			
			1: lithogenic	2: organic	3: carbonate	4: opal
Th	EP	20	259 ± 35	8 ± 16	1.9 ± 1.3	0 ± 2
		43	176 ± 15	0 ± 5	0.93 ± 0.32	0.19 ± 0.08
		MAB	9.4 ± 0.7	16.2 ± 3.7	1.8 ± 1.0	2.4 ± 1.3
Pa	EP	21	15.8 ± 2.5	2.4 ± 1.3	0 ± 0.1	0.60 ± 0.18
		41	10.1 ± 7.6	0 ± 2	0.07 ± 0.23	0.91 ± 0.05
		MAB	0.71 ± 0.07	1.3 ± 0.5	0.25 ± 0.11	0.11 ± 0.27
Be	EP	20	0.87 ± 1.24	1.8 ± 0.6	0 ± 0.05	0.31 ± 0.08
		47	7.1 ± 1.8	0 ± 0.8	0 ± 0.13	0.67 ± 0.03
		MAB	1.3 ± 0.1	1.4 ± 0.6	0.59 ± 0.17	0.43 ± 0.20

The $k_i(\text{Th})$ for lithogenic clay [simplified as $k_1(\text{Th})$ hereafter] from EP and SO regions are in the order of $2 \cdot 10^8$ g/g (Table 1a), in close agreement with the estimate by Luo and Ku [2]. The $k_1(\text{Th})$ from MAB is in the order of 10^7 g/g, in good agreement with the estimate by Chase et al. [4] and Luo and Ku [3]. In general, $k_1(\text{Th})$ are one to two orders of magnitude higher than $k_1(\text{Pa})$ and $k_1(\text{Be})$ [simplified as $k_1(\text{Pa}, \text{Be})$ hereafter] among three regions. Among all four end members, $k_1(\text{Th}, \text{Pa})$ are the highest in EP and SO. One interesting result is that $k_2(\text{Th}, \text{Pa}, \text{Be})$ (for organic carbon) are the highest among four end members in MAB. In the EP region, $k_2(\text{Th}, \text{Pa}, \text{Be})$ also have high values (even though their uncertainties can be high) as compared with those for carbonate and opal. Therefore, one cannot ignore the contribution of organic matter to the observed K_d . As also demonstrated by Quigley et al. [5], polysaccharides in the colloidal organic matter have very high K_d value ($\sim 10^8$) for ^{234}Th . Even though $k_2(\text{Th}, \text{Pa}, \text{Be})$ in SO are zero, they all have large uncertainties. One also notices the following relationships in Table 1a: $k_3(\text{Th})$ (for carbonate) $> k_4(\text{Th})$ (for opal) and $0 \approx k_3(\text{Pa}, \text{Be}) < k_4(\text{Pa}, \text{Be})$ in EP and SO; and $k_3(\text{Th}, \text{Pa}, \text{Be}) \approx k_4(\text{Th}, \text{Pa}, \text{Be})$ in MAB. Even though Luo and Ku [2] did not include the organic carbon in their three-end-member mixing model, the relative magnitudes of their $k_i(\text{Th}, \text{Pa}, \text{Be})$ for the other three end members obtained from the combined data from EP and SO regions (Table 1 in [2]) are similar to the averaged $k_i(\text{Th}, \text{Pa}, \text{Be})$ values for EP and SO regions (Table 1a).

Substituting k_i values from Table 1a into Eq. (1a), one can obtain the model-predicted K_d (designated as K_d^*) for each sample. The observed K_d and predicted K_d^* values are compared in Fig. 2a–c. Most of the predicted K_d^* have the percent residue or deviation $[=100 \cdot (K_d^* - K_d)/K_d]$ within $\pm 40\%$ of the observed K_d (within the two dotted lines of Fig. 2a–c). The $\pm 40\%$ deviation of K_d^* from K_d indicates that the present four-end-member mixing model is adequate but not perfect. The model must have missed some

other important controlling factors. The high model-derived $k_1(\text{Th, Pa})$ values in EP and SO as compared to those in MAB may reflect difference in particle size and concentration, chemical composition, and residence time of suspended lithogenic particles in the water column. As cautioned by Chase et al. [1], their defined $K_d (=X/C)$ is only a “pseudo”- K_d , because the total concentration of a given nuclide (C) in water column includes not only dissolved species but also colloidal and particulate species. The relative propor-

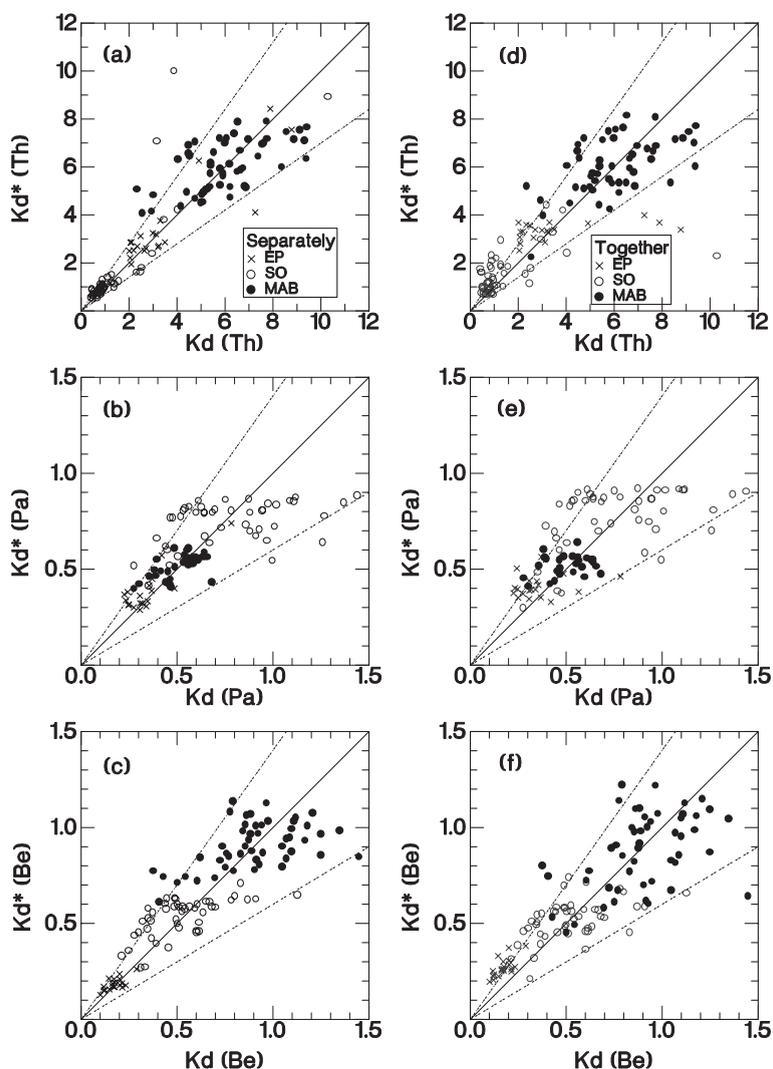


Fig. 2. Comparison of the observed K_d and model-derived K_d^* for (a) Th, (b) Pa, and (c) Be for data from three regions treated separately; (d) Th, (e) Pa, and (f) Be for all data from three regions treated together. All are in units of 10^6 g/g. Two dotted lines in each diagram represent $\pm 40\%$ deviation of K_d^* from K_d .

Table 1b

Average percent contents (\tilde{f}_i) of four end members in sediment-trap materials from different regions [1], and the average percent contributions \bar{F}_i ($=\tilde{f}_i \cdot k_i / \sum \tilde{f}_i \cdot k_i$) of four end members to the average bulk distribution coefficients ($\bar{K}_d \approx \bar{K}_d^* = \sum \tilde{f}_i \cdot k_i$) of Th, Pa, and Be in three regions

Region	\tilde{f}_i (wt %)			
	1: lithogenic	2: organic	3: carbonate	4: opal
EP	0.63 ± 0.59	5.8 ± 1.6	68.6 ± 7.5	24.9 ± 7.5
SO	0.72 ± 1.08	4.8 ± 2.6	23.0 ± 18.8	71.5 ± 19.9
MAB	38.6 ± 16.7	8.0 ± 5.0	32.0 ± 14.6	21.5 ± 12.2

Region	\bar{K}_d (10 ⁶ g/g)	\bar{F}_i (%) ^a			
		1: lithogenic	2: organic	3: carbonate	4: opal
EP	3.6 ± 1.8 (Th)	48 ± 7	14 ± 27	38 ± 26	0 ± 13
SO	1.5 ± 1.6 (Th)	79 ± 7	0 ± 13	13 ± 5	8 ± 4
MAB	6.0 ± 1.7 (Th)	60 ± 5	22 ± 5	10 ± 5	9 ± 5
EP	0.35 ± 0.13 (Pa)	26 ± 4	36 ± 19	0 ± 15	38 ± 12
SO	0.80 ± 0.34 (Pa)	10 ± 7	0 ± 11	2 ± 7	88 ± 5
MAB	0.51 ± 0.11 (Pa)	57 ± 6	22 ± 8	17 ± 7	5 ± 12
EP	0.17 ± 0.05 (Be)	3 ± 4	56 ± 19	0 ± 15	41 ± 11
SO	0.53 ± 0.19 (Be)	10 ± 3	0 ± 7	0 ± 15	90 ± 4
MAB	0.90 ± 0.23 (Be)	57 ± 5	12 ± 5	21 ± 6	10 ± 5

^a Uncertainties reflect only those of k_i in Table 1a.

tions of those species do vary geographically [6–8]. For example, MAB is closer to land; thus, one may expect high colloidal and particulate concentrations, which could cause high C and low K_d . Another big unknown is the kinetic (or non-equilibrium) effect between sediment-trap materials and surrounding water during the adsorption/desorption processes [1]. Finally, the model's assumption that all k_i are constants for a chosen region may not be strictly true. Certainly, further studies are needed.

Table 1b summarizes the average percent contents of four end members (\tilde{f}_i) and the average observed bulk distribution coefficients \bar{K}_d of Th, Pa, and Be from three regions separately. By combining \tilde{f}_i and \bar{K}_d with k_i values from Table 1a, one can estimate the average percent contributions ($\bar{F}_i = \tilde{f}_i \cdot k_i / \sum \tilde{f}_i \cdot k_i$) of four end members to the calculated \bar{K}_d^* ($=\sum \tilde{f}_i \cdot k_i \approx \bar{K}_d$) or observed \bar{K}_d of Th, Pa, and Be from three regions as shown in Table 1b. Uncertainties of \bar{F}_i reflect only those of k_i in Table 1a. In the EP region, lithogenic clay (\bar{F}_1) and carbonate (\bar{F}_3) are the major contributors to \bar{K}_d (Th), while organic carbon (\bar{F}_2) and opal (\bar{F}_4) are the major contributors to \bar{K}_d (Pa, Be) among four end members (Table 1b). The uncertainty of \bar{F}_3 is, however,

rather large. The observed fractionation trend that $\bar{K}_d(\text{Th}) > \bar{K}_d(\text{Pa}) > \bar{K}_d(\text{Be})$ in EP region (Table 1b) is consistent with $k_1(\text{Th}) > k_1(\text{Pa}) > k_1(\text{Be})$, $k_3(\text{Th}) > k_3(\text{Pa}, \text{Be}) \approx 0$, and $k_{2,4}(\text{Pa}) > k_{2,4}(\text{Be})$ in the region. In the SO region, lithogenic clay (\bar{F}_1) is the major contributor to $\bar{K}_d(\text{Th})$, while only opal (\bar{F}_4) is the major contributor to $\bar{K}_d(\text{Pa}, \text{Be})$. The observed fractionation trend that $\bar{K}_d(\text{Th}) > \bar{K}_d(\text{Pa}) \geq \bar{K}_d(\text{Be})$ in SO is consistent with $k_1(\text{Th}) > k_1(\text{Pa}) \geq k_1(\text{Be})$, and $k_4(\text{Pa}) > k_4(\text{Be})$ in SO (Table 1a). In MAB, lithogenic clay (\bar{F}_1) is the major contributor to $\bar{K}_d(\text{Th}, \text{Pa}, \text{Be})$. However, contributions from other end members are also appreciable. The observed fractionation trend that

Table 2a

Model-predicted distribution coefficients (k_i ; in units of 10⁶ g/g) of ²³⁰Th, ²³¹Pa, and ¹⁰Be for four end members of sediment-trap materials for all data from three regions

Z	Case	k_i (10 ⁶ g/g)			
		1: lithogenic	2: organic	3: carbonate	4: opal
Th	121	9.8 ± 0.6	12.9 ± 3.3	3.8 ± 0.5	0.00 ± 0.35
Pa	94	0.61 ± 0.12	0.0 ± 0.85	0.21 ± 0.09	1.00 ± 0.07
Be	117	1.51 ± 0.08	2.0 ± 0.4	0.01 ± 0.06	0.57 ± 0.04

Table 2b

Average percent contents (\bar{f}_i) of four end members in sediment-trap materials and the average percent contributions $\bar{F}_i (= \bar{f}_i \cdot k_i / \sum \bar{f}_i \cdot k_i)$ of four end members to the average bulk distribution coefficients ($\bar{K}_d \approx \bar{K}_d^* = \sum \bar{f}_i \cdot k_i$) of Th, Pa, and Be for all data from three regions

All data	\bar{f}_i (wt %)			
	1: lithogenic	2: organic	3: carbonate	4: opal
	17.3 ± 21.8	6.62 ± 4.44	35.5 ± 22.5	41.6 ± 28.2

\bar{K}_d (10 ⁶ g/g)	\bar{F}_i (%) ^a			
	1: lithogenic	2: organic	3: carbonate	4: opal
3.8 ± 2.6 (Th)	43 ± 3	22 ± 6	35 ± 5	0 ± 4
0.60 ± 0.31 (Pa)	18 ± 4	0 ± 9	12 ± 6	70 ± 5
0.59 ± 0.34 (Be)	41 ± 2	21 ± 4	1 ± 4	37 ± 3

^a Uncertainties reflect only those of k_i in Table 2a.

$\bar{K}_d(\text{Th}) > \bar{K}_d(\text{Pa}) < \bar{K}_d(\text{Be})$ in MAB is consistent with $k_i(\text{Th}) > k_i(\text{Pa}) < k_i(\text{Be})$ for all end members (Table 1a).

The k_i values obtained from the nonlinear regression on all data from three regions together are summarized in Table 2a as functions of nuclides and end members. The $k_2(\text{Th}, \text{Be})$ (for organic fraction) obtained from all data are the highest among the four end members, confirming the importance of organic matter. The $k_1(\text{Th}, \text{Be})$ obtained from all data (Table 2a) are similar to that from MAB (Table 1a). It is explainable by the fact that \bar{f}_1 from EP and SO are extremely small and $K_d(\text{Th}, \text{Be})$ are the highest in MAB among three regions (Table 1b); thus, the data from MAB dominate the outcome of $k_1(\text{Th}, \text{Be})$ during the nonlinear regression analysis on all data. It is not coincident that the $K_d(\text{Th})$ of 10×10^6 g/g given by [1] and [4] agrees with those obtained from MAB and all data here. Likewise, $k_4(\text{Pa})$ for all data (Table 2a) is similar to that from SO region (Table 1a). Because SO has the highest $K_d(\text{Pa})$ and \bar{f}_4 (Table 1b) among three regions, thus, the data from SO more or less determined the outcome of $k_4(\text{Pa})$ for all data. The predicted $K_d^*(\text{Th}, \text{Pa}, \text{Be})$ from Eq. (1a) using k_i from Table 2a for all data are compared with the observed $K_d(\text{Th}, \text{Pa}, \text{Be})$ in Fig. 2d–f. One half of $K_d^*(\text{Th})$ data from SO (Fig. 2d) and more than half of $K_d^*(\text{Be})$ from EP (Fig. 2f) lie outside of the ±40% deviation lines.

Therefore, the model fits for all data are not as good as the results obtained from treating the data from three regions separately (Fig. 2a,c) (Table 2b).

3. Conclusions

In order to elucidate the relationship between the components of sediment-trap materials and K_d of nuclides, one cannot ignore the organic matter component.

The 20-fold difference in $k_1(\text{Th})$ value obtained by Chase et al. [1] and Luo and Ku [2,3] is mainly caused by the way they chose the sample population. The former used all data from three regions (EP, SO, and MAB) together and the latter treated the data from three regions separately. Both ways were adopted in this paper.

Both f_i and $k_i(\text{Th}, \text{Pa}, \text{Be})$ of four end members (lithogenic clay, organic carbon, carbonate and opal) in sediment-trap materials contribute to the varied degree of fractionation among Th, Pa, and Be in three regions, when the data from three regions are treated separately. The opal-to-carbonate [1] or opal-to-lithogenic clay [2] ratio alone does not provide a full picture.

The $k_i(\text{Th}, \text{Pa}, \text{Be})$ obtained for all data can be biased by extreme values of f_i and/or $K_d(\text{Th}, \text{Pa}, \text{Be})$ from one of three regions.

Separation of dissolved, colloidal, and particulate species in the water column; and fuller characterization of particles in terms of grain size, chemical composition, etc. are necessary steps to understand better the factors controlling the bulk distribution coefficients of tracers in the ocean.

Acknowledgements

Discussions with Drs. Robert Anderson, Zanna Chase, Teh-lung Ku, Shangde Luo and Peter Santschi were most fruitful. Their thoughtful comments clarified some disputed interpretations. Dr. Chase kindly provided the correct version of Appendix Table 1 in [1]. Editorial assistance from Diane Henderson is indispensable. This work is supported by NOAA grant GC02-386, and is SOEST contribution 6442.

References

- [1] Z. Chase, R.F. Anderson, M.Q. Fleisher, P.W. Kubik, The influence of particle composition and particle flux on scavenging of Th, Pa, and Be in the ocean, *Earth Planet. Sci. Lett.* 204 (2002) 215–229.
- [2] S. Luo, T.L. Ku, On the importance of opal, carbonate, and lithogenic clays in scavenging and fractionating ^{230}Th , ^{231}Pa and ^{10}Be in the ocean, *Earth Planet. Sci. Lett.* 220 (2004) 201–211.
- [3] S. Luo, T.L. Ku, Reply to comment on “On the importance of opal, carbonate, and lithogenic clays in scavenging and fractionating ^{230}Th , ^{231}Pa and ^{10}Be in the ocean”, *Earth Planet. Sci. Lett.* 220 (2004) 223–229.
- [4] Z. Chase, R.F. Anderson, Comment on “On the importance of opal, carbonate, and lithogenic clays in scavenging and fractionating ^{230}Th , ^{231}Pa and ^{10}Be in the ocean” by S. Luo and T.-L. Ku, *Earth Planet. Sci. Lett.* 220 (2004) 213–222.
- [5] M.S. Quigley, P.H. Santschi, C.C. Hung, Importance of acid polysaccharides for ^{234}Th complexation to marine organic matter, *Limnol. Oceanogr.* 47 (2002) 367–377.
- [6] M.L. Wells, Marine colloids and trace metals, in: D.A. Hansell, C.A. Carlson (Eds.), *Biogeochemistry of Marine Dissolved Organic Matter*, Academic Press, San Diego, 2002, pp. 367–404.
- [7] L. Guo, P.H. Santschi, M. Baskaran, A. Zindler, Distribution of dissolved and particulate ^{230}Th and ^{232}Th in seawater from the Gulf of Mexico and off Cape Hatteras as measured by SIMS, *Earth Planet. Sci. Lett.* 133 (1995) 117–128.
- [8] M.P. Bacon, R.F. Anderson, Distribution of thorium isotopes between dissolved and particulate forms in the deep sea, *J. Geophys. Res.* 87 (1982) 2045–2056.