

## Control of Pa/Th ratio by particulate chemical composition in the ocean

Laodong Guo,<sup>1</sup> Min Chen,<sup>2</sup> and Celine Gueguen<sup>1</sup>

Received 12 June 2002; accepted 27 August 2002; published 19 October 2002.

[1] Controlled laboratory experiments were carried out using pure sorbents to examine the interactions of  $^{234}\text{Th}$  (or  $^{233}\text{Pa}$ ) with particle surfaces and whether there is a fractionation between  $^{234}\text{Th}$  and  $^{233}\text{Pa}$  by particulate chemical composition. Our results show that the adsorption of  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  on particle surfaces is highly selective and compound specific, resulting in a fractionation of  $^{233}\text{Pa}/^{234}\text{Th}$  ratio, especially on  $\text{SiO}_2$  ( $K_d$  ratio,  $K_{d-233\text{Pa}}/K_{d-234\text{Th}}$ , = 10) and  $\text{CaCO}_3$  ( $K_d$  ratio,  $K_{d-233\text{Pa}}/K_{d-234\text{Th}}$ , = 0.01) surfaces. These new results agree well with previously published field observations that showed an increase of  $^{231}\text{Pa}/^{230}\text{Th}$  ratio (or  $K_d$  of  $^{231}\text{Pa}$ ) with increasing opal abundance and decreasing carbonate content in oceanic particles. In addition, they highlight the complications of using  $^{231}\text{Pa}/^{230}\text{Th}$  ratio as a proxy and have implications for both oceanography and trace element geochemistry although more studies are needed to further examine the influence of natural organic matter on the fractionation of Th/Pa ratios. **INDEX TERMS:** 4875 Oceanography: Biological and Chemical: Trace elements; 4825 Oceanography: Biological and Chemical: Geochemistry; 4866 Oceanography: Biological and Chemical: Sorptive scavenging; 4860 Oceanography: Biological and Chemical: Radioactivity and radioisotopes; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615). **Citation:** Guo, L., M. Chen, and C. Gueguen, Control of Pa/Th ratio by particulate chemical composition in the ocean, *Geophys. Res. Lett.*, 29(20), 1961, doi:10.1029/2002GL015666, 2002.

### 1. Introduction

[2] The  $^{231}\text{Pa}/^{230}\text{Th}$  ratio has been used as a proxy in ocean circulation [Scholten *et al.*, 1995; Yu *et al.*, 1996; Marchal *et al.*, 2000; Moran *et al.*, 2001], paleoproductivity [Lao *et al.*, 1992; Francois *et al.*, 1993; Kumar *et al.*, 1993, 1995] and ocean scavenging [Anderson *et al.*, 1983; Nozaki and Nakanishi, 1985]. However, the molecular mechanisms of these applications are not well understood. It has been found that  $^{231}\text{Pa}/^{230}\text{Th}$  ratios in oceanic particles and sediments are not constant and can deviate significantly from their productive ratio in the water column [Yu *et al.*, 1996; Walter *et al.*, 1997, 1999, 2001]. Fractionation between  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  within the ocean basin constitutes the foundation of using these isotopes as tracers in the ocean circulation [Yu *et al.*, 1996] and boundary scavenging [Bacon *et al.*, 1988; Anderson *et al.*, 1994]. In addition,

an observed correlation between  $^{231}\text{Pa}/^{230}\text{Th}$  ratio and particulate matter flux has led to recent applications of  $^{231}\text{Pa}/^{230}\text{Th}$  ratio as a paleoproductivity proxy in the ocean [e.g., Lao *et al.*, 1992; Francois *et al.*, 1993; Kumar *et al.*, 1993, 1995]. Nevertheless, this application assumes a constant fractionation on  $^{231}\text{Pa}/^{230}\text{Th}$  regardless of types of particles or chemical composition, which is not supported by many field studies [Anderson *et al.*, 1983; Rutgers van der Loeff and Berger, 1993; Kumar *et al.*, 1995; Luo and Ku, 1999].

[3] It is generally assumed that adsorption of Th (IV) and Pa (IV, V) on marine particle surfaces is a non-selective physicochemical process [e.g., Quigley *et al.*, 1996], and chemical composition of marine particles, such as silica, does not fractionate  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  [Anderson *et al.*, 1992; Walter *et al.*, 1999]. However, many field observations suggest either a preferential scavenging of  $^{231}\text{Pa}$  by biogenic opal [DeMaster, 1979; Taguchi *et al.*, 1989; Walter *et al.*, 1999, 2001] or a chemical composition influence on  $^{231}\text{Pa}/^{230}\text{Th}$  ratio [Walter *et al.*, 1997; Luo and Ku, 1999; Walter *et al.*, 2001; Chase *et al.*, 2001]. In addition, recent field and laboratory studies both point to a selective and compound specific interaction of  $^{234}\text{Th}$  with marine organic matter [Guo *et al.*, 2002; Quigley *et al.*, 2002]. Unfortunately, interactions of Pa with marine particles have not been systematically investigated [Nyffeler *et al.*, 1984; Anderson *et al.*, 1992]. Applications of  $^{231}\text{Pa}/^{230}\text{Th}$  ratios and the interpretation of field data require not only field investigations but also controlled laboratory experiments to examine possible mechanisms. Whether Pa is fractionated with respect to Th during binding with different marine particles is largely unknown, but is relevant to the use of Pa/Th ratio as a proxy in oceanography.

### 2. Methods

[4]  $^{233}\text{Pa}$  ( $t_{1/2} = 27$  d) and  $^{234}\text{Th}$  ( $t_{1/2} = 24$  d) were used in the controlled laboratory experiments to examine the fractionation of  $^{233}\text{Pa}/^{234}\text{Th}$  ratios on different types of inorganic and organic sorbents (Table 1).  $^{233}\text{Pa}$  was separated from its parent nuclide  $^{237}\text{Np}$  ( $t_{1/2} = 2.14 \times 10^6$  y) (Isotope Products, CA) according to procedures described in Luo [1988] and Zheng *et al.* [1990]. Activity concentrations of  $^{233}\text{Pa}$  were determined by a HP-Ge well detector (Canberra Industries) at 300 KeV (6.62%) and 312 KeV (38.6%).  $^{234}\text{Th}$  was milked from its mother nuclide  $^{238}\text{U}$  ( $t_{1/2} = 4.47 \times 10^9$  y) (Sigma Chemical) using the procedures described in Quigley *et al.* [2001] and measured by a HP-Ge well detector at 63 KeV. Types of sorbents used in adsorption experiments and other detailed information are listed in Table 1. Sorbents used included various inorganic particles, such as  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ,  $\text{MnO}_2$ , and  $\text{Fe}_2\text{O}_3$ , and

<sup>1</sup>International Arctic Research Center, University of Alaska Fairbanks, AK, USA.

<sup>2</sup>Department of Oceanography, Xiamen University, Xiamen, China.

**Table 1.** Types of Sorbents, Mass Balance (%) and Values of Partition Coefficient ( $K_d$  or  $K_c$ ) of  $^{234}\text{Th}$  and  $^{233}\text{Pa}$ 

Type of Sorbents (CAS #)	Description	$^{234}\text{Th}$		$^{233}\text{Pa}$	
		Mass Balance (%)	$\log K_d$	Mass Balance (%)	$\log K_d$
MnO <sub>2</sub> (1313139)	<5 $\mu\text{m}$ powder	106 $\pm$ 16	6.14 $\pm$ 0.31	108 $\pm$ 7	6.20 $\pm$ 0.41
Fe <sub>2</sub> O <sub>3</sub> (1309371)	<5 $\mu\text{m}$ powder	94 $\pm$ 6	5.83 $\pm$ 0.02	97 $\pm$ 6	5.15 $\pm$ 0.12
CaCO <sub>3</sub> (471341)	powder	99 $\pm$ 6	5.60 $\pm$ 0.02	101 $\pm$ 2	3.68 $\pm$ 0.23
Humic acid (68131044)	Sodium-salt	80 $\pm$ 20	5.58 $\pm$ 0.01	104 $\pm$ 2	4.31 $\pm$ 0.21
Chitin (1398614)	Coarse flakes, 99% acetylated	108 $\pm$ 14	3.50 $\pm$ 0.73	96 $\pm$ 5	3.69 $\pm$ 0.67
SiO <sub>2</sub> (14808607)	1–5 $\mu\text{m}$ , Amorphous	108 $\pm$ 4	3.98 $\pm$ 0.03	108 $\pm$ 7	5.09 $\pm$ 0.72
Carrageenan Type V (9062071)	Acid polysaccharides	111 $\pm$ 6	7.78 $\pm$ 0.12	111 $\pm$ 7	7.49 $\pm$ 0.17

No chemical pretreatment was used for sorbents before sorption experiments. Data ( $\pm$ ) are those from replicate or duplicate results.

different organic substances, such as humic acids, chitin, and carrageenan type V (acid polysaccharides). No chemical pretreatment was used for sorbents before Th (IV) and Pa (IV, V) sorption experiments. Predetermined amounts of organic or inorganic sorbents were added to artificial seawater [Horne, 1969] in Teflon beakers with a final total solid concentration of about 0.1 mg/ml. Then, a spike of  $^{233}\text{Pa}$  or  $^{234}\text{Th}$  radiotracer was added to adsorption systems. After equilibrium (2 h) aliquots of the suspensions were filtered or ultrafiltered to separate particulate (0.4  $\mu\text{m}$  filter-retained) or colloidal (1 kDa filter-retained) from dissolved (filtrate, <0.4  $\mu\text{m}$  or ultrafiltrate, <1 kDa) phases. Activity concentrations of  $^{233}\text{Pa}$  or  $^{234}\text{Th}$  were measured in the filter-retained particles and filtrate. Aliquots of total suspension solutions were also measured for  $^{233}\text{Pa}$  or  $^{234}\text{Th}$  to monitor the mass balance of both radiotracers. All adsorption experiments were carried out in triplicate or duplicate.

[5] Total recovery of radiotracers from both filter-retained and filtrate fractions compared with that in suspension solution gave rise to a satisfactory mass balance for both  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  (Table 1). Mass balance data ranged from 96% to 111% for  $^{233}\text{Pa}$  while they varied from 80% to 111% for  $^{234}\text{Th}$  depending on sorbents. These mass balance results are mostly within  $\pm 10\%$ . Lower recovery was measured in the adsorption experiment of  $^{234}\text{Th}$  on humic substances, likely due to the loss of humic substances to the walls.

[6] The concentration of filterable suspended particles was determined by weigh difference on dried filter samples for the calculation of partition coefficients of  $^{233}\text{Pa}$  and  $^{234}\text{Th}$ . However, the mass concentration of carrageenan was based on the added powder weight.

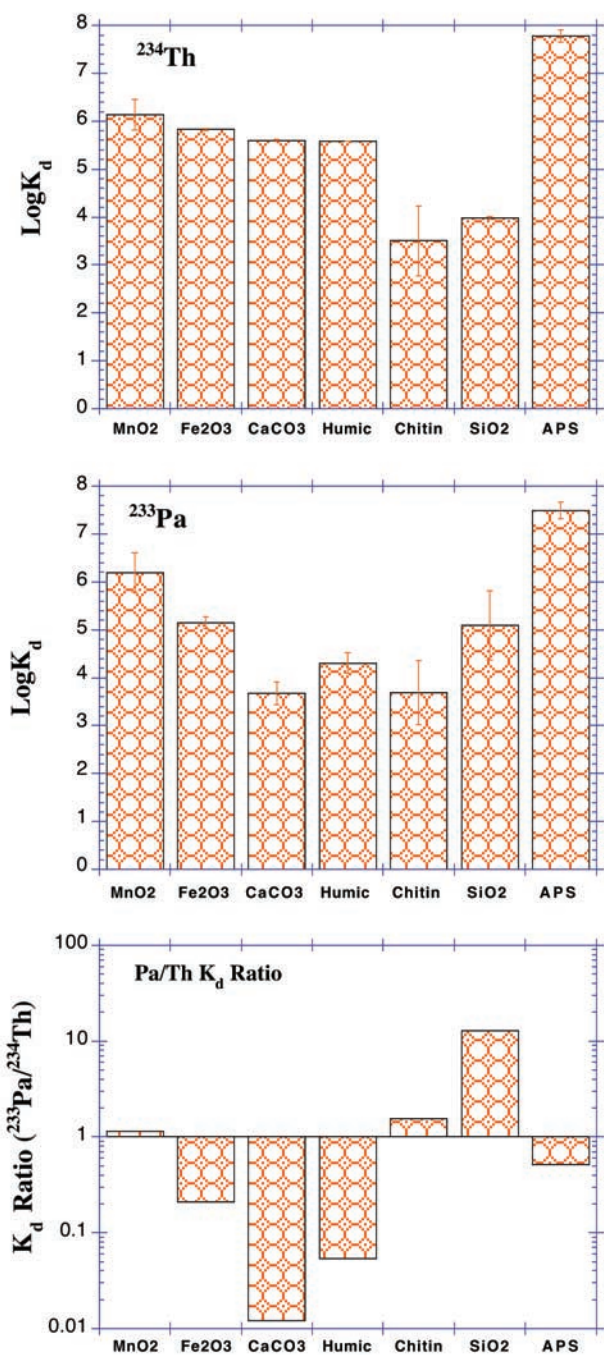
### 3. Results and Discussion

[7] Values of partitioning coefficient,  $K_d$ , of  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  between dissolved and particulate (or colloidal) phases, were distinctly different on various particulate phases. For example, measured  $K_d$  values for both  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  span 3 to 4 orders of magnitude, varying from  $10^{3.7}$  to  $10^{7.5}$  for  $^{233}\text{Pa}$  and from  $10^{3.5}$  to  $10^{7.8}$  for  $^{234}\text{Th}$  on different particle surfaces (Table 1 and Figure 1). Most importantly, while most sorbents had similar  $K_d$  values for both  $^{234}\text{Th}$  and  $^{233}\text{Pa}$ , SiO<sub>2</sub> and CaCO<sub>3</sub>, on the other hand, demonstrated significant fractionation between  $^{234}\text{Th}$  and  $^{233}\text{Pa}$  (Figure 1). Measured  $K_d$  value for  $^{234}\text{Th}$  on SiO<sub>2</sub> was  $10^{3.98}$  but was  $10^{5.09}$  for  $^{233}\text{Pa}$ , resulting in a fractionation factor (or  $K_d$  ratio of  $^{233}\text{Pa}$  over  $^{234}\text{Th}$ ) of  $\sim 13$  (Figure 1). In contrast to SiO<sub>2</sub>, the opposite is true for CaCO<sub>3</sub>. A

significant higher  $K_d$  value was observed for  $^{234}\text{Th}$  ( $10^{5.6}$ ), but lower  $K_d$  value for  $^{233}\text{Pa}$  ( $10^{3.7}$ ) on CaCO<sub>3</sub>, with a fractionation factor of  $\sim 0.012$  ( $K_d$  ratio of  $^{233}\text{Pa}$  over  $^{234}\text{Th}$ ). These results indicate that particle types and thus chemical composition of particles could cause significant fractionation between  $^{233}\text{Pa}$  and  $^{234}\text{Th}$ . While SiO<sub>2</sub> has a high affinity for  $^{233}\text{Pa}$ , the affinity of CaCO<sub>3</sub> for  $^{233}\text{Pa}$  is low. In other words, SiO<sub>2</sub> particles preferentially sorb or scavenge  $^{233}\text{Pa}$  whereas CaCO<sub>3</sub> selectively interacts with  $^{234}\text{Th}$ . These are direct evidence that fractionation between  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  could be controlled by the abundance of SiO<sub>2</sub> and CaCO<sub>3</sub> of oceanic particles, even though sorbents used in our experiments may not be representative of natural marine particles and marine organic matter may affect the fractionation of Pa/Th ratios.

[8] Interestingly, not all the experimental organic components used appear to have equal adsorption effect. They seem to have distinctively different affinity for these two radionuclides, Th (IV) and Pa (IV, V). Carrageenan (type V), a mixture of sulfated acid polysaccharides (APS) extracted from seaweed, had the highest  $K_d$  values for both  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  (up to  $10^{7.49}$  and  $10^{7.78}$ , respectively) within all sorbents tested. However, chitin, a cellulose-like biopolymeric organic compound, had very low  $K_d$  values for both  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  ( $10^{3.69}$  and  $10^{3.50}$ , respectively). Difference in  $K_d$  values of  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  was 3–4 orders of magnitude between the two different organic sorbents (chitin vs. acid polysaccharides). The enhancement of Th and Pa adsorption on carrageenan (APS) surfaces likely resulted from the presence of strong acidic functional group [Quigley *et al.*, 2002; Santschi *et al.*, 2002]. In addition, oxidation state differences between Th (IV) and Pa (IV, V) may cause fractionation between Th and Pa isotopes as well. However, our results showing fractionation for both  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  are consistent with recent studies that demonstrate that acid polysaccharides are the effective organic component in the scavenging of Th (IV) isotopes [e.g., Guo *et al.*, 2002; Quigley *et al.*, 2002].

[9] Even though chemical composition affects the adsorption of  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  on particle surfaces, it will not fractionate the ratio of  $^{231}\text{Pa}/^{230}\text{Th}$  without fractionation between  $^{231}\text{Pa}$  and  $^{230}\text{Th}$ . While most inorganic (MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>) and organic (chitin and carrageenan) sorbents discriminated little between  $^{233}\text{Pa}$  and  $^{234}\text{Th}$ , the fractionation of  $^{233}\text{Pa}$  and  $^{234}\text{Th}$  caused by SiO<sub>2</sub> and CaCO<sub>3</sub> was significant, resulting in distinctly different  $K_d$  values between  $^{233}\text{Pa}$  and  $^{234}\text{Th}$ . Since SiO<sub>2</sub> and CaCO<sub>3</sub>, which cause fractionation of  $^{233}\text{Pa}/^{234}\text{Th}$  ratio, are two of the most abundant biogenic solid components, opal and carbonate, in



**Figure 1.** Variations of partitioning coefficient ( $K_d$ ) between dissolved and particulate phases and fractionation of  $^{233}\text{Pa}/^{234}\text{Th}$  ratios among different adsorbents in terms of  $K_d$  ratio. Sorbents used include MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, humic acid, chitin, SiO<sub>2</sub>, and acid polysaccharides (APS, carrageenan Type 5) (see Table 1). Note that SiO<sub>2</sub> had a positive effect on the  $^{233}\text{Pa}/^{234}\text{Th}$   $K_d$  ratio while CaCO<sub>3</sub> (and likely humic acid) reduced the  $^{233}\text{Pa}/^{234}\text{Th}$   $K_d$  ratio. In addition, MnO<sub>2</sub> and chitin had little effect on the fractionation of  $^{233}\text{Pa}/^{234}\text{Th}$ .

the ocean, especially in the Southern Ocean [DeMaster, 1979], ratios of  $^{231}\text{Pa}/^{230}\text{Th}$  could vary with the abundance of opal and calcium carbonate in oceanic particles [Walter *et al.*, 1999; Chase *et al.*, 2001]. Due to the complex nature of

marine particles and possible organic and inorganic coatings, the effect of marine organic matter on Th and Pa adsorption need to be further studied.

[10] Based on  $K_d$  data of  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  from field studies,  $^{231}\text{Pa}$  was found to have higher  $K_d$  values than  $^{230}\text{Th}$  when extrapolated to a 100% of opal content in oceanic particles [Chase *et al.*, 2001]. However,  $K_d$  value of  $^{231}\text{Pa}$  was significantly lower than that of  $^{230}\text{Th}$  if particles are composed of 100% of carbonate. Our conclusions that SiO<sub>2</sub> preferentially sorbs  $^{233}\text{Pa}$  while CaCO<sub>3</sub> preferentially sorbs  $^{234}\text{Th}$ , are therefore consistent with those field results [Chase *et al.*, 2001]. Furthermore, the interpretation of many field observations [Walter *et al.*, 1997, 2001] on  $^{231}\text{Pa}/^{230}\text{Th}$  ratio in oceanic particles requires that SiO<sub>2</sub> (opal) fractionates on  $^{231}\text{Pa}$  and  $^{230}\text{Th}$ . Indeed, using available literature data for both  $^{231}\text{Pa}/^{230}\text{Th}$  ratio and opal content of oceanic particles [Walter *et al.*, 1999], a significant correlation ( $n = 9$ ,  $p < 0.05$ ) between excess  $^{231}\text{Pa}/^{230}\text{Th}$  ratio and opal abundance can be revealed. This correlation further supports our laboratory results depicted in Figure 1. Thus, our results showing a fractionation of  $^{233}\text{Pa}/^{234}\text{Th}$  ratio by SiO<sub>2</sub> and CaCO<sub>3</sub> not only challenge the use of  $^{231}\text{Pa}/^{230}\text{Th}$  ratio as a proxy in paleoproductivity but also have significant implications for both oceanography and geochemistry.

[11] **Acknowledgments.** We thank two anonymous reviewers for critical comments. This work was supported, in part, by the U.S. NSF (OCE-9906823), Japan Frontier Observational Research System for Global Change/IARC, and a Swiss NSF fellowship.

## References

- Anderson, R. F., M. B. Bacon, and P. G. Brewer, Removal of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  from the open ocean, *Earth Planet Sci. Lett.*, 62, 7–23, 1983.
- Anderson, R. F., M. Q. Fleisher, P. E. Biscay, N. Kumar, B. Dittrich, P. Kubik, and M. Suter, Anomalous boundary scavenging in the Middle Atlantic Bight: evidence from  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ ,  $^{10}\text{Be}$  and  $^{210}\text{Pb}$ , *Deep-Sea Res. II*, 41, 537–561, 1994.
- Anderson, H. L., R. Francois, and S. B. Moran, Experimental evidence for different adsorption of Th and Pa on different solid phases in seawater, *EOS, Trans. Amer. Geophys. Union*, 73(S43), 270, 1992.
- Bacon, M. P., Tracers of chemical scavenging in the ocean: boundary effects and large-scale chemical fractionation. Philosophical Transactions of the Royal Society of London, A320, 187–200, 1988.
- Chase, Z., R. F. Anderson, M. Q. Fleisher, P. Kubik, and P. Scherrer, The influence of particulate composition on scavenging of Th, Pa, and Be in the ocean, *EOS*, 82(47), F619, 2001.
- DeMaster, D. J., The marine budgets of silica and 32-Si, Ph.D. thesis, Yale University, New Haven, pp. 308, 1979.
- Francois, R., M. P. Bacon, M. Altabet, and L. D. Labeyrie, Glacial/interglacial changes in sediment rain rate in the SW Indian sector of subantarctic waters as recorded by  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ , U and  $\delta^{15}\text{N}$ , *Paleoceanography*, 8, 611–629, 1993.
- Guo, L., C. C. Hung, P. H. Santschi, and I. D. Walsh, Scavenging of  $^{234}\text{Th}$  and its relationship to acid polysaccharide abundance in the Gulf of Mexico, *Mar. Chem.*, 78, 103–119, 2002.
- Home, R. A., Marine Chemistry, Wiley Interscience, 1969.
- Kumar, N., R. Gwiazda, R. F. Anderson, and P. N. Froelich,  $^{231}\text{Pa}/^{230}\text{Th}$  ratios in sediments as a proxy for past changes in Southern Ocean productivity, *Nature*, 362, 45–48, 1993.
- Kumar, N., R. F. Anderson, R. A. Mortlock, P. N. Froelich, P. Kubik, B. Dittrich-Hannen, and M. Suter, Increased biological productivity and export production in the glacial Southern Ocean, *Nature*, 378, 675–680, 1995.
- Lao, Y., R. F. Anderson, and W. S. Broecker, Boundary scavenging and deep-sea sediment dating: constraints from excess  $^{230}\text{Th}$  and  $^{231}\text{Pa}$ , *Paleoceanography*, 7, 783–789, 1992.
- Luo, S., Growth dynamics of deep-sea Mn nodules and its implications for paleoceanography: Chemical and isotopic evidences, Ph.D. thesis, Xiamen University, 1988.

- Luo, S., and T.-L. Ku, Oceanic  $^{231}\text{Pa}/^{230}\text{Th}$  ratio influenced by particle composition and remineralization, *Earth Planet. Sci. Lett.*, *167*, 183–195, 1999.
- Marchal, O., R. Francois, T. F. Stocker, and F. Joos, Ocean thermohaline circulation and sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratio, *Paleoceanography*, *15*, 625–641, 2000.
- Moran, S. B., C.-C. Shen, S. E. Weinstein, L. H. Hettlinger, J. H. Hoff, H. N. Edmonds, and R. L. Edwards, Constraints on deep water age and particle flux in the Equatorial and South Atlantic Ocean based on seawater  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  data, *Geophys. Res. Lett.*, *28*, 3437–3440, 2001.
- Nozaki, Y., and T. Nakanishi,  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  profiles in the open ocean water column, *Deep-Sea Res.*, *32*, 1209–1220, 1985.
- Nyffeler, U. P., Y. H. Li, and P. H. Santschi, A kinetic approach to describe trace-element distribution between particles and solution in natural aquatic system, *Geochim. Cosmochim. Acta*, *48*, 1513–1522, 1984.
- Quigley, M. S., B. D. Honeyman, and P. H. Santschi, Thorium sorption in the marine environment: Equilibrium partitioning at the Hematite/water interface, sorption/desorption kinetics and particle tracing, *Aquatic Geochem.*, *1*, 277–301, 1996.
- Quigley, M. S., P. H. Santschi, L. Guo, and B. D. Honeyman, Sorption irreversibility and coagulation behavior of  $^{234}\text{Th}$  with marine organic matter, *Mar. Chem.*, *76*, 27–45, 2001.
- Quigley, M. S., P. H. Santschi, C.-C. Hung, L. Guo, and B. D. Honeyman, Importance of polysaccharides for  $^{234}\text{Th}$  complexation to marine organic matter, *Limnol. Oceanogr.*, *47*, 367–377, 2002.
- Rutgers van der Loeff, M. M., and G. W. Berger, Scavenging of  $^{231}\text{Pa}/^{230}\text{Th}$  near the Antarctic Polar Front in the South Atlantic, *Deep-Sea Res.*, *40*, 339–357, 1993.
- Santschi, P. H., C. C. Hung, G. Schultz, N. Alvarado-Quiroz, L. Guo, J. Pinckney, and I. Walsh, Control of acid polysaccharide production,  $^{234}\text{Th}$  and POC export fluxes by marine organisms, *Geophys. Res. Lett.*, *29*, (in press), 2002.
- Scholten, J. C., M. M. Rutgers van der Loeff, and A. Michel, Distribution of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  in the water column in relation to the ventilation of the deep Arctic basins, *Deep-Sea Res. II*, *42*, 1519–1531, 1995.
- Taguchi, K., K. Harada, and S. Tsunogai, Particulate removal of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  in the biological productive northern North Pacific, *Earth Planet. Sci. Lett.*, *93*, 223–232, 1989.
- Walter, J. H., M. M. Rutgers Van der Loeff, and H. Hoeltzen, Enhanced scavenging of  $^{231}\text{Pa}$  relative to  $^{230}\text{Th}$  in the South Atlantic south of the polar front: implications for the use of the  $^{231}\text{Pa}/^{230}\text{Th}$  ratio as a paleo-productivity proxy, *Earth Planet. Sci. Lett.*, *149*, 85–100, 1997.
- Walter, H.-J., M. M. Rutgers Van der Loeff and R. Francois, Reliability of the  $^{231}\text{Pa}/^{230}\text{Th}$  activity ratio as a tracer for bioproductivity of the ocean. In: “Use of proxies in paleoceanography: examples from the South Atlantic”, edited by G. Fisher and G. Wefer, Springer-Verlag Berlin Heidelberg, pp. 393–408, 1999.
- Walter, H. J., W. Geibert, M. M. Rutgers Van der Loeff, G. Fisher, and U. Bathmann, Shallow vs. deep-water scavenging of  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  in radionuclide enriched waters of the Atlantic sector of the Southern Ocean, *Deep-Sea Res. I*, *48*, 471–493, 2001.
- Yu, E.-F., R. Francois, and M. P. Bacon, Similar rates of modern and last-glacial ocean thermohaline circulation inferred from radiochemical data, *Nature*, *378*, 689–694, 1996.
- Zheng, A., W. Shi, and Y. Huang, The separation of high purity  $^{233}\text{Pa}$  from  $^{237}\text{Np}$ , *Atomic Energy Sci. Technol.*, *24*, 69–72, 1990.

---

L. Guo and C. Gueguen, International Arctic Research Center, University of Alaska Fairbanks, AK 99775, USA. (guol@iarc.uaf.edu)  
 M. Chen, Department of Oceanography, Xiamen University, Xiamen, 361005, China.