

On the importance of the decay of ^{234}Th in determining size-fractionated $\text{C}/^{234}\text{Th}$ ratio on marine particles

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Received 4 August 2006; revised 13 October 2006; accepted 24 October 2006; published 2 December 2006.

[1] Accurate determination of the $\text{POC}/^{234}\text{Th}$ ratio on sinking particles is essential for the application of ^{234}Th as a proxy for the export of particulate organic carbon (POC) from the upper ocean. Previous studies have shown that $\text{POC}/^{234}\text{Th}$ ratios may vary by as much as two orders of magnitude, but the mechanism for this variability remains poorly understood. In this study, $\text{POC}/^{234}\text{Th}$ and $\text{POC}/^{228}\text{Th}$ ratios in three particle size classes were examined for samples collected from the upper 500 m at a station in the South China Sea. Our results indicate that changes in the $\text{POC}/^{234}\text{Th}$ ratio with particle size at a given depth are mostly driven by simple decay of ^{234}Th . In fact, various trends in the $\text{POC}/^{234}\text{Th}$ ratio versus particle size are explained by a combination of ^{234}Th decay and the preferential remineralization of POC relative to Th during particle aggregation. We also observed a trend of decreasing $^{234}\text{Th}/^{228}\text{Th}$ ratios with particle size. This trend is consistent with results expected from a Brownian-pumping model.

Citation: Cai, P., M. Dai, W. Chen, T. Tang, and K. Zhou (2006), On the importance of the decay of ^{234}Th in determining size-fractionated $\text{C}/^{234}\text{Th}$ ratio on marine particles, *Geophys. Res. Lett.*, 33, L23602, doi:10.1029/2006GL027792.

1. Introduction

[2] Over the past decade, the naturally occurring radioisotope, ^{234}Th ($t_{1/2} = 24.1$ d), has been widely used to quantify particulate organic carbon (POC) export in the upper ocean. The application of this approach requires measurement of both the depth profile of ^{234}Th , which is used to calculate ^{234}Th fluxes, and an estimate of the $\text{POC}/^{234}\text{Th}$ ratio on sinking particles to empirically derive POC export. Field observations, however, have shown that the $\text{POC}/^{234}\text{Th}$ ratio on marine particles may vary from 1 to $>100 \mu\text{mol dpm}^{-1}$. More specifically, researchers have observed various trends of $\text{POC}/^{234}\text{Th}$ ratio with particle size (see review by Buesseler *et al.* [2006]). These observations have led to the recent discussion regarding the accuracy of the ^{234}Th approach [e.g., Benitez-Nelson and Charette, 2004; Moran *et al.*, 2003, 2004].

[3] To explain how the $\text{POC}/^{234}\text{Th}$ ratios change with particle size, several processes have been invoked, such as changes in the volume:surface area (V:SA) ratio of marine particles, rapid abiotic aggregation of small particles into larger ones, and preferential degradation or assimilation of POC relative to ^{234}Th [Buesseler *et al.*, 2006]. We suggest

that an additional mechanism should be considered, the decay of ^{234}Th . This is simply because ^{234}Th has a relatively short half-life ($t_{1/2} = 24.1$ d), whereas in the upper ocean, processes such as particle aggregation and export generally occur over a time scale of days to weeks [e.g., Honeyman and Santschi, 1989; Murray *et al.*, 1989]. In a closed system, the decay of ^{234}Th is expected to result in an increase in $\text{POC}/^{234}\text{Th}$ ratios with particle size if one assumes negligible remineralization of POC during particle aggregation. In this study, we have designed a field experiment by applying a longer-lived Th isotope, ^{228}Th ($t_{1/2} = 1.91$ a) coupled with ^{234}Th . Since both ^{234}Th and ^{228}Th are radiogenic, i.e., ^{234}Th is produced through in-situ decay of dissolved ^{238}U whereas ^{228}Th is through decay of dissolved ^{228}Ra , their geochemical behaviors in seawater should be similar. Thus, determinations of size-fractionated $^{234}\text{Th}/^{228}\text{Th}$ ratio should lend insights into the possible role of the decay of ^{234}Th in regulating $\text{POC}/^{234}\text{Th}$ ratio on marine particles.

2. Methods

[4] Samples in this study were collected at South East Asia Time-Series Station (SEATS; 18°N , 116°E) on a cruise in May 2005 on board R/V Dongfanghong II. SEATS is located in the northern South China Sea, and the water depth at this location is 3841 m. A large volume (500 L) of seawater was sampled at 13, 30, 52, 80, 110, 125, 150, 175, 200, 230, 260, 290, 350, 410, 450 and 500 m with an in-situ pump (McLane Lab) equipped with 142 mm diameter filtration holders. Seawater was pumped sequentially through a $53 \mu\text{m}$ Nitex screen, a $10 \mu\text{m}$ Nitex screen, a $1.0 \mu\text{m}$ (nominal pore size) quartz fiber filter (QMA, Whatman), and two 5-inch MnO_2 -impregnated cartridges. The pump flow rates were $4\text{--}7 \text{ L min}^{-1}$. During deployment of the in-situ pump, 4 L of seawater were collected for total ^{234}Th analyses at the same depths using Go-Flo bottles attached on a CTD rosette sampler. After sample collection, particles on the 53 and $10 \mu\text{m}$ pore size Nitex screens were re-suspended by ultrasonication in filtered seawater and re-collected on 47-mm $1.0 \mu\text{m}$ QMA filters. The 142-mm QMA filters as well as the 47-mm QMA filters were dried overnight, and a 22-mm subsample was cut from each filter and prepared for beta counting. The remaining QMA filter material was used for the determination of natural ^{228}Th . Analysis of particulate ^{234}Th activities were performed at sea with gas-flow proportional beta counters (RisØ GM-5-25) following the methods described in Cai *et al.* [2006a]. After beta counting, the subsamples were then used for POC measurement. POC analysis was accomplished with a PE-2400 SERIES II CHNS/O analyzer according to the JGOFS protocols [Knap *et al.*, 1996].

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Table 1. Size Fractionated ^{234}Th , ^{228}Th and POC Concentration in the Upper 500 m at SEATS in the South China Sea^a

Depth, m	^{234}Th , dpm l ⁻¹					^{228}Th , dpm m ⁻³					POC, μM		
	<1 μm	1–10 μm	10–53 μm	>53 μm	<1 μm	1–10 μm	10–53 μm	>53 μm	1–10 μm	10–53 μm	>53 μm		
13	1.823 ± 0.089	0.173 ± 0.007	0.0109 ± 0.0009	0.0142 ± 0.0013	16.98 ± 1.01	1.547 ± 0.053	0.166 ± 0.013	0.419 ± 0.021	0.83	0.103	0.102		
30	1.982 ± 0.111	0.223 ± 0.010	0.0229 ± 0.0007	0.0331 ± 0.0014	15.92 ± 1.77	1.800 ± 0.059	0.277 ± 0.013	0.528 ± 0.024	1.02	0.120	0.156		
52	2.041 ± 0.094	0.311 ± 0.009	0.0510 ± 0.0013	0.0585 ± 0.0005	11.84 ± 0.76	1.844 ± 0.063	0.362 ± 0.018	0.616 ± 0.026	0.90	0.118	0.127		
80	1.522 ± 0.072	0.154 ± 0.008	0.0309 ± 0.0006	0.0545 ± 0.0018	5.31 ± 0.34	0.608 ± 0.022	0.194 ± 0.009	0.577 ± 0.027	0.69	0.078	0.100		
110	2.531 ± 0.102	0.195 ± 0.005	0.0315 ± 0.0007	0.0366 ± 0.0014	7.76 ± 0.51	0.710 ± 0.025	0.165 ± 0.008	0.263 ± 0.013	0.33	0.053	0.048		
125	2.359 ± 0.090	0.198 ± 0.012	0.0214 ± 0.0009	0.0280 ± 0.0006	7.59 ± 0.56	0.797 ± 0.028	0.119 ± 0.006	0.386 ± 0.019	0.30	0.037	0.041		
150	2.196 ± 0.086	0.212 ± 0.006	0.0314 ± 0.0020	0.0135 ± 0.0009	8.04 ± 0.46	0.915 ± 0.031	0.170 ± 0.009	0.209 ± 0.011	0.28	0.055	0.017		
175	2.841 ± 0.116	0.217 ± 0.007	0.0384 ± 0.0016	0.0195 ± 0.0014	7.79 ± 0.37	0.953 ± 0.032	0.194 ± 0.010	0.187 ± 0.009	0.28	0.038	0.023		
200	2.051 ± 0.086	0.205 ± 0.009	0.0226 ± 0.0003	0.0168 ± 0.0004	6.44 ± 0.33	1.196 ± 0.041	0.189 ± 0.009	0.181 ± 0.008	0.24	0.043	0.037		
230	2.180 ± 0.092	0.219 ± 0.009	0.0247 ± 0.0008	0.0165 ± 0.0011	7.83 ± 0.42	1.218 ± 0.044	0.209 ± 0.010	0.392 ± 0.019	0.24	0.043	0.022		
260	2.225 ± 0.082	0.194 ± 0.008	0.0238 ± 0.0005	0.0198 ± 0.0016	6.05 ± 0.30	1.215 ± 0.043	0.280 ± 0.012	0.234 ± 0.010	0.23	0.040	0.021		
290	3.280 ± 0.128	0.209 ± 0.009	0.0313 ± 0.0004	0.0165 ± 0.0010	7.09 ± 0.51	1.327 ± 0.047	0.257 ± 0.012	0.312 ± 0.014	0.45	0.043	0.038		
350	2.505 ± 0.097	0.202 ± 0.009	0.0343 ± 0.0009	0.0214 ± 0.0006	4.53 ± 0.27	1.014 ± 0.035	0.302 ± 0.014	0.209 ± 0.011	0.26	0.041	0.023		
410	2.331 ± 0.087	0.269 ± 0.006	NA	0.0147 ± 0.0005	6.30 ± 0.33	1.168 ± 0.039	NA	0.200 ± 0.011	0.28	NA	0.018		
450	2.444 ± 0.103	0.240 ± 0.009	0.0206 ± 0.0003	0.0211 ± 0.0006	5.06 ± 0.50	1.110 ± 0.039	0.167 ± 0.008	0.227 ± 0.011	0.23	0.036	0.023		
500	2.273 ± 0.095	0.228 ± 0.005	0.0267 ± 0.0011	0.0168 ± 0.0009	4.48 ± 0.27	1.132 ± 0.039	0.232 ± 0.011	0.188 ± 0.009	0.41	0.034	0.021		

^aNA means not available due to accidental loss of the sample during ultrasonication.

[5] Analysis for total ^{234}Th in 4-L samples was based on the small volume MnO_2 coprecipitation technique following the procedure described by *Cai et al.* [2006b]. Dissolved ^{234}Th activity was estimated by the difference between total and particulate ^{234}Th . For the analysis of particulate ^{228}Th , approximate 4–5 dpm of ^{230}Th were added as a yield tracer to the remaining QMA filters. The subsequent procedure for the isolation of Th isotopes was according to *Anderson and Fler* [1982]. Thorium isotopes (^{228}Th and ^{234}Th) on MnO_2 cartridges, meanwhile, were leached using 2 N HNO_3 and H_2O_2 mixture [*Cai et al.*, 2006a]. Finally, Th was extracted into a 0.25 M TTA/benzene solution, and evaporated onto a stainless steel disc. The discs were counted by alpha spectrometry in ultra ion-planted detectors (Octète™ PC) until a minimum of 500 counts of ^{228}Th alpha was reached. The ^{228}Th peak was corrected for the underlying ^{224}Ra activity by the analysis of the dominant ^{224}Ra alpha at 5.7 MeV (this correction is typically <5%). Blank activity in the QMA filter was determined to be <2% of the particulate ^{228}Th activities. The collection efficiencies for dissolved ^{228}Th on MnO_2 cartridges were estimated from the ^{234}Th measurements on MnO_2 cartridges and in seawater [*Cai et al.*, 2006a]. Thorium-228 and -234 activities were both decay-corrected to the midpoint of sampling. The associated error represents one sigma uncertainty derived from counting statistics.

3. Results and Discussion

3.1. Size Fractionated ^{234}Th , ^{228}Th and POC Concentrations

[6] Dissolved ^{234}Th activities (<1 μm fraction) in the upper 500 m at SEATS varied from 1.522 dpm l⁻¹ to 3.280 dpm l⁻¹ (Table 1). Particulate ^{234}Th activities ranged from 0.0142 dpm l⁻¹ to 0.0585 dpm l⁻¹ on large particles collected on the >53 μm Nitex screens and between 0.0109 and 0.051 dpm l⁻¹ on medium size class particles collected on the 10–53 μm Nitex screens, whereas ^{234}Th activities measured on the 1–10 μm QMA filters were about ten times higher and ranged from 0.154 dpm l⁻¹ to 0.311 dpm l⁻¹. Dissolved ^{228}Th activities ranged from 16.98 dpm m⁻³ to 4.48 dpm m⁻³. Particulate ^{228}Th activities determined on the 1–10 μm QMA filters varied from 0.608 dpm m⁻³ to 1.844 dpm m⁻³ and showed a subsurface minimum between 80 m and 175 m, possibly due to rapid particle aggregation in this depth interval. The 10–53 μm Nitex screens had ^{228}Th activities that ranged from 0.119 dpm m⁻³ to 0.362 dpm m⁻³, and on average, were about 50% lower than those measured on the >53 μm Nitex screens. POC determined on the 1–10 μm QMA filters varied from 0.23 to 1.02 μM , whereas those measured on the 10–53 and >53 μm Nitex screens ranged from 0.034 to 0.120 μM , and between 0.017 and 0.156 μM respectively. POC concentrations in all particle size classes generally tended to decrease with depth.

[7] Overall, total ^{234}Th in the upper 100 m was deficient with respect to its parent nuclide, ^{238}U , which was estimated to be around 2.42 dpm l⁻¹ from salinity measurements at this location [*Chen et al.*, 1986]. Below 100 m, secular equilibrium was generally reached except at 175 m and 300 m. Radium-228 activities at this location decreased from ~80 dpm m⁻³ in the upper 50 m to ~5 dpm m⁻³ at

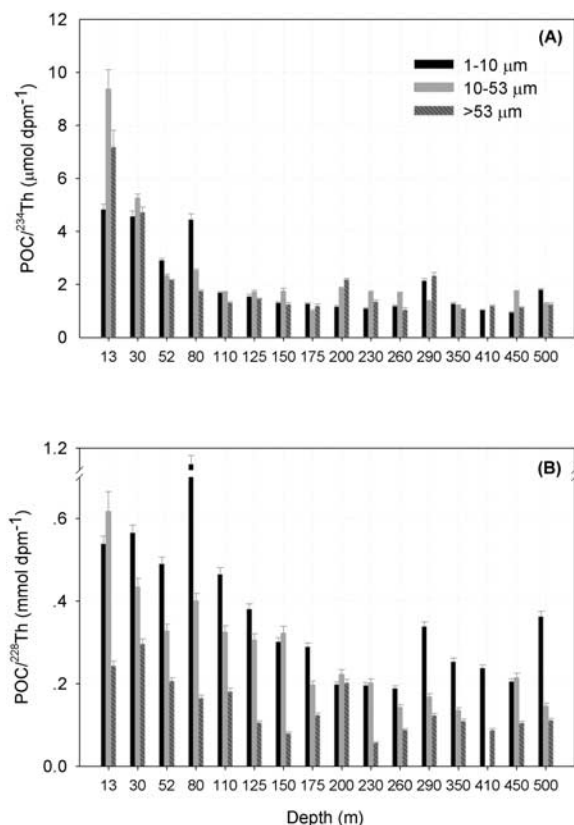


Figure 1. Size fractionated POC/Th ratios versus depth at SEATS in the South China Sea. (a) $\text{POC}/^{234}\text{Th}$, (b) $\text{POC}/^{228}\text{Th}$.

500 m (P. Cai et al., unpublished data, 2006). Total ^{228}Th in the upper 100 m also showed deficit with respect to ^{228}Ra , but to a considerably larger extent than ^{234}Th and ^{238}U . Below 200 m, total ^{228}Th tended to be in excess with respect to ^{228}Ra . This general characteristic has been observed at a station close to the present study site in the northern South China Sea [Lv, 2005], and at equatorial Pacific by Luo et al. [1995], suggesting that ^{234}Th and ^{228}Th and their parent nuclides in certain environmental settings may be at steady state.

[8] Assuming constant distribution of ^{228}Ra over the scavenging time scale of ^{228}Th , we can estimate the residence times of ^{234}Th and ^{228}Th in the euphotic zone using Equation 3 presented by Luo et al. [1995]. Such an exercise showed that both isotopes have similar residence times (1.26 ± 0.34 vs. 0.97 ± 0.07 yr). A similar conclusion was reached by Luo et al. [1995]. This implies that the geochemical behaviors of these two isotopes are similar, such that at least over the time scale of the mean life of ^{234}Th , seasonal changes and advective/diffusive transport are unlikely to play a significant role. Note that Luo et al. [1995] observed differences in the behavior between ^{228}Th and ^{230}Th in the upper ocean. Based upon the consideration that ^{230}Th has a significantly longer residence time and thus records a longer history than ^{228}Th does, these researchers ascribed the difference to diffusive and advective input of ^{230}Th .

3.2. POC/Th Versus Particle Size

[9] As most researchers are concerned with the application of ^{234}Th as a tracer for sinking particles, we will only

examine the POC/Th ratios on particles of size $\geq 1 \mu\text{m}$, which are thought to dominate the particle export in the upper ocean. The size-fractionated $\text{POC}/^{234}\text{Th}$ ratios varied from 0.95 to $9.4 \mu\text{mol dpm}^{-1}$ (Figure 1a). The lower limit was among the lowest $\text{POC}/^{234}\text{Th}$ ratios ever measured, and can be ascribed to efficient recycling of nutrients and carbon in this regime [e.g., Liu et al., 2002]. For all the size classes, $\text{POC}/^{234}\text{Th}$ ratios generally tended to decrease with depth. This was presumably due to preferential remineralization of POC relative to ^{234}Th . Alternatively, it can be explained by changes in surface binding ligands with depth, or simply increasing ^{234}Th activities at depth (see review by Buesseler et al. [2006]).

[10] Various trends in $\text{POC}/^{234}\text{Th}$ ratios with particle size and depth are observed (Figure 1a). These include a $\text{POC}/^{234}\text{Th}$ ratio decrease with particle size (52–110 m, 350, and 500 m), a $\text{POC}/^{234}\text{Th}$ ratio increase with particle size (200 m), or a constant $\text{POC}/^{234}\text{Th}$ ratio with particle size (30, 125, 175, 410 m). All of these trends have been observed previously [e.g., Buesseler et al., 2006; Passow et al., 2006]. In contrast, $\text{POC}/^{228}\text{Th}$ ratios generally tended to decrease with particle size (Figure 1b). The only exception to this pattern is at 200 m, where $\text{POC}/^{228}\text{Th}$ ratio was roughly invariant. Since the half-life of ^{228}Th is much longer than that of ^{234}Th , and likely longer than the time scale over which particle coagulation and aggregation occur, the $\text{POC}/^{228}\text{Th}$ ratio thus may be approximated as an analogue of decay-corrected $\text{POC}/^{234}\text{Th}$ ratio. It is now apparent that though there may be various trends of decay-uncorrected $\text{POC}/^{234}\text{Th}$ with particle size, decay-corrected $\text{POC}/^{234}\text{Th}$ ratios tended to decrease with particle size. The decrease in POC/Th ratio with particle size can be achieved via preferential remineralization of POC relative to Th during particle coagulation and aggregation. The invariant $\text{POC}/^{228}\text{Th}$ ratio with particle size at 200 m may be simply due to parallel remineralization of POC and Th at this depth.

3.3. $^{234}\text{Th}/^{228}\text{Th}$ Versus Particle Size

[11] Size-fractionated $^{234}\text{Th}/^{228}\text{Th}$ ratios varied by more than an order of magnitude, from a low of 34 to a high of 553. Substantial variability was also evident within a given particle size class (Figure 2). This is due to the fact that ^{234}Th and ^{228}Th have different source in seawater; ^{234}Th is produced through the decay of conservative ^{238}U , whereas ^{228}Th is added to seawater via the decay of ^{228}Ra , whose activity decreases from the surface ocean to a mid-water minimum (P. Cai et al., unpublished data, 2006). As a result, $^{234}\text{Th}/^{228}\text{Th}$ ratios in dissolved phase vary substantially with depth (Figure 2), causing a similar variability in particulate $^{234}\text{Th}/^{228}\text{Th}$ ratios [e.g., Bacon and Anderson, 1982]. Nevertheless, at any given depth $^{234}\text{Th}/^{228}\text{Th}$ ratios consistently decreased with particle size. On average, $^{234}\text{Th}/^{228}\text{Th}$ ratios on small, medium and large size class particles were 197, 133, and 81 respectively, whereas in the dissolved phase, the value was 332. The largest difference in $^{234}\text{Th}/^{228}\text{Th}$ ratios between different size class particles occurred at 300 m, where the $^{234}\text{Th}/^{228}\text{Th}$ ratio for particles $>53 \mu\text{m}$ was almost 9 times lower than in the dissolved phase. The decrease in $^{234}\text{Th}/^{228}\text{Th}$ ratios with particle size is consistent with the hypothesis of a so-called Brownian-pumping model, in which trace metals are expected to be transferred by coagulation up the particle size spectrum, from colloids

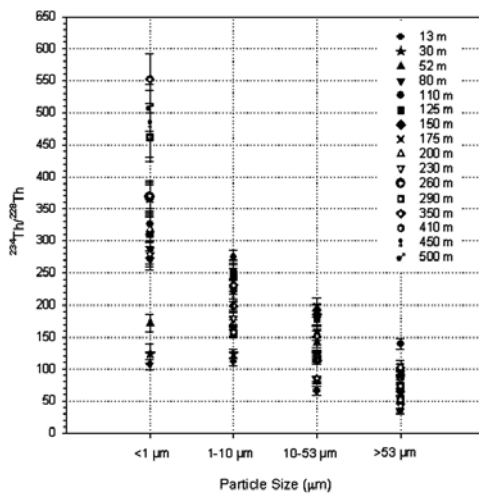


Figure 2. $^{234}\text{Th}/^{228}\text{Th}$ ratios versus particle size at SEATS in the South China Sea. Note that $^{234}\text{Th}/^{228}\text{Th}$ ratios in the dissolved fraction ($<1\ \mu\text{m}$) are also shown.

to small, and then to large particles [Honeyman and Santschi, 1989]. This trend is also expected from a reversible model for particle aggregation and disaggregation [e.g., Cochran *et al.*, 1993] if one assumes that aggregation $>$ disaggregation, i.e., that there is a net forward flow of small particles towards larger particles.

[12] Since the geochemical behaviors of ^{234}Th and ^{228}Th are similar, changes in size fractionated $^{234}\text{Th}/^{228}\text{Th}$ ratio at a given depth can be expressed as the following equation if there is no more particle-water exchange after coagulation:

$$R_p = R_d \times \text{EXP}[-(\lambda_{234} - \lambda_{228})t] \quad (1)$$

where R_d and R_p represent $^{234}\text{Th}/^{228}\text{Th}$ ratios in the dissolved and particulate phases, respectively; λ_{234} and λ_{228} are decay constants for ^{234}Th and ^{228}Th ; t is the time for particle coagulation. As $\lambda_{234} \gg \lambda_{228}$, equation (1) can be simplified to

$$R_p = R_d \times \text{EXP}[-\lambda_{234}t] \quad (2)$$

Equation (2) suggests that variations in $^{234}\text{Th}/^{228}\text{Th}$ ratio are solely due to the decay of ^{234}Th . In this context, variations in $^{234}\text{Th}/^{228}\text{Th}$ ratio may quantitatively reflect changes in size fractionated $\text{C}/^{234}\text{Th}$ ratio that are caused by the decay of ^{234}Th (Figure 2). Equation (2) also suggests that $^{234}\text{Th}/^{228}\text{Th}$ ratio is a potentially useful in situ “coagulation meters” for marine particles in a steady state environment, as t (the time for particle coagulation) can be easily estimated if size-fractionated $^{234}\text{Th}/^{228}\text{Th}$ ratios are known. In the present case, we utilized the $^{234}\text{Th}/^{228}\text{Th}$ ratios in the dissolved phase and on the large particles to determine t . Results suggest that t varied from 21 to 75 d at different depths.

4. Summary

[13] Despite over a decade using ^{234}Th and $\text{POC}/^{234}\text{Th}$ ratios to determine export rates of POC from the upper ocean, mechanisms for the variability in $\text{POC}/^{234}\text{Th}$ ratio on

marine particles remain poorly understood. In this study, we have examined, for the first time, the $\text{POC}/^{234}\text{Th}$ and $\text{POC}/^{228}\text{Th}$ ratios in three particle size classes for samples collected from the upper 500 m at a station in the South China Sea. Our results clearly demonstrate that changes in $\text{POC}/^{234}\text{Th}$ ratio with particle size at a given depth are mostly driven by simple decay of ^{234}Th . In fact, various trends in the $\text{POC}/^{234}\text{Th}$ ratio versus particle size observed in this study can be explained by a combination of ^{234}Th decay and the preferential remineralization of POC relative to Th during particle aggregation.

[14] Nevertheless, our results do not necessarily mean that other processes are not important. However, without considering the effect of the decay, our interpretation for the variability in the size-fractionated $\text{POC}/^{234}\text{Th}$ ratios may be biased. For example, if volume:surface area (V:SA) played a role and the decay of ^{234}Th were insignificant, one would expect to see invariant $^{234}\text{Th}/^{228}\text{Th}$ ratios on different size class particles. This, however, contradicts our observations. We contend that size-fractionated $\text{POC}/^{234}\text{Th}$ and $\text{POC}/^{228}\text{Th}$ should be investigated over a wider range of oceanographic settings in order to fully understand the role of the decay of ^{234}Th .

[15] **Acknowledgments.** This work was supported by the Natural Science Foundation of China (NSFC) through grants 40676045, 40206011, 90211020, 40490264 and 40521003, and by the Ministry of Education through the Program for Changjiang Scholars and Innovative Research Team in University. We are grateful to M. M. Rutgers van der Loeff, C. Lamborg and an anonymous reviewer for their constructive comments. We thank the crew of Dongfanghong II for their assistance in sample collection during the cruise.

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