### Influence of particle composition on thorium scavenging in the marginal China seas

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#### Abstract

Thorium-234 and particle composition (organic matter, biogenic silica, carbonate and lithogenic component) were examined in the East China Sea (ECS) and the northern South China Sea (NSCS) in order to constrain the particle types scavenging thorium isotopes. Good positive correlations between particulate organic matter (POM) or carbonate and thorium-234 in suspended particulate matter (SPM) indicates that POM and carbonate are efficient to scavenge thorium-234. No relationship between biogenic silica and thorium-234 suggests that geochemical behavior of thorium-234 may be not influenced by biogenic silica. A simple model was used to evaluate the affinity of thorium-234 to different particle components. The results show that POM is the most efficient scavenger for thorium-234 in the ECS and the NSCS, followed by carbonate. The authors' results lend support to the utility of thorium-234 as a proxy of POC and carbonate in the upper layer. However, the strong dependence of thorium scavenging on particle composition challenges thorium-230 as a constant flux proxy.

Key words: POC, biogenic silica, thorium, carbonate, particle composition

#### 1 Introduction

Thorium isotopes (thorium-228, thorium-230 and thorium-234) are naturally occurred radionuclides in the ocean. Owing to their constant production rates and the known sources in the ocean, one can calculate particle fluxes based on the radioactive disequilibria between thorium and their precursor (uranium isotopes). Actually, there are very few natural tools that can convert concentrations into fluxes in the ocean (Geibert and Usbeck, 2004). Therefore, thorium isotopes, especially thorium-234 and thorium-230, have been widely used to evaluate the fluxes of biogenic particles and trace metals. Thorium-234  $(T_{1/2}=24.1 \text{ d})$ has usually been used to estimate fluxes of particulate organic carbon (Buesseler et al., 1992; Eppley, 1989), particulate inorganic carbon (Bacon et al., 1996), biogenic silica (Rutgers van der Loeff et al., 2002; Buesseler et al., 2001), tracer metals (Gustafsson et al., 2000) and persistent organic pollutants (Gustafsson et al., 1997a, b). The basic principle for flux calculation is to multiply thorium-234 flux by its ratio to other elements on particles. However, recent studies suggest that the ratios were affected by particle size, sampling depth, studied regions and sampling methods (Buesseler et al., 2006). How these factors produce the effect of the ratios of thorium-234 on other elements and then the calculated fluxes become a focus of thorium-234 application and is not well understood up to now. In fact, almost all of the influencing factors resulted from the unique fact that is the interaction between thorium-234 and different particle chemical components. Consequently, the reliability or validity of thorium-234 flux approach is subject to the particle chemical composition essentially.

Thorium-230 ( $T_{1/2}=75\,400\,$  a) was widely used as a proxy in paleoproductivity (Kumar et al., 1995; Kumar et al., 1993; Francois et al., 1993), constantflux calibration (Francois et al., 1990; Suman and Bacon, 1989) and ocean circulation (Moran et al., 2001; Yu et al., 1996). These applications assume that the thorium-230 removal to be independent of particle chemical composition, and approximately equal to its production rate from uranium-234 in the overlying water column. However, many recent field and laboratory studies suggest that thorium affinity to different

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particle components (such as particulate organic matter, carbonate, biogenic silica, lithogenic matter, etc.) was different (Li, 2005; Ray-Barman et al., 2005; Geibert and Usbeck, 2004; Chase et al., 2002; Guo et al., 2002; Luo and Ku, 1999). An important question is whether composition-dependent scavenging of thorium affects the utility of thorium-230 as a proxy as pointed out by Chase et al. (2002).

In this paper, we have presented a set of data obtained in the East China Sea (ECS) and the northern South China Sea (NSCS) that allows the interaction between thorium-234 and particle chemical components to be examined. Our results will shed light on the question linked to the utilities of thorium-234 and thorium-230 as flux proxies in the ocean.

#### 2 Sampling and analyses

#### 2.1 Sampling sites

Figure 1 shows the collection sites in this study. Among the eight stations occupied for thorium-234 and particle composition measurements, three depth profiles (Stas S0508, S0703 and S1002) were obtained with Rosette casts in the ECS from June to July 2006. Only surface samples were collected at other stations (Stas D15, D16, D18, D20 and D22) in the NSCS from July to August 2006.



**Fig.1.** Locations of sampling stations in the East China Sea (Stas S1002, S0703 and S0508) and the South China Sea (Stas D15, D16, D18, D20 and D22).

#### 2.2 Thorium-234 analysis

Thorium-234 analysis was conducted with a  $MnO_2$ -coprecipitation technique described by Ma et al. (2005). Briefly, two liters of seawater was added

with drops of concentrated ammonia, 25  $\mu$ l of concentrated KMnO<sub>4</sub> solution and 10  $\mu$ l of concentrated MnCl<sub>2</sub> solution. The formed MnO<sub>2</sub> precipitate carrying thorium was allowed to settle for 2 h and filtered on a 47 mm GF/F filter. Filters containing MnO<sub>2</sub> precipitate and suspended particulate matter were dried and beta-counted as soon as possible. After decay of thorium-234 (>150 d), a second beta-counting was required to correct for the contribution of other beta emitters than thorium-234/protactinium-234m (Rutgers van der Loeff et al., 2002). The thorium-234 counting errors were less than  $\pm 5\%$ , and the thorium-234 activities were corrected to the sampling mid-time. The study areas were characterized by high particle concentration (with the mean of  $0.005 \ 4 \ \text{kg/m}^3$ ), in this condition, particulate thorium-234 (in  $Bq/m^3$ ) makes up about 90% of the total thorium-234 (Chen, 1996), herein total thorium-234 measured reflects the particulate thorium-234 actually.

### 2.3 POC, biogenic silica and carbonate analysis

Samples for particulate organic carbon and carbonate were taken from the same Rosette cast for the thorium sampling. One to two liters of water were filtered using pre-combusted 47 mm GF/F filters (at 500°C for 4 h). The filters were stored frozen until determination. POC filters were fumed with concentrated HCl to remove inorganic carbonates, and analyzed in Perkin Elmer CHN analyzer. Carbonate filters were not treated with any acid but other procedures were the same to that of POC. Particulate inorganic carbon (PIC) was calculated as the difference between bulk carbons obtained from carbonate filters and POC. The carbonate fraction was calculated as follow: CaCO<sub>3</sub>= $8.33 \times$ PIC (Ray-Barman et al., 2005).

Biogenic silica analysis was conducted using the double wet-alkaline digestion method (Ragueneau et al., 2005). In brief, a polycarbonate membrane (0.4  $\mu$ m pore-size and 47 mm diameter) containing suspended particulate matter was firstly digested with 0.2 mol/dm<sup>3</sup> NaOH in a polymethylpentene centrifuge tube at 100°C for 40 min. At the end of this digestion, silicic concentration in the supernatant was analyzed. After rinsed and dried, the filter was secondly digested identical to the first one. The biogenic silica concentration was corrected for mineral interference determined by the second digestion.

Lithogenic content was estimated as  $100-(2.4 \times BSi+carbonate+2 \times organic carbon)$  (Chase et al., 2002). Where 2.4 was conversion factor between Si<sub>opal</sub> and opal (Mortlock and Froelich, 1989), which was also proposed by JGOFS, 2 is the mass ratio of organic matter to organic carbon (Buffle, 1990). Hereby, lithogenic component was comprised of minerals mainly.

#### 3 Results and discussion

### 3.1 Role of bulk particle in geochemical cycling of thorium

In general, thorium isotopes except thorium-232 in the ocean are produced in situ by uranium isotopes and removed from the water column by particle scavenging and sinking. A good positive correlation between thorium-234 activity in seawater and the concentrations of suspended particulate matter (SPM) was observed (Fig. 2), which reflected the important role of SPM in regulating the geochemical behavior of



**Fig.2.** Relationship between thorium-234 specific activity and the concentrations of suspended particle matter in the ECS and the NSCS.

thorium-234 in the study sea areas. In order to examine particle scavenging to thorium-234, ratios of thorium-234 activity to particle concentrations (in Bq/kg) were adopted in the following (Fig. 3). Because total thorium-234 reflected particulate thorium-234 actually, ratios of total thorium-234 to particle concentration indicated similar implications to that of particulate thorium-234 to particle concentration essentially. The SPM collected by filters is composed of fecal pellets, marine snow, detritus and individual foraminifera in variable proportions. Although each type of particles was derived from different sources, it was a practical and efficient way to classify them based on their chemical compositions, such as particulate organic matter (POC), biogenic silica (BSi), carbonate and lithogenic component. By means of this classification, it will be possible to study the role of different components in thorium-234 scavenging. In the following, we will focus on the relationship between thorium and the contents of different components.

#### 3.2 Role of different particulate components

#### on thorium scavenging

#### 3.2.1 POC

A good positive correlation between thorium-234 and POC was observed (Fig. 3a), which gave a support to the use of thorium-234 as a POC flux proxy at least in the East China Sea. Disequilibria between thorium-234 and uranium-238 have been widely used to estimate POC export flux out of the euphotic zone, though a few of studies suggest that thorium-234 possibly tracks the total mass flux rather more closely than the POC flux (Shimmield et al., 1995; Murray et al., 1989). More efficient scavenging of thorium-234 in the upper ocean layer was ascribed to the enriched organic ligands in the particulate matter produced by biological activity (Ray-Barman et al., 2005; Quigley et al., 2001). Because POC consists of many organic compounds, and different compounds have different affinity to thorium, the observed correlation between thorium-234 and POC may change with POC composition. Polysaccharides have been considered to play an important role in thorium-234 scavenging and have been studied mostly (Guo, Hung et al., 2002; Quigley et al., 2002). However, a little was known about the role of other organic compounds (such as pigments, fatty acid, amino acid and humic acid etc.) in thorium-234 scavenging (Stewart et al., 2007; Guo, Chen et al., 2002). More in-depth studies were needed for accurately evaluating different organic compounds in thorium scavenging. During particulate settling, organic ligands in POM decreased rapidly by degradation or remineralization (Hirose and Tanoue, 1998), and thus the scavenging efficiency of thorium to POC may become weakened gradually. Considering the sorption irreversibility of thorium-234 with marine organic matter (Quigley et al., 2001) and the lost of thorium-234 by radioactive decay, the correlation between POC and thorium-234 may change or disappear in mesopelagic waters. This can be elucidated by another thorium isotope of thorium-230 which is produced in situ by uranium-234 decay and is almost independent of its disintegration in the ocean. Lack of correlation between excessive thorium-230 and POC in sediment



**Fig.3.** Thorium-234 as a function of particle compositions. (a. POC, b. lithogenic component, c. carbonate and d. biogenic silica)

trap samples at least below 400 m in the northeastern Atlantic POMME experiment verified that thorium scavenging by particulate organic matter in mesopelagic waters was less efficient than that in surface bio-productive water (Ray-Barman et al., 2005). On the other hand, a four-end-member mixing model proposed by Li (2005) suggests that the role of organic matter in thorium-230 scavenging can not be ignored though it is less efficient in the mesopelagic waters. 3.2.2 Lithogenic material

There is an inverse linearly relationship between thorium-234 and the lithogenic fraction (Fig. 3b), which indicates that the bulk lithogenic material act as a dilute reagent in thorium-234 specific activities. However, this inverse relation can not infer information on the role of lithogenic component in scavenging thorium-234. This relation can result from the following mechanisms. On the one hand, high SPM concentration may exceed the amount which is enough to scavenge bulk thorium-234. As a result, lithogenic appears to be a dilute reagent. In this condition, actual relation has been concealed and apparent relation does not illustrate the scavenging of lithogenic component to thorium-234. On the other hand, lithogenic regime is a complicated system consisting of minerals, MnO<sub>2</sub>,  $Fe(OH)_3$ , etc. This relationship may change with the changing of the fraction of each substance in lithogenic components due to their different scavenging efficiencies for thorium as revealed by controlled experiments (Geibert and Usbeck, 2004; Guo, Chen et al., 2002) and in situ investigation (Ray-Barman et al., 2005; Luo and Ku, 1999).

Partition coefficients,  $K_{\rm d}$ , of thorium listed in Table 1 indicate obvious difference among the affinities of thorium to different lithogenic substances. The highest  $K_{\rm d}$  values were observed for thorium on MnO<sub>2</sub>. It is well known that thorium-234 in seawater is usually enriched by manganese oxide-impregnated cartridges (Buesseler et al., 2001; Buesseler et al., 2000) or  $MnO_2$ precipitation (Ma et al., 2005; Rutgers van der Loeff et al., 2002). The strong affinity of  $MnO_2$  for thorium was not surprising. In contrast,  $K_{\rm d}$  values on smectite, a standard for determination of clay minerals via X-ray diffraction, are three to four orders of magnitude less than that on  $MnO_2$  (Table 1), indicating relative weak affinities of this lithogenic mineral for thorium. If the affinities of other lithogenic substances for thorium lie between smectite and  $MnO_2$ ,  $K_d$  values for thorium on bulk, lithogenic component would vary from  $10^6$ to  $10^{10}$ . The in situ data of  $K_{\rm d}$  which lied between

this range (Table 1) approved this assumption. Obviously, correlations between lithogenic components and thorium will depend on the lithogenic composition. On the one hand, good positive correlations between lithogenic component and thorium have been observed in the Pacific and Atlantic Oceans (Ray-Barman et al., 2005; Luo and Ku, 1999). Ray-Barman et al. (2005) pointed out that this positive correlation reflected the correlation between manganese content and thorium. Namely, thorium scavenging by lithogenic matter depends on the manganese-related coatings outside the particles. On the other hand, manganese was not always correlated with the load of lithogenic components. Manganese was enriched in small suspended particles and can be incorporated into sinking particulate throughout the water column by coagulation or aggregation (Ray-Barman et al., 2005). On this condition manganese was wrapped by other substances and has little chance to contact with dissolved thorium, as a consequence negative correlation between lithogenic component and thorium was observed. Considering only a little studies have been conducted on the influence of lithogenic composition on thorium scavenging in recent years and the complications of lithogenic component, further studies are required to evaluate accurately which substances are the major thorium-234 scavenger in lithogenic materials.

Table 1. Partition coefficients of thorium between particulate components and seawater

Components	Locations	Radionuclide	$K_{ m d}/$	Reference	
			$\rm dm^3 \cdot kg^{-1}$		
Opal	EqPac and MAB	thorium-230	$0.4 \times 10^{6}$	Chase et al. $(2002)$	
	EqPac and North Atlantic	thorium-230	$2.5{ imes}10^6$	Luo and Ku (2004)	
Carbonate	EqPac. and MAB	thorium-230	$9.0 \times 10^6$	Chase et al. $(2002)$	
	EqPac and North Atlantic	thorium-230	$1.0 \times 10^{6}$	Luo and Ku $(2004)$	
Lithogenic	EqPac and North Atlantic	thorium-230	$230 \times 10^{6}$	Luo and Ku $(2004)$	
	EqPac. and MAB	thorium-230	$10 \times 10^6$	Chase et al. $(2002)$	
$MnO_2$	NE Atlantic Ocean	thorium-230	$(2-2.5) \times 10^{10}$	Ray-Barman et al. $(2005)$	
	Western Mediterranean Sea	thorium-230	$(0.4-0.6) \times 10^{10}$	Ray-Barman et al. $(2002)$	
Smectite	Controlled experiments	thorium- $234$	$7.1 \times 10^6$	Geibert and Usbeck (2004)	
SPM	Southern South China Sea	thorium-234	$0.07 \times 10^{6}$	Chen (1996)	
	Northeastern South China Sea	thorium-234	$0.45 \times 10^{6}$	Chen (1996)	
	Xiamen Bay, China	thorium-234	$0.49 \times 10^{6}$	Chen (1996)	
	Jiulong River Estuary, China	thorium-234	$0.14 \times 10^{6}$	Chen (1996)	
	Coastal ocean to open ocean	thorium- $234$	$(0.003\ 210) \times 10^6$	Honeyman and Santschi $(1989)$	

#### 3.2.3 Carbonate

Good positive correlation between thorium-234 and carbonate contents (Fig. 3c) suggests that  $CaCO_3$ is an important thorium-234 scavenger in the ECS and the NSCS. This is consistent with the reported results from the Southern Ocean and the Equatorial Pacific, where the strong correlation between excessive thorium-230 and  $CaCO_3$  was used to approve that  $CaCO_3$  could be an important thorium-230 carrier (Luo and Ku, 2004; Chase et al., 2002). Controlled experiments show that  $CaCO_3$  selectively interacts with thorium-234 in contrast to  $SiO_2$  (Guo, Chen et al., 2002), which was also confirmed by the higher partition coefficients of thorium between  $CaCO_3$  and solution observed in situ (Table 1). In general, CaCO<sub>3</sub> remains stable over much of the water column whereas particulate organic matter is expected to experience more dissolution with depth (Ray-Barman

et al., 2005). This implies that the role of  $CaCO_3$  in regulating thorium scavenging may be more notable in mesopelagic waters. On the other hand, thorium-230 produced in water column was usually removed to local sediments (Yu et al., 2001; Walter et al., 1997; Kumar et al., 1993) and the standing crops of thorium-230 increase linearly with increasing depth (Edmonds et al., 1998); both lend support to the importance of  $CaCO_3$  in thorium scavenging in deep water. Actually, the above information can be found in the previous studies, in which  $CaCO_3$  and lithogenic materials have been expected to scavenge thorium efficiently in mesopelagic and deep water where POC were barren relative to upper layer (Luo and Ku, 2004; Chase et al., 2002). Our results provided a further evidence for this expectation.

3.2.4 Biogenic silica

The lack of correlation between thorium-234

activities and BSi contents suggests that BSi is not the main thorium-234 carrier (Fig. 3d). Although little study was conducted on the influence of biogenic silica on thorium-234 scavenging, this relation can be illustrated by other thorium isotope such as thorium-230. The inverse correlations between excessive thorium-230 and BSi observed in the northeastern Atlantic (Ray-Barman et al., 2005), the Southern Ocean and the equatorial Pacific Ocean (Chase et al., 2002) indicate that thorium-230 has a lower affinity to BSi than other components. A combined model also confirms that opal (i.e.,  $BSiO_2 \cdot xH_2O$ ) is a weak scavenger for thorium-230 (Siddall et al., 2005). However, these results do not exclude the probability that a good positive correlation between thorium-234 activities and BSi contents can be found. In some environments where particulate organic carbon coupled with biogenic silica closely (i.e., nearly constant POC/BSi ratio occurred), a positive correlation may occur. The euphotic layer in some sea areas belongs to these environments. The relationship between thorium and BSi in these environments reflects the connection between POC and thorium indeed. With the particulate organic matter degradation and the dissolution of opal during particle settling, this relation would disappear within the mesopelagic water as a result of the decoupling of POC and BSi.

# 3.2.5 Comparison of thorium affinity to different particle components

Since POC,  $CaCO_3$  and lithogenic matter in particles play important roles in regulating thorium-234 scavenging just as stated above, a three end-member model was proposed to distinguish the affinities of thorium-234 to different particle components (i.e., POC, CaCO<sub>3</sub> and lithogenic matter). The multiple regression equation is

$$A_{\rm Th-234} = a \rm POC + b \rm CaCO_3 + c \rm Lith,$$
(1)

where  $A_{\rm Th-234}$  is the thorium-234 activity; a, b and c are coefficients of multiple regression; and POC, CaCO<sub>3</sub> and Lith denote the contents of particulate organic carbon, calcium carbonate and lithogenic matter. The regression analyses show that affinities of thorium-234 to different chemical components varied greatly (Table 2). POC had the strongest preference for thorium-234 than inorganic components, followed by carbonate. Recent studies suggest that both of lithogenic component and CaCO<sub>3</sub> were the major carriers for thorium-230 in mesopelagic water (Li, 2005; Chase et al., 2002; Luo and Ku, 1999). Considering that thorium-230 scavenging predominantly occurred in mesopelagic water rather than in surface water, and POM degraded mainly in upper ocean while refractory inorganic matter such as  $CaCO_3$  and lithogenic experience a little loss throughout the water column, our results provide additional evidence for the important role of lithogenic and  $CaCO_3$  in thorium-230 scavenging in mesopelagic water.

Table 2. Multiple regression results for thorium-234 activities as a function of POC,  $CaCO_3$  and lithogenic contents

Component	Coefficient	$\pm SE$	n	$r^2$	F	Р
POC	$a \ 2.71$	$\pm 0.61$				
$CaCO_3$	$b \ 0.84$	$\pm 0.28$	19	0.86	30.58	$< 0.000 \ 1$
Lithogenic	$c \ 0.64$	$\pm 0.25$				

# 3.3 Implications for thorium as particle flux proxy

Thorium-234 was widely used as a tracer for POC flux in the euphotic layer (Burd and Honda, 2007; Kawakami and Honda, 2007; Buesseler et al., 2006; Cochran et al., 2000). POC flux out of the euphotic layer was estimated by the POC/thorium-234 ratio in the particles at export interface multiplied by thorium-234 export flux (Buesseler et al., 1992). This application is based on the assumption that thorium-234 is scavenged by particulate organic matter or certain correlation between thorium-234 and POM exists. As stated above, our results support thorium-234 as a proxy for POC export flux. In addition, the correlations between thorium-234 and carbonate or lithogenic matter highlighted the use of thorium-234 as a tracer for inorganic component flux though more studies are needed in the future.

Thorium-230 has been widely used to calibrate particle flux and sediment focusing or winnowing with the assumption that its removal from water column is roughly equal to its production in the overlying water column whatever the particle chemical composition variation (Hoffmann and McManus, 2007; Moran et al., 2001; Walter et al., 1997; Yu et al., 1996; Francois et al., 1990). However, our results suggest that thorium scavenging in seawater was affected by particle chemical composition. For example, in sea areas with the particle regime mainly comprised of biogenic silica, thorium-230 scavenging will be less efficiency, and the particulate fluxes calculated by normalizing to thorium-230 production will be over-estimated. In sea areas with particulate organic matter dominating the particle regime, particulate fluxes normalized to thorium-230 will be underestimated. The enhanced scavenging of thorium-230 in the western Northwest Pacific Ocean highlighted this situation (Yamada and Zheng, 2007). It is obvious whether the thorium-230 was suitable as a constant flux proxy or a calibrated standard will depend on particle composition in the study sea areas.

#### 4 Conclusions

Relationships between particle chemical compositions and thorium-234 show that thorium-234 was scavenged strongly by particulate organic matter, followed by carbonate in the East China Sea (ECS) and the northern South China Sea (NSCS). These results provided evidence for thorium-234 as a proxy of POC and carbonate export in the study sea areas. Although inverse relation has been observed between thorium-234 and lithogenic component, any conclusions can not be drawn due to the high particle concentrations in the study sea areas and complication of lithogenic components. Lithogenic components and carbonate play more important role in thorium scavenging in the mesopelagic water due to POM degradation during particle settling. Biogenic silica was not an efficient scavenger for thorium-234 in seawater. This study places an important constraint on the use of thorium isotopes as the flux proxy of particulate component in the ocean.

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