

Organic carbon to ^{234}Th ratios of marine organic matter

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Abstract

Uncertainties in the determinations of particulate organic carbon flux from measurements of the disequilibrium between ^{234}Th and its mother isotope uranium depend largely on the determination of the organic carbon to $^{234}\text{thorium}$ ($\text{OC} : ^{234}\text{Th}$) ratio. The variability of the $\text{OC} : ^{234}\text{Th}$ ratio in different size fractions of suspended matter, ranging from the truly dissolved (<3 or 10 kDa) fraction to several millimeter sized marine snow, as well as from sediment trap material was assessed during an eight-day cruise off the coast of California in Spring 1997. The affinity of polysaccharide particles called TEP (transparent exopolymer particles) and inorganic clays to ^{234}Th was investigated through correlations. The observed decrease in the $\text{OC} : ^{234}\text{Th}$ ratio with size, within the truly dissolved to small particle size range, is consistent with concepts of irreversible colloidal aggregation of non-porous nano-aggregates. No consistent trend in the $\text{OC} : ^{234}\text{Th}$ ratio was observed for particles between 1 or 10 to 6000 μm . Origin and fate of marine particles belonging to this size range are diverse and interactions with ^{234}Th too complex to expect a consistent relationship between $\text{OC} : ^{234}\text{Th}$ ratio and size, if all categories of particles are included. The relationship between OC and ^{234}Th was significant when data from the truly dissolved fraction were excluded. However, variability was very large, implying that OC flux calculations using different collection methods (e.g. sediment trap, Niskin bottles or pumps) would differ significantly. Therefore a large uncertainty in OC flux calculations based on the ^{234}Th method exist due to individual decisions as to which types or size classes of particles best represent sinking material in a specific area. Preferential binding of ^{234}Th to specific substance classes could explain the high variability in the relationship between OC and ^{234}Th . At 15 m, in the absence of lithogenic material, the $\text{OC} : ^{234}\text{Th}$ ratio was a function of the fraction of TEP or TEP-precursors in OC , confirming that acidic polysaccharides have a high affinity for ^{234}Th and that TEP carry a ligand for ^{234}Th . Preferential binding to TEP might change distribution patterns of ^{234}Th considerably, as TEP may sink when included in large aggregates, or remain suspended or even ascend when existing as individual particles or microaggregates. In the presence of lithogenic matter, at depths below 30 m, the ratio between ^{234}Th and OC was linearly related to the ratio between aluminosilicates and C. The affinity of inorganic substances to ^{234}Th is known to be relatively low, suggesting that a coating of acidic polysaccharides was responsible for the apparently high affinity between ^{234}Th and lithogenic material. Overall, $\text{OC} : ^{234}\text{Th}$ ratios of all material collected during this investigation can best be explained by differential binding of ^{234}Th to both TEP and TEP-precursors, as well as to lithogenic minerals, which were very abundant in an intermediate nepheloid layer between 50 and 90 m.

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1. Introduction

Knowledge of the mechanisms that drive the flux of carbon to the deep sea is an important prerequisite for understanding the marine carbon cycle and thus the potential impacts of rising atmospheric CO₂ concentrations. Sediment traps have been used to estimate particulate organic carbon (POC) flux within the water column for decades. Since the early nineties, POC flux has also been estimated from the disequilibrium between ²³⁴Th and its mother isotope ²³⁸U (Buesseler et al., 1992; Murray et al., 1996). The difference between the calculated ²³⁴Th flux and that measured by traps has been interpreted to be the result of under- or over-collection by traps (Buesseler, 1991). However, problems with flux estimates from the thorium method also became apparent (Buesseler et al., 1992, 1995; Murray et al., 1996) in part because of the uncertainty about whether ²³⁴Th is an appropriate tracer for POC, or whether ²³⁴Th may be a better tracer for mass (e.g. surface area) than POC (Murray et al., 1989). Answers to these questions are urgently needed as the uncertainties in the determinations of POC flux from ²³⁴Th measurements depend largely on the determination of the OC:²³⁴Th ratio used to make this conversion.

The OC:²³⁴Th ratio can be highly variable in both space and time and with particle collection method, introducing a large uncertainty in flux estimates using ²³⁴Th deficiencies. The reasons for this variability are not well understood (Buesseler et al., 2006-this issue; Moran et al., 2003; Santschi et al., 2006-this issue). It has been postulated that the OC:²³⁴Th ratio should increase with particle size, but opposite trends have also been observed (Buesseler et al., 2006-this issue). Potential causes for this variability include: the lifetime of particles in the surface with respect to sinking, the surface to volume ratio of particles, biases during particle collection and differential binding to specific substance classes. Phytoplankton may scavenge thorium (Fisher et al., 1987) and mineral composition and particle flux may impact the rate at which thorium is scavenged from the water column (Chase et al., 2002, 2003). Furthermore, preferential binding to acidic polysaccharides has been postulated (Niven et al., 1995) and established both in situ and in the laboratory (Guo et al., 2002b,c; Quigley et al., 2002).

Acidic polysaccharides, which are released by phytoplankton and bacteria, form surface active transparent exopolymer particles, called TEP (Passow, 2002b). TEP are highly surface active, or “sticky”, promoting coagulation, and form the matrix of marine snow (Passow et al., 1994). Thus, these particles may contain or

carry a ligand for ²³⁴Th that may substantially impact the distribution of ²³⁴Th. When incorporated into marine snow, TEP belong to the pool of large sinking particles, however, individual TEP may also belong to the pool of small suspended particles, which may ascend to surface waters, as their density is lighter than sea water (Azetsu-Scott and Passow, 2004). Precursors of TEP belong to the colloidal pool (Passow, 2000).

Using data collected during an eight-day cruise in the Santa Barbara Channel we will show how the OC:²³⁴Th ratio varies with particle size, from the truly dissolved (ultrafiltrate) fraction to millimeter-sized marine snow. We will also investigate the possibilities of differential binding of ²³⁴Th to TEP and lithogenic material and discuss possible effects on the distribution and sinking of ²³⁴Th in the water.

2. Methods

2.1. Sample collection

We determined the OC:²³⁴Th ratio in colloidal and particulate organic matter by a variety of means in the Santa Barbara Channel, off Santa Barbara (34°15.0'N, 119°54.5'W) during April 1–9, 1997 as part of a collaborative study between the University of Washington and the University of California, Santa Barbara. Sampling was conducted from the *R/V Point Sur*. Vertical profiles of temperature and salinity (SBE-19 CTD), beam attenuation (SeaTech transmissometer at 550 nm), and fluorescence (SeaCat fluorometer) were determined several times daily. We measured aluminosilicates (Al) as a proxy for clays, TEP and TEP-propensity, as well as POC and dissolved organic carbon (DOC), nutrients, chlorophyll *a* (chl. *a*) and total, particulate and dissolved ²³⁴Th. Different types of samples were collected, using a variety of methods (Table 1). Each type of sample was collected 3–8 times during the 8-day period and as no temporal trend was visible data from different days were averaged, with given errors representing one standard deviation between samples (Table 1).

Water column samples (WC_{Niskin}) for determination of total, dissolved and particulate ²³⁴Th, as well as TEP, OC, chl. *a*, nutrients and Al were collected using 30 l Niskin bottles from 6 depths (0, 15, 30, 45, 60, 75 m) along the track of a drifting sediment trap (Table 1). Approximately 10 l of seawater were taken for total ²³⁴Th and 20 l were pressure filtered through a 1-μm Nuclepore filter for determination of dissolved ²³⁴Th (filtrate) and particulate ²³⁴Th.

Table 1
Sample collection during the R/V Point Sur research cruise (1–9 April 1997)

Collection method	Sampling dates and number of samples	Depths	Size fractions (μm)	Parameters
WC _{Niskin} (Niskin bottles, small volume filtration)	2–8; $n=8$	0, 15, 30, 45, 60, 75 m	$>0.8 \mu\text{m}$	OC, ^{234}Th , TEP,
WC _{LVF 1–53} (LVF 1–53 μm) and WC _{LVF >53} (LVF >53 μm)	2–8; $n=11$ (15 m); $n=2$ (55 and 75 m, each)	15, 55, 75 m	1–53 μm > 53 μm	^{234}Th , Al, Ca, DW, Cl, OC*
Marine snow, Hand-collected	3, 4, 5; $n=3$	10–20 m	$>1–7 \text{ mm}$	OC, ^{234}Th , TEP, DW, Cl,
Sinking particles, Sediment traps	4–6, 7–9; $n=2$ each depth	75, 150 m	Sinking particles	OC, ^{234}Th , TEP, Al, DW, Cl, LSi [#] , BSi [#]
Ultrafiltration, Niskin bottles	2, 3, 4, 6, 7, 8; $n=6$ (5 for TEP)	15 m	Total, $<1, <0.2 \mu\text{m}$, <10 or 3 kDa (alternate days)	OC, ^{234}Th , TEP

Ca = calcium carbonate, Cl = chloride, DW = dry weight, LSi = lithogenic silica, BSi = biogenic silica, OC = organic carbon. n = number of samples. Averages of results from samples of different days are given, thus the number of samples are treated as “replicates”.

* Calculated by difference from DW, Al, calcium carbonate, biogenic and lithogenic silicate and salt.

LSi+BSi lithogenic and biogenic silica determined by Shipe and Brzezinski (2001).

Suspended matter was also collected using a large volume in-situ filtration system (LVFS). The LVFS consisted of a baffling system, a 53 μm Nitex screen pre-filter and two 1 μm quartz filters (Bishop et al., 1999). Samples were collected for 1 h (filtered volume: 1012–2896 l, median 1462 l at a flow rate of 17–51 l min^{-1} , median: 24 l min^{-1}), the filters rinsed with 30 ml of weak (1%) NaHCO_3 solution to remove salt, vacuumed to dryness, and dried at 50 °C for 24 h. Subsamples of the 1- μm (WC_{1–53}) and the 53- μm (WC_{>53}) filters were analyzed for mass, ^{234}Th , Al, calcium, chloride (for sea salt correction). POC estimates were obtained by difference after accounting for the Al, calcium carbonate and biogenic silica mass fractions. For details on biogenic silica determinations, see Shipe (2000).

Marine snow was hand collected at depths of 10–20 m by scuba divers using 60 ml syringes. Aggregates were selected underwater in three size categories (small, medium, large), which were determined each day by divers as described in Alldredge (1989). Aliquots of aggregate slurry from each size category, containing between 30 and 234 aggregates each, were analyzed for mass, ^{234}Th and chloride, POC, and TEP. Representative aggregates from each size category were sized each day. Aggregate sizes varied between days and an aggregate considered “small” one day could be qualified as “medium” the next. Data are presented following the actual sizes determined, independent of collection day or collection category.

On six days ultrafiltration exercises were conducted. Water from six 30 l Niskin bottles collected at 15 m was pressure filtered sequentially through a 1 μm Nuclepore filter and a 0.2 μm Millipore filter into 20 l polyethylene cubitainers. Subsamples for <1 and $<0.2 \mu\text{m}$ size fractions were taken. Colloidal separation proceeded over

approximately 6 h as $<0.2 \mu\text{m}$ filtered water was pumped across either a 1 or 3 kDa (on alternate days) Amicon cross-flow ultra-filtration cartridge using a Teflon bellows pump. The ultra-filtered (<1 or <3 kDa) fraction was collected in a second polycarbonate tank. When the colloidal fraction (>1 or 3 kDa and $<0.2 \mu\text{m}$) was concentrated down to approximately 2–3 l, cross-flow filtration was terminated. Triplicates of the ultra-filtered fraction, a single colloidal fraction and three sequential acid rinses of the two tanks and the cross-flow filtration system (1 N HCl in artificial seawater) were analyzed for OC, ^{234}Th and TEP-propensity (TEP-propensity was not determined in the acid rinses).

Two 51-h deployments of Particle Interceptor Traps (aspect ratio of 8:1, diameter 7 cm), were conducted at 75 and 150 m to collect sinking particles. Trap material was picked for swimmers (which were rare in these samples) and then analyzed for ^{234}Th , mass, chloride (for salt correction), Al, POC and TEP. Traps were poisoned with a 15 cm thick brine layer (50 ppt above ambient salinity). No corrections for possible dissolution of material in traps were made (Antia, 2005; Hung et al., 2004). Large particles, including zooplankton were collected with a 333- μm net (diameter: 1 m) between 75 m and the surface.

2.2. Analysis

Seawater for nutrient analysis ($\text{NO}_3 + \text{NO}_2$, PO_4 and H_4SiO_4) was filtered through 0.2 μm pore size syringe filters and stored frozen ($-30 \text{ }^\circ\text{C}$) until analysis by flow injection (Johnson et al., 1985). Chlorophyll *a* and phaeopigments were measured in triplicate using standard fluorometric methods (Parsons et al., 1984). Du-

plicate 500–750 ml samples for particulate OC were filtered onto Whatman GF/F glass-fiber filters, stored frozen, and analyzed on a Control Equipment Corporation CHN Analyzer, Model 440XA, according to Sharp (1991). Samples for particle mass were filtered onto preweighed Nuclepore filters, dried in a desiccator and reweighed on a Cahn electrobalance. Dissolved OC concentrations were measured on acidified/purged samples using a Shimadzu TOC-5000 high-temperature catalytic oxidation analyzer (Benner and Hedges, 1993). ^{234}Th samples were processed by acidification with HCl, and the addition of an FeCl and ^{230}Th efficiency tracer. Samples were then neutralized with NH_3 and $\text{Fe}(\text{OH})_3$ precipitated. Further separation was conducted using acidification and ion exchange chromatography, and samples were plated on platinum disks and alpha and beta counted (Anderson and Fleer, 1982; Dunne et al., 2000; Murray et al., 1996). Filters for particulate ^{234}Th were analyzed in full after digestion using a boiling concentrated acid mixture. The efficiency of ^{234}Th recovery was determined using a ^{230}Th yield tracer with subsequent beta and alpha counting. Analytical uncertainty in ^{234}Th was 0.12 dpm l^{-1} or 6% of the total. ^{238}U was derived from salinity (Chen et al., 1986). Al was determined by flame atomic absorption spectrometry. TEP in seawater was measured colorimetrically on four replicates as described in Passow and Alldredge (1995) and in sedimented material after Passow et al. (2001) using Gum Xanthan as a standard. TEP concentrations are given as the concentration of Gum Xanthan per liter ($\mu\text{gXeq l}^{-1}$) with the equivalent Alcian Blue staining capacity as measured by adsorption at 787 nm. As the number of sites, which bind to Alcian Blue per carbon is unknown for marine polysaccharides and is likely to vary as polysaccharide composition varies, the carbon content of TEP cannot be determined. Xeq is an arbitrary unit to calibrate the Alcian Blue solution. Simultaneous measurements of clean TEP and POC have shown that $1 \mu\text{g Xeq l}^{-1}$ on average equals about $0.7 \mu\text{g l}^{-1}$ OC in several systems measured (Engel and Passow, 2001).

TEP-propensity estimates the relative concentration of TEP-precursors that can form TEP by measuring the spontaneous production of new TEP after removal of ambient TEP (Passow, 2000, 2002a). TEP-propensity does not yield the actual concentration of precursor material, but under similar physico-chemical conditions (pH, pressure) the ratio between measured TEP-propensity and TEP-precursors should be constant once equilibrium conditions are reached. In unpublished experiments with 0.2- μm filtered seawater, equilibrium conditions were reached after 5–6 h (UP), which is

similar to results with nano-gels (Chin et al., 1998; Verdugo et al., 2004). TEP-propensity was estimated by measuring TEP concentrations on 0.2- μm filters 24 h (total, <1 and $<0.2 \mu\text{m}$) or 48 h (colloidal and ultra-filtered fraction) after fractionation of samples.

3. Results and discussion

3.1. Characteristics of the study area

The Santa Barbara Channel is a 100 km long, 45 km wide, and 500 m deep basin that constitutes the northern end of the Southern California Bight. It is bordered to the north by the mainland US and by the Channel Islands to the south. Westerly winds promote episodic, local upwelling events, which result in large diatom blooms (Dugdale and Wilkerson, 1989). Our study was conducted between such upwelling events. In fact, our sampling was during a period of very strong westerly winds that had disrupted a bloom that had developed the previous week and continued again the week after. As a result of wind induced mixing, surface values of nitrate were high, ranging between 2.6 and $7.5 \mu\text{M}$. The subsurface chlorophyll maximum averaged $0.9 \mu\text{g/l}$ at 14 m and chlorophyll inventories in the euphotic zone (0–60 m; 0.1% light level) varied between 22 and 39 mg m^{-2} . The standing stock of TEP was extremely low with $<5 \text{ g Xeq m}^{-2}$ and surface concentrations ($40\text{--}100 \mu\text{g Xeq l}^{-1}$) were only slightly elevated compared to concentrations below the chlorophyll maximum. Vertical patterns in the concentration of TEP were similar to those found during low-productivity seasons in the same area (Passow et al., 2001) and consistent with the low chlorophyll and the high nutrient concentrations observed. A persistent intermediate nepheloid layer between depths of 50 and 90 m was apparent in beam attenuation. Particulate attenuations at this depth were approximately twice that at depths above and below. In the upper 30 m average lithogenic silica concentrations were below $0.1 \mu\text{M}$, but increased to $1.0 \mu\text{M}$ at 75 m with maximum values of $1.6 \mu\text{M}$ (Shipe, 2000). This is consistent with previous research that have found terrigenous inputs to be a major contributor to overall flux in this area (Dymond et al., 1981; Fleischer, 1972). The average 0–75 m total ^{234}Th was $2.04 \pm 0.26 \text{ dpm/l}$ ($n=12$). Total ^{234}Th activities were strongly deficient relative to ^{238}U in the mixed layer above 40–60 m. Below the mixed layer, ^{234}Th activities approached to equilibrium with ^{238}U . Dissolved ^{234}Th activities were constant (1.4 dpm/l) throughout the upper 100 m. Particulate ^{234}Th activities were extremely low at the surface ($<0.2 \text{ dpm/l}$) and

increased to a subsurface maximum (>0.4 dpm/l) between 50 and 80 m. This subsurface maximum coincided with the intermediate nepheloid layer shown in beam attenuation and lithogenic particle distributions from silica and Al. As has been observed previously (Dunne et al., 1997), bottle dissolved and particulate ^{234}Th activities are typically found not to sum to the directly measured total ^{234}Th activity. The sums of dissolved plus particulate ^{234}Th activities ranged from 62% to 117% of total ^{234}Th activities with an average value of 83%. Given the tendency for dissolved ^{234}Th to adsorb on filtration surfaces, we suggest that the difference between total ^{234}Th activity and the sum of dissolved and particulate ^{234}Th activities is due to adsorption of dissolved ^{234}Th during filtration.

3.2. Methodological concerns: mass balance for ultrafiltration

The loss of material when using cross flow ultrafiltration is a major concern (e.g. Dai and Benitez-Nelson, 2001). A mass balance for the averages of the six ultra-filtrations is given in Table 2, with colloidal matter representing material between 10 or 3 kDa and 0.2 μm . Colloidal matter using both cut-offs are included in the average values as there was no significant difference in the fractionation whether a 10 or 3 kDa filter membrane was used. Total recovery rate was 98% for the carbon and 90% for ^{234}Th , which lie within the range found in other studies (Dai and Benitez-Nelson, 2001; Guo et al., 1997). The directly measured colloidal fraction was quite small for both OC (6% of the <0.2 μm fraction) and ^{234}Th (5% of the <0.2 μm fraction), which lies within the lower end of the range found in other studies (Dai and Benitez-Nelson, 2001; Guo et al., 1997). The ultrafiltered fraction contributed 88% and 42% OC and ^{234}Th , respectively to the dissolved (<0.2 μm) fraction. A small fraction of the OC (4% of total) and a large fraction of ^{234}Th (42% of total) were subsequently

recovered in the acid rinses of the membranes and containers. Total losses to the filter membranes and containers between 20% and 35% are common (Dai and Benitez-Nelson, 2001; Guo et al., 1997). The source of this fraction can't be determined unequivocally. The colloidal fraction of ^{234}Th retrieved in the acid rinses in our study can be estimated assuming that the OC: ^{234}Th ratio of the colloidal fraction reflects that of all colloidal material, and using the OC content in the acid rinses. Under that assumption the amount of ^{234}Th in the acid rinse that originally belonged to the colloidal fraction is 0.036 dpm l^{-1} . This would imply that >92% of the ^{234}Th retrieved in the acid rinses belonged in the ultrafiltered rather than the colloidal fraction. If, however, it is assumed that a fraction of the colloidal material is extremely sticky, and that the OC: ^{234}Th ratio measured in the colloidal fraction does not represent this sticky fraction, a much larger portion of the ^{234}Th retrieved in the acid rinses would belong to the colloidal fraction. In other studies the ^{234}Th has been ascribed to the colloidal fraction (Guo et al., 1997) or ignored in further calculation (Dai and Benitez-Nelson, 2001). Assuming that in our study the ^{234}Th recovered during acid rinses, belonged totally to the colloidal fraction, this fraction would contain 47% of dissolved ^{234}Th , which lies in the same range as values found in the Gulf of Mexico or the Middle Atlantic Bight (Guo et al., 1997). In graphics and calculations presented here, we will, however, only consider the ^{234}Th directly measured in the colloidal fraction as colloidal, and the fraction measured in the truly dissolved fraction as truly dissolved, ignoring the ^{234}Th retrieved in the acid rinses.

3.3. The OC: ^{234}Th ratio and particle selectivity of different collection devices

The OC: ^{234}Th ratios of samples collected by different methods at 75 m were slightly lower for sinking ($5 \pm 1 \mu\text{m dpm}^{-1}$) versus suspended large ($\text{WC}_{\text{LVF}>53} = 8 \mu\text{m dpm}^{-1}$) or suspended small ($\text{WC}_{\text{Niskin}} = 9 \pm 2 \mu\text{m dpm}^{-1}$) particles, but did not differ from each other significantly (t -test, $\alpha = 0.01$) (Table 3). An earlier study found OC: ^{234}Th ratios in sediment trap material to be intermediate between small and large suspended particles, which exhibited a decreasing ratio with increasing size (Hung et al., 2004). An OC: ^{234}Th ratio of material collected in traps intermediate to different suspended particles or the same as suspended particles would be expected.

Differences between samples collected by different methods were larger and their variability higher for

Table 2
Mass balance for ultrafiltration exercises ($n=6$)

Size fraction	OC (μM)	%	^{234}Th (dpm l^{-1})	%
Dissolved (<0.2 μm)	113.6 ± 4.8	100	1.07 ± 0.16	100
Colloidal (>3–10 KDa; <0.2 μm)	7.0 ± 1.2	6	0.05 ± 0.05	5
Truly dissolved (<3–10 KDa)	99.9 ± 7.2	88	0.45 ± 0.19	42
Acid rinse	4.9 ± 2.8	4	0.45 ± 0.13	42
Total recovery		98		90

Table 3
OC:²³⁴Th ratio in particles collected by different methods

Method	Depth	OC: ²³⁴ Th ($\mu\text{mol dpm}^{-1}$)	<i>n</i>
WC _{Niskin}	75 m	9 ± 2	3
Traps	75 m	5 ± 1	4
WC _{LVF>53 μm}	75 m	8	1
WC _{Niskin}	10–20 m	150 ± 31*	3
WC _{LVF 1–53 μm}	15 m	41 ± 18	10
WC _{LVF>53 μm}	15 m	64 ± 42	10
Hand-collected snow	10–20 m	37 ± 10	12
WC _{total}	15 m	68 ± 8	5
Net >333 μm	0–75 m	3000	1

n = number of samples.

*182 ± 125, *n* = 6 including surface values.

samples collected from the upper 20 m (Table 3). The OC:²³⁴Th ratios of hand collected marine snow and large particles WC_{LVF>53} were statistically (*t*-test $\alpha=0.01$) the same (37 ± 10 and 64 ± 42), but both values differed significantly (*t*-test $\alpha=0.01$) from the ratio in water collected with Niskin bottles at 10–20 m (WC_{Niskin} 10–20 m: 150 ± 31). The OC:²³⁴Th ratio in unfiltered water (WC_{Total}: 68 ± 8) from 15 m was statistically lower than WC_{Niskin}, but statistically in the same range as WC_{LVF1–53} (15m: 41 ± 18) and even WC_{LVF>53} and marine snow. Thus WC_{Niskin} were the only samples, which were statistically clearly different from other samples at 10–20 m. Different types of filters collect varying amounts of “dissolved” material that adsorbs to the filter membranes, or POC may be lost into solution during filtration. The usage of different filters for the OC and thorium determinations as here for the WC_{Niskin} samples (Whatman GF/F versus 1- μm Nuclepore filter) is thus especially problematic, even if both have a similar nominal pore size (0.8 to 1.0 μm). Overestimates of OC and thorium on GF/F compared to membrane filters have been shown (Buesseler et al., 2006-this issue; Moran et al., 1999; Rutgers Van der Loeff et al., 2006-this issue) and artificially high OC:²³⁴Th ratios may be the result of such filter biases. This could explain the high OC:²³⁴Th ratio we found in WC_{Niskin} samples compared to other similar samples, like WC_{LVF1–53} or WC_{Total}. The OC:²³⁴Th ratio of material caught in a zooplankton net was very high, almost 2 orders of magnitude higher than the ratios of the other samples.

The decrease of the OC:²³⁴Th ratio and a simultaneous decrease in the variability with depth have been observed in many other regions of the ocean (Buesseler et al., 2006-this issue). Biological processes that alter the size of particles (e.g. growth, division, production of feces, and fragmentation of snow due to feeding) are

appreciably more important in surface waters than at depth. A higher variability in the relationship with age and size of particles may thus be expected in surface waters, where biological activity is high.

Part of the variability, however, stems from collecting different types of particles while using different sampling approaches. Among others, the differing filter cut-offs, characteristics of the filters (Moran et al., 1999), the stickiness of particles (Logan, 1993), and the sample volume determine the class of particles present in the sample. Buesseler et al. (2006-this issue) give a detailed discussion on biases due to collection methods and filter types. Here, we will discuss only the effect of the sampling device on the type of material expected in the different samples. Unfiltered water sampled with Niskin bottles (WC_{Total}) includes both colloidal and particulate matter, whereas filtered samples (WC_{Niskin}), theoretically exclude colloidal matter. The volume of water analyzed for the total sample was, however, too small to quantitatively sample large particles and the characteristics of WC_{Total} or WC_{Niskin} cannot be expected to include characteristics of particles collected with the large volume filtration system. Particles in WC_{Niskin} may be considered “small” compared to WC_{LVF>53} or even WC_{LVF1–53}, because medium-sized or large particles are too rare to be found at representative amounts in the volumes filtered onto GF/F. Organisms, small fecal pellets and detritus particles should dominate WC_{Niskin} and WC_{LVF1–53} samples, with rarer particles missing in WC_{Niskin}. WC_{LVF>53 μm} should include representative amounts of large particles (large feces, feeding structures, sturdy aggregates) because of the large volume filtered. Fragile marine snow could, however, be destroyed by the turbulence near the filter with the possible consequence that some of the material stemming from such a large aggregate is lost from the WC_{LVF>53} samples. Hand collected marine snow biases towards snow of the upper 20 m, as collection at greater depth is not feasible and selects for large snow, but ensures that all of the material belonging to a large aggregate is collected quantitatively. Traps theoretically collect all sinking material, but can also collect migrating organisms. In practice, traps have been found to over- and under-collect and it is currently unclear to what degree collection is selective for certain particle types. As aggregates are too fragile to be sampled by nets zooplankton dominate net samples.

3.4. OC:²³⁴Th as a function of particle size

The average OC:²³⁴Th ratios of samples collected at about 15 m depth in different size categories (ultrafil-

tration results, WC_{Niskin} and $WC_{LVF1-53}$, $WC_{LVF>53}$, marine snow) are depicted in Fig. 1a. The $OC:^{234}Th$ ratio decreased from the truly dissolved (ultrafiltered) fraction to the “small” particulate fraction, but remained more or less the same in all larger size fractions, including different sizes of marine snow. The dependence of the $OC:^{234}Th$ on particle sizes between 1 and 100 μm have been studied many times before; (for review see Buesseler et al., 2006-this issue). Decreasing $OC:^{234}Th$ ratios with particle size for particles 1–100

μm has been observed, but most other studies suggest that the $OC:^{234}Th$ ratio remains constant or increases with size in this size range (Buesseler et al., 2006-this issue). The $OC:^{234}Th$ ratio of material $< 1 \mu m$ has been studied less frequently. Both ^{234}Th and OC in the truly dissolved (ultrafiltrate) and the colloidal (1 or 3 kDa to 0.2 μm), as well as the particulate fraction were determined by Guo et al. (1997) and by Dai and Benitez-Nelson (2001) and changes in the $OC:^{234}Th$ of material $< 1 \mu m$ can be calculated from the data in their tables.

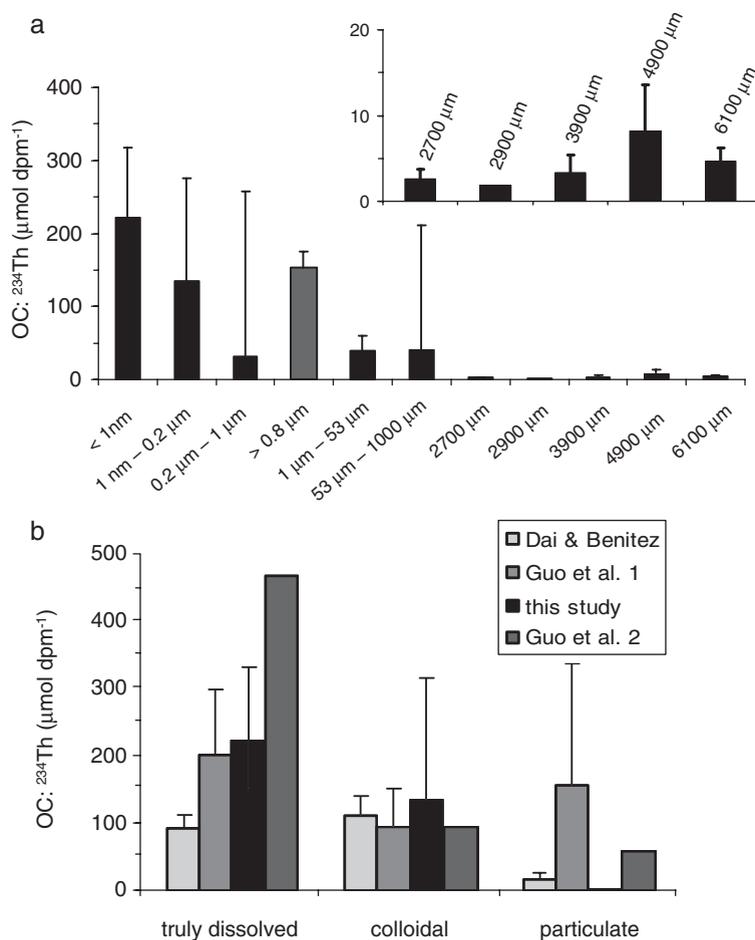


Fig. 1. a) The $OC:^{234}Th$ relationship as a function of size ranging from truly dissolved (ultrafiltered) material to large marine snow. The inset is an expansion for marine snow. All data stem from samples collected at 10–20 m depths. The first three columns depict average results of 5 ultrafiltration exercises, the next column (hatched) presents average data from WC_{Niskin} , and the following 2 columns show averages from WC_{LVF} and the last 5 columns present data of hand-collected marine snow. Marine snow was presented according to its real size, independent of the collection category. (WC_{Niskin}) may include a methodological bias (see text). Error lines represent standard deviations between samples, error propagation is included. b) The $OC:^{234}Th$ ratio of truly dissolved, colloidal and particulate material is shown. The particulate fraction of our study is too small ($3 \mu mol dpm^{-1}$) to show up in the graph. Data calculated from Dai and Benitez-Nelson (2001) (Tables 2 and 3) and Guo et al. (1997) (Tables 3, 4 and 5) are presented. The lower cut-off was 1 kDa for both, the upper cut off was 1 and 0.2 μm for data from Dai and Benitez-Nelson and Guo et al., respectively. Our data ranged from 3 or 10 kDa to 0.2 μm . All samples were collected from the surface ocean (≤ 30 m). The data by Dai and Benitez-Nelson were collected at $42^{\circ}29'N$ and $69^{\circ}44'W$ ($n=4$). Data by Guo et al. 1 were collected in July 1994 in the Middle Atlantic Bight ($n=2$) and that of Guo et al. 2 in October 1993 in the Gulf of Mexico ($n=1$). Our data was collected in April 1997 in the Santa Barbara Channel ($n=6$). Error lines as above.

Average OC:²³⁴Th ratios of these data are presented in Fig. 1b. All samples were collected from the upper water layer (≤ 30 m). Dai and Benitez-Nelson did not attribute the ²³⁴Th recovered in the rinse water to any fraction, whereas it was added to the colloidal fraction in the data sets of Guo et al. (1997). Three out of four data sets show the same trend, of highest OC:²³⁴Th ratios in the truly dissolved fraction (<1 or 3 kDa) and smallest ratios in the particulate phase (>0.2 or 1 μm), with intermediate ratios in the colloidal phase. Values of the particulate fraction of the Mid-Atlantic Bight data are higher than those of the colloidal fraction, but variability is so high, that this is not significant. To our knowledge, no other OC:²³⁴Th data on hand-collected marine snow exists. Our data suggest no consistent trend in the OC:²³⁴Th ratio with size of marine snow (Fig. 1a, inset). Variability of characteristics of marine snow is always high. Especially in the surface ocean, marine snow is constantly formed and destroyed and it is unlikely that size of marine snow is a function of its age. Summarizing trends in the OC:²³⁴Th ratio over the whole size spectrum of marine material, a decrease in the OC:²³⁴Th ratio may be expected between the truly dissolved, the colloidal and the particulate fraction up to a size of about 1 or 10 μm . The ratio appears more variable and either increases or remains constant with size for larger particles (see also Buesseler et al., 2006-this issue), including large marine snow.

A previously published model, predicts a generalized curve where the OC:²³⁴Th ratio decreases with increasing particle size up to about 10 μm -particles, and remains constant thereafter (Burd et al., 2000). The model is driven by adsorption and aggregation, ignoring biological processes like degradation or remineralization. The agreement between model and data in the lower size range suggest that biological processes may be of secondary importance and that the changes in the OC:²³⁴Th ratio at the lower end of the spectrum is largely explainable by the physical, size-dependant processes of aggregation and adsorption. Decreasing OC:²³⁴Th ratios with increasing size of colloidal matter are consistent with the concept of irreversible colloidal aggregation of non-porous nano-aggregates. Aggregation of colloids to nano-aggregates has been shown (Chin et al., 1998; Passow, 2000).

The variability in the OC:²³⁴Th versus size relationship for particles >10 μm may result from the large variety of particle types belonging to this particulate size class. Large fecal pellets appear to have a very low OC:²³⁴Th ratio (Dunne et al., 2000). This might be expected for fresh feces, as POC loss during

digestion is high because of selective OC assimilation by copepods (Buesseler et al., 2006-this issue). With increasing age the ratio of large pellets should increase due to decay of ²³⁴Th and a small surface area compared to volume. Aggregates are fractal and very porous, with larger ones being more porous than smaller ones (Alldredge, 1998). The flux of solutes into aggregates is mostly based on diffusion (Jannasch et al., 1988), with diffusion rates similar to those in seawater (Ploug, 2001). Moreover, aggregates fragment and disaggregate during sedimentation (Dilling, 1997; Dilling and Alldredge, 2000; Dilling et al., 1998). Thus, from a theoretical point of view the OC:²³⁴Th ratio of aggregates would depend on aggregate composition, age, and effective porosity, e.g. if the inside surfaces of an aggregate is accessible for ²³⁴Th binding on time scales of fragmentation and re-aggregation relative to the decay of ²³⁴Th. Large phytoplankton cells or feeding structures will exhibit yet another behavior with regard to their OC:²³⁴Th ratio. ²³⁴Th may bind to phytoplankton and protozooplankton directly (Buesseler et al., 1998; Fisher et al., 1987). The relationship between OC:²³⁴Th ratio and marine organisms has also been suggested to be based on the production of acidic polysaccharides by phytoplankton (Santschi et al., 2003). Contradictory findings regarding the relationship of the OC:²³⁴Th ratio versus particle size for particles >1 μm may thus easily reflect differences in the dominating particle type, even if no differences in the affinity of ²³⁴Th to different substances are assumed.

3.5. OC:²³⁴Th ratio as a function of TEP or clay concentration

A plot of ²³⁴Th as a function of OC of all samples (Fig. 2) suggests a significant relationship ($r^2=0.7$, $n=22$) between ²³⁴Th and C, if the truly dissolved fraction (data point with 100 μM OC vs. 0.45 dpm l^{-1} ²³⁴Th) is ignored. However, variability is too high to use this relationship for reliable C-flux estimates from ²³⁴Th deficiencies. Usually OC flux is calculated from ²³⁴Th deficiency based on OC:²³⁴Th ratios of samples collected using sediment traps, LVFS, or Niskin bottles. The large variability in the regression based on all types of data indicates that the calculated OC flux would differ significantly depending on the particular method of collection used. The high variability in the OC:²³⁴Th ratio may reflect specific binding of ²³⁴Th to certain organic and inorganic substance classes. TEP and their colloidal precursors are rich in acidic polysaccharides (Alldredge et al., 1993), and a

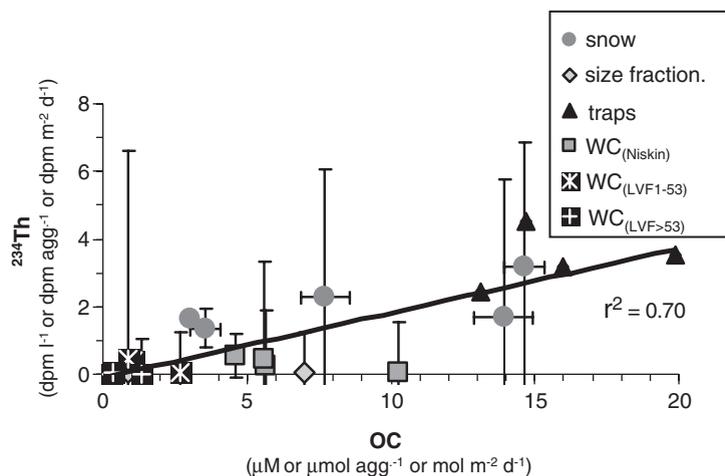


Fig. 2. The overall relationship between ^{234}Th and OC is depicted. All averages of all data are included in the graph and regression, except the average value of the truly dissolved fraction, which with a C content of $99.9\ \mu\text{M}$ and a ^{234}Th content of $0.45\ \text{dpm l}^{-1}$ is off scale and not included in the regression. Error lines as in Fig. 1 are symmetrical.

high affinity of ^{234}Th to acidic polysaccharides has been suggested both in situ and in laboratory experiments (Guo et al., 2002a; Quigley et al., 2002). In our study, the average OC: ^{234}Th ratio of the truly dissolved fraction (<3 or $10\ \text{kDa}$), colloids (3 or $10\ \text{kDa}$ – $0.2\ \mu\text{m}$), small particulates (0.2 – $1.0\ \mu\text{m}$) up to medium sized particles (1 – $53\ \mu\text{m}$) is a linear function ($r^2=0.92$) of the TEP:OC ratio (Fig. 3a). The OC: ^{234}Th ratio of small particles $\text{WC}_{\text{Niskin}}$ from $15\ \text{m}$ also falls within that relationship. This implies that in the upper $15\ \text{m}$ ^{234}Th binding was a function of the OC fraction, which consists of TEP or TEP-precursors, independent of the size of the material, ranging from the colloidal to large particles. A linear relationship between the ^{234}Th :OC ratio and the fraction of acidic polysaccharides within the pool of OC was also found for sinking and suspended particles in the Gulf of Mexico (Santschi et al., 2003), confirming that thorium binds preferentially to the acidic polysaccharide fraction of OC (Santschi et al., 2006-this issue). A direct comparison of results with regards to the relationships between the OC: ^{234}Th ratio and TEP or acidic polysaccharide content is impossible, as different methods and standards were used to determine the acidic polysaccharide fraction. Specific binding of ^{234}Th to TEP will impact distribution patterns of ^{234}Th . TEP are not only associated with sinking marine snow, but also exist as individual particles, which can have a positive buoyancy and even accumulate at the surface (Azetsu-Scott and Passow, 2004). Accumulation of TEP and ^{234}Th in the surface layer has been observed during a spring bloom in a coastal area (Azetsu-Scott and Niven, 2005). Such upward transport of ^{234}Th would, if large enough to

be significant, further complicate the use of ^{234}Th deficiency to calculate C-flux.

No relationship existed in our study between the OC: ^{234}Th ratio and the percentage of TEP in C, for particles below $30\ \text{m}$, for sinking particles (trap data), or marine snow. Marine snow, trap samples and samples from below $15\ \text{m}$ all displayed a much smaller OC: ^{234}Th ratio than expected from TEP contribution (Fig. 3a). The OC: ^{234}Th ratios of the trap and $\text{WC}_{\text{LVF1-53}}$ samples from below $30\ \text{m}$, exhibited a linear relationship with the relative amount of Al in the water, with trap material being relatively enriched in ^{234}Th compared to suspended material (Fig. 3b). Thus samples from below $30\ \text{m}$ suggest preferential binding of ^{234}Th to lithogenic material, with particles rich in ^{234}Th and lithogenic material sinking preferentially. Particle–water partitioning coefficients for thorium adsorption to inorganic phases are, however, only moderate, whereas those to acidic polysaccharides are high (for overview see Santschi et al., 2006-this issue). All non-living surfaces in the ocean are rapidly coated with acidic polysaccharides and other surface active substances (Decho, 1990). Assuming that binding between acidic polysaccharides and ^{234}Th depends on the surface area of the acidic polysaccharides, the binding capacity of a certain amount of acidic polysaccharides would be appreciably larger if they existed as a thin surface layer coating particles, rather than as TEP, which are essentially acidic polysaccharide aggregates. A relatively small amount of Alcian Blue stainable material would thus be able to bind large amounts of ^{234}Th in the presence of fine lithogenic particles. In terms of total mass, such a monolayer

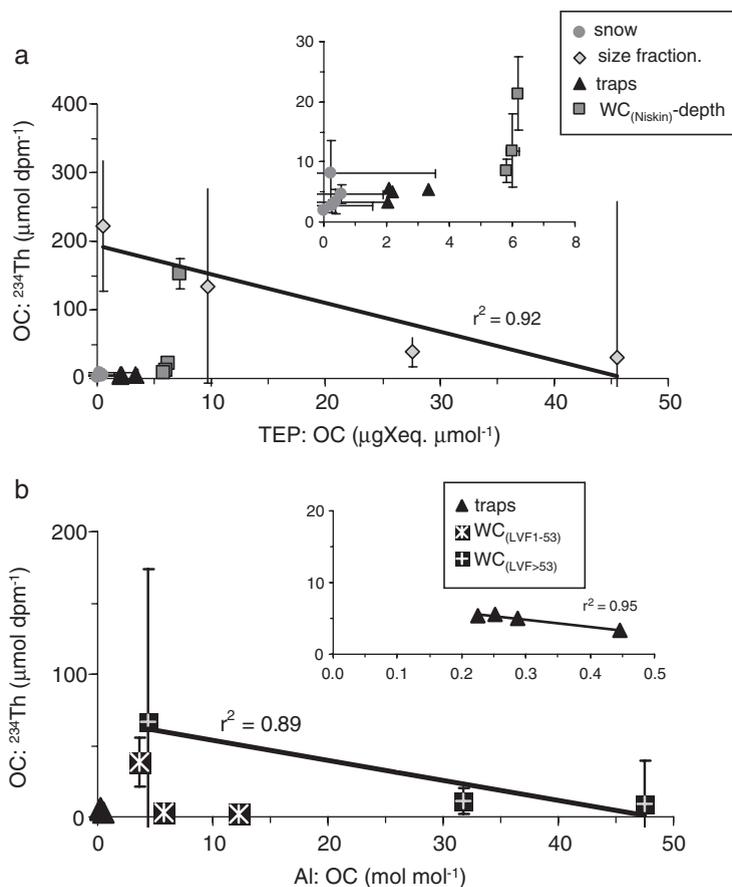


Fig. 3. a) Average OC:²³⁴Th ratio versus the fractions of TEP+TEP-precursors in C. Inset is an expansion of the low TEP: OC ratios. The regression is calculated from size-fractionated samples (truly dissolved to 1–53 μm) and the near surface sample of WC_{Niskin} fits the regression as well. Samples from below 30 m, trap samples and marine snow show no correlation between the OC:²³⁴Th ratio and the TEP+TEP-precursors to OC ratio. Error lines as above. Traps are depicted individually as each collection period integrated over 2 days. b) The average OC:²³⁴Th ratios versus the ratios of Al:C. Inset is an expansion showing Al:OC ratios two orders of magnitude smaller. Regressions for trap samples and for WC_{LVF>53}, respectively, are also depicted.

coating of the lithogenic material would be negligible. The presence of lithogenic material would then mask the relationship between acidic polysaccharides and ²³⁴Th, as seen in our data. The relationship between lower OC:²³⁴Th ratios and lithogenic material in traps suggests that clay settled preferentially relative to other suspended material. Aggregates are known to scavenge clay particles promoting their sedimentation (Kumar et al., 1998; Passow et al., 2001). Unfortunately Al determinations of marine snow exist only for one sampling day. But those three data points (3 size classes) all fall between suspended and trap samples with regards to their OC:²³⁴Th vs. Al:OC relationship. As marine snow was collected above 30 m depths where clay concentrations were low, these aggregates must have scavenged ²³⁴Th labeled clay very efficiently, which would be expected for large organic aggregates.

3.6. Thorium in trap material

Material collected in sediment traps consisted of OC, lithogenic material and biominerals (mostly calcium carbonate, some opal). Our data allow the calculation of the respective contributions of these different substances to trap material by assuming that (1) the characteristics of hand-collected marine snow from the surface ocean represent those of OC in traps, that (2) the contribution of lithogenic material can be estimated from measurements of aluminosilicates or lithogenic silicates in traps, and that (3) biogenic minerals contain neither OC nor bind ²³⁴Th. The relatively high OC content of marine snow suggests that the fraction of biogenic material in marine snow at the surface was low. Visual examination also demonstrated that the snow was predominately detrital, not diatom dominated, strengthening the assumption that the marine snow

Table 4

End-member calculation estimating the contributions of OC, Al and bio-minerals in traps (OC_{trap}, Al_{trap}, BioMin_{trap}, respectively) and the fractionation of ²³⁴Th, OC, DW and TEP between these three components of trap material, as well as the ratios of material of the three components

	Units	Traps <i>total</i>	OC* _{trap}	Al _{trap}	BioMin _{trap}
²³⁴ Th	dpm m ⁻² d ⁻¹	3419	399	3020	0
OC	nmol OC m ⁻² d ⁻¹	15.9	14.7	1.2	0
DW	mg m ⁻² d ⁻¹	2887	443	1390	1054
TEP	mgXeq m ⁻² d ⁻¹	37.5	45.9	<i>Very small</i>	<i>Very small</i>
²³⁴ Th:DW	dpm mg ⁻¹	1.2	0.9	2.2	0
OC: ²³⁴ Th	μmol dpm ⁻¹	4.6	33, 37	0.4	0
TEP: ²³⁴ Th	μg Xeq dpm ⁻¹	10	115	<i>Very small</i>	<i>Very small</i>

DW= Dry weight; OC= organic carbon; Al= alumino silicates, Bio.Min= biogenic minerals.

*Values from hand-collected snow. **Bold** = measured, *italics* = calculated values, the others are based on assumptions. As more measurements existed than were necessary to solve the equations a calculated and a measured value exist for the OC:²³⁴Th ratio of OC_{trap}, showing a relatively high degree of consistency. The TEP content of OC derived from snow was higher than the TEP content in traps, implying that the amount of TEP that settled associated with alumino silicates or biogenic minerals was very small. These are back-of-the-envelope calculations and the uncertainty associated with the assumptions (see text) are large and not quantifiable compared to standard deviations of calculations, thus no error range is given.

consisted predominantly of OC, with diatom frustules contributing very little. Estimates of lithogenic material using Al gave similar values to those using measured lithogenic silicates, and both are consistent with earlier measurements in the area, justifying the second assumption as well. The third assumption is the hardest to justify, as evidence suggests that thorium is scavenged by opal, and especially by carbonate and lithogenic material (e.g. Chase et al., 2002). But binding of ²³⁴Th to mineral particles depends also highly on the sea water, giving strong evidence that colloidal matter determines binding of ²³⁴Th to minerals (Geibert and Usbeck, 2004). This study further suggests that variations in DOC composition may be controlling the adsorption of ²³⁴Th onto mineral (biominerals and lithogenic minerals) particles (Geibert and Usbeck, 2004). In the following calculation we will initially assume that binding of ²³⁴Th to biominerals can be neglected, but discuss both cases later.

Using the three assumptions the partitioning of ²³⁴Th in traps is estimated using the following three equations, where DW_{trap}, DW_{POC}, DW_{AlSi}, and DW_{BioMin} stand for the dry weight of trap material, OC, Al and biominerals, respectively. The carbon content of trap material, particulate organic carbon and alumino-silicates is labeled as C_{trap}, C_{POC}, and C_{AlSi}, respectively. And Th_{trap}, Th_{POC}, and Th_{AlSi} stand for the thorium content of trap material, OC and Al.

$$DW_{\text{trap}} = DW_{\text{POC}} + DW_{\text{AlSi}} + DW_{\text{BioMin}} \quad (1)$$

$$C_{\text{trap}} = C_{\text{POC}} + C_{\text{AlSi}} \quad (2)$$

$$Th_{\text{trap}} = Th_{\text{POC}} + Th_{\text{AlSi}} \quad (3)$$

The average OC content of snow and trap material, respectively, was 39.8% and 8.3% of DW calculated

using DW and OC measurements of snow and trap material. From Al (4.79 mmol m⁻² d⁻¹, MW ≈ 280) and silicate measurements (Shipe and Brzezinski, 2001) in trap material, the DW of lithogenic material can be estimated to be 1390 mg m⁻² d⁻¹ (Table 4), which is supported by other studies showing that in this area the terrigenous mineral component accounts for about 53% of the sinking mass flux (Dymond et al., 1981; Fleischer, 1972; Thunell, 1998). Using the assumption that the OC content of alumino silicates (surface coating) is 1% of DW (Eganhouse and Venkatesan, 1993), the remaining data for Table 4 can be calculated without further assumptions.

During sedimentation, marine snow from the surface will aggregate with all particles present (Passow et al., 2001). A large fraction of the lithogenic material present in the deeper water in the Santa Barbara Basin (Dymond et al., 1981) is too small to sink at significant speeds, unless in association with organic aggregates (Passow et al., 2001). Thus the lithogenic material, and presumably the biogenic material, must all have arrived in the traps as part of marine snow. This, however, does not alter the end-member calculations from above, which give an estimate of the mechanism of ²³⁴Th transport.

Calculations presented in Table 4 indicate that 89% of all ²³⁴Th in traps was associated with lithogenic material rather than with OC (no ²³⁴Th is associated with biominerals, according to assumption 3). If binding of ²³⁴Th to biominerals is allowed, about 89% of all ²³⁴Th in traps reaches these associated with mineral particles (either with biominerals or with lithogenic material). The trap data thus indicate that lithogenic material (or lithogenic+biominerals) scavenged ²³⁴Th more effectively than OC. Or, alternatively that polysaccharides scavenged ²³⁴Th more effectively when

coating minerals, than as TEP, which are polysaccharide particles. This latter interpretation is consistent with that of Geibert and Usbeck (2004). The concentration of acidic polysaccharides that would coat lithogenic material is too small to be determined by our back-of-the-envelope calculation above. But if our argument is correct, the OC:²³⁴Th ratio will be small in the presence of minerals. Moreover, ²³⁴Th will be enriched in traps, when these lithogenic particles are scavenged by fast sinking marine snow.

Further studies will be necessary to understand the mechanisms driving the specific binding of ²³⁴Th. If ²³⁴Th binds preferentially to acidic polysaccharides as we (and others) suggest then ²³⁴Th would track extracellular acidic polysaccharides rather than OC. A roughly constant relationship between the fraction of extracellular acidic polysaccharides and OC would allow ²³⁴Th to track OC reasonably well. On average, the fraction of extracellular acidic polysaccharides of particulate organic matter may be fairly constant. In surface waters, where biological production and destruction rates of organic matter are high, the fraction of extracellular acidic polysaccharides varies, as can be deduced from varying concentrations of TEP in surface waters (Passow, 2002b). At depth, the ratio of extracellular acidic polysaccharides to POC is presumably more constant. Consequently ²³⁴Th may trace OC at depth reasonably well as has been suggested (Bruland et al., 1981; Santschi et al., 1999), and this would explain the relative success the thorium method has had in determining POC flux to date. However, in regions affected by the cycling of lithogenic material, ²³⁴Th would track the surface area of these particles, because they are coated with a thin layer of extracellular acidic polysaccharides. This may also be true in the presence of other inorganic particles, like calcium carbonate. Such an interpretation is supported by experiments by Geibert and Usbeck (2004), where in the absence of inorganic particles, ²³⁴Th was retrieved in the particulate phase, presumably complexed with TEP or TEP-like particles, which had formed from colloids. In the presence of inorganic particles, ²³⁴Th appeared associated with inorganic particles, possibly because they were coated with colloidal matter (Geibert and Usbeck, 2004, but see Santschi et al., 2006-this issue). This implies that the relationship between ²³⁴Th and extracellular acidic polysaccharides is not constant, and partially depends on the presence of inorganic particles. As fine lithogenic particles only sink at significant speeds when scavenged by large organic aggregates, ²³⁴Th labeled inorganic particles would sink in association with sinking POC. Neverthe-

less, it appears unlikely that ²³⁴Th tracks sinking OC very well, if polysaccharide coated inorganic particles are abundant.

4. Conclusions

Our field study indicates that in the absence of inorganic particles, ²³⁴Th affinity is high for TEP and their precursors with the result that ²³⁴Th may be associated with large, rapidly sinking TEP-rich aggregates, with small suspended particles coated with TEP-like substances, or with TEP that float upward accumulating in the surface layer of the ocean. ²³⁴Th also exhibited a high affinity for lithogenic particles, possibly due to an organic coating of inorganic particle surfaces. As fine lithogenic material is effectively scavenged by marine snow, an enrichment of ²³⁴Th in sinking matter may be the result. It appears that the OC:²³⁴Th ratio depends largely on the types of particles present, rather than on size per se, except in size classes smaller than about 1 μm. The complexity of the dynamics impacting particle generation and destruction as well as differences in specific binding rates of ²³⁴Th, and the largely unknown impact of the coatings of colloidal matter, prevent a simple relationship between the OC:²³⁴Th ratio and particle size. Few processes impacting ²³⁴Th binding change continuously with particle size over the spectrum from colloidal to marine snow sized material.

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