Effects of particle composition on thorium scavenging in the North Atlantic

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Abstract

The dependence of thorium scavenging by particles on particle composition is examined at selected stations of the U.S. GEOTRACES North Atlantic Section (GA03). Scavenging is here described by the apparent, first-order rate constant of Th adsorption onto particles (k_1), as estimated from an inversion of Th radioisotope and radioactive parent data. Our k_1 estimates are regressed against particle phase data using two different models. Model I considers biogenic particles (POC + PIC + bSi), lithogenic particles, Mn (oxyhydr)oxides, and Fe (oxyhydr)oxides as regressors, and k_1 as the regressand. Model II considers ln(POC + PIC + bSi), ln(lithogenic particles), ln(Mn (oxyhydr)oxides), and ln(Fe (oxyhydr)oxides) as regressors, and ln(k_1) as the regressand, where ln() denotes the natural logarithm. Thus, models I and II posit that the effects of particle phases on k_1 are, respectively, additive and multiplicative. These models are applied to three groups of stations: (i) all selected stations, (ii) stations west of the Mauritanian upwelling region ("western stations"), and (iii) stations within that region ("eastern stations").

We find that model II appears to better describe the effect of particle composition on k_1 than model I. Particle composition explains a larger fraction of the variance of k_1 for the eastern stations ($R^2 = 0.60$ for model I and 0.67 for model II) than for the western stations ($R^2 = 0.26$ for model I and 0.39 for model II). When considering all stations, the variance of k_1 explained by particle composition is intermediate ($R^2 = 0.50$ for model I and 0.51 for model II). According to model II, the variance of k_1 explained by particle composition is predominantly due to biogenic particles at the eastern stations and to Mn (oxyhydr)oxides at the western stations. Additionally, we find that particle composition does not explain a significantly different proportion of variance of k_1 than particle concentration. It is thus concluded that, at our selected stations, (i) biogenic particles and Mn (oxyhydr)oxides more strongly influence Th scavenging than any other phases considered and (ii) particle composition and particle concentration have comparable effects on this process.
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1. INTRODUCTION

The high particle reactivity of radioactive thorium isotopes in seawater has resulted in their widespread use in eval-

uating processes affecting marine particles. Examples include the use of ^{234}Th to estimate the export of particulate matter from the surface ocean (Bhat et al., 1969; Coale and Bruland, 1987; Buesseler et al., 1992; Buesseler et al., 2006), and the applications of ^{230}Th to paleo-oceanography, including for estimating past changes in sediment redistribution (François et al., 2004). However, the use of thorium isotopes to investigate these processes depends partly on our understanding of how the metal attaches to particles. In seawater, thorium exists in the +IV oxidation state (Choppin and

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Wong, 1998) and has a strong binding affinity to oxygen containing compounds (Santschi et al., 2006). Thus, one may expect the affinity of thorium for particles to depend on their chemical composition and surface charge.

Previous studies have examined the dependence of Th scavenging on particle composition. Balistrieri et al. (1981) found that stability constants for the adsorption of thorium onto particles in the deep subtropical North Atlantic were closer in magnitude to those for the adsorption of Th onto organic compounds than to those for metal oxides. Using sediment trap data from a variety of regions including the Equatorial Pacific, the Southern Ocean, and the North Atlantic, Chase et al. (2002) explored the relationship between the partition coefficient for ^{230}Th, K_D, and particle composition (in their study, K_D was defined as A_{p*}/A_d, where A_{p*} is the ^{230}Th activity per gram of particles in the sediment trap, and A_d is the ^{230}Th activity per gram of seawater 1000 m above the trap). They found that K_D is positively correlated with $CaCO_3$ weight fraction (% $CaCO_3$) ($r^2 = 0.66$), weakly and positively correlated % lithogenic material ($r^2 = 0.15$), negatively correlated with % biogenic silica ($r^2 = 0.59$), and not significantly correlated with % particulate organic matter. Using the data of Chase et al. (2002) from the North Atlantic, Equatorial Pacific, and Southern Ocean, together with data from the Arabian Sea, Scholten et al. (2005) reported that K_D exhibits significant positive correlation with % $CaCO_3$ ($r^2 = 0.37$), % particulate organic carbon ($r^2 = 0.11$), and % lithogenic material ($r^2 = 0.34$), and a significant negative correlation with % biogenic silica ($r^2 = 0.40$). However, each of these correlations were only significant when including data from the Southern Ocean; upon removing this dataset, only a weak, negative relationship between K_D and % biogenic silica was apparent ($r^2 = 0.08$) (Scholten et al., 2005). Further restricting the analysis to datasets from the North Atlantic, including the Middle Atlantic Bight (Biscaye et al., 1988), the Sargasso Sea (Anderson et al., 1983), and stations near the Canary Islands (Scholten et al., 2001), K_D shows significant, but weak, positive relationships with % $CaCO_3$ ($r^2 = 0.05$) and % lithogenic material ($r^2 = 0.11$), and no significant relationship with % particulate organic carbon and % biogenic silica (Fig. S1; K_D and particle composition data from Chase et al., 2002).

Roy-Barman et al. (2005) found that the relationship between the fraction of thorium present in particles and the particle composition varies between Th isotopes. From ^{230,234}Th data collected by sediment traps deployed in the Northeast Atlantic, they found particulate ^{230}Th (in units of dpm/gram of particles) to show the strongest (positive) correlation with lithogenic material and particulate Mn, whereas particulate ^{234}Th (dpm/gram of particles) showed the strongest (positive) correlation with particulate organic carbon. They also found biogenic opal to have little or no correlation with either particulate ^{230}Th or ^{234}Th. From sediment traps deployed from 2000 to 2003 as part of the Oceanic Flux Program off Bermuda (at 500, 1500, and 3200 m), Roberts et al. (2009) reported only a significant positive relationship between K_D and % total carbohydrate content of particles. However, from data collected from the

same program between 2005 and 2007, Chuang et al. (2013) found the strongest positive relationship between K_D and % $CaCO_3$, although they speculated that such a relationship was caused by the coating of this mineral phase by various biopolymers.

The recent radionuclide and particle concentration dataset obtained along the U.S. GEOTRACES North Atlantic transect (GA03) provides a unique opportunity to study the dependence of Th scavenging on particle composition in oceanic waters. Lam et al. (2015) have reported measurements of small (0.8–51 μm) and large ($\geqslant 51$ μm) bulk particle concentrations as well as particle phase concentrations, including particulate organic carbon (POC), particulate inorganic carbon (PIC), biogenic opal (bSi), lithogenic material, and manganese and iron (oxyhydr)oxides, obtained along GA03. Hayes et al. (2015a) have used the ^{230}Th (Hayes et al., 2015b) and particle (Lam et al., 2015) data from GA03 to determine how particle composition affects the partitioning of Th between particulate and dissolved phases. They estimated the distribution coefficient for ^{230}Th from $K_D = A_p/(A_d P)$, where A_p is the ^{230}Th activity in the particulate phase (dpm/m^3), A_d is the ^{230}Th activity in the dissolved phase (dpm/m^3), and P is bulk particle concentration (μg/kg). They found that K_D is largest for Mn and Fe (oxyhydr)oxides (116.8 g/g and 32.8 g/g, respectively), and smallest for particulate organic matter (0.3 g/g). They could not derive significant values of K_D for opal, consistent with a similar result obtained for trap particles (Roy-Barman et al., 2005).

Importantly, most of pre-existing studies focused on the effects of particle composition on the partitioning of thorium between the dissolved and particulate phases, rather than on the kinetics of sorption reactions. Below the euphotic zone, thorium is generally thought to undergo a reversible exchange with slowly sinking particles (Nozaki et al., 1981; Bacon and Anderson, 1982). In this model, thorium cycling is governed by three parameters: the rate constant of Th adsorption onto particles (k_1), the rate constant of Th desorption from particles (k_{-1}), and the particle sinking speed (w). A more complete treatment includes in addition the rate constant of Th release from particles during particle degradation (β_{-1}; Clegg et al., 1991a). The quantities k_1, k_{-1}, and β_{-1} should be viewed as apparent, first-order rate constants given the various assumptions in the model, such as the consideration of only one particle class. Under a set of assumptions, including steady state, three of these rate parameters are related to K_D by the expression $K_D = k_1/((k_{-1} + \beta_{-1})P)$ (Honeyman et al., 1988; Lerner et al., 2017). Thus, the processes of thorium adsorption, thorium desorption, and particle degradation may each influence the observed partitioning of the metal between the dissolved and particulate forms.

Several studies have investigated the effects of particle concentration on estimates of k_1 in oceanic waters. Bacon and Anderson (1982) found a linear relationship between k_1 and P from samples taken from the Guatemala and Panama Basins. Honeyman et al. (1988) proposed that k_1 could be related to particle concentration as $k_1 = k_{1,c}P^b$, where $k_{1,c}$ and b are positive constants. If $b < 1$, then K_D