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Water column distribution of ^{230}Th and ^{232}Th in the Black Sea

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Abstract—Profiles of ^{230}Th and ^{232}Th at a station in the western central Black Sea were determined using a highly sensitive mass spectrometry method. Compared with most open ocean and coastal waters, concentrations of "dissolved" ($<0.4\,\mu$m) ^{230}Th and ^{232}Th in the Black Sea are significantly higher, primarily due to lower scavenging rate in this predominantly anoxic environment. Above the anoxic zone (0–95 m) about 42% of ^{230}Th and 57% of ^{232}Th are in the particulate form, compared with 9 and 21%, respectively, in the anoxic zone. The distribution indicates that a sizable fraction of particulate Th is associated with Mn-containing particles at the O_2–H_2S interface just above the anoxic zone, which is released into solution when such particles are transported across the redox boundary and are dissolved in the anoxic zone. From the partitioning and isotopic composition of Th between dissolved and particulate phases, it is estimated that approximately 20–40% of the dissolved ^{230}Th in the water column is terrigenous. The residence time of dissolved Th in the Black Sea water column is 43–48 years, compared with 6–20 years for the same depth range elsewhere in the world oceans.

INTRODUCTION

THE Black Sea is by far the largest anoxic basin in the world. It is an ideal environment for studying the geochemical cycling of elements across the oxic–anoxic interface, a subject that has long intrigued oceanographers. During the R.V. *Knorr* expedition to the Black Sea in June 1988, the water column at Sta. BS3-2 (42°50′N, 32°00′E) in the central western basin (Fig. 1) was sampled, with especially detailed resolution across the O_2–H_2S transition zone, for the analyses of isotopes of uranium and thorium, ^{210}Pb and ^{210}Po. This constitutes the most comprehensive study of scavenging processes in the water column of anoxic environments using natural decay-series isotopes. The data on uranium isotopes, ^{234}Th, ^{210}Pb and ^{210}Po have been reported previously (WEI, 1990; WEI and MURRAY, 1991; WEI and MURRAY, in press). The newly acquired ^{230}Th and ^{232}Th data are integrated with the previous ^{234}Th data and discussed in this paper.

^{234}Th ($T_{1/2}$ = 24.1 days) and a major portion of ^{230}Th ($T_{1/2}$ = 75,200 years) are produced in seawater from the decay of ^{238}U and ^{234}U, respectively, whereas ^{232}Th ($T_{1/2} = 1.4 \times 10^{10}$ years) in the ocean is derived from continents via fluvial and aeolian pathways. If Th

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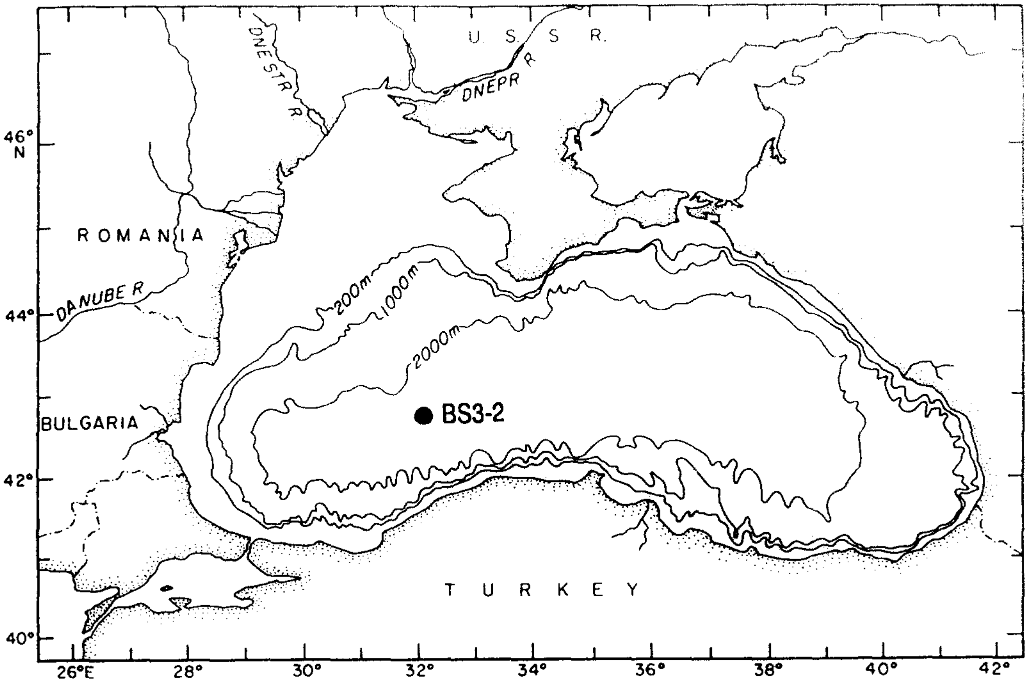

Fig. 1. Location of the sampling station (BS3-2) in the Black Sea.

isotopes are used as tracers to study chemical scavenging processes in the oceanic water column in a comprehensive manner, it is necessary to combine these three Th isotopes. This is because ^{234}Th is too short-lived to be applicable to the deep ocean where scavenging rates are usually slow. Conversely, ^{230}Th is too long-lived to be useful as a sensitive tracer for studying chemical scavenging in the surface ocean where scavenging rates are typically fast. However, ^{230}Th has an additional continental source from the surface. In order to resolve the two components of ^{230}Th, it is necessary to invoke ^{232}Th, the only nonradiogenic isotope of Th, which is derived only from lands. If Th isotopes are used as proxies to study the cycling of trace metals, it is especially important to include ^{232}Th which serves as a necessary link between most trace metals and radiogenic Th isotopes (Huh and Bacon, 1985).

Figure 2 shows profiles of salinity and potential temperature at the time of the cruise. Salinity increased from 18.2‰ at the surface to 22.3‰ at the bottom, with the halocline layer centered at *ca* 50 m. Potential temperature decreased from 17.5°C at surface to a minimum of 7°C at 45 m and then increased to 9°C throughout the rest of the water column. These structures produce a layer of high stability at the base of the oxic zone which has important bearings on metal scavenging and particle cycling, as discussed later.

Figure 3 shows profiles of oxygen and sulfide. Dissolved oxygen is high in the surface with a photosynthetically-produced maximum at 10 m. Oxygen then decreases rapidly to less than 10 μM at 55 m and less than 5 μM between 55 and 95 m. Sulfide first becomes detectable at about 95 m and increases almost linearly with depth. Based on the distribution of these two redox-sensitive species, the water column can be viewed as a

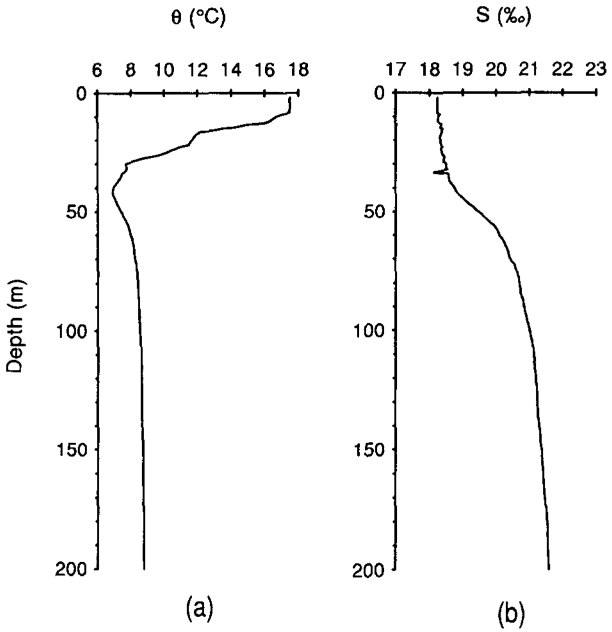

Fig. 2. Profiles of (a) potential temperature and (b) salinity at BS3-2.

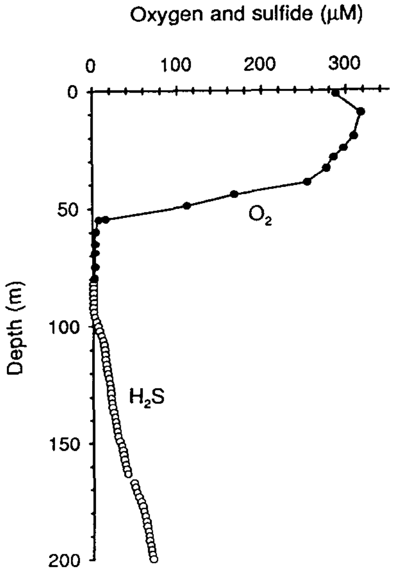

Fig. 3. Profiles of oxygen and sulfide at BS3-2.

three layered system, with the oxic zone from the surface to 55 m, the "suboxic" zone from 55 to 95 m, and the anoxic zone below 95 m (Murray *et al.*, 1989).

METHODS

Water samples were collected using 30-l Niskin bottles mounted on a CTD rossette. These bottles were outfitted with Teflon-coated stainless steel springs. Nitrogen gas was used to pressure filter (at 12 psi) seawater through 0.4-μm Nuclepore filters. The filtrates were drawn into 1-l polyethylene bottles, and immediately spiked with 1 dpm ^{229}Th and acidified to pH ~2 using double distilled HCl. The filters were rinsed with about 15 ml of deionized water to remove sea salt and stored in Petri dishes.

In the laboratory, after the addition and equilibration of 1 mg Fe carrier, concentrated ULTREX NH_4OH was added to the water samples to raise the pH to ~7 and effect the adsorption and coprecipitation of Th isotopes with $Fe(OH)_3$. Following a 24-h equilibration in a water bath of 60°C, the precipitates were collected by centrifugation, washed with D.I. water by resuspension, and re-centrifuged. The coprecipitation and washing procedure is a major step to remove alkali- and alkaline earth samples, which constitute the major cations in seawater. After dissolving the "salt-free" precipitates in 2 ml of 8 N HCl, the samples were ready for the subsequent ion exchange procedures to purify Th.

Three successive ion-exchange columns were used to separate literally the entire periodic table of elements from Th. All columns are loaded with anion exchange resin (AG1 × 8, 100–200 mesh) and washed sequentially with D.I. water, 8 N HCl, and D.I. water again. The columns were converted to required forms just prior to use. The first column (Bio-Rad 10-ml polypropylene column) was loaded with 2 ml of resin (wet volume) and conditioned with 8 N HCl. The second column was identical to the first one, except that it is conditioned with 8 N HNO_3. The third and final column was a 1-ml "micro-column" packed with 0.2 ml resin and pre-conditioned with 8 N HNO_3. The 0.2-ml capacity column was fabricated from a 2-ml polyethylene Pasteur pipet by cutting the top third of the pipet bulb and trimming 20 mm from the tip. The tip was fitted with a 4 mm diameter frit (1/16 in. thickness, 35 μm pore size).

The 2 ml sample solution (in 8 N HCl) was loaded to the first column and the eluate containing Th was collected with a 10 ml Teflon beaker. After all sample solution had passed through, the column was washed with 5 ml of 8 N HCl which was also collected in the same beaker. The eluate was then evaporated to dryness. The first column retained and separated the Fe carrier, and most other metals in the periodic table, from Th. Elements eluted off the column along with Th were any remaining alkali- and alkaline earth metals, and a few other trace metals in seawater such as Al, Sc, and rare earths.

After the eluate from the first column was evaporated to incipient dryness, the sample was transposed to nitric form with 2 ml of 8 N HNO_3. The solution was then charged to the second column. Th was retained on the column, whereas metals not separated from Th in the first column passed through the second column. Following the passage of the sample solution, the column was washed with 10 ml of 8 N HNO_3. The Th was eluted off the column with two 2-ml increments of 8 N HCl, which was collected in the original Teflon beaker and evaporated to dryness.

Normally the sample was rather clean at this point. However, it was necessary to perform a final micro-column operation to ensure purification and facilitate the preparation of sample source for mass spectrometry. This was done by dissolving the dry-down spot from the previous step by ~0.5 ml of 8 N HNO_3 and passing the solution through the micro-column. After washing the column with 1 ml of 8 N HNO_3, Th was eluted off the column with 0.5 ml of 1 N HCl. The eluate was dripped directly from the column tip onto a Teflon pad which was mounted on a glass pedestal. The pad was 1/16 in. thick, 3/4 in. diameter, with a conical depression in the center to hold 0.5 ml of solution.

The filter samples were transferred to Teflon beakers and spiked with 1 dpm ^{229}Th and 1 mg Fe carrier in the laboratory. The polycarbonate matrices were decomposed by soaking in NH_4OH with gentle heating to evaporate NH_4OH. Then a mixture of HNO_3, HCl and HF was used to digest the particulates. After total dissolution of the filter samples, the chemical procedures were the same as described above for seawater samples.

In handling and processing the samples, clean-room practices should be stringently observed to avoid contamination and minimize blank levels. The sample bottles and all labware were pre-cleaned by acid-leaching. The chemical procedures were always performed in a laminar-flow hood. The acids and NH_4OH used were of ULTREX grade or double distilled.

The Th isotopic analysis was performed at Battelle Pacific Northwest Laboratory using a three-stage mass spectrometer. Detailed procedures for source preparation and loading will be reported separately (HUH *et al.*, in preparation).

RESULTS AND DISCUSSION

Concentrations of ^{230}Th, ^{232}Th and the ^{230}Th/^{232}Th activity ratio in the dissolved and particulate forms are listed in Table 1, and the profiles are shown in Figs 4 and 5. Where appropriate in the following discussion, the notations $^{230}Th_d$, $^{232}Th_d$, $^{230}Th_p$ and $^{232}Th_p$ will be used to represent dissolved ^{230}Th, dissolved ^{232}Th, particulate ^{230}Th and particulate ^{232}Th, respectively. Note that the terms "dissolved" and particulate used in this paper are only operationally defined, as based on filtration using 0.4-μm membrane filters.

Dissolved ^{230}Th *and* ^{232}Th

Profiles of $^{230}Th_d$ and $^{232}Th_d$ are strikingly similar (Fig. 4). Both show the following features: (i) a decrease, by a factor of more than two, from the surface to a broad minimum centered around 70 m; (ii) a distinct subsurface peak at 45 m superimposed on the above trend; and (iii) a sharp increase with depth in the mid-water column from 70 to 400 m (for ^{232}Th) or 800 m (for ^{230}Th).

Concentrations of $^{232}Th_d$ in the water column vary between 5×10^{-5} and 3.3×10^{-4} dpm kg^{-1}, averaging 1.5×10^{-4} dpm kg^{-1}. These values are significantly higher than $^{232}Th_d$ in most other deep ocean and coastal waters reported recently (e.g. HUH and BACON, 1985; HUH and BEASLEY, 1987; NOZAKI and YAMADA, 1987; HUH *et al.*, 1989; CHUN, 1989). However, compared with ^{232}Th data reported three decades ago for 11 locations in the Black Sea (LAZAREV *et al.*, 1961), data presented here are one to two orders of magnitude lower. As discussed in HUH *et al.* (1989), we believe the earlier measurements are erroneously high due to sampling and analytical contamination.

If $^{230}Th_d$ concentrations at the same depths in the water column are compared, the Black Sea data at BS3-2 are very close to those in the Arctic Ocean (BACON *et al.*, 1989), and are much higher than all available data from elsewhere (e.g. NOZAKI *et al.*, 1981; BACON and ANDERSON, 1982; NOZAKI and NAKANISHI, 1985; HUH and BEASLEY, 1987; MURNANE *et al.*, *Table* 1. *Distribution of total suspended matter* (*TSM*) *and concentrations of* ^{230}Th *and* ^{232}Th *in dissolved and particulate forms in the water column of Sta. BS3-2* (42°50′N, 32°00′E) *in the central western Black Sea. The listed standard deviations* ($\pm 1\sigma$) *are based on propagated error from counting statistics, including* ±1.6% *uncertainty from the* ^{229}Th *spike activity*

		Dissolved			Particulate		
Depth (m)	TSM (mg l^{-1})	^{232}Th (dpm/10^3 kg)	^{230}Th (dpm/10^3 kg)	^{230}Th/^{232}Th	^{232}Th (dpm/10^3 kg)	^{230}Th (dpm/10^3 kg)	^{230}Th/^{232}Th
10	0.57	0.1272 ± 0.0021	0.272 ± 0.010	2.14 ± 0.06	—	—	—
20	0.25	0.1079 ± 0.0018	0.255 ± 0.011	2.36 ± 0.07	0.2100 ± 0.0034	0.169 ± 0.015	0.80 ± 0.07
30	0.24	0.0933 ± 0.0015	0.183 ± 0.019	1.95 ± 0.11	—	—	—
40	0.12	0.0660 ± 0.0011	0.159 ± 0.007	2.42 ± 0.11	0.0642 ± 0.0022	0.077 ± 0.008	1.20 ± 0.13
45	0.13	0.3345 ± 0.0055	0.368 ± 0.035	1.10 ± 0.06	—	—	—
60	0.05	0.0558 ± 0.0009	0.133 ± 0.017	2.38 ± 0.39	0.0980 ± 0.0018	0.102 ± 0.015	1.04 ± 0.15
70	0.11	0.0671 ± 0.0011	0.121 ± 0.005	1.81 ± 0.06	—	—	—
80	0.17	0.0518 ± 0.0008	0.148 ± 0.004	2.83 ± 0.06	0.1940 ± 0.0032	0.252 ± 0.016	1.30 ± 0.08
90	0.11	0.0683 ± 0.0011	0.170 ± 0.010	2.48 ± 0.11	—	—	—
100	0.01	0.0864 ± 0.0014	0.192 ± 0.014	2.22 ± 0.17	0.1109 ± 0.0018	0.112 ± 0.020	1.01 ± 0.18
110	0.03	0.0790 ± 0.0013	0.207 ± 0.007	2.63 ± 0.06	—	—	—
120	0.04	0.1002 ± 0.0017	0.264 ± 0.008	2.35 ± 0.06	0.0833 ± 0.0017	0.100 ± 0.005	1.20 ± 0.06
130	0.09	0.1038 ± 0.0017	0.269 ± 0.008	2.59 ± 0.07	—	—	—
140	0.06	0.1124 ± 0.0018	0.355 ± 0.015	3.15 ± 0.13	0.0538 ± 0.0012	0.078 ± 0.010	1.45 ± 0.19
170	0.11	0.1463 ± 0.0024	0.437 ± 0.018	2.92 ± 0.05	—	—	—
200	0.06	0.1550 ± 0.0035	0.584 ± 0.053	3.97 ± 0.35	0.0745 ± 0.0016	0.105 ± 0.020	1.41 ± 0.27
400	0.07	0.2397 ± 0.0039	0.713 ± 0.024	2.98 ± 0.06	—	—	—
800	0.08	0.2063 ± 0.0033	0.855 ± 0.026	4.15 ± 0.11	0.0510 ± 0.0011	0.076 ± 0.010	1.50 ± 0.20
2076	0.05	0.2176 ± 0.0036	0.847 ± 0.028	3.89 ± 0.09	—	—	—

1990; Clegg *et al.*, 1991). Mechanisms leading to the similar ^{230}Th$_d$ concentrations in the Arctic Ocean and Black Sea are conceivably different in these two settings. The high ^{230}Th$_d$ concentrations in the Arctic Ocean can be attributed to extremely low particle flux and hence low scavenging rates (Bacon *et al.*, 1989). In the Black Sea, the flux of particles is relatively high, while the production rate of ^{230}Th is atypically low due to the low uranium concentration (3.3 ppb in typical seawater vs 1.3–2.1 ppb in Black Sea water; Wei and Murray, 1991). The higher-than-usual ^{230}Th$_d$ concentrations in Black Sea are related to the redox chemistry in this special environment (discussed later).

Except at 45 m, the ^{230}Th$_d$/^{232}Th$_d$ activity ratio increases with depth by a factor of 2 (Fig. 4), from 2 to 4, indicating the increased contribution of radiogenic ^{230}Th with depth (discussed later). The anomalously low ^{230}Th$_d$/^{232}Th$_d$ at 45 m (1.1) is similar to the ^{230}Th$_p$/^{232}Th$_p$ ratio in the upper water column (see later), which, coupled with high ^{230}Th$_d$ and ^{232}Th$_d$ concentrations at that depth clearly indicate the effect of particles. As noted earlier, at BS3-2, 45 m is the depth of the highest density gradient (hence static stability) in the water column. Such a correlation (between ^{232}Th maximum and density gradient) has also been noted elsewhere (Huh and Bacon, 1985; Chun, 1989) and it alludes to the possible effect of less than 0.4-μm or colloidal-sized particles in the "dissolved" fraction (Honeyman and Santschi, 1991). It is interesting to note that the concentration of filtered particles in the oxic zone is characterized by a pronounced decrease from 0.57 mg l^{-1} at 10 m to 0.04 mg l^{-1} at 55 m (Wei and Murray, 1991), suggesting the production of <0.4-μm particles at the expense of >0.4-μm particles and remineralization of particles. This

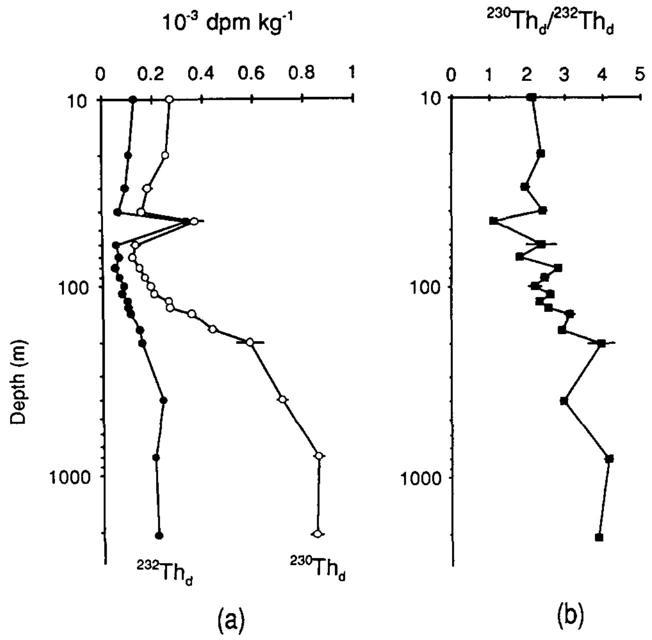

Fig. 4. Profiles of (a) dissolved ^{230}Th and ^{232}Th and (b) dissolved ^{230}Th/^{232}Th ratio at BS3-2. The depth axis is a log scale.

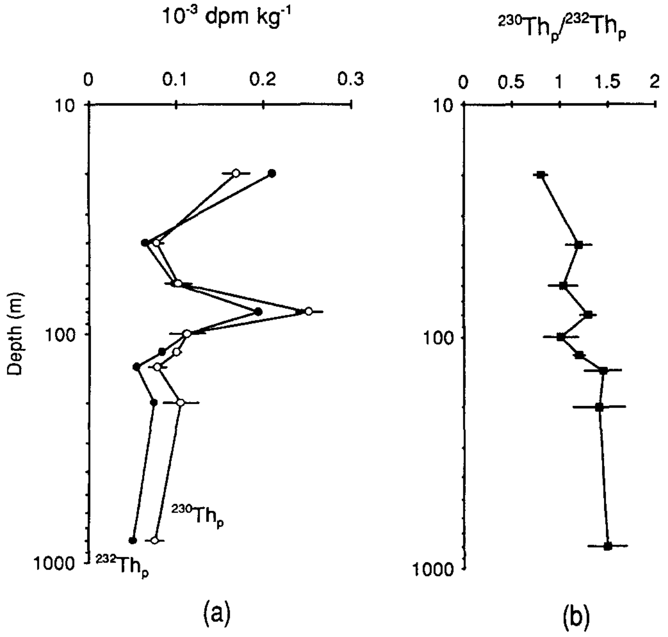

Fig. 5. Profiles of (a) particulate ^{230}Th and ^{232}Th and (b) particulate ^{230}Th/^{232}Th ratio at BS3-2. The depth axis is a log scale.

disaggregation/remineralization process may be microbially mediated (CHO and AZAM, 1988). Reduced particle size and an established strong pycnocline will retard particulate settling and water mixing, thereby maintaining a layer of increased concentration of "dissolved" matter in the region of high density gradient. The secondary phosphate maximum (CODISPOTI *et al.*, 1991) and subsurface maxima of $NO_3^- + NO_2^-$ and *in situ* fluorescence (KARL and KNAUER, 1991) found near 45 m at BS3-2 may be related to this speculated process. This hypothesis is consistent with the model prediction of CLEGG and WHITFIELD (1990) which showed that the highest disaggregation and remineralization rates occur at a subsurface depth.

The decrease with depth of dissolved ^{230}Th and ^{232}Th in the upper water column reflects input at surface of continental detritus via aeolian (HACISALIHOĞLU *et al.*, 1991) and/or riverine (LEWIS and LANDING, 1991) pathways. Based on ancillary data, an attempt is made to estimate the fraction of ^{232}Th in freshly delivered alumino-silicates that is soluble on contact with surface seawater. Although there is no data on the flux of continental materials at the site, a first order approximation can be made by assuming that it is similar to the deposition rate of bottom sediments. At an adjacent station (BS4-9), BARNES and COCHRAN (1991) estimated, based on ^{210}Pb stratigraphy, an apparent sedimentation rate of 40 cm ky^{-1}. In order to convert this apparent sedimentation rate to mass accumulation rate, we need to know the porosity of wet sediments and the density of dry sediments. Although porosity was not directly determined on the BS4-9 core, it is reasonable to assume a value of 85–90% as estimated for the upper 10 cm of other cores in the deep Black Sea (ROSS and DEGENS, 1974; CALVERT *et al.*, 1987; CRUSIUS and ANDERSON, 1991). As for dry sediment density, a value of 2.5 g cm^{-3} is assumed. From these, a mass accumulation rate of 0.01–0.015 g cm^{-2} y^{-1} is obtained. Multiplying the mass accumulation rate by the concentration of ^{232}Th, which averages 1.0 dpm g^{-1} with little variation in the upper 10 cm (BARNES and COCHRAN, 1991), results in 0.01–0.015 dpm cm^{-2} y^{-1} as the total flux of ^{232}Th. The question then follows is: what is the flux of dissolved ^{232}Th to the surface water? This can be estimated from the inventory and residence time of dissolved ^{232}Th in the surface water based on the steady-state assumption. The inventory of dissolved ^{232}Th in the upper 40 m is 0.00042 dpm cm^{-2}. The residence time of dissolved ^{232}Th in surface water should be the same as that of ^{234}Th in theory, which in the upper 40 m is about 100 days (WEI and MURRAY, 1991). Thus, the dissolution flux of ^{232}Th from terrigenous material is estimated to be 1.5×10^{-3} dpm cm^{-2} y^{-1}, which accounts for 9–13% of the total ^{232}Th delivered to the surface Black Sea. Considering the uncertainties involved in the calculation, the result seems to be fairly reasonable; it is not inconsistent with the percentages of leachable Al in aeolian dusts (5–15%) determined from seawater leaching experiments by MARING and DUCE (1987).

Radiogenic vs terrigenous contribution of dissolved ^{230}Th

There are two sources of $^{230}Th_d$ in seawater: radiogenic and terrigenous. The radiogenic component is produced from the decay of ^{234}U in seawater; and the terrigenous component is derived from leaching by seawater of particles of continental origin, as discussed earlier. Because $^{232}Th_d$ has only the continental source, the terrigenous component of $^{230}Th_d$ can be estimated from the concentration of $^{232}Th_d$ and the ^{230}Th/^{232}Th ratio in continental detritus, i.e.

$$(^{230}\mathrm{Th_d})_{\mathrm{terrigenous}} = {}^{232}\mathrm{Th_d} \times (^{230}\mathrm{Th}/^{232}\mathrm{Th})_{\mathrm{continental\ detritus}}.$$

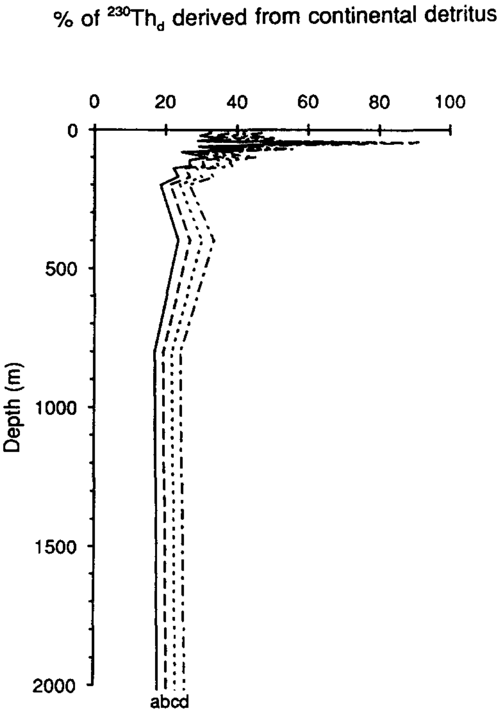

Fig. 6. Variation with depth of the terrigenous component of dissolved ^{230}Th as a fraction of total dissolved ^{230}Th at each depth. The four profiles are calculated by varying the $^{230}Th/^{232}Th$ ratio of the source material from (a) 0.7 to (d) 1.0.

The radiogenic component of $^{230}Th_d$ can then be calculated by subtracting the terrigenous component from the measured, total ^{230}Th:

$$(^{230}Th_d)_{radiogenic} = {}^{230}Th_d - (^{230}Th_d)_{terrigenous}.$$

The question then is the $^{230}Th/^{232}Th$ ratio in the source material. This ratio can be reasonably constrained by the following considerations. The $^{230}Th/^{232}Th$ ratio in surface sediments, which is 1.47 ± 0.15 ($n = 5$) in the top 10 cm of BS4-9, is identical to those (1.45 ± 0.05; $n = 3$) in suspended particles in the anoxic zone. Because these values carry a considerable signal of radiogenic ^{230}Th, they should be considered as upper limits for $^{230}Th/^{232}Th$ in continental detritus. The lowest particulate $^{230}Th/^{232}Th$ ratio observed in the oxic zone is 0.80 ± 0.07 (Table 1). If 0.8 is taken as the $^{230}Th/^{232}Th$ ratio in continental detritus, it is calculated that the terrigenous component of $^{2320}Th_d$ decreases from ~40% near the surface to ~20% below 800 m. Figure 6 shows that the result does not change dramatically if the ratio is varied between 0.7 and 1, which we believe should bracket the real $^{230}Th/^{232}Th$ ratio in freshly delivered continental material.

Particulate ^{230}Th *and* ^{232}Th

Due to a mishap in the chemical analysis, half of the filter samples, which were processed in a batch, were lost. Despite the poor sample resolution in the particulate Th profile, there

Table 2. Water column inventories of ^{230}Th *and* ^{232}Th *at Sta. BS3-2*

	Inventory (dpm m^{-2})			
	^{230}Th		^{232}Th	
Depth range	Dissolved	Particulate	Dissolved	Particulate
0–55 m (oxic)	13.1	7.2	7.2	8.2
55–95 m (suboxic)	6.3	6.7	3.2	5.6
95–2076 m (anoxic)	1560	160	410	110

still exist some phenomena that can be discerned. The available data show a general correspondence between the concentrations of particulate Th and total suspended matter, and suggest the existence of near surface maxima and subsurface maxima around 80 m (Table 1 and Fig. 5). It is important to note that the subsurface maxima of particulate ^{230}Th and ^{232}Th appear to coincide with the maxima of particulate Mn (LEWIS and LANDING, 1991) and particulate ^{234}Th (WEI and MURRAY, 1991) found at 70–80 m. Below 80 m, there exists a strong positive correlation ($r = 0.99$) between particulate ^{230}Th and particulate Mn: $^{230}\mathrm{Th_p} = 0.021\ \mathrm{Mn_p} + 0.078$; $n = 6$. Because the samples for both measurements were collected from the same station at the same time, the coherence provides evidence of scavenging of dissolved Th by Mn-containing particles at the redox boundary and recycling of Th along with Mn in the anoxic deep water.

In the oxic and suboxic zones, $^{232}\mathrm{Th_p}$ is higher than $^{232}\mathrm{Th_d}$ whereas $^{230}\mathrm{Th_p}$ is fairly comparable to $^{230}\mathrm{Th_d}$. The trend is clearly reversed in the anoxic zone where both isotopes show much lower concentration in the particulate form than in the dissolved form. This is similar to the observation made in Saanich Inlet (CHUN and HUH, 1988), and reflects the fact that, as an A-type metal, Th is not efficiently scavenged by sulfides.

Inventories of dissolved and particulate ^{230}Th and ^{232}Th in the oxic (0–55 m), suboxic (55–95 m), and anoxic (95–2076 m) zones are estimated, as given in Table 2. The data show that in the oxic and sub-oxic zones combined, 42% of ^{230}Th and 57% of ^{232}Th are in the particulate form. By comparison, only 9% of ^{230}Th and 21% of ^{232}Th are in the particulate form in the anoxic zone. We believe the major carrier phase of particulate Th is Mn-oxyhydroxides in the suboxic zone and alumino-silicates in the oxic and anoxic zones.

The $^{230}\mathrm{Th_p}/^{232}\mathrm{Th_p}$ activity ratio increases from 0.8 near surface to 1.5 at depth, which is in parallel with the increase of $^{230}\mathrm{Th_d}/^{232}\mathrm{Th_d}$ from 2 to 4. The correspondence between these two ratios is consistent with the thinking that the adsorption of Th by suspended particles is a reversible process (BACON and ANDERSON, 1982; MOORE and HUNTER, 1985).

Fluxes and residence times of dissolved Th *isotopes*

The residence times of dissolved Th below the euphotic zone are normally too long to be derived from the ^{238}U–^{234}Th disequilibrium. The problem can be overcome using the ^{234}U–^{230}Th disequilibrium. Because only the radiogenic component of $^{230}\mathrm{Th_d}$ is relevant to this application, the terrigenous component must be subtracted from the total $^{230}\mathrm{Th_d}$. Assuming that the ^{230}Th/^{232}Th ratio in terrigenous particles is 0.7–1, the inventory of radiogenic $^{230}\mathrm{Th_d}$ in the water column can be calculated to be 1160–1290 dpm m^{-2} using the method discussed earlier. The production rate of ^{230}Th in the water column, based on the detailed ^{234}U data (Wei and Murray, 1991), is 26.8 dpm m^{-2} y^{-1}. Thus, the residence time of dissolved ^{230}Th in the water column (0–2076 m) is 43–48 years, compared with 6–20 years calculated from data for the same depth range at other open-ocean sites (Nozaki *et al.*, 1981, 1987; Bacon and Anderson, 1982; Nozaki and Nakanishi, 1985; Cochran *et al.*, 1987; Clegg *et al.*, 1991).

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