

Th and Pa Isotopes in the Waters of the Western Margin of the Pacific near Japan: Evidence for Release of ^{228}Ra and ^{227}Ac from Slope Sediments*

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Abstract: Using the moored MnO_2 -fiber method, we have obtained 38 determinations of Th and Pa isotope concentrations from 18 sites along the margin of the western North Pacific near Japan, from water depths of 1,330 to 5,873 m. From our data, we are able to show that (1) ^{228}Ra and ^{227}Ac are being supplied to the seawater from the slope sediments of Honshu, Japan, (2) our ^{230}Th and ^{231}Pa concentrations match those obtained by *in situ* pumping with a MnO_2 -fiber adsorber in the Japan and Izu-Ogasawara trenches but are significantly higher than those from the Panama and Guatemala basins, and (3) our ^{232}Th concentrations show a similar systematic decrease with depth as do those of trace metals like Mn, Al, Te and Bi whose concentrations are strongly controlled by particulate matter scavenging.

In contrast, our data fail to show (1) that enhanced removal of ^{230}Th and ^{231}Pa by scavenging from the water column is taking place near the western margins and (2) that ^{231}Pa is being removed in preference to ^{230}Th from the water column to the marginal sediments. This is probably due to rapid mixing of the deep waters as compared to the scavenging rates of ^{230}Th and ^{231}Pa in the water column and at the sediment/seawater interface.

1. Introduction

Depth profiles of reactive metals in the open seas have usually been discussed in terms of vertical processes, both physical and biological, often involving scavenging by particulate matter. Yet it is now recognized that lateral transport along isopycnals coupled with uptake or release of elements at oceanic margins may have an adverse effect on elemental distributions even in mid-oceanic regions far away from any topographic margins.

Significant evidence for this boundary effect has been obtained through investigations of the disequilibria of the U/Th decay series nuclides in seawater. It is well known that ^{228}Ra ($t_{1/2} = 5.7$ years) has a higher concentration (in fact reaches maximum concentrations) in both surface and bottom waters of the open oceans (Moore, 1969). In open ocean surface waters, its high concentration is ascribed to lateral input

from the continental shelf where it is added to the water from underlying sediments. In bottom waters, its concentration maximum may be the result of supply from the underlying sediments and isopycnal transport from nearby slopes. ^{227}Ac ($t_{1/2} = 21.8$ years) shows a similar pattern in deep waters. Nozaki (1984) has observed that ^{227}Ac exists in excess over its parent ^{231}Pa in North Pacific deep waters, much like ^{228}Ra . This excess ^{227}Ac probably also derives from a bottom sediment source.

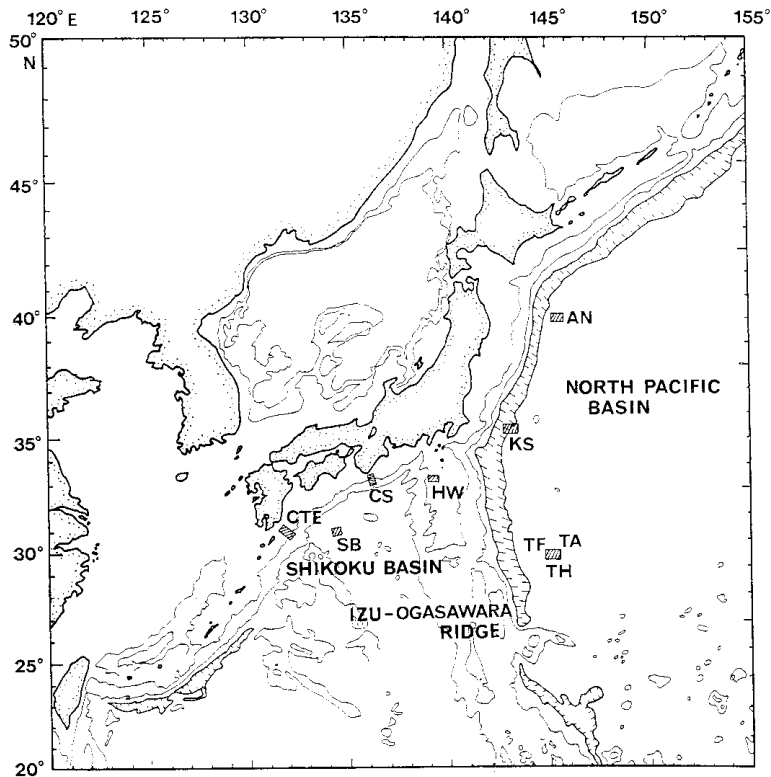
Evidence for elemental uptake at oceanic margins was also shown by the various GEOSECS ^{210}Pb measurements (Bacon *et al.*, 1976; Spencer *et al.*, 1981; Nozaki *et al.*, 1980; Cochran *et al.*, 1983). These studies indicated that the deficiency of reactive ^{210}Pb in seawater relative to its soluble precursor ^{228}Ra generally gets larger from the interior towards the margins of ocean basins, which suggests that the scavenging of ^{210}Pb is intensified near or at the sediment-seawater interface. Investigations of ^{230}Th and ^{231}Pa , both reactive daughters of dissolved uranium (^{234}U and ^{235}U , respectively), have

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Table 1. Location, water depth, and dates of sampling and analysis for the MnO₂-fiber mooring experiments.

Site Name	Location		Water depth (m)	Duration of deployment (m/d/yr)	Date of analysis (m/d/yr)
	Latitude	Longitude			
CTE-1	30°48'N	131°41'E	1500	11/14/83— 4/12/84	4/30/84
CTE-2	30°45'N	131°45'E	1620	11/14/83— 4/12/84	4/30/84
CS-2	33°05'N	135°45'E	2640	11/03/83—12/07/84	1/30/85
CS-3	32°52'N	135°45'E	3600	11/03/83—12/07/84	1/13/85
CS-4	32°38'N	135°44'E	4670	11/04/83—12/07/84	1/13/85
CS-5	32°45'N	136°15'E	4500	11/04/83—12/06/84	1/16/85
SB-1	31°16'N	134°08'E	4480	11/02/83—12/09/84	12/25/84
SB-2	30°43'N	134°05'E	4450	11/02/83—12/09/84	12/25/84
SB-3	31°02'N	135°35'E	4500	11/02/83—12/09/84	12/25/84
TA-23	30°00'N	145°00'E	5780	3/12/82— 5/10/83	5/25/83
TF-23	30°00'N	145°00'E	5910	3/12/82— 5/10/83	5/25/83
TH-23	29°30'N	145°20'E	5846	3/12/82— 7/19/82	5/25/83
HW-1	33°00'N	139°00'E	1800	5/09/84— 5/23/85	7/01/85
KS-2	35°55'N	142°20'E	4328	5/13/84— 5/24/85	7/01/85
KS-3	35°50'N	142°32'E	5127	5/13/84— 5/25/85	7/01/85
KS-4	35°48'N	142°40'E	3500	5/13/84— 5/25/85	7/01/85
KS-5	35°45'N	142°47'E	5050	5/14/84— 5/24/85	7/01/85
AN-5	40°00'N	145°28'E	5270	9/04/84— 4/15/85	5/20/85

Fig. 1. Location map for MnO₂-fiber mooring experiments.

offered further evidence regarding the importance of horizontal transport. Despite being produced uniformly within the ocean by uranium decay and removed by scavenging with short residence times less than a few hundred years, these nuclides take different pathways to their depositional sink. Yang *et al.* (1986) have shown that ^{231}Pa is enriched relative to ^{230}Th in the sediments of a highly depositional environment

such as the ocean margins and the Antarctic regions. Other studies of ^{230}Th and ^{231}Pa in particulate matter (Anderson *et al.*, 1983a, b) and in seawater (Nozaki and Nakanishi, 1985) have also demonstrated that there is a net transport of ^{231}Pa from the mid-ocean to regions where it is more intensively scavenged.

Thus, the processes controlling uptake and release of elements at the oceanic margins are

Table 2. Th and Pa isotope concentrations (dpm/10³kg) in seawater obtained by moored MnO₂-fiber method.

	Depth (m)	Distance above bottom (m)	^{232}Th	^{230}Th	^{233}Th (as ^{233}Ra)	^{227}Th (as ^{227}Ac)	^{231}Pa
CTE-1	1470	30	n.a.	0.32±0.07	0.59±0.13	0.71±0.16	0.32±0.10
CTE-2	1590	30	n.a.	0.30±0.04	0.53±0.07	0.42±0.07	0.26±0.06
CS-2	1835	805	0.070±0.018	0.56±0.05	2.01±0.26	1.01±0.14	0.39±0.07
	2215	425	0.039±0.010	0.89±0.08	1.84±0.22	1.42±0.18	0.75±0.19
CS-3	2595	1005	0.035±0.008	0.35±0.04	1.03±0.10	0.87±0.09	0.30±0.06
	3175	425	0.020±0.004	0.53±0.03	1.24±0.10	1.22±0.10	0.22±0.03
CS-4	3565	1105	0.029±0.009	0.94±0.06	1.66±0.14	1.48±0.13	0.41±0.05
	4245	425	0.020±0.012	0.86±0.03	1.90±0.08	1.59±0.07	0.32±0.03
CS-5	3395	1105	0.034±0.005	0.84±0.03	1.75±0.09	1.09±0.07	0.26±0.03
	4075	425	0.040±0.011	1.04±0.07	2.00±0.19	2.30±0.21	0.59±0.07
SB-1	4055	425	0.019±0.004	0.47±0.03	0.96±0.07	0.86±0.07	0.18±0.03
SB-2	4025	425	0.007±0.003	0.32±0.03	0.80±0.09	0.72±0.08	0.11±0.02
SB-3	4075	425	0.009±0.002	0.30±0.01	0.59±0.03	0.45±0.03	0.09±0.03
TA23	3965	1815	0.007±0.002	1.12±0.09	0.98±0.09	1.13±0.10	0.56±0.07
	4165	1615	0.011±0.004	1.19±0.08	1.19±0.08	1.07±0.10	0.48±0.05
	4565	1215	0.015±0.004	1.49±0.12	1.48±0.13	1.52±0.14	0.37±0.04
	4965	815	0.026±0.003	1.71±0.11	2.14±0.13	2.10±0.18	0.57±0.06
	5170	610	0.020±0.003	1.69±0.09	2.21±0.11	1.99±0.16	0.44±0.05
	5370	410	0.022±0.006	1.90±0.11	2.83±0.14	2.12±0.21	0.55±0.05
	5575	205	0.033±0.006	1.94±0.16	3.08±0.21	2.42±0.20	0.50±0.06
	5725	55	0.033±0.004	2.34±0.07	3.91±0.09	2.58±0.16	0.69±0.09
TF23	5668	242	0.022±0.005	1.32±0.10	2.13±0.13	0.70±0.18	0.57±0.06
	5873	37	0.019±0.005	0.94±0.10	2.16±0.14	1.66±0.19	0.34±0.01
TH23	5605	241	0.034±0.006	1.79±0.10	2.77±0.13	2.50±0.18	0.58±0.04
	5810	36	0.033±0.011	1.54±0.13	2.78±0.19	2.36±0.26	0.43±0.04
HW-1	1675	125	n.a.	0.14±0.02	0.35±0.04	n.a.	n.a.
KS-2	4223	105	n.a.	0.72±0.13	1.19±0.23	1.38±0.27	0.32±0.07
KS-3	5022	105	n.a.	0.81±0.11	1.40±0.19	0.95±0.13	0.33±0.05
KS-4	3395	105	n.a.	0.47±0.05	0.25±0.03	0.31±0.03	0.29±0.03
	3495	5	n.a.	0.55±0.08	0.29±0.04	0.34±0.05	0.28±0.04
KS-5	4945	105	n.a.	0.61±0.10	1.01±0.16	0.86±0.14	0.26±0.04
	5045	5	n.a.	0.81±0.16	1.56±0.31	1.41±0.28	0.27±0.05
AN-5	1330	3940	n.a.	0.12±0.01	0.84±0.09	0.05±0.01	0.09±0.01
	1480	3790	n.a.	0.10±0.01	0.62±0.06	0.09±0.01	0.07±0.01
	1580	3680	n.a.	0.18±0.06	0.67±0.24	0.09±0.03	0.09±0.05
	2980	2290	n.a.	0.58±0.06	0.44±0.05	0.47±0.05	0.40±0.05
	4780	490	n.a.	0.97±0.15	1.70±0.27	1.51±0.24	0.44±0.08
	5230	40	n.a.	1.55±0.39	3.16±0.81	1.46±0.37	0.59±0.15

n.a.=not analyzed

important for our understanding of elemental distributions in the ocean. In this study, we have measured Th and Pa isotope concentrations in seawater from near the slopes of the western boundary of the Pacific Ocean near Japan. Our results clearly indicate that ^{227}Ac and ^{228}Ra are being released from the slope sediments.

2. Methodology and results

We extracted Th and Pa isotopes *in situ* from large volumes of seawater using Mn-impregnated fibers onto which they were adsorbed over several months, analyzed their isotopic composition, and estimated their seawater concentrations relative to dissolved ^{234}Th in the water (Nozaki, 1983). Locations for and the durations of the MnO_2 -fiber mooring experiments are given in Table 1 and Fig. 1. Stations CTE, CS, and HW are located on the slopes of the Shikoku Basin and the Izu-Ogasawara Ridge. All other stations are more than 50 miles away from their nearest slopes. A detailed description of our analytical procedure may be found in Nozaki (1983). We have made three assumptions in calculating α -emitting Th isotope concentrations from our raw data; 1) the rate of nuclide adsorption is constant over the period of the mooring experiments, 2) the MnO_2 -fibers adsorb the nuclides only in dissolved form and 3) dis-

solved ^{234}Th concentration is 2.2 dpm kg^{-1} . For ^{231}Pa , it is further assumed that there is no fractionation between Th and Pa during adsorption onto the MnO_2 -fiber (Anderson *et al.*, 1983b). Some criticisms regarding the validity of these assumptions will be discussed below. The results are given in Table 2 together with a ± 1 sigma counting error margin.

Our fundamental premise in interpreting short-lived ^{228}Th ($t_{1/2}=1.91$ years) and ^{227}Th ($t_{1/2}=18.7$ days) data is that they represent equilibrium concentrations with their parents, ^{228}Ra and ^{227}Ac , in the water. As a check, we made repeat measurements of Th isotopes on the MnO_2 -fiber samples for site TA-23. Approximately a half of each MnO_2 -fiber sample was analyzed soon after the sample recovery without using any Th yield tracer. No correction for the decay or growth of ^{227}Th and ^{228}Th during sampling was made under an assumption that they are in equilibrium with their parents, ^{227}Ac and ^{228}Ra in the sample. This assumption is based on the laboratory study of Reid *et al.* (1979) showing that MnO_2 -fibers strongly adsorb Ra and Ac isotopes in seawater and on the expectation that short-lived Th isotopes should be in equilibrium with their parent nuclides, based on ^{230}Th box-model scavenging residence time of ~ 30 years (Nozaki *et al.*, 1981) in deep

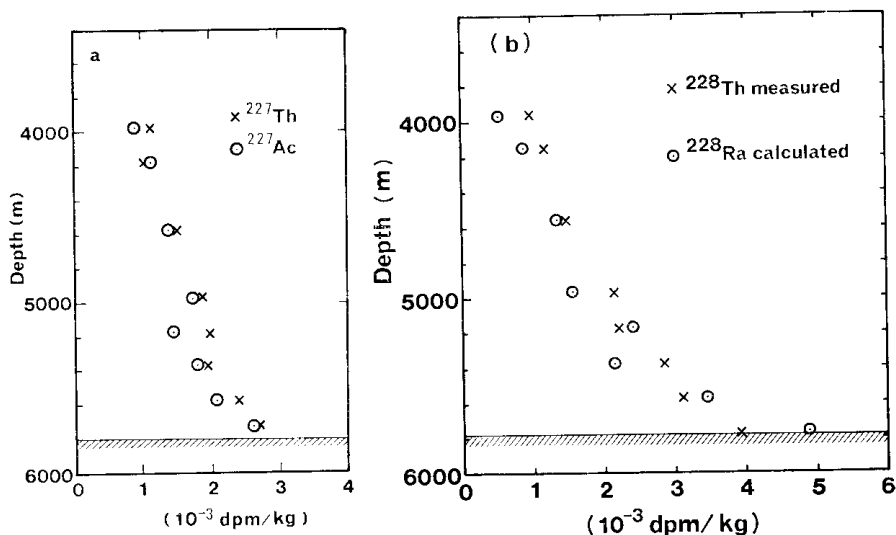


Fig. 2. Selected isotope concentrations plotted against depth for site TA-23 (see Fig. 1 for location): a. ^{227}Th and ^{227}Ac (both measured), b. ^{228}Th (measured) and ^{228}Ra (calculated). See text for ^{228}Ra calculations.

ocean waters. The α -emitting Th data for site TA-23 were reported earlier by Nozaki and Horibe (1983) and are given in Table 2. The remaining half of each MnO_2 -fiber was analyzed again for Th isotopes and ^{231}Pa about 2.5 years after the first measurement. In the meantime, the ^{227}Th should have attained secular equilibrium with the ^{227}Ac in the sample even if it had not been in equilibrium at the time of sample recovery. A ^{232}Th spike (and a ^{233}Pa spike) were used, because the initial ^{234}Th had decayed out of the sample. (The exact values of chemical yield for both Th and Pa were also required for calculating ^{231}Pa concentrations.) We calculated ^{231}Pa (Table 2) and ^{227}Th (as ^{227}Ac) concentrations from their activity ratios with respect to ^{230}Th multiplying by the ^{230}Th concentration obtained earlier. The repeat measurements show good agreement for ^{227}Th (Fig. 2a) and hence our ^{227}Th data can be regarded as ^{227}Ac concentrations.

Confirming the ^{228}Th - ^{228}Ra relationship in our data is somewhat difficult, because the ^{228}Ra concentrations were not determined. However, based on the repeat measurements on ^{228}Th for site TA-23, it is possible to estimate ^{228}Ra concentrations from the equation given by,

$$A^0_{\text{Ra-228}} = \left[\left(\frac{A^t_{\text{Th-228}}}{A_{\text{Th-230}}} \right) - \left(\frac{A^0_{\text{Th-228}}}{A_{\text{Th-230}}} \right) e^{-\lambda_{\text{Th-228}} t} \right] \\ \times \frac{(\lambda_{\text{Th-228}} - \lambda_{\text{Ra-228}}) A_{\text{Th-230}}}{\lambda_{\text{Th-228}} (e^{-\lambda_{\text{Ra-228}} t} - e^{-\lambda_{\text{Th-228}} t})}$$

where A^t is the activity on the MnO_2 -fiber after the time, t , elapsed from sample recovery to analysis, A^0 is the initial activity, when recovered, and λ is the decay constant of the nuclide designated. It is assumed that there is no fractionation between Ra and Th during their adsorption onto the MnO_2 -fiber. For site TA-23, the calculated ^{228}Ra concentration is approximately equal to the ^{228}Th concentration in the water (Fig. 2b) based on the uncertainties in the calculation (3–10% for ^{228}Th and 7–30% for ^{228}Ra due to one sigma counting error). This is also expected from that the ^{230}Th concentrations for site TA-23 are higher than 1×10^{-3} dpm kg^{-1} in the seawater (Table 2) corresponding to box-model scavenging residence time for ^{230}Th of longer than 40 years and that if this ^{230}Th scavenging residence time is applicable to ^{228}Th ,

there should be no deficiency of ^{228}Th relative to ^{228}Ra for deep waters. Therefore, we assume as a first order approximation that our ^{228}Th data from other sites are also equal to the equilibrium values of ^{228}Ra in seawater.

At the SB sites, our Th and Pa data are anomalously low compared to those of other sites (Figs. 4 and 6), which requires some explanation. Current meter records around the SB sites indicate that the bottom currents were extraordinarily high in the two months preceding recovery of the moorings (Fukasawa, personal communication). Therefore, it is likely that more seawater came into contact with the MnO_2 -fiber attached to the mooring during the last two months than over the previous months of the mooring experiment. This implies that our assumption of constant uptake rate of nuclides by the MnO_2 -fibers is invalid, and causes an underestimate of the α -emitting nuclide concentrations. Nevertheless, nuclide ratios such as $^{227}\text{Th}/^{228}\text{Th}$ and $^{230}\text{Th}/^{231}\text{Pa}$ would not be affected by this.

In discussing these results hereafter, we use the convention of parenthesis in identifying the activity ratio.

3. Discussion

3.1. Evidence for ^{227}Ac and ^{228}Ra release from slope sediments

We have separated our ^{227}Ac and ^{228}Th (as ^{228}Ra) data, from the Shikoku Basin and from the North Pacific east of the Japan and Izu-Ogasawara trenches, into two groups (Fig. 3 and 4) based on the hypothesis that the gyre circulation of the deep water in our study area is divided in two by the Izu-Ogasawara Ridge which extends southward from Honshu (Teramoto, personal communication). In the eastern data group (Fig. 3), both ^{227}Ac and ^{228}Th (as ^{228}Ra) concentrations decrease exponentially with distance from the bottom suggesting that they are being supplied from deep-sea sediments. These profiles are comparable to those reported earlier for open ocean regions of the North Pacific (Nozaki *et al.*, 1981; Nozaki, 1984; Nozaki and Nakanishi, 1985). In order to explain the profiles by a simple vertical eddy diffusion model (Nozaki, 1984), the vertical diffusion coefficient needs to be as large as several tens of square

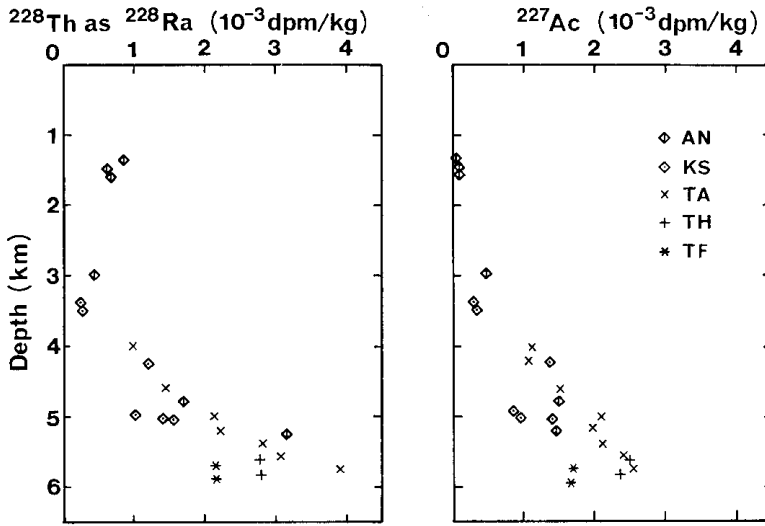


Fig. 3. Concentration-depth plots for ^{228}Th (as ^{228}Ra) and ^{227}Ac in the Northwest Pacific Basin. Labels represent different sites; locations in Fig. 1.

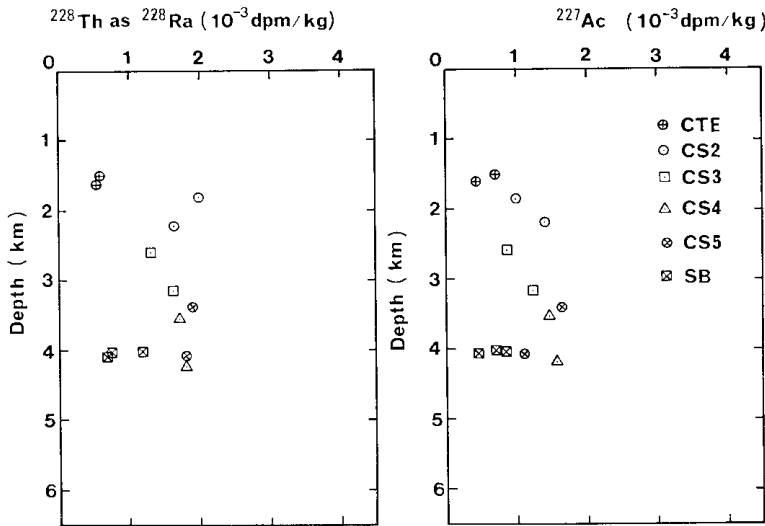


Fig. 4. Concentration-depth plots for ^{228}Th (as ^{228}Ra) and ^{227}Ac along the slope of Shikoku Basin (site CTE, CS, SB: see Fig. 1 for locations).

centimeters per second. Although this value for diffusivity is too high according to physical oceanographers (*e.g.* Armi, 1979; Sarmiento and Rooth, 1980), it is difficult to see from these data alone how significantly the profiles are affected by the lateral input of ^{227}Ac and ^{228}Ra from nearby slopes.

On the other hand, in the western data group (Fig. 4) both ^{227}Ac and ^{228}Th (as ^{228}Ra) are significantly higher than those of their parents

throughout the water column. This strongly suggests that ^{227}Ac and ^{228}Ra are being supplied from the slope sediments to the water. It seems unlikely that the observed high concentrations of ^{227}Ac and ^{228}Th (as ^{228}Ra) are being supplied by upwelling of bottom water along the slopes. If upwelling were occurring, then we would expect high ^{230}Th and $(^{230}\text{Th}/^{231}\text{Pa})$ ratios on the MnO_2 -fibers because bottom water has higher ^{230}Th and $(^{230}\text{Th}/^{231}\text{Pa})$ ratio than

shallow water, but we do not see this. Instead, the ^{230}Th concentration and the ($^{230}\text{Th}/^{231}\text{Pa}$) ratio systematically increase with depth (Table 2 and Figs. 6 and 8). If their source is not upwelling, then the high ^{227}Ac and ^{228}Th (as ^{228}Ra) concentrations must have another source which is apparently isopycnal transport from mid-depth waters where they are supplied to the water column by the slope sediments. Therefore, these nuclides may be useful for the study of basin-scale circulation and mixing of deep waters, in particular for the North Pacific, because it will still be many years before we will be able to detect conservative anthropogenic tracers in deep water there.

The relationship between ^{227}Ac and ^{228}Th (as ^{228}Ra) is shown in Fig. 5. Most data seem to follow an approximately linear trend suggesting that both of these nuclides are being supplied from similar sediment sources in the basins. Three samples from shallow depths (1,330–1,580 m) at site AN-5 however are exceptions and show significant deviation from the general linear trend. This may be because ^{228}Ra is being supplied to these depths from shallow depth sediments without accompanying ^{227}Ac in signifi-

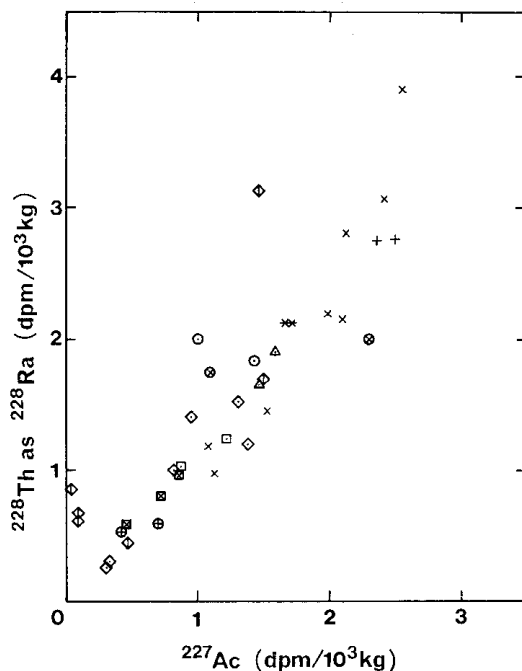


Fig. 5. Correlation diagram between ^{228}Th (as ^{228}Ra) and ^{227}Ac . Symbols as in Figs. 3 and 4.

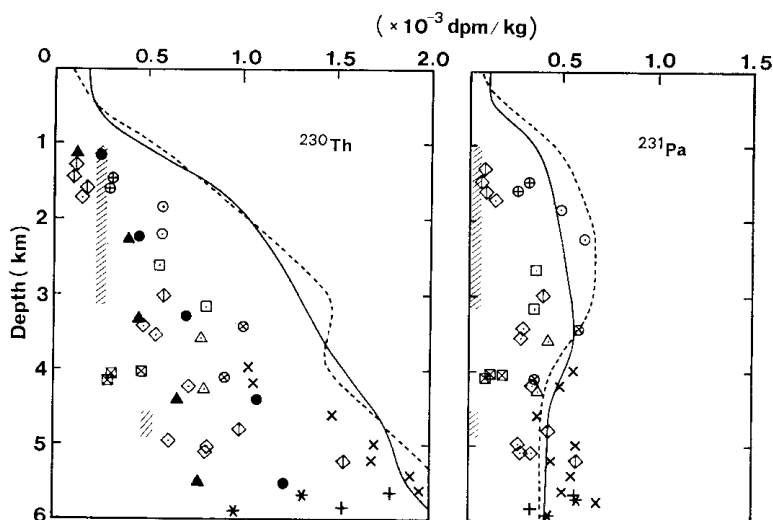


Fig. 6. Concentration-depth plots of dissolved ^{230}Th and ^{231}Pa in the study area compared to Panama and Guatemala basin data from Anderson *et al.* (1983b) (shaded areas) and two open ocean profiles from Nozaki and Nakanishi (1985) (solid and dotted curves). Dissolved ^{230}Th data from *in situ* pump samples (Nozaki *et al.* 1987) are also shown for sites AN-1 (solid circles) and AN-4 (solid triangles). Other symbols as in Figs. 3 and 4.

cant quantities. Indeed we see no significant excess ^{227}Ac in the surface waters of the regions either (Nozaki, 1984).

3.2. ^{230}Th and ^{231}Pa profiles

All ^{230}Th and ^{231}Pa data are plotted in Fig. 6 as a function of depth. The ^{230}Th concentrations tend to increase with depth, although the data points are somewhat scattered as a result of local effects. On the other hand, the ^{231}Pa concentrations are nearly constant below 2,000 m. Let us compare our ^{230}Th and ^{231}Pa data with the results obtained by other techniques. Anderson *et al.* (1983b) and Nozaki *et al.* (1987) used an *in-situ* pumping system and a membrane filtration unit along with the MnO_2 -adsorber. Because their samples are filtered of particulate matter, their data represent only dissolved nuclide concentrations. As shown in Fig. 6, our ^{230}Th data are comparable to those of Nozaki *et al.* (1987) for the Japan and Izu-Ogasawara trench stations but significantly higher than those in the Guatemala and Panama basins (Anderson *et al.*, 1983b). Our ^{231}Pa data are also strikingly different from those in the Guatemala and Panama basins. These suggests that different scavenging regimes are operating for ^{230}Th and ^{231}Pa in the western North Pacific and in the Guatemala and Panama basins.

In contrast to the MnO_2 -fiber extraction techniques, Nozaki and Nakanishi (1985) chemically processed large-volume unfiltered seawater samples and obtained total ^{230}Th and ^{231}Pa concentrations in the open ocean regions of the western North Pacific. Our dissolved ^{230}Th concentrations are lower than their total ^{230}Th concentrations for any given depth horizon, whereas our dissolved ^{231}Pa data are comparable to their total ^{231}Pa concentrations (Fig. 6). This can be ascribed to the higher affinity of ^{230}Th to particles than that of ^{231}Pa and not to an intensified scavenging of ^{230}Th near the ocean boundaries. Nozaki *et al.* (1987) have found that approximately 30% of the ^{230}Th in seawater is associated with particulate matter. Using the ratio of particle/seawater distribution coefficients, $K_D^{\text{Th}}/K_D^{\text{Pa}}=10$ (Nozaki and Nakanishi, 1985), the particle association of ^{231}Pa is calculated to be only 3%. If we take these nuclide concentrations bound to particles into account, we would expect a linearly increasing

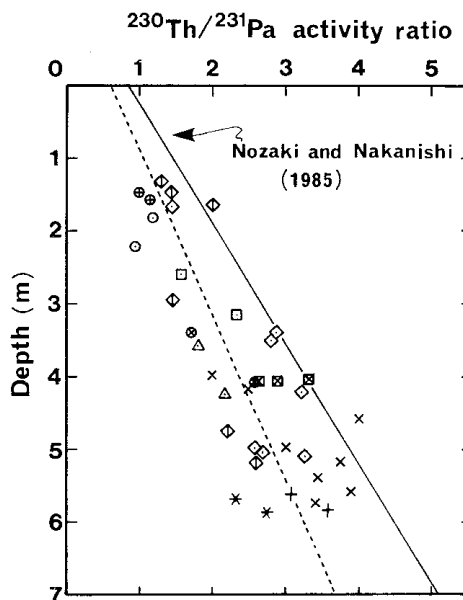


Fig. 7. The ($^{230}\text{Th}/^{231}\text{Pa}$) ratio as a function of depth. The solid line shows total ($^{230}\text{Th}/^{231}\text{Pa}$) ratio (Nozaki and Nakanishi, 1985). The dotted line is based on the calculated dissolved ($^{230}\text{Th}/^{231}\text{Pa}$) ratio assuming that particulate nuclide fractions are 30% for ^{230}Th and 3% for ^{231}Pa (Nozaki and Nakanishi, 1985). Symbols as in Figs. 3 and 4.

trend of dissolved ($^{230}\text{Th}/^{231}\text{Pa}$) ratio with depth based on the previous observation of Nozaki and Nakanishi (1985). Our data are consistent with this trend (Fig. 7).

3.3. Is ^{231}Pa removed preferentially relative to ^{230}Th at the western margins?

Yang *et al.* (1986) have mapped the ($^{230}\text{Th}_{\text{xs}}/^{231}\text{Pa}_{\text{xs}}$) ratio in deep-sea surface sediments of the Pacific Ocean and found that the sediments of the western North Pacific are enriched in ^{231}Pa relative to ^{230}Th . Such enrichment of ^{231}Pa has also been found in materials collected by sediment traps in the Panama Basin (Anderson *et al.*, 1983b) and in Antarctic sediments (DeMaster, 1979). Based on Panama and Guatemala Basin data, Anderson *et al.* (1983b) hypothesized that coating of particles by manganese oxides changed their surface adsorption characteristics such that adsorption of ^{230}Th and ^{231}Pa from seawater was nonbiased ($K_D^{\text{Th}}/K_D^{\text{Pa}}=1$). Such alteration in surface chemistry of particles may not be occurring in the western North

Pacific because of its relatively low-productivity and oxygenated environment. Indeed, the ^{230}Th and ^{231}Pa concentrations obtained here are higher than those of the eastern marginal basins (Fig. 6) and do not reveal any indication of enhanced scavenging of these two nuclides from the water column. Yang *et al.* (1986) then postulated that ^{231}Pa might be preferentially taken up from seawater at the sediment-seawater interface, as apparently occurs for ^{210}Pb (Bacon *et al.*, 1976; Spencer *et al.*, 1981).

Our ^{230}Th and ^{231}Pa data do not also show any evidence for a preferential removal of ^{231}Pa relative to ^{230}Th from the water column. This may be because the deep water is being mixed so rapidly that we could not detect the concentration gradients of ^{230}Th and ^{231}Pa from open oceans towards the western margins. Recently, Shimmield *et al.* (1986) demonstrated that the flux of ^{230}Th and ^{231}Pa at the sediment/water interface rapidly increases inshore based on their study of Baja California sediments. In order to clarify the behaviour of ^{230}Th and ^{231}Pa near the western North Pacific, more comprehensive study particularly on sedimentary deposits is needed.

3.4. Depth-profile of ^{232}Th

Unlike other isotopes of thorium (*e.g.* ^{234}Th , ^{230}Th , ^{228}Th) which are produced by the decay of the parent nuclides in seawater, ^{232}Th is delivered to the ocean by continental weathering. Because of its long half-life (1.4×10^{10} years) and its poor solubility in seawater, the radioactivity of ^{232}Th in seawater is extremely low and has long been difficult to accurately determine by counting of α -activity. However, MnO_2 -fiber techniques now make it possible to extract Th from large volume seawater samples of $>10^3$ liters, and hence significantly improve the signal to noise ratio for ^{232}Th detection. Results of MnO_2 -fiber extraction and α -counting of ^{232}Th have been reported by Moore (1981), Bacon and Anderson (1982), Nozaki and Horibe (1983) and Anderson *et al.* (1983b).

Figure 8 shows ^{232}Th data obtained in this study from both moored MnO_2 -fibers and those based on the *in situ* pumping method (Nozaki *et al.*, 1987). The agreement of the two sets of the data suggests again that the MnO_2 -fiber methods determine *dissolved* Th concentration

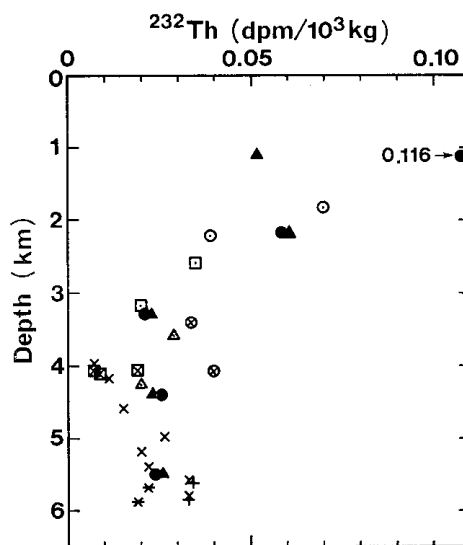


Fig. 8. ^{232}Th concentration plotted against depth. Solid circles and triangles are those obtained by *in situ* pumping for stations AN-1 and AN-4, respectively (Nozaki *et al.*, 1987). Other symbols as in Figs. 3 and 4.

in seawater. The mean concentration below 3 km is 0.023 ± 0.010 dpm/ 10^3 kg which is comparable to mean concentrations reported for eastern Pacific deep waters (Moore, 1981; Bacon and Anderson, 1982). Our western North Pacific data also show excellent agreement with the Atlantic data of Chen *et al.* (1986) which they obtained by a precise mass-spectrometric technique. One measurement in southeast of Hawaii at a depth of 2,789 m by Anderson *et al.* (1983) gave an upper limit of <0.002 dpm/ 10^3 kg for deep water. The geochemical significance of this low ^{232}Th concentration as compared to the mean western Pacific deep water ^{232}Th concentration needs to be further investigated. Somewhat lower values (~ 0.003 dpm/ 10^3 kg) have been reported for Caribbean deep waters because of the relatively short residence time of Th in that basin (Huh and Bacon, 1985).

Although our investigation was confined to samples from depths below 1 km, our ^{232}Th concentration values seems to systematically decrease with depth. This pattern of decreasing ^{232}Th concentration with depth resembles those of some reactive metals like Mn (Landing and Bruland, 1980), Al (Orians and Bruland, 1986), Te (Lee and Edmond, 1985) and Bi (Lee *et al.*,

1986), whose oceanic distributions are largely controlled by scavenging of particulate matter. Interestingly, the ^{232}Th profile also resembles that of anthropogenically supplied Pb and Pu, but this may be fortuitous. Many of these heavy metals appear to reach the oceans from atmospheric sources. Because of the extremely short residence time of Th that may be carried by rivers to coastal waters (Aller and Cochran, 1976), eolian input is also likely to be the most significant source of Th for the open oceans.

4. Conclusions

In this paper, we have presented new measurements of dissolved Th and Pa isotope concentrations in seawater very close to the western edge of the North Pacific. From these data, we conclude:

1) ^{226}Ra and ^{227}Ac are clearly being supplied to overlying seawater from the slope sediments of Honshu, Japan. As a consequence, these nuclides can serve as useful tracers for the study of basin-scale circulation and mixing of deep water.

2) Our dissolved ^{230}Th and ^{231}Pa concentrations are comparable to those deduced from published data from open ocean regions but significantly higher than those of hemipelagic regions like the Panama and Guatemala basins. Our data do not clearly demonstrate that Th and Pa isotopes are more effectively scavenged from the water column in near the western margins than in the open oceans.

3) ^{232}Th concentration appears to decrease from shallow depth waters to nearly constant value of $0.3 \text{ p mol kg}^{-1}$ below 3 km, paralleling similar decreases in concentration with depth for the reactive heavy metals, such as Mn, Al, Te and Bi whose concentrations are predominantly controlled by particulate scavenging.

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日本付近太平洋西縁の海水中の Th および Pa 同位体： 陸棚斜面堆積物から ^{228}Ra と ^{227}Ac の放出についての証拠

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要旨: マンガン・ファイバー係留濃縮法を用いて日本付近の太平洋西縁に沿う18か所において水深 1,330-5,873 m から得た 38 試料について, Th および Pa 同位体の海水中の濃度を測定した. その結果, (1) 本州陸棚斜面の堆積物から ^{228}Ra と ^{227}Ac が海水に供給されていること, (2) 得られた ^{230}Th と ^{231}Pa 濃度は, 日本海溝と伊豆小笠原海溝で MnO_2 ・ファイバーを現場水中ポンプ法で得た結果と一致したが, パナマ・ガテマラ海盆での値

よりは明らかに高いこと, および (3) ^{232}Th 濃度はスキャベンジングに強く支配される Mn, Al, Bi, Te などに似て深くなるにつれて低くなることがわかった。

しかし, われわれの ^{230}Th と ^{231}Pa の結果は (1) 西縁附近の海水からこれらの核種がより活発に除去されていることや, (2) ^{231}Pa が ^{230}Th より優先的に海水から堆積物へ除かれていることを明確に示してはいない. これはおそらく海水や堆積物-海水境界面での ^{230}Th と ^{231}Pa のスキャベンジングの速度に比べて深層海水がより速く混合しているからであろう。

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