Tracers of Chemical Scavenging in the Ocean: Boundary Effects and Large-Scale Chemical Fractionation [and Discussion]

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Tracers of chemical scavenging in the ocean: boundary effects and large-scale chemical fractionation

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Several nuclides in the natural radioactive decay series display a strong non-conservative behaviour in the oceanic water column because of their removal to the sediments by uptake at the solid–solution interface. This removal process is commonly referred to as scavenging, and it is believed to be important in governing the behaviour of many heavy metals and other trace substances in the ocean. Measurements of radioactive disequilibrium in seawater yield estimates of the rate at which scavenging occurs. Results show that removal times by scavenging are comparable to within-basin lateral mixing times. It follows that the distribution of the scavenged tracers should be sensitive to the spatial distribution of their sinks, and this has been demonstrated by observation, most notably in the case of ^{210}Pb. The distribution of ^{210}Pb suggests a strong control by intensified uptake at boundaries, especially at the ocean margins. This conclusion has been confirmed by sediment traps and by measurements of ^{210}Pb accumulations in the sediment column. A similar phenomenon of intensified scavenging at ocean margins has been observed for ^{231}Pa. Studies with ^{230}Th, on the other hand, show that its delivery to the sediments is mainly caused by the local flux of sinking particles. Thus two transport pathways for removal by scavenging are envisioned, one with a strong horizontal component due to the intensified uptake at the margins and the other with a strong vertical component due to the particle flux. Important large-scale chemical fractionations, best illustrated by comparative studies of ^{230}Th and ^{231}Pa, are produced by differential partitioning of elements between these two pathways. Model calculations suggest that horizontal mixing rate and particle flux are important variables controlling the partitioning of reactive chemical substances between pelagic sediments of the interior ocean and hemipelagic sediments of the ocean margins. Changes in the extent of this partitioning through time may be recorded as changes in the ^{230}Th/^{231}Pa ratio through the sediment column.

1. Introduction

Geochemists have long recognized the importance of adsorption at solid surfaces in the long-term control of trace-metal concentrations in the ocean (Goldschmidt 1954; Goldberg 1954; Krauskopf 1956; Turekian 1977). The removal of chemical substances from the oceanic water column by uptake on the surfaces of particles and subsequent delivery to the sediments is commonly referred to as chemical scavenging. Certain nuclides belonging to the natural radioactive decay series can serve as tracers that allow the estimation of scavenging rates and the delineation of transport pathways. This information is important to our understanding of how the oceans assimilate materials added to them. An important outcome of recent tracer studies is the conclusion that chemical scavenging is intensified at the ocean margins and that there occur significant net fluxes of some tracers from the ocean interior into the sediments accumulating at the margins. In this paper I summarize the evidence supporting that conclusion and examine some of its consequences.

2. RADIOACTIVE DISEQUILIBRIUM IN THE OCEAN

The ability to infer rates of oceanic processes, such as chemical scavenging, from simple concentration measurements in seawater derives from the existence of radioactive disequilibrium within a decay series. Figure 1 illustrates the radioactive disequilibria that occur within the ^{238}U series in deep-ocean water. It can be seen that the daughter nuclides ^{230}Th and ^{210}Pb are markedly depleted relative to their parent nuclides in the decay series. Additional examples of radioactive daughter depletions are found in the ^{232}Th and ^{235}U series. The depletions are caused by the continual scavenging of the daughter nuclides, and it can easily be shown that the rate of removal J_d of a daughter nuclide is proportional to the difference between parent activity A_p and daughter activity A_d:

$$J_d = \lambda_d (A_p - A_d), \tag{1}$$

where λ_d is the radioactive decay constant of the daughter.
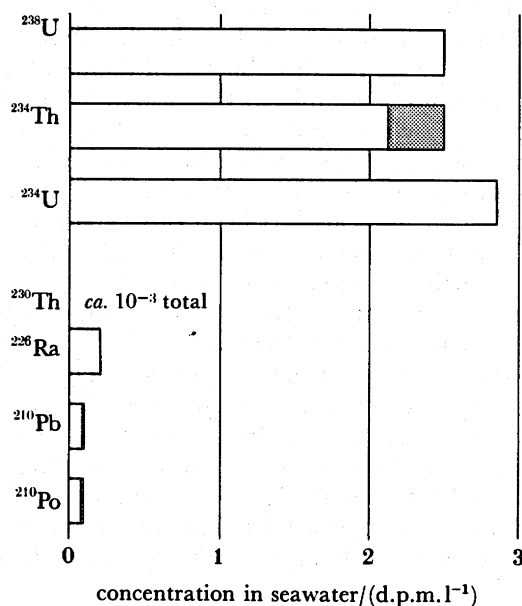

FIGURE 1. Concentrations of the longer-lived members of the ^{238}U decay series in seawater arranged in descending order within the series. The values chosen are representative of deep ocean water. Somewhat different relations are found in the surface waters. Shaded areas represent the suspended particulate fraction. Deficiencies of ^{230}Th and ^{210}Pb relative to their parent nuclides result from scavenging. A ^{234}Th deficiency is not found because of the short half-life, but a significant uptake by the suspended particles is evident. (1 d.p.m. (disintegration per minute) = 60 Bq.)

The first study of radioactive disequilibrium to estimate rate of removal by scavenging was done by Moore & Sackett (1964), who, on the basis of ^{230}Th–^{234}U and ^{231}Pa–^{235}U measurements, showed that the residence time of Th and Pa with respect to scavenging in the deep sea is less than 100 years. The discovery by Craig et al. (1973) of a ^{210}Pb–^{226}Ra disequilibrium in the deep sea showed the residence time of Pb to be approximately 50 years, much shorter than had previously been believed. Numerous subsequent investigations have confirmed these results and developed the use of these radionuclides as chemical tracers in the ocean (see reviews by Cochran 1982; Bacon 1984).

3. Intensified scavenging at ocean margins

The measurements of radioactive disequilibrium discussed above can yield exact and unambiguous determinations of removal rates, but the mechanisms and sites of removal that are deduced from them can depend on differing interpretations. In earlier studies it was usually assumed implicitly that the removal from a given column of water was accomplished entirely by the vertical flux of particles through that column. More recently, however, several lines of evidence have converged to show that chemical scavenging occurs more rapidly at the ocean margins than in the ocean interior and that, for some chemical species, much of the removal from the interior is caused by lateral transport to sites of intensified scavenging at the margins.
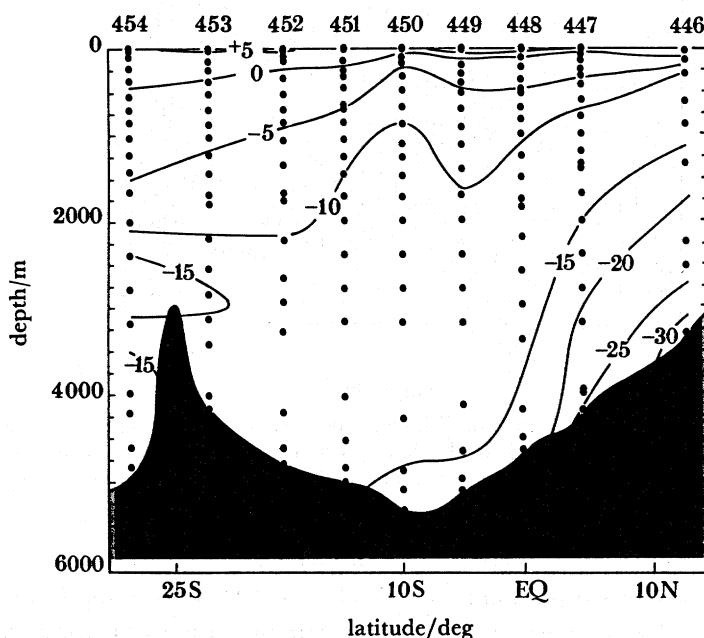

FIGURE 2. Vertical section showing the ^{210}Pb–^{226}Ra activity difference (disintegrations per minute per 100 kg) in the central Indian Ocean. From Cochran *et al.* (1983).

Figure 2 is a vertical section of the activity difference ^{210}Pb–^{226}Ra measured in the central Indian Ocean. Positive values (i.e. excess ^{210}Pb) are found at the ocean surface because of ^{210}Pb supply from the atmosphere. At depth are found the systematic ^{210}Pb deficiencies due to scavenging. The apparent rate of scavenging, as measured by the activity difference (equation (1)), increases towards the seafloor and is greatest at the northern end of the section at the station closest to land. As a result there is a horizontal gradient of decreasing ^{210}Pb concentration towards the ocean margin in the north, and it is expected that a net flux of ^{210}Pb from the ocean interior into the margin sediments must occur. Other examples of this phenomenon have been published by Bacon *et al.* (1976), Nozaki *et al.* (1980) and Spencer *et al.* (1981).

A net transport of ^{210}Pb to the margin should support an accumulation of ^{210}Pb in the margin sediments that exceeds the local rate of supply. There are no data yet available to test this hypothesis in the northern Indian Ocean, but a good example from the west coast of the U.S.A. has been given by Carpenter *et al.* (1981) and is shown here in figure 3. The expected
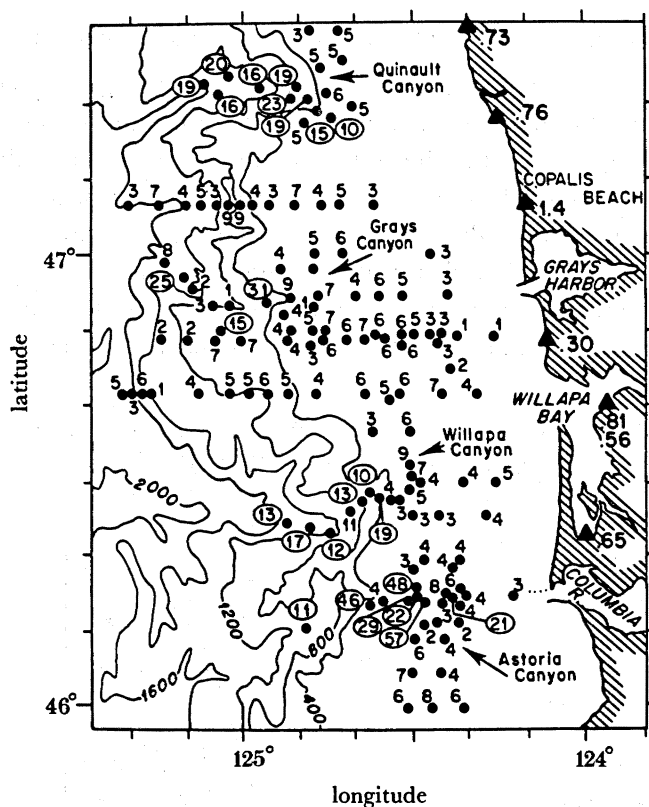
FIGURE 3. Accumulation rates of ^{210}Pb (in units of disintegrations per minute per square centimetre per year) in sediments off the coast of Washington, U.S.A. The flux expected from atmospheric deposition is estimated from soil profiles on land (triangles) and is less than 1 d.p.m. cm^{-2} a^{-1}. From Carpenter *et al.* (1981).

accumulation rate of ^{210}Pb in these sediments, mainly the ^{210}Pb that is deposited from the atmosphere, is approximately 1 d.p.m. cm^{-2} a^{-1}.† The measured accumulations usually exceed this value severalfold, and some very large values occur in canyons on the continental slope. It can be shown that the contribution of ^{210}Pb by rivers is small, and one is forced to conclude that most of the ^{210}Pb that is accumulating in these sediments is derived from offshore. More recently Buesseler *et al.* (1985/86) have compiled data from the east coast of the U.S.A. that show smaller accumulations of ^{210}Pb than are observed on the west coast. It remains to be determined which location is more representative of ocean margins in general.

Recent years have seen an impressive development in the use of deep-sea sediment traps to measure the vertical transport of materials by the flux of particles. Sediment traps provide the opportunity to compare direct measurements of radionuclide fluxes with predictions from radioactive disequilibrium measurements in the overlying water. Such a comparison for three radionuclides is shown in table 1. In the case of ^{230}Th, more than 70 % of the expected flux is found in the trap. In contrast, much smaller fractions of the expected amounts of ^{231}Pa and ^{210}Pb are found. The result for ^{210}Pb is consistent with the observations discussed above, which indicate that much of the ^{210}Pb escapes uptake by the vertical flux of particles and is lost from the ocean interior by lateral transport and deposition in sediments accumulating at the margins. It appears that a similar percentage of the ^{231}Pa may be lost in the same way.

† 1 d.p.m. (disintegration per minute) = 60 Bq.

TABLE 1. RADIONUCLIDE FLUXES AT 3200 m, SARGASSO SEA NEAR BERMUDA

(Fluxes are given in units of disintegrations per minute per square metre per year. Measured fluxes are one-year averaged values from Bacon et al. (1985).)

nuclide	half-life/years	known scavenging rate[a]	measured flux	measured/expected
^{230}Th	75 200	84	60	0.71
^{231}Pa	32 500	7.8	2.8	0.36
^{210}Pb	22.3	11 900	3500	0.29

[a] Expected fluxes based on radioactive disequilibrium in overlying water column. The value for ^{210}Pb includes the atmospheric input.

4. ^{230}Th/^{231}Pa FRACTIONATION

(a) Historical review

The long-lived radionuclides ^{230}Th and ^{231}Pa have an extended history of use in the estimation of deep-sea sediment accumulation rates (Ku 1976; Cochran 1982). They are produced in seawater from the decay of isotopes of U, which is a conservative element, and thus have a source that is uniformly dispersed throughout the oceans. Because of their efficient scavenging from the water column, ^{230}Th and ^{231}Pa accumulate in the sediments. The reduction of their activities downcore due to radioactive decay gives a measure of sediment accumulation rate, if the accumulation rate is assumed to be constant with time.

In the 1960s it was independently suggested by Sackett (1960) and by Rosholt et al. (1961) that measurements of the ^{230}Th/^{231}Pa ratio in sediments should allow an absolute age determination and not require the assumption of constant accumulation rate. Because of the different half-lives of the two nuclides, the ratio increases with age at a known rate, and the ratio at zero age should be equal to the production-rate ratio, which is rigidly fixed at a value of 11 (activity ratio) by the ^{234}U/^{235}U ratio in seawater. Actual measurements in surface sediments, however, gave results that departed markedly from this value. In pelagic sediments the ^{230}Th/^{231}Pa ratio at the surface was usually found to exceed the production-rate ratio, often by a factor of 2 or 3 (Ku 1966). The later work on ^{210}Pb and the finding of its intensified scavenging at the ocean margins led to the suggestion that ^{231}Pa might be similarly affected (Bacon et al. 1976). The work of Anderson et al. (1983a, b) confirmed this by showing low ^{231}Pa in the vertical flux of particles collected by sediment traps at mid-ocean sites (see also table 1) and by showing significant horizontal ^{231}Pa concentration gradients indicating a net transport to the margins. DeMaster (1981), Shimmield et al. (1986) and Yang et al. (1986) have shown that surface sediments around the margins of the Pacific Ocean usually contain ^{230}Th/^{231}Pa ratios that are substantially lower than the production-rate ratio, in contrast with the abyssal sediments underlying the interior regions.

In figure 4 is reproduced the map of ^{230}Th/^{231}Pa ratios in surface sediments from the Pacific Ocean that was published by Yang et al. (1986). It is clear from this map that the redistribution processes described above have a large, ocean-wide impact. Relative to ^{230}Th, ^{231}Pa is systemically depleted in sediments from the centre of the ocean and enriched in sediments at the margins. This large-scale chemical fractionation comes about because of the differential partitioning of the two elements between a vertical flux due to uptake by the downward flux of particles and a lateral flux driven by intensified uptake at the margins. The differential partitioning is caused by differences in reactivity between the two elements. Figure 5 summarizes results of ^{230}Th/^{231}Pa ratio measurements in deep Pacific waters, which show that the
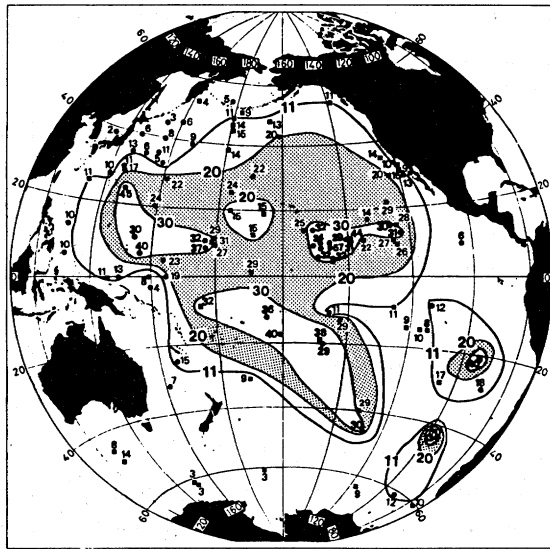
FIGURE 4. Activity ratios $^{230}Th/^{231}Pa$ in Pacific Ocean surface sediments.
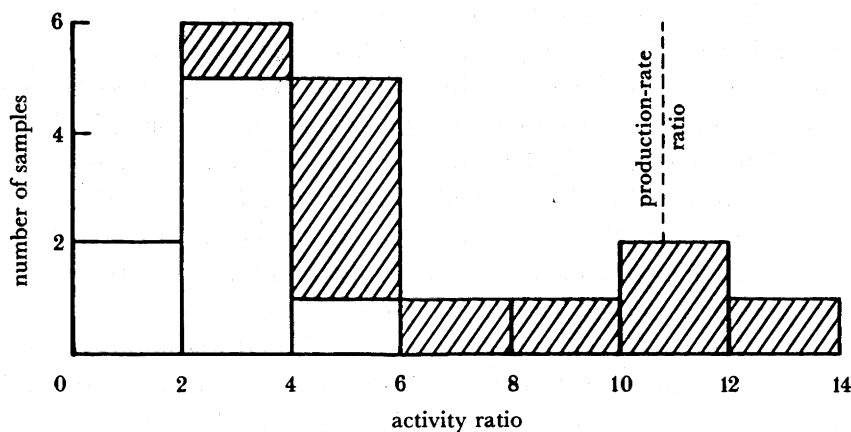The production-rate ratio is 11. From Yang *et al.* (1986).

FIGURE 5. Summary of $^{230}Th/^{231}Pa$ ratios measured in deep water from the Pacific Ocean. Samples less than 1000 m below the surface and less than 1000 m above the bottom were not included. Open areas, interior Pacific (Nozaki & Nakanishi 1985); shaded areas, Guatemala/Panama basins (Anderson *et al.* 1983b).

ratio is usually less than half the production-rate ratio. This implies a longer oceanic residence time for Pa than for Th, allowing a larger fraction of the Pa to be transported to sites of intensified removal at the ocean margins. In what follows I attempt to formalize and quantify the description of the Th/Pa fractionation process with a simple analytical model.

(b) Pacific Ocean model

Figure 6 is an idealized representation of the Pacific Ocean in which an interior box I and a margin box M are defined by the 4000 m isobath. From the data of Kossinna (1921; cited in Sverdrup *et al.* 1942, p. 21), 20% of the volume of the ocean is assigned to M and 65% to I. A third box, B, contains waters below 4000 m, which make up 15% of the total volume. Horizontal fluid exchange between I and M occurs at the rate v_{ex}, but vertical exchange
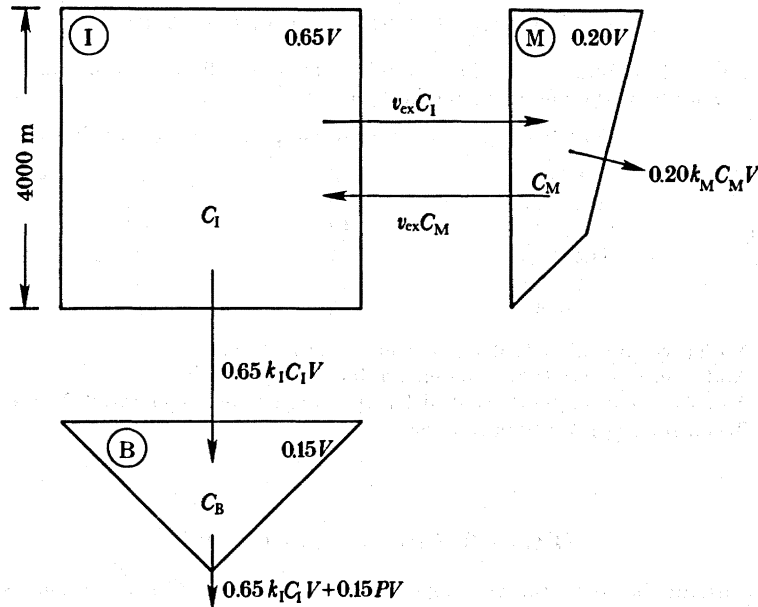
FIGURE 6. Pacific Ocean box model. See text for explanation.

between I and B is ignored. Each box has average tracer concentrations, C, and scavenging rates are assumed to be proportional to tracer concentration and given by rate coefficients k. Because of the long half-lives of ^{230}Th and ^{231}Pa, radioactive decay is negligible, and the sum of the deposited fluxes out of M and B ($0.20\ k_M C_M V + 0.65\ k_I C_I V + 0.15\ PV$) must balance the total *in situ* tracer production PV.

Steady-state material balance is assumed to hold for each of the tracers in I and M as follows.

$$0.65\,P^{Th}V = 0.65\,k_I^{Th}\,C_I^{Th}\,V + v_{ex}(C_I^{Th} - C_M^{Th}), \tag{2}$$

$$0.65\,P^{Pa}V = 0.65\,k_I^{Pa}\,C_I^{Pa}\,V + v_{ex}(C_I^{Pa} - C_M^{Pa}), \tag{3}$$

$$0.20\,P^{Th}V + v_{ex}(C_I^{Th} - C_M^{Th}) = 0.20\,k_M^{Th}\,C_M^{Th}\,V, \tag{4}$$

$$0.20\,P^{Pa}V + v_{ex}(C_I^{Pa} - C_M^{Pa}) = 0.20\,k_M^{Pa}\,C_M^{Pa}\,V. \tag{5}$$

The concentrations C are all measurable quantities. It is also possible to obtain a measure of the deposited flux ratio R from measurements of ^{230}Th/^{231}Pa ratios in sediment traps or in surface sediments:

$$R_I = k_I^{Th}\,C_I^{Th}/k_I^{Pa}\,C_I^{Pa}, \tag{6}$$

$$R_M = k_M^{Th}\,C_M^{Th}/k_M^{Pa}\,C_M^{Pa}. \tag{7}$$

(Strictly speaking, the ratio found in surface sediments is not an exact measure of R_I as defined here, because of the additional deposition of tracer produced in the bottom box B. Surface-sediment ratios can also be modified by bioturbation. In the calculations that follow sediment-trap data are used to define R_I and R_M. Note that a knowledge of the sediment trapping efficiency is not required.) Table 2 summarizes the data that are available and the values that were chosen for making computations. It is obvious that the data base is very small, and quantitative conclusions based on it must be regarded as tentative and subject to revision as more data become available.

TABLE 2. DATA USED IN MODEL CALCULATIONS

(The range and number of samples refer to those samples that were collected in mid-water, more than 1000 m below the surface and more than 1000 m above the bottom.)

quantity	reported range	number of samples	selected value	reference
C_I^{Th} (d.p.m. m^{-3})	0.8–1.8	8	1.2	[a]
C_I^{Pa} (d.p.m. m^{-3})	0.41–0.69	9	0.53	[a]
C_M^{Th} (d.p.m. m^{-3})	0.21–0.62	12	0.35	[b]
C_M^{Pa} (d.p.m. m^{-3})	0.044–0.113	11	0.058	[b]
R_I	21–35	11	26	[c, d]
R_M	5–8	5	7	[b]

[a] Nozaki & Nakanishi (1985); central, western Pacific.
[b] Anderson et al. (1983b); Guatemala and Panama basins.
[c] Anderson et al. (1983a); central Pacific, Sargasso Sea, equatorial Atlantic.
[d] Bacon et al. (1985); Sargasso Sea.

TABLE 3. MODEL PARAMETERS

(P^{Th} and P^{Pa} are constants based on the U isotope content of seawater. Other parameters were calculated as described in the text.)

production rates/(d.p.m. m^{-3} a^{-1})
$$P^{Th} = 0.0261$$
$$P^{Pa} = 0.00242$$

rate constants/a^{-1}	reciprocals/years
$v_{ex}/V = 0.0014$	710
$k_I^{Th} = 0.020$	50
$k_M^{Th} = 0.092$	11
$k_I^{Pa} = 0.0026$	380
$k_M^{Pa} = 0.10$	10

(c) Model results

The system described by equations (2–7) is overdetermined. The procedure that was followed was to use (2), (3) and (6) for the interior box to solve for v_{ex}/V by eliminating k_I^{Th} and k_I^{Pa}. The value obtained was 0.0021 a^{-1}. The procedure was then repeated with (4), (5) and (7) for the margin box and yielded the value 0.00075 a^{-1}. The discrepancy between these two estimates of v_{ex}/V could be eliminated by adjusting the starting concentrations in table 2. However, for purposes of the illustrative calculations shown below, I adopted the simpler procedure of taking the average value 0.0014 a^{-1}, and the scavenging rate coefficients k were then determined uniquely from (2–5). The values obtained are listed in table 3. They show that, within the interior ocean, Th is more efficiently scavenged than is Pa ($k_I^{Th} > k_I^{Pa}$). As pointed out by Anderson et al. (1983a), this is consistent with suspended-particle data showing that Th is bound more strongly by the particles than is Pa (i.e. a larger distribution coefficient K_d for Th than for Pa). At the ocean margin, scavenging of both nuclides is, as expected, more rapid than it is in the interior ($k_M > k_I$), and the contrast between Th and Pa has now virtually disappeared ($k_M^{Th} \approx k_M^{Pa}$). This result was also found by Anderson et al. (1983b), who attributed it to an abundance of manganese-oxide surfaces, with similar distribution coefficients for both Th and Pa, in suspended particles in the Guatemala and Panama basins. Whether or not these qualitative differences in particle-surface chemistry between ocean interior and ocean margin are truly representative of the whole ocean, or whether the Guatemala and Panama basins are

a unique environment because of their very high biological productivity, is an important unanswered question (Yang *et al.* 1986).

Having computed values for the model parameters from the existing data, we can now examine how sensitive the observed chemical fractionation between the two elements might be to oceanographic change. This is of interest for understanding how the chemistry of the present ocean is controlled, and it is also of interest for examining whether past changes in oceanographic conditions might have been recorded as variations in the ^{230}Th/^{231}Pa ratio in the sediment column. Horizontal mixing rate must be an important variable controlling the degree of fractionation, and I have performed a series of computations to illustrate this. The scavenging rate coefficients k were all held constant at the values listed in table 3, and v_{ex}/V was allowed to vary. Figure 7 shows how the deposited fluxes of each tracer out of each box respond, and figure 8 shows explicitly how the ultimate fate of each tracer is controlled by the mixing rate. At very low mixing rates an exact balance between *in situ* production and the deposited flux is approached, and in figure 7 the curves for both the interior and margin boxes converge to the production-rate line. As mixing rate increases, there is increasing loss of tracer from the interior to the margin, and the curves diverge. The shaded region on each plot includes the selected value of v_{ex}/V (0.0014 a^{-1}) and threefold variations about it (*ca.* ± 0.5 log unit). It is intended to represent a reasonable range of oceanographic conditions. Within this range the degree of ^{231}Pa transfer from interior to margin is quite sensitive to the mixing rate, and large transfers can occur. Over the same range, ^{230}Th deposition is less sensitive to change, and one would expect more spatial uniformity in its flux to the underlying sediments.

Figure 9 shows the effect of horizontal mixing rate on the ^{230}Th/^{231}Pa ratio in the deposited flux. It is this ratio that is preserved in deep-sea sediments and potentially could give a measure
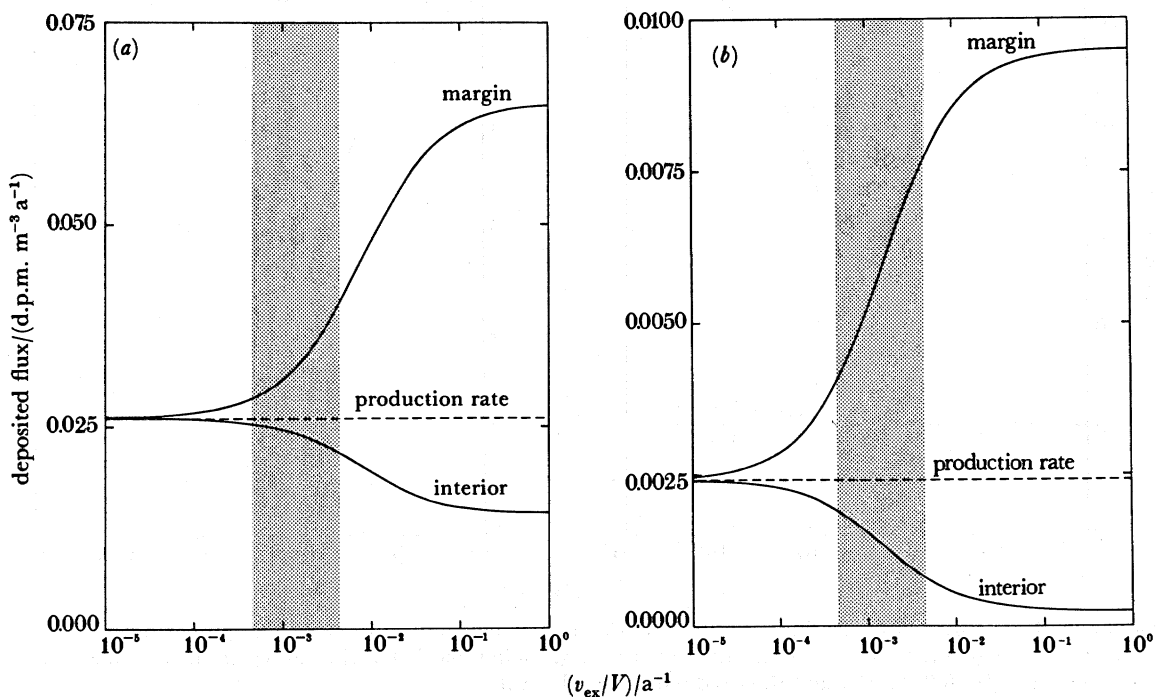

FIGURE 7. Deposited flux of (*a*) Th and (*b*) Pa against mixing rate. Scavenging rates are held constant at the values given in table 3. The shaded regions include the selected value of v_{ex}/V (0.0014 a^{-1}) and threefold variations about it.
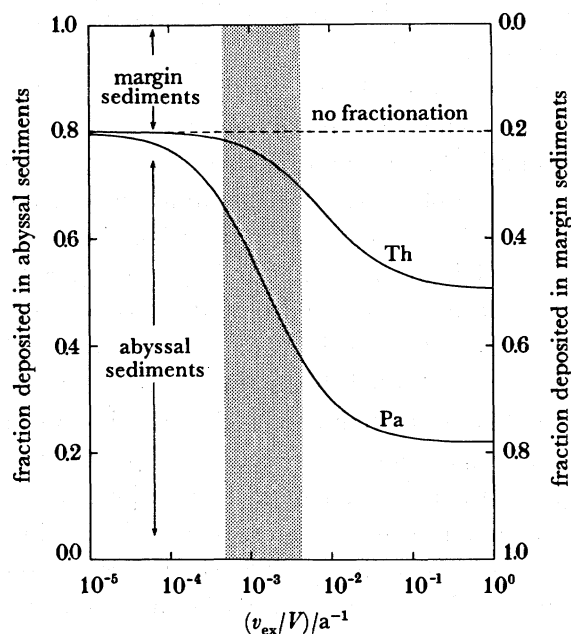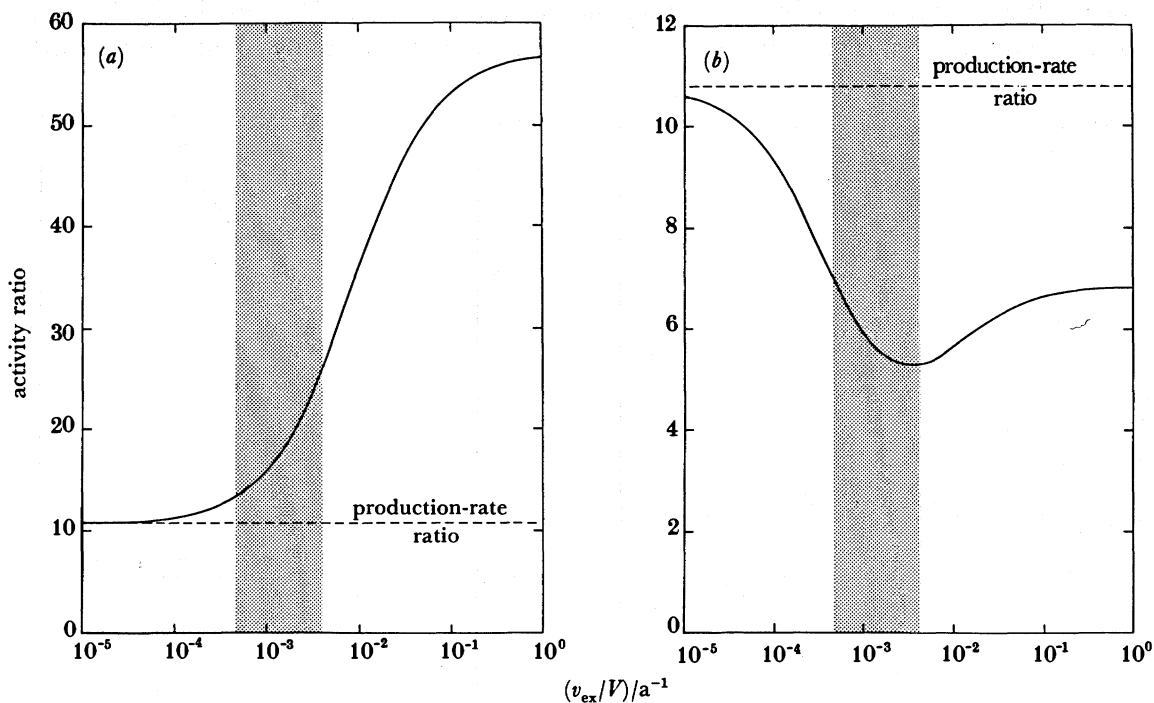
FIGURE 8. Distribution of tracer inventory between abyssal and margin sediments against mixing rate. The inventories include the amounts produced in the bottom box $(0.15\,PV)$. Scavenging rates are held constant at the values given in table 3. The shaded region includes the selected value of v_{ex}/V $(0.0014\ \mathrm{a}^{-1})$ and threefold variations about it.

FIGURE 9. Deposited $^{230}\mathrm{Th}/^{231}\mathrm{Pa}$ flux ratio (a) from the interior box and (b) from the margin box against mixing rate. Scavenging rates are held constant at the values given in table 3. The shaded regions include the selected value of v_{ex}/V $(0.0014\ \mathrm{a}^{-1})$ and threefold variations about it.

of past environmental change. In the interior (figure 9a) the ratio is very sensitive to mixing rate, and it is not surprising that the ratio method for dating deep-sea sediments has not proven, in most cases, to be superior to methods based on individual radionuclides (Ku 1976). Irregular (non-monotonic) downcore variations in ^{230}Th/^{231}Pa were found by Bacon & Rosholt (1982) in a core from the Bermuda Rise, indicating past variations in the deposited flux ratio. At the ocean margin (figure 9b) there is a minimum in the curve, and the flux ratio is less sensitive to the exchange rate (note the difference in scale of the vertical axis between figures 9a and b).

It follows from the existence of a strong boundary scavenging effect that the oceanic residence time of a scavenged element should be dependent on the rate of large-scale mixing. The residence time of a tracer in a multi-compartment system is given by

$$\tau = \sum_i C_i V_i / PV, \tag{8}$$

where C_i is the tracer concentration in each compartment, V_i is the volume of each compartment, P is the uniform rate of tracer production, and V is the total volume of the system. In the present case, (8) becomes

$$\tau = (0.20\,C_{\mathrm{M}} + 0.65\,C_{\mathrm{I}} + 0.15\,P/k_{\mathrm{I}})/P. \tag{9}$$

As shown in figure 10, a significant dependence on horizontal mixing rate is indeed found for Pa. The dependence is much weaker for the more reactive element Th. (In equation (9) it is assumed that the scavenging rate coefficient in the bottom box B is the same as in the interior box I.)

The other important variable that controls the degree of fractionation between Th and Pa is the scavenging rate. It would be possible to examine the effect of varying each of the four
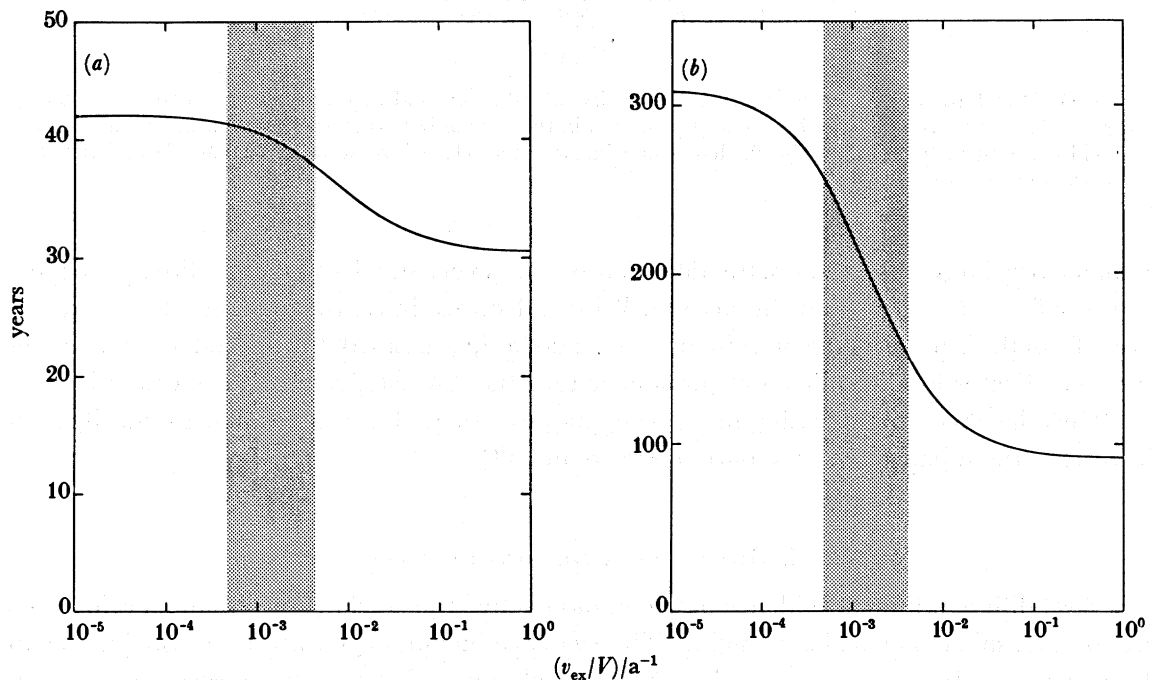

FIGURE 10. Oceanic residence time of (a) Th and (b) Pa against mixing rate. Scavenging rates are held constant at the values given in table 3. The shaded regions include the selected value of v_{ex}/V (0.0014 a^{-1}) and threefold variations about it.

k values independently, but because of space and time limitations I chose for present purposes to examine just the effect of varying the total scavenging rate while holding constant the relative proportions of the individual k values. In other words, I maintained the proportions $k_I^{Th}:k_M^{Th}:k_I^{Pa}:k_M^{Pa} = 1:4.6:0.13:5$, as they are in table 3, while simultaneously varying all of the k values. This would represent the effect of ocean-wide variations in scavenging rate due to changes in biological productivity or sedimentation rate but without considering changes in their spatial distribution. The mixing rate v_{ex}/V was held constant at 0.0014 a^{-1}. I use just one figure to illustrate the effects of varying the scavenging rate. Figure 11 shows that as the scavenging rate
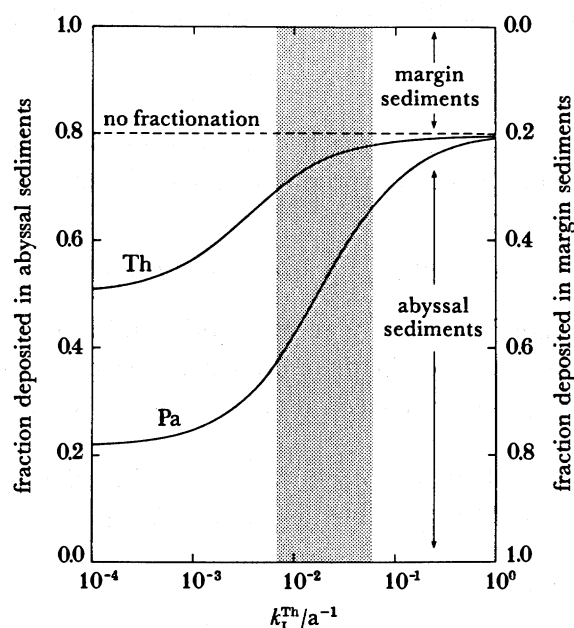

FIGURE 11. Distribution of tracer inventory between abyssal sediments and margin sediments against scavenging rate. The inventories include the amounts produced in the bottom box (0.15 PV). The exchange rate v_{ex}/V is held constant at 0.0014 a^{-1}. The shaded region includes the selected value of k_I^{Th} (0.020 a^{-1}) and threefold variations about it.

becomes very large, the extent of fractionation becomes very small and there is little net export of tracer from the interior to the margin. With a decrease in scavenging rate, the export of tracer from the interior to the margin increases, and, as in the case of the dependence on mixing rate, the effect is found to be more pronounced for the less reactive element Pa than it is for Th. Thus the effects of increasing the scavenging rate are qualitatively similar to the effects of decreasing the mixing rate (compare figures 8 and 11).

5. SUMMARY AND CONCLUSIONS

Several different lines of evidence based on radioactive tracers show the ocean margins to be sites of intensified chemical scavenging. The evidence includes concentration distributions in the water column, inventories in the sediment column and direct flux measurements with sediment traps. Because of the strong boundary effect, the oceanic residence time of a scavenged element is dependent on oceanic mixing rate.

The observed fractionation of ^{230}Th and ^{231}Pa in the oceans is explained by a differential partitioning of the two elements between a vertical flux via sinking particles and a horizontal flux to ocean-margin sinks. Two conditions bring this partitioning about: (1) a difference in reactivity towards particle surfaces between the two elements and (2) the existence of different regions of the ocean, characterized by different scavenging rates for reactive elements, that are coupled by horizontal exchange. Under these two conditions, there is a natural tendency for the less reactive element to accumulate preferentially in the region where the scavenging rate is higher (see also Broecker & Peng 1982, pp. 208–210).

Model calculations suggest that horizontal mixing rate is an important variable controlling the fractionation between ^{230}Th and ^{231}Pa. It may seem surprising to conclude that tracers displaying such strongly non-conservative behaviour could play a useful role in the study of ocean mixing rates. The simple calculations presented here, however, suggest that once the concentrations of the tracers in the water column and their ratio in the deposited flux are fixed by measurement, the allowable range of mixing rates is quite narrow. The potential for using the tracers in this way should be explored further with more sophisticated models.

Results of the model calculations indicate that the ^{230}Th/^{231}Pa ratio in the deposited flux should be sensitive to oceanographic change. Systematic downcore variations should be sought in deep-sea sediments to ascertain whether systematic glacial-to-interglacial variations occurred.

Additional examples of large-scale chemical fractionation should be sought among elements known to be controlled by scavenging. Possible candidates might be the cosmogenic radionuclides ^{26}Al (possibly a highly reactive element like Th) and ^{10}Be (possibly a less reactive element like Pa). A second possibility would be a comparison between tetravalent Ce and the trivalent rare-earth elements, the tetravalent Ce being more reactive.

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Discussion

W. ROETHER (*University of Bremen, F.R.G.*). I am somewhat surprised by the high margin–interior exchange timescale (*ca.* 700 years) that Dr Bacon derives. Would Dr Bacon's data, considering data uncertainties, be consistent also with appreciably smaller values (i.e. by a factor of two or three), or might it be an artefact of restricting oneself to essentially a two-box model approach?

M. P. BACON. The parameter V/v_{ex} is a measure of the time for fluid exchange between interior box and margin box. With $V/v_{ex} = 710$ years, and with the volumes of the interior and margin boxes equal to $0.65V$ and $0.20V$, respectively, the value $V/v_{ex} = 710$ years means that water in the interior box is replaced every 460 years by water from the margin box and that water in the margin box is, in turn, replaced every 140 years by water from the interior box. The result obtained in the calculations is sensitive to the assumed concentration difference between the two boxes. My suspicion is that the Guatemala Basin concentration values may be atypically low, even for ocean margins, and that I therefore may have over-estimated the concentration difference and hence the exchange time. A value lower by a factor of two or three would be within the present range of uncertainty. Additional concentration data would considerably improve the constraints we have on the exchange time.

H. ELDERFIELD (*Department of Earth Sciences, University of Cambridge, U.K.*). I was very interested by Dr Bacon's examination of the relation between Th and Pa deposition fluxes in the ocean interior and on margins and ocean mixing rates in terms of the evidence it might give for palaeo-oceanographic changes. Of course, other factors will affect the contrast in radionuclide fluxes, such as changes in productivity. For example, the effect of more rapid mixing could be offset by increased productivity of ocean margins.

M. P. BACON. Dr Elderfield is correct in stating that more than one variable could be involved in governing the Th/Pa ratio deposited to the sediment, and a unique interpretation of downcore variations in the ratio would not be possible without additional information. The determination of past changes in the rates of oceanic processes is difficult, and the interpretation of other indicators can also be ambiguous. So I believe it is worthwhile to explore the development of other possible tools, such as the one I am suggesting here. A logical first step is to find out whether a systematic glacial-to-interglacial variation in the ratio can be observed in pelagic and hemipelagic sediment cores.