

THORIUM ISOTOPES IN THE MARINE ENVIRONMENT

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Analyses of thorium isotopes isolated from fractions of a North Pacific Core, representing authigenic and detrital minerals, indicated that there were movements of ^{228}Ra within the sedimentary column, that the thorium comes to the deposit primarily from sea water, that there is no evidence for the migration of thorium isotopes within the sedimentary column, and that there is a continued growth of phillipsite at depths in the column. Finally, there appeared to be a preferential accommodation of ^{231}Pa and/or ^{227}Ac in the phillipsite, the authigenic zeolite, relative to the detrital minerals. The high values of the $^{228}\text{Th}/^{232}\text{Th}$ ratios in sea water may be influenced by the contribution of ^{228}Th arising from ^{228}Ra migration through the water-sediment interface.

1. Introduction

Characteristically, the concentrations of thorium isotopes in various marine systems do not reflect radioactive equilibrium with members of the radioactive series to which they belong. For example, the excess of ^{228}Th over the amount expected from radioactive equilibrium with ^{228}Th in waters of the Atlantic [1] and of the Pacific [2] has been explained by the entry of ^{228}Ra from the particulate phases containing ^{228}Th falling through the water column [2] or from the river introduction of ^{228}Ra [1]. Neither explanation is satisfying in a quantitative way (see below) and it seemed appropriate at this time to consider the possibility of a significant input from the sediments themselves, as suggested by Moore and Sackett [1]. Such a concept implies a mobility within the deposits of the isotopes of thorium and/or of their predecessors in the radioactive decay series. To ascertain the validity of this idea, a study of the distribution of such isotopes between the authigenic and detrital minerals of a deposit appeared promising. The former solid phases can accommodate migrat-

ing species within their crystal lattices, while the latter can absorb such materials upon their surface. Preferential accumulation or release of thorium isotopes or their parents within the three natural *radioactive decay series* (^{238}U , ^{235}U and ^{232}Th) may then be reflected in variations in isotopic ratios between different mineral components of the deposits.

2. Experimental work

The sediment cores JYN V-49P and JYN V-49PG taken on an expedition of the Scripps Institution of Oceanography at $17^{\circ}10'\text{N}$ and $132^{\circ}50'\text{W}$ from a depth of 5188 m, were chosen for this work inasmuch as they contained well developed crystals of authigenic zeolite phillipsite in a matrix of continentally derived minerals. The phillipsite ranged in size from 8 to 32μ . The silt fraction was dominated by quartz and feldspars, while the clay minerals were represented by illite, montmorillonite and chlorite. There was no measurable calcium carbonate.

Three isolates of thorium isotopes were obtained from the cores: (1) from a complete dissolution of the phillipsite; (2) from a hot 6N HCl leaching of the entire sample; and (3) from the total dissolution of

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the less than 2 micron size fraction.

The phillipsite was presumed to reflect a purely authigenic mineral; the less than 2 micron size fraction, primarily detrital minerals; and the leaching of the entire sample a tie-in with previous results.

The methods for the isolation of the thorium isotopes are described in ref. [3] and for the radioactive assay of the samples in ref. [4]. The results of the work are given in tables 1 and 2 and figs. 1 and 2.

3. Interpretation of the results

The ^{230}Th and ^{232}Th in the sediment are primarily derived from sea water. This conclusion derives from the observation that the $^{230}\text{Th}/^{232}\text{Th}$ ratios in the upper 20 cm of the core were identical within experimental error in all three isolates (table 1). They yield a sedimentation rate of $0.7 \text{ mm}/10^3 \text{ yr}$ (fig. 1). The extrapolation of the $^{230}\text{Th}/^{232}\text{Th}$ curve of the sediment surface (fig. 1) gives a value for the ratio of 38, consistent with previously determined values for sediments in this general area (ref. [3], p. 437). The geographical control upon the surface sediment values of the ratio is presumed to conform to variations in the ratio in the waters adjacent to the deposits. The uniformity in the ratio from the three isolates of the sediment clearly suggests that the thorium in the detrital minerals has been accommodated by sorption processes upon their surfaces while, in the authigenic mineral phillipsite, it may well be built into the lattice. At depths in the core where uranium-supported ^{230}Th becomes significant, below 20 cm, the ratio in the phillipsite becomes higher than in the other two phases. The difference can be attributed to variations in the $^{238}\text{U}/^{232}\text{Th}$ ratio. Since the ^{232}Th concentrations in the three phases are similar, the ^{238}U contents probably determine the ratios. The phillipsites, presumably with more ^{238}U than the other two phases, have higher values of the ratio.

There is no evidence in the present study for the migration of ^{232}Th or ^{230}Th in the sedimentary column. The migration concept is sometimes evoked by those who find the ionium/thorium rates of accumulation in pelagic sediments unacceptable (see e.g. ref. [6]). The conclusion that the ^{232}Th and the ^{230}Th are immobile in the deposits is essentially a

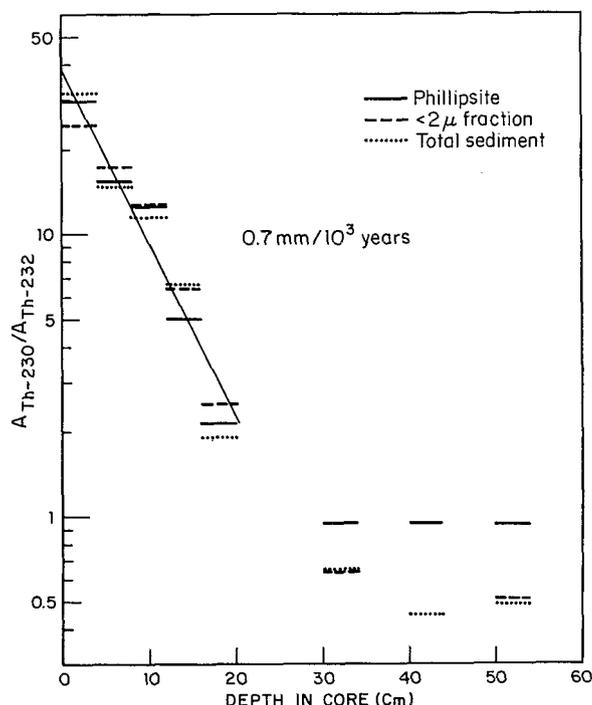


Fig. 1. The $^{230}\text{Th}/^{232}\text{Th}$ activity ratio in the three isolates of the core as a function of depth in the core.

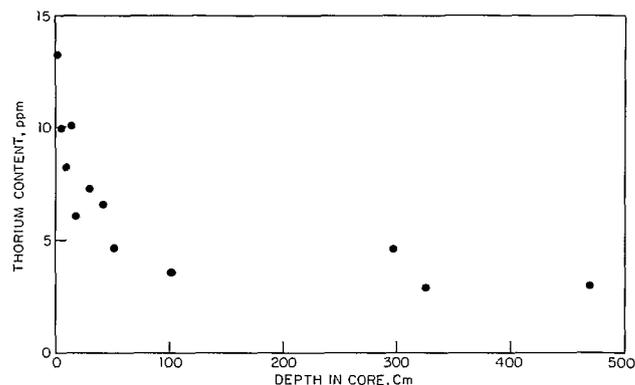


Fig. 2. The thorium concentration of the phillipsite as a function of depth in the sedimentary column.

corollary of the one in the previous paragraph.

There is a movement of ^{228}Ra from the detrital minerals to the interstitial water and a subsequent and preferential uptake of it and/or its daughter ^{228}Th by the phillipsite. The $^{228}\text{Th}/^{232}\text{Th}$ ratios in the phillipsite

Table 1
The distribution of thorium isotopes in JYN V-49 sedimentary phases

Depth in core (cm)	Thorium concentration (ppm)			$^{230}\text{Th}/^{232}\text{Th}$ (dpm/dpm)			$^{228}\text{Th}/^{232}\text{Th}$ (dpm/dpm)		
	Phillipsite	Leachate	$< 2\mu$	Phillipsite	Leachate	$< 2\mu$	Phillipsite	Leachate	$< 2\mu$
0-4	13.2	10.1	10.0	29.7	31.8	24.2	5.6	1.02	0.94
4-8	10.0	8.8	12.6	15.3	24.7	17.5	7.1	1.07	0.93
8-12	8.2	9.8	10.6	12.4	11.4	12.6	7.9	1.08	0.90
12-16	10.1	11.2	12.0	5.0	6.7	6.4	9.9	1.05	0.92
16-20	6.0	13.2	12.7	2.15	1.9	2.5	9.8	1.10	0.88
30-34	7.3	12.2	14.5	0.95	0.65	0.64	9.6	1.18	0.75
40-44	6.4	12.3		0.95	0.43		9.6	1.03	
50-54	4.6	11.4	12.3	0.94	0.49	0.51	7.4	1.10	0.86
100-105	3.6			0.48			9.8		
290-295	4.7						7.0		
324-331	2.95			0.66			7.6		
470-475	3.0			0.78			8.2		

The samples from depths greater than 100 cm were retrieved from the piston core (49P) while the samples from the surface to 54 cm came from the pilot gravity core 9 (49G).

cluster about a value of 9, while in the leached total fractions the ratios seem to be a little less than unity (table 1). Such a situation can arise if the ^{228}Ra formed from the decay of ^{232}Th in the detrital minerals readily enters the pore waters and migrates within the interstitial solution. Subsequently the probability of accommodation of ^{228}Ra and/or ^{228}Th in the phillipsite is high. Quantitatively the phillipsite accounts for about 3 wt% of the total sediment. Thus there is about thirty times more ^{232}Th yielding its ^{228}Ra in the detrital phases than in the phillipsite. If about one third of the ^{228}Th formed in this system is subsequently incorporated in the phillipsite, the observed distributions of the thorium isotopes in the sedimentary components are reasonable. The $^{228}\text{Th}/^{232}\text{Th}$ ratios in the acid extracts of the total sample, values slightly higher than one, most probably result from the preferential acid leaching of the ^{228}Th in compa-

ison to its parent ^{232}Th , a situation not different from that of the leaching of ^{234}U in relation to ^{238}U from solid phases [5]. The ratio value, slightly less than unity, in the total sample under 2 microns in size clearly indicates the consequences of the migration process — the depletion in ^{228}Th relation to ^{232}Th .

There is a continued growth of phillipsite within the sedimentary column. Such a concept explains the decrease in the ^{232}Th contents of the phillipsites with depth in the core (fig. 2). At any given stratum in the sedimentary column, the initial formation of phillipsite can be assumed to have removed most of the thorium from the interstitial solution. Subsequent crystal growth, utilizing dissolved species of such elements as aluminum, silicon, sodium and potassium, results in the decrease of the thorium concentration for the entire mineral. Fig. 2 suggests that

Table 2
The activities of ^{227}Th , normalized to the time of isolation of thorium isotopes

Depth interval (cm)	^{227}Th in dpm/g			^{230}Th in dpm/g		
	Phillipsite	Leachate	$\leq 2\mu$	Phillipsite	Leachate	$< 2\mu$
0-4	24	3.7	4.0	94	77	58
4-8	23	2.2	2.0	37	52	53
8-12	21	2.3	3.1	25	27	32

the formation of phillipsite continues at least down to 100 cm, or assuming a sedimentation rate down to this level of 0.7 mm/100 yr, about one million or so years.

There is a preferential accommodation of ^{231}Pa and/or ^{227}Ac in the phillipsite relative to the detrital minerals. Table 2 presents a typical pattern for the distribution of ^{227}Th , normalized to the time of isolation of thorium isotopes, among the three separates from the core. This nuclide is presumed to be in radioactive equilibrium with ^{231}Pa and/or ^{227}Ac . Clearly, there is a marked enrichment of ^{227}Th in the phillipsite, relative to the detrital minerals, utilizing ^{230}Th as a base for comparison. This could result from a preferential uptake of either the ^{231}Pa or ^{227}Ac or of both.

Such differing chemical behavior of protoactinium and thorium might explain the anomalies in the $^{231}\text{Pa}/^{230}\text{Th}$ geochronologies for deep-sea cores. Sackett [6] has observed a differential accumulation of these nuclides in ferro-manganese mineral formation. The relative constancy of the ^{227}Th in the three fractions remains unresolved.

4. Implications to the $^{228}\text{Th}/^{232}\text{Th}$ ratios in sea water

The high values of the $^{228}\text{Th}/^{232}\text{Th}$ ratios in sea water may be influenced by contributions of ^{228}Th from the overlying waters by the migrations of ^{228}Ra through the water sediment interface. Koczy [7] has postulated a migration of ^{226}Ra within the deposits and through the interface on the basis of the distribution of this nuclear species in depth profiles from various parts of the world ocean, while Goldberg and Koide [8] utilized such movements of radium to explain the disequilibrium between ^{230}Th and ^{210}Pb in the upper 15 cm or so of Indian Ocean sediments.

The ocean water disequilibrium of ^{228}Th with respect to ^{232}Th is most difficult to explain by river entry of thorium isotopes. The very short half-lives of ^{228}Th (1.9 years) and ^{228}Ra (6.7 years) in conjunction with a residence time of thorium species in sea water of 60 or 70 years requires an excess of ^{228}Ra over ^{232}Th in river waters of orders of magnitude, a situation in which a mechanism does not as yet exist.

The entry of ^{228}Ra from the suspended phases in sea water is also not quantitatively attractive. Consider our present core which accumulates at 7×10^{-5} cm/yr or, with a particulate matter density of 2 g/cm³ and a water content of 50% at a rate of 7×10^{-5} g/yr/cm². If we assume that the average lifetime of the solid phases in water is 2 yr, then the 550 l water column in principle can receive ^{228}Ra from 1.4×10^{-4} g of sediment. Assuming 10 parts per million of thorium in these solid phases, then each liter of sea water can accumulate ^{228}Ra from 2.5×10^{-12} g of Th. However, the Th contents of sea waters appear to be of the order of $n \times 10^{-10}$ g/l; too high to allow such a model to account for the activity ratio $^{228}\text{Th}/^{232}\text{Th}$ attaining values of 20 to 30.

Clearly, the migration of ^{228}Ra through the oceanic sea floor into the overlying waters can provide an additional source of ^{228}Th . The quantitative aspects of this problem can only be considered with further experimental work on different types of pelagic sediments.

Acknowledgements

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