

## THORIUM AND URANIUM IN MARINE BARITE

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Analyses of thorium and uranium from deep-sea barites and their sediments show that: (1) Marine barites concentrate thorium relative to their bulk sediments and appear to be growing near the sediment surface. However, some barites are found associated with ferromanganese deposits, and these barites, like continental varieties, are depleted in thorium and may reflect formation or alteration from effects of volcanic processes. (2) While marine barites show  $^{230}\text{Th}/^{232}\text{Th}$  depositional rates analogous to their sediments, they have distinctly lower isotope ratios which may reflect their formation from deep-sea or pore water. (3) Marine barites, like phillipsites and sea water, contain excess amounts of  $^{228}\text{Th}$  and are probably undergoing a continuous exchange chemistry within the thorium series as the result of  $^{228}\text{Ra}$  mobilization in the sedimentary column.

### 1. Introduction

There has been mounting evidence within the last decade that the thorium and uranium decay series in the ocean display chemistries that often result in striking examples of radioactive disequilibrium. The formation of authigenic minerals in marine sediments offer promising systems to study the solution chemistry and special reactivities within the series. The precipitation of marine barite might appear as one of the more ideal systems to investigate such phenomena.

The low [1, 2] or undetectable [3] concentrations of thorium in the sea water column is evidence of its reactivity and preference for particulate phases. The  $^{230}\text{Th}$  isotope is stripped from its soluble  $^{234}\text{U}$  parent by fall-out of authigenic or detrital particulates while  $^{232}\text{Th}$  and  $^{228}\text{Th}$  isotopes enter in the form of weathered detrital minerals [4]. Sedimentary chronology utilizing this excess  $^{230}\text{Th}$  has been widely applied [4] and verified [5-9]. The different transport paths for the  $^{230}\text{Th}$  and  $^{232}\text{Th}$  isotopes have been proposed to

contribute a higher  $^{230}\text{Th}/^{232}\text{Th}$  in surface water than deep waters [10]. Also the  $^{228}\text{Th}$  isotope exhibits up to ten fold excesses in the water column over the parent  $^{232}\text{Th}$  [1, 2], as a probable result of the solubility and mobility of its  $^{228}\text{Ra}$  parent [11]. This excess is even more striking when one considers the half life for equilibration would be only tens of years.

Bernat and Goldberg [12, 13] proposed that the limiting amounts of available thorium cause a decrease in thorium concentrations of growing authigenic minerals such as marine phillipsite. The tens of ppm of thorium in fish bone debris suggest that at least one other authigenic phase is competing for these thorium supplies. They also showed that marine phillipsite exhibits a  $^{228}\text{Th}$  excess probably because migrating  $^{228}\text{Ra}$  is continually exchanged in the zeolite phase.

Marine barite is reported to be a potential receptor for large amounts (tens of ppm) of thorium while incorporating normal sediment concentrations of uranium [2, 14]. In marine barites isolated from one Atlantic core Somayajulu and Goldberg [2] found that the thorium concentration decreased with depth in the sediment column. Also the barites displayed  $^{230}\text{Th}/^{232}\text{Th}$  ratios co-linear with but lower than the bulk sediments, a possible reflection of the initial

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lower ratios for deep ocean waters where barite formation might have taken place [10].

The objectives of this paper are first to confirm whether marine barites of the Pacific hold in detail the unique records of oceanic thorium chemistry, as found for the one Atlantic sample. Second, there are potential records of  $^{228}\text{Th}$  excesses in barites considering radium as one of the more ideal substituents for the host cation barium. Third, the ionium/thorium chronology of marine barites should indicate the histories of mineral formation relative to sediment deposition.

## 2. Experimental

Marine barites were separated from the sediments by a selective chemical leaching technique using hydrofluoric acid followed by heavy liquid separation [15]. The abundance of barite in the sediment was calculated gravimetrically with yields certified better than 90%. The sediment cores investigated in detail were Piquero 1 ( $9^{\circ}57' \text{ N}$ ;  $113^{\circ}05' \text{ W}$ ) and Dragon 1 ( $9^{\circ}10' \text{ N}$ ;  $119^{\circ}30' \text{ W}$ ), both from barite deposits associated with mixed silica-carbonate oozes of the eastern equatorial Pacific [16].

The barite analyses for Th and U were performed by chemical separation and alpha spectrometry. Fifty to one hundred milligrams of barite were placed in 20–50 mesh Biorad AG-50 cation exchange resin which was previously washed in 0.5 N hot oxalic acid. The mixture was placed in teflon-sealed pyrex vials with 500 cpm of  $^{234}\text{Th}$  and 3.5 cpm of  $^{232}\text{U}$  as tracers and heated at  $100^{\circ}\text{C}$  for three days with intermittent agitation, after which dissolution was usually complete. The sulphate supernatant liquid plus non-barite mineral residue was filtered through a membrane with pore space less than  $0.45 \mu$ . This residue was weighed with the difference from the original sample weight being the amount of barite dissolved. This undissolved mineral impurity was 0–5% anatase and rutile in all cases.

The resin was washed with water and the uranium extracted with 6 N HCl. Thorium was then extracted with hot 0.5 N oxalic acid. Uranium was purified by adsorption from 9 N HCl on the AG-1 anion resin (200–400) mesh and extracted with warm water. Iron contamination was removed by extracting into

4 methyl-2 pentanone from a 6 N HCl sample solution. The uranium was further purified by extraction at pH 3 into 0.4 N TTA (thenoyl-trifluoroacetone) and back into 2 N  $\text{HNO}_3$ . The solution was wet ashed (via  $\text{HClO}_4$  and  $\text{HNO}_3$ ) and electroplated according to Koide and Goldberg [17]. The thorium fraction was purified by adsorption on AG-50 cation resin (200–400 mesh), in a 4 N HCl solution, and removed with 0.5 N oxalic acid. Further purification involved extraction at pH 2 into 0.25 N TTA and back into 2 N  $\text{HNO}_3$ . The final solution was electroplated according to Goldberg and Koide [4].

Both the Th and U separates were alpha particle counted for several days using a Nuclear Diode surface barrier detector connected to a 512 channel Nuclear Data Analyzer. Thorium yields were computed after counting the beta activity of the  $^{234}\text{Th}$  on a Geiger Muller counter, and uranium yields calculated from the alpha activity of the  $^{232}\text{U}$  tracer. Errors quoted are statistical after yield, counter background, and blank corrections. Several of the larger crystalline barites, separated only by heavy liquids without leaching chemistry, gave comparable results. The bulk samples were analyzed according to Goldberg and Koide [4] which uses a 6N HCl leaching procedure followed by chemical separation and electroplating.

## 3. Results and interpretations

The results for Th and U in marine barites and their bulk sediments are listed in table 1. The uranium contents range from 0.2–5.0 ppm which are comparable to the 1–2 ppm average of most marine sediments [18]. The thorium levels for marine barites average about 30 ppm, in general agreement with the previous results [2, 14]. However, there seems to be some significant trends in the large range of 2–100 ppm.

(1) Barites from the pelagic oozes of the equatorial Pacific seem to concentrate thorium relative to bulk sediments. These barites display the typical 30 ppm value and are a rather widespread and uniform phenomenon in this area [15, 16]. Most probably these are marine barites forming in a normal marine environment from barium concentrations provided by biological detritus [15].

(2) With sediment burial there is a decrease in the

Table 1 - Thorium, thorium isotopes and uranium in marine barites and bulk sediments.

Sample	*Type	Section(cm) <sup>3</sup>		Th(ppm)		Activity ratios (dpm/dpm)				U(ppm)		
		Barite	Bulk	Barite	Barite	Bulk	230 Th/232 Th		228 Th/232 Th			
							Barite	Bulk	Barite		Bulk	
Piquero I (9°57'N, 113°05'W)	EEP	4-14	0-2			4.3		77.1	1.18			
			0.90	95±14			4.5±0.7		3.4±0.6	1.02	19±4	
				7.5-9			3.5		63.8	1.02		
				12-14			2.8		48.5	1.02		
			14-24		0.87	50±9	3.2	4.2±0.9	48.4	4.9±0.9	1.20	13±2
			24-34		1.1	53±8	3.2	4.1±0.7	48.4	3.8±0.7	1.20	4.2±0.7
				18-19.5			3.2		48.4		1.20	
				23.5-24			4.4		45.4		0.97	
				30-31			4.1		41.4		1.1	
				34-44	1.9	24±4		4.4±0.8		4.9±0.5		1.5±0.3
				44-64	3.0	29±2		1.1±0.1		3.1±0.7		-
				71-72			5.3		13.5		1.0	
				64-84	1.7	28±2		0.8±0.1		3.6±0.4		2.6±0.5
				84-104	2.6	23±2		1.1±0.2		3.3±0.6		5.4±0.5
		104-124	3.0	22±3		1.2±0.2		1.9±0.4		7.1±0.9		
		124-144	2.6	40±5		0.64±0.13		1.2±0.3		6.2±1.5		
				141-145			4.7	5.1		1.0		
Dragon I (9°09'N, 119°30'W)	EEP	0-2	0-2	0.7	42±6	5.0	36±5	66.1	2.0±0.6	1.0	4.9±0.6	
			5-7	0.6	31±5	4.5	12±2	30.7	3.7±1.0	1.8	1.1±0.4	
		10-20	0.4	26±2		0.59±0.09		1.6±0.2		< 1		
					11-12			2.5	2.3		1.8	
				14-16			3.6	4.3		1.6		
				23-24			4.7	7.9		1.3		
				40-42			3.4	1.4		1.1		
				50-10	0.7	14±1		0.29±0.12		1.9±0.3		< 1
			4.8	7.3±1.3	(7-10)	29.0	139	-	1.0	-		
RIS 56 (13°S, 105°W)	EPR	0-18										
RIS 58 (5°S, 105°W)	EPR	59-84		1.3	37±5		18±3	-	21±4	-	4±2	
Piquero II (8°S, 108°W)	EPR	0-2		0.47	4.2±1.1		44±12	-	11±5	-	0.6±0.3	
PROA 101 P (7°N, 17°W)	LB	6-10				10.6		1.28		1.0		
						16.0		0.70		1.0		
						9.7		1.30		1.0		
		83-97	2.2	4.2±1.7		1.5±0.9		21±12		< 0.1		
		124-134	3.4	8.6±4.4		45±23		6		0.5±0.2		
		215			20		0.40					
Dodo 8 (18°N, 158°W)	LB	Mn crust	1.7	8,2±6		11±8		23		0.7±0.4		
Chub 34 (8°N, 127°W)	LB	97	1.8	11±2		1.5±0.4		19		0.9±0.4		
Colo.-Sterling		Con. mental (radioactive hot spring)	-	1.3±0.9		1.3		11		0.15		

\*Type: EEP = East Equatorial Pacific, EPR = East Pacific Rise, LB = Large Barites.

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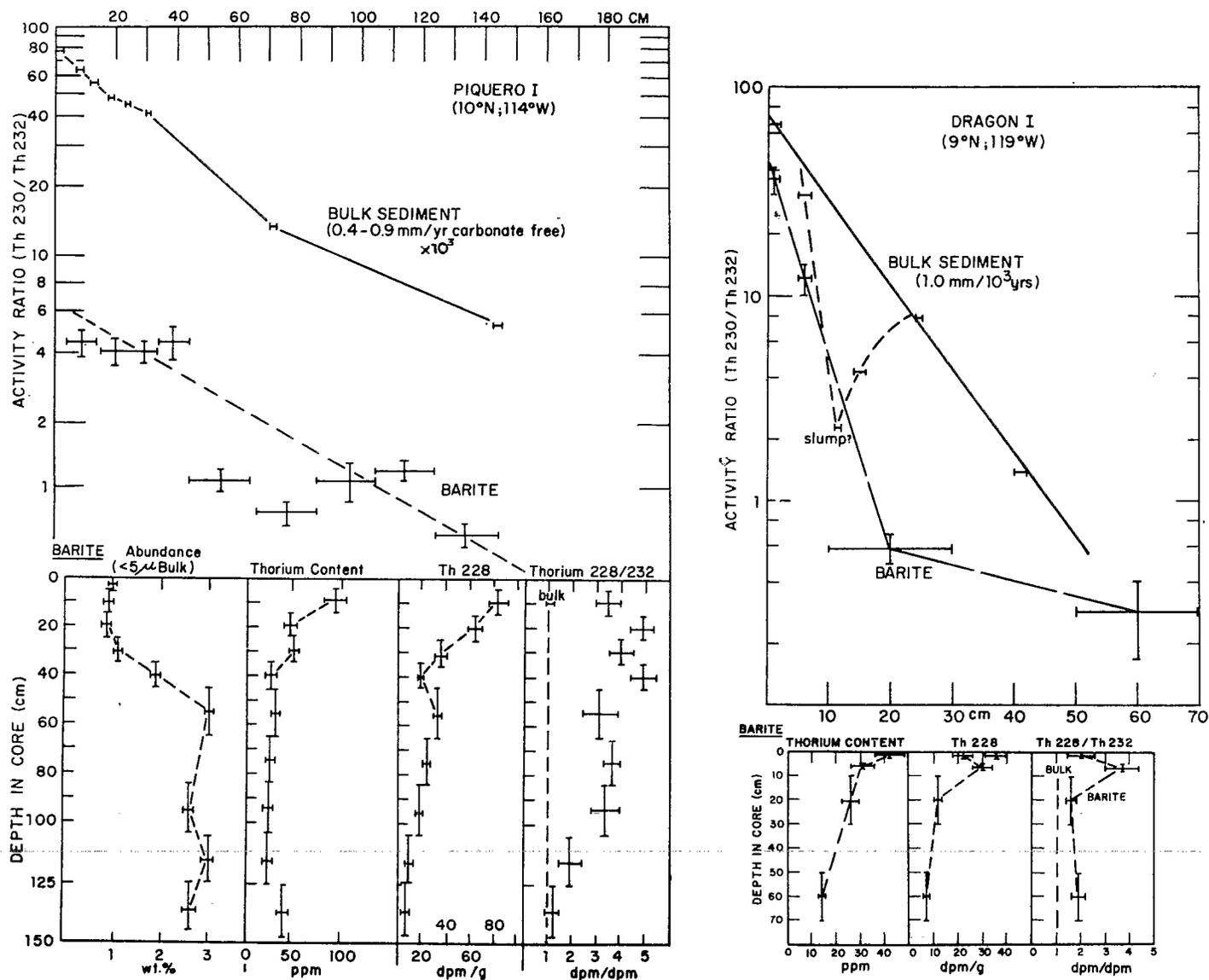


Fig. 1. Thorium isotopes in barite cores of the eastern Pacific: (a) Piquero I (10°N; 114°W), (b) Dragon I (9°N; 119°W).

concentration of thorium with a corresponding increase in the absolute amounts of barites (figs. 1a and 1b). Marine barites, as for phillipsite [12, 13], are suggested to be forming and growing diagenetically in surface marine sediments. Likewise the supplies of available Th appear limited during growth. These supplies of  $^{232}\text{Th}$  should be provided by continental minerals [4], and their availability may be enhanced during the early stages of burial which are accompanied by diagenesis of minerals and marine organic compounds. Alternatively, marine barites may nucleate and grow around another thorium-rich phase such as apatite, fish debris, or zircon.

(3) Some barites from the East Pacific Rise or of a large crystallinity contain lower than average thorium concentration and are depleted relative to the bulk phases. These barites may form or are altered under conditions not normal to the marine environment. They are all closely associated with ferromanganese phases which may be the direct or indirect chemical consequence of volcanic activity ([19] and associated refs.). In particular, the large barite crystals of PROA 101 P were abnormally associated with a majority of palygorskite and sepiolite bulk phases which may be attributable to reactions between hydrothermal solutions and sea water [20]. Such barites bear a closer resemblance to continental and marine borderland varieties which, having been magmatically derived, contain appreciably less thorium than most deep-sea varieties, ([14], and one entry in table 1).

(4) Marine barites display a  $^{230}\text{Th}/^{232}\text{Th}$  depositional rate comparable to their bulk phases, but with a distinctly lower nuclide ratio in the sulphate phase. The results of table 1 are illustrated in figs. 1a and 1b for cores Piquero 1 and Dragon 1. These cores display carbonate-free sedimentation rates of 0.7 and 1.0 mm/ $10^3$  yr respectively for both the sediments and their isolated barites. While these rates have some irregularities, they are quite typical for the eastern Pacific as confirmed by other methods [5–8]. In Piquero 1 the rate for barites is achieved after 50 cm of burial which being associated with increasing barite content seems to represent the zone where barite is diagenetically formed during the initial stages of sediment deposition. The evident distinction however lies in a uniquely lower  $^{230}\text{Th}/^{232}\text{Th}$  ratio of these marine barites compared to their coexisting sediments.

The difference in  $^{230}\text{Th}/^{232}\text{Th}$  ratios between the

barites and bulk sediments is difficult to explain and appears unique for deep-sea authigenic minerals studied so far [12, 13]. While a detailed mechanism may be conjectural with respect to existing knowledge, one explanation might be barite precipitation from deep-sea or pore waters which have an isotope ratio which differs from that of surface waters where the bulk of the sediments are assumed to derive their thorium nuclides. Such a difference in isotopic ratios between surface and deep water was predicted by Goldberg et al. [10], who suggested a biological or detrital transport of  $^{232}\text{Th}$  from surface waters where it is derived from continental runoff, while  $^{230}\text{Th}$  forms uniformly in the whole water column from its homogeneously dissolved uranium 234 parent. Alternatively, there could be excess supplies of  $^{232}\text{Th}$  in the sediment systems relative to bottom waters from the proximity and early diagenesis of the detrital mineral sources. The net result would be a lower  $^{230}\text{Th}/^{232}\text{Th}$  ratio in deep waters or pore waters relative to surface waters. The difference between the  $^{230}\text{Th}/^{232}\text{Th}$  ratio in barite and its bulk sediment at the core top indicate this isotope ratio to be unique from the beginning of sedimentation and barite formation. In any case, barites forming at the ocean bottom should reflect thorium isotopes from deep or pore waters, and these seem to be unique from those supplies for the sediments.

(5) The  $^{228}\text{Th}/^{232}\text{Th}$  ratio in marine barites is conspicuously out of radioactive equilibrium in the barites and higher than the nearly equilibrated bulk sediments. This is also the case for phillipsite [12]. Since radium appears to be preferentially leached and mobilized in the interstitial water [11], the  $^{228}\text{Ra}$  parent could be extracted and coprecipitated by marine barite in excess amount. Actually, one cannot differentiate between the uptake of either the  $^{228}\text{Ra}$  or  $^{228}\text{Th}$ , but the evidence for large scale radium migration is the stronger. The short half-life of both nuclides (7 and 2 years respectively) restricts such processes to a rather rapid exchange between barite, pore waters and bulk phases.

#### 4. Conclusions

Marine barites concentrate thorium relative to bulk sediments under normal conditions of deep-sea pelagic

sedimentation. They also appear to grow near the top of the sediment and give rates of deposition equivalent to their sediments. In selected cases where barites are associated with ferromanganese deposits, processes associated with volcanism may contribute to barite formation or alteration making them similar to continental analogues which have depleted thorium contents. During formation, barites inherit a lower  $^{230}\text{Th}/^{232}\text{Th}$  ratio that seems to be unique to a deep-sea location. Barites also incorporate excess activities of  $^{228}\text{Th}$ . In this respect they resemble other authigenic minerals and sea water which maintain disequilibrium in the thorium decay series.

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