

# BARIUM IN THE ANTARCTIC OCEAN AND IMPLICATIONS REGARDING THE MARINE GEOCHEMISTRY OF Ba AND $^{226}\text{Ra}$ \*

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Received 11 July 1972

Revised version received 22 May 1973

Ba distribution in the ocean correlates linearly with that of  $^{226}\text{Ra}$ , reflecting little fractionation of the two elements in their uptake by marine organisms. The weight ratio of  $^{226}\text{Ra}/\text{Ba}$  is estimated to be  $(0.714 \pm 0.08) \times 10^{-8}$ . A wide range of Ba/Si and Ra/Si values is noted in siliceous plankton collected from different oceans. This corroborates with the observations that, although silica co-varies with Ba and  $^{226}\text{Ra}$ , the Ba/Si and  $^{226}\text{Ra}/\text{Si}$  ratios in seawater vary from one area to another. Sediment pore water contains higher Ba concentrations than the overlying seawater. The resulting diffusive flux of Ba through the sediment-sea interface is estimated to be no more than 20% of the river input. The apparent oversaturation of dissolved Ba in pore fluids with respect to barite supports the idea that complexing of Ba with organic ligands may be important. Box model calculations show that: (1) on a per unit area basis,  $^{226}\text{Ra}$  flux from the continental shelf sediments is higher than that from the deep sea floor; (2) in the deep ocean, the magnitude of diffusive input of  $^{226}\text{Ra}$  from sediments is about equal to the loss due to radioactive decay.

## 1. Introduction

Early attempts to establish a correlation between barium and radium distribution in the ocean were inconclusive [1,2]. Recent studies, however, seem to have affirmed such a correlation in the Pacific and the Atlantic [3–5]. Here, we report a study on the In-

dian-Antarctic Ocean south of the Australian Continent. The samples from this region were taken during cruise 35 of USNS *Eltanin*. Results of this study relating to radium have been previously reported [6], and the data for barium are presented in this communication.

Barium concentration measurements were carried out on two profiles taken across the Antarctic Convergence and on pore fluids extracted from a sediment core retrieved from the same general area. Our measuring techniques followed those of Wolgemuth

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and Broecker [3]. In the laboratory, samples were "spiked" with a  $^{135}\text{Ba}$ -enriched solution of known concentration and isotopic composition. Barium was separated from other sea salts on a cation exchange column and then measured by solid-source mass-spectrometry.

## 2. Correlation between Ba and $^{226}\text{Ra}$ distributions

Results on the two ocean profiles are listed in table 1. They are also plotted against depth in fig. 1, together with some data recently published for the Atlantic and the Pacific Oceans. For comparison, radium data from the same stations are shown in fig. 2. Similarities between these two sets of data are evident. It appears that to the north of the Antarctic Convergence, Ba and  $^{226}\text{Ra}$  in the surface oceans are rather uniform. South of the Convergence, their varia-

TABLE 1  
Barium concentration in the Indian-Antarctic Ocean\*

Depth (m)	Temp. (C°)	Salinity (‰)	Ba ( $\mu\text{g}/\text{kg}$ )
EL35-I (South of Antarctic convergence 56°02'S, 128°09'E, 4483 meters)			
5	1.05	33.89	10.3
100	0.97	33.89	10.3
492	2.34	34.56	12.1
734	2.28	34.63	11.8
1088	2.14	34.72	11.6
2082	1.28	34.73	13.6
4085	0.22	34.68	14.3
4533	0.02	34.68	14.1
EL35-II (North of Antarctic convergence 47°38'S, 128°04'E, 3990 meters)			
5	8.23	34.60	7.4
240	8.28	34.60	7.3
490	8.33	34.60	7.2
740	7.33	34.49	7.9
991	4.95	34.37	8.7
1954	2.52	34.65	12.4
2946	1.82	34.76	12.9
3704	1.02	34.72	14.4

\* Temperature and salinity data are from S.S. Jacobs, P.M. Bruchhausen and E.B. Bauer, *Eltanin Reports, Cruises 32-36, Stations EL35-869 and EL35-874, 1968* (Lamont-Doherty Geological Observatory 1970).

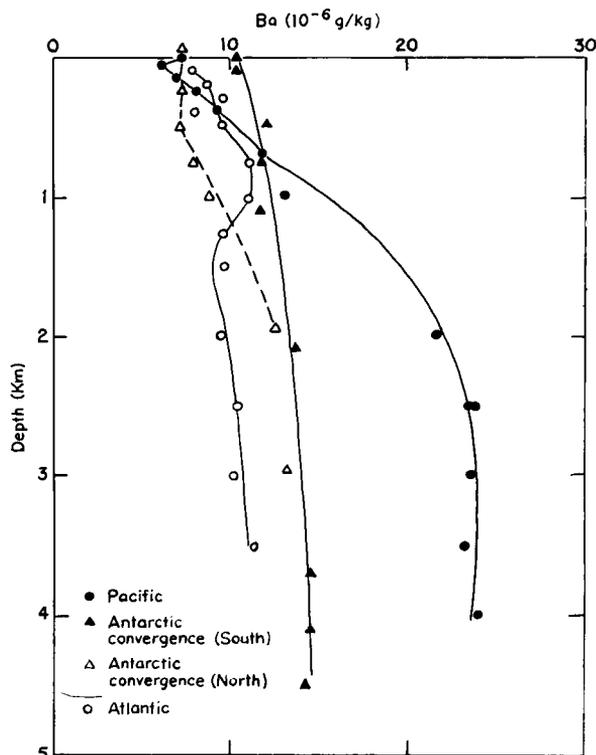


Fig. 1. Vertical distribution of Ba in the ocean. Pacific data: Wolgemuth (4); Atlantic data: Wolgemuth and Broecker (3); Antarctic: this work.

tions with depth are small due to upwelling of deep water in the Circumpolar region. In the deep oceans, both elements increase from the Atlantic to the Pacific via the Antarctic. The average increment between the Antarctic and the Pacific deep waters is about 2.5 times the one between the deep North Atlantic and the Antarctic.

The correlation plot of Ba and Ra (fig. 3) shows that the Antarctic data fall neatly on a straight line passing through the zero origin with a slope of  $0.714 \pm 0.08 \times 10^{-8} \text{ g Ra/g Ba}$ . Data of Geosecs I and III in the Pacific Ocean and that of the Project Bomex in the Atlantic Ocean more or less also fall on a straight line which has the same slope as the Antarctic line but does not pass through the zero origin. Whether or not the "offset" of the two parallel lines shown in fig. 3 is real cannot be ascertained at this time. The data are drawn from different sources and there have been discrepancies among different laboratories. For exam-

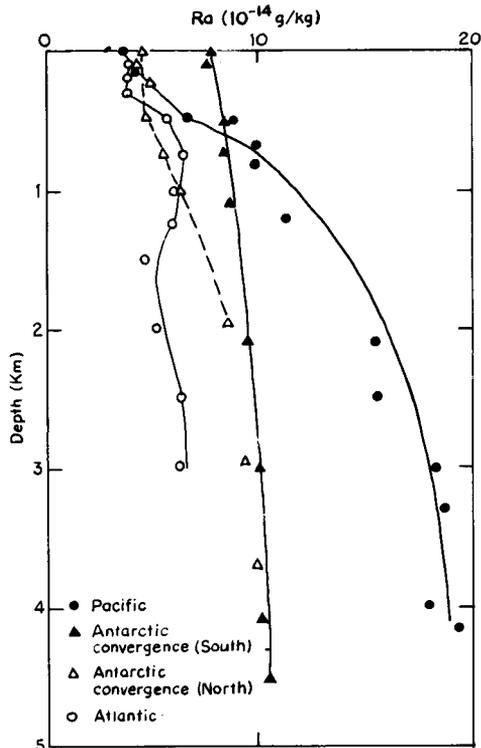


Fig. 2. Vertical distribution of Ra in the ocean. Pacific data: Ku's analyses in Broecker et al., [7]; Atlantic data: Broecker and Peng [5]; Antarctic: Ku et al. [6].

ple, the Geosecs I inter-laboratory calibration of  $^{226}\text{Ra}$  [7] has shown that Chung's measurements consistently give values about 1 to  $1.7 \times 10^{-14}$  g Ra/kg lower than Ku's. If this amount of correction is applied to either Chung's Geosecs data or Ku's Antarctic results, the Pacific and Antarctic points will fall on a single straight line. Disagreements in the analytical results of barium also exist. In a recent paper, Bender et al. [10] suspected that the Geosecs I Ba data of Wolgemuth [4] could be about  $2 \mu\text{g Ba/kg}$  too high due to the presence of undetected blanks. This is still unclear, as recent work of Bernat et al. [12] and Church and Wolgemuth [11] tend to support Wolgemuth's results. If one were to subtract  $2 \mu\text{g Ba/kg}$  from Wolgemuth's values, one would find that, at a given  $^{226}\text{Ra}$  concentration, the Geosecs III values of Bacon and Edmond [9] are much too high in comparison with Wolgemuth's Geosecs I results. Thus

improvement of accuracy in both  $^{226}\text{Ra}$  and Ba measurements should first be made before attempting to look into the fine structure of the Ra–Ba correlation curve.

Two statements, however, can be made here. Firstly, the available data do suggest that the oceanic occurrence of the two alkaline-earth elements bears a rather constant ratio ( $\text{Ra/Ba} \sim 0.71 \times 10^{-8}$  by weight) and this can be taken to imply that, in being taken up by marine organisms, Ba and  $^{226}\text{Ra}$  are scarcely fractionated. Secondly, in view of the dissimilarities in the geochemistries of Ba and  $^{226}\text{Ra}$ , Ba entering the ocean largely from rivers while  $^{226}\text{Ra}$  mainly injected from bottom sediments and radioactive, the observed linear correlation is in fact somewhat unexpected. One could anticipate deviations from perfect linearity to occur, especially for the Pacific where the "residence time" of the deep water is long. As will be shown later in our discussion of the major oceanic cycles of the two elements, their differences are minimized by the fact that radioactive decay loss of  $^{226}\text{Ra}$  in the deep ocean is about equal to the gain from sediment input.

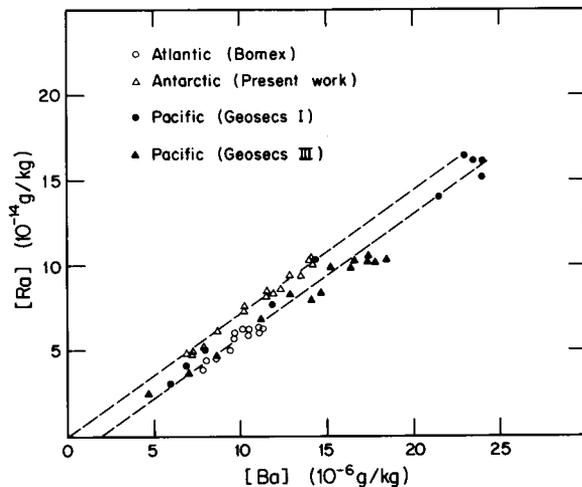


Fig. 3. Correlation plot of Ba and Ra concentrations in the world oceans. Sources of data: Atlantic (Bomex): Wolgemuth and Broecker [3] and Broecker and Peng [5]; Antarctic: this work and Ku et al. [6], Pacific (Geosecs I): Wolgemuth [4] and Chung's data in Broecker et al. [7], Pacific (Geosecs III): Bacon and Edmond [9] and Craig et al. [8]. Both dash-lines give a slope of  $0.714 \times 10^{-8}$  g Ra/g Ba.

### 3. Ba/Si and $^{226}\text{Ra}/\text{Si}$ in siliceous plankton and in the ocean

The increase of Ba and Ra with depth has been explained by biological uptake of these elements in surface waters and their subsequent release into the deep ocean upon dissolution of the settling organic particles [2, 14]. Both Ku et al. [6] and Wolgemuth and Broecker [3] suggested that these settling organic particles are mainly siliceous plankton. The suggestion has since gained its support from the linear relationship held by Ba–Si and Ra–Si in the oceans, as noted by Edmond and his coworkers [9,13]. Table 2 summarizes the slopes of the Ba–Si and Ra–Si linear

TABLE 2  
Ra/Si and Ba/Si ratios in the ocean

Region	$10^{-11}$ g Ra/g Si	$10^{-3}$ g Ba/g Si
Antarctic of Convergence	3.0	4.2
Antarctic of Convergence	1.1	1.6
Pacific (Geosecs I and III)	2.6	3.6

TABLE 3  
Published Ba and Ra data on diatom samples

Material (locality)	References	$10^{-3}$ g Ba/g ash	$10^{-3}$ g Ba/g Si*
<i>Chaetoceros</i> (Black Sea)	[15, 16]	4	9.5
<i>Rhizosolenia</i> (Black Sea)	[15, 16]	20~30	48~72
Diatomaceous ooze (N. Pacific)	[17]	–	3.1

Material (locality)	References	$10^{-11}$ g Ra/g dry matter	$10^{-11}$ g Ra/g Si**
Mixed diatom (Atlantic)	[18–22]	$0.2 \pm 0.1$	$0.9 \pm 0.4$
Diatoms, mainly <i>Chaetoceros</i> and <i>Rhizosolenia</i> (Atlantic)	[22]	0.77	3.3
Diatoms, mainly <i>Rhizosolenia</i> (Atlantic)	[22]	3.8	16.3

\* Assuming the ash contains 90% of  $\text{SiO}_2$  in weight [23].

\*\* Assuming the dry matter consists of 50% of  $\text{SiO}_2$  in weight [23].

plots for three oceanic areas. One notes that even though the Ra/Ba ratio is shown to be fairly constant throughout the ocean, the Ba/Si and Ra/Si ratios do not; they vary from one region to another. If the argument for siliceous plankton transfer is correct, then large variations of Ba/Si and Ra/Si are expected to be found in these plankton organisms. Data on the Ba and Ra contents of siliceous plankton are very scanty. In table 3 we summarize the reported data for diatom samples. Indeed, a wide range of Ba/Si is encountered. It is plausible that a mixture of relatively Ba- and Ra-enriched diatoms (e.g. *Chaetoceros* and *Rhizosolenia*) with species of presumably low Ba and Ra could account for the observed Ba/Si and Ra/Si ratios in different oceans. It should be interesting to make measurements of Ba and Ra on the siliceous samples in the future and compare their Ra/Ba ratios with those found in seawater.

### 4. Cycles of Ba and $^{226}\text{Ra}$ in the sea

Wolgemuth and Broecker [3] suggest that the first order characteristics of the geochemical cycle of Ba in the sea is best understood by considering a single two-box mixing model. Following these authors, we will discuss the marine cycles of both Ba and Ra using the model approach. In our two-box model for Ba (fig. 4A), the only difference from the calculations of Wolgemuth and Broecker [3] lies in our choosing the average values for the world ocean rather than for the Pacific Ocean alone. We obtain the concentrations of Ba in the warm surface ocean  $[\text{Ba}]_s$  and in the cold deep ocean  $[\text{Ba}]_D$  by averaging the more recent Ba data [this work, 3,4,9] which are weighed according to the relative volumes of the different oceans (Pacific and Indian : Atlantic : Antarctic = 0.61 : 0.27 : 0.12). The water exchange rate,  $R$ , is taken to be 3.2 m/yr (corresponding to a deep water residence time of 1100 yr). As shown in fig. 4A, our estimates differ only slightly from those of Wolgemuth and Broecker [3]. Of the  $4.12 \mu\text{g Ba/cm}^2/\text{yr}$  transferred from the surface to the ocean in association with falling particles, only 15% reaches the sea floor; the rest being recycled in the sea. Pore water data (shown later) indicate that there may also be a flux of Ba from the sediments to the ocean. But such an input is relatively small compared with the fluxes indicated in fig. 4A.

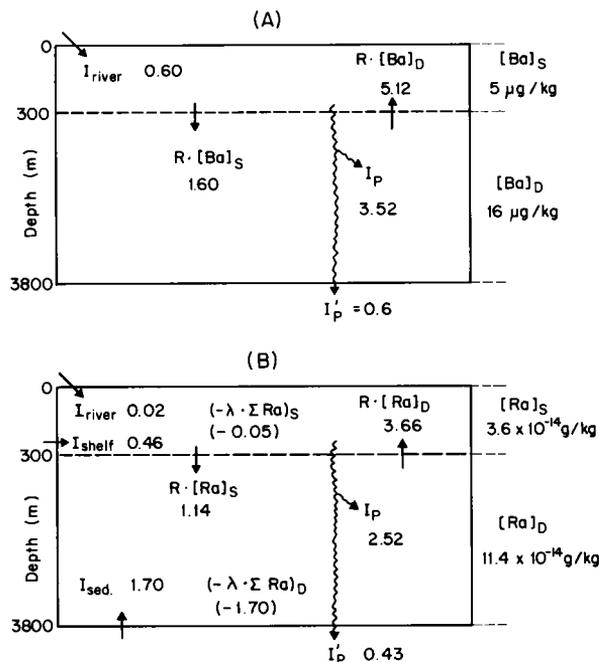


Fig. 4. (A) Two-box model depicting the marine cycle of Ba.  $I_{river}$  = river input,  $I_p$  = particulate Ba that redissolves =  $R \cdot [Ba]_D - [Ba]_S$ ,  $I'_p$  = particulate Ba that falls to the deep sea. All numbers shown are in the unit of  $\mu\text{g Ba/cm}^2/\text{yr}$ . (B) Two-box model depicting the marine cycle of  $^{226}\text{Ra}$ .  $I_{shelf}$  = input from shelf sediments,  $I_{sed}$  = input from deep-sea sediments,  $(-\lambda \cdot \Sigma \text{Ra})_S$  and  $(-\lambda \cdot \Sigma \text{Ra})_D$  = decay of  $^{226}\text{Ra}$  in the surface box and in the deep box, respectively. All numbers shown are in the unit of  $10^{-14} \text{ g Ra/cm}^2/\text{yr}$ .

Similar calculations are made for  $^{226}\text{Ra}$  (fig. 4B). To obtain the  $^{226}\text{Ra}$  contents of the surface ocean  $[Ra]_S$ , and the deep ocean  $[Ra]_D$ , we multiply the corresponding Ba concentrations of fig. 4A by  $0.714 \times 10^{-8} \text{ g Ra/g Ba}$ . The river input of  $^{226}\text{Ra}$  of  $0.02 \pm 0.01 \times 10^{-14} \text{ g Ra/cm}^2/\text{yr}$  reported by Moore [24] is adopted here. In the model the in situ radioactive decay of  $^{226}\text{Ra}$ ,  $-\lambda \cdot \Sigma \text{Ra}$ , is accordingly taken into account. The model depicts that a steady state distribution of  $^{226}\text{Ra}$  requires a flux of  $0.46 \times 10^{-14} \text{ g Ra/cm}^2/\text{yr}$  from the continental shelf sediments of the surface ocean as opposed to a flux of  $1.7 \times 10^{-14} \text{ g Ra/cm}^2/\text{yr}$  from the sea floor to the deep ocean. Since the area of the ocean floor above a water depth of 300 m is only about 10% of the entire ocean, the actual  $^{226}\text{Ra}$  flux from the shelf sediments should be averaged about  $4.6 \times 10^{-14} \text{ g Ra per cm}^2$  of the continental shelf each year. This is almost three times the fluxes from deep-sea sediments. Although it is well

known that shelf sediments act as the major source supplying  $^{228}\text{Ra}$  to the surface sea [25–28], the conclusion put forth here to indicate shelf sediments being also an important source for  $^{226}\text{Ra}$  has not been readily visualized.

## 5. Barium in pore fluids

Pore water samples from the Antarctic core ( $60^\circ\text{S}$ ,  $126^\circ\text{E}$ , water depth 4500 m) were collected on board USNS *Eltanin* soon after the core was raised. Table 4 presents pertinent chemical data for these samples. Total  $\text{CO}_2$  ( $\Sigma \text{CO}_2$ ) was measured by the infrared technique [29],  $\text{Cl}^-$  by silver nitrate titration and  $\text{SO}_4^{2-}$  by the  $\text{BaSO}_4$  gravimetric method [30]. Also indicated in the table are representative analytical errors. We have also measured  $\text{K}^+$ ,  $\text{Mg}^{++}$ , and  $\text{Ca}^{++}$ . Within experimental uncertainties of 5 to 10%, their concentrations are not different from those of the seawater above.

Much higher Ba contents than those in seawater are found in these pore fluids. Above the 260 cm level in the core, they contain 26 to  $40 \mu\text{g Ba/kg}$ , which is still lower than the saturation value of 45 to  $50 \mu\text{g Ba/kg}$  for Ba in seawater in equilibrium with pure barite at  $1^\circ\text{C}$  and 500 atm [11]. Below 260 cm, however, Ba increase sharply to 190 to  $280 \mu\text{g Ba/kg}$  with no accompanying decrease in  $\text{SO}_4^{2-}$  concentration. The sharp increase cannot be due to experimental mishaps as the order of analysis for the samples was random with respect to their depth designations.

Interstitial Ba and  $\text{SO}_4^{2-}$  have also been reported for the JOIDES cores. The majority of the JOIDES samples contain 50 to  $200 \mu\text{g Ba/kg}$ . Several samples with very low  $[\text{SO}_4^{2-}]$  show high  $[\text{Ba}^{++}]$  up to  $8 \text{ mg Ba/kg}$  (30). A plot of  $[\text{Ba}^{++}]$  against  $[\text{SO}_4^{2-}]$  for the JOIDES results is shown in fig. 5. Two “saturation” lines are shown. The solid line represents the apparent solubility product of barite in seawater, i.e.,  $K_{s,p} = ([\text{Ba}^{++}][\text{SO}_4^{2-}])_{\text{saturation}}$ , at  $1^\circ\text{C}$  and 500 bars. It has a value of  $13.5 \times 10^{-5} (\text{g/kg})^2$  [11]. The dashed line denotes the condition at  $25^\circ\text{C}$  and 1 bar. It has a value of  $9.7 \times 10^{-5} (\text{g/kg})^2$  [11]. Thus the points above the lines are “supersaturated” and those below are “undersaturated”. The remarkable fact is that almost all the data points lie above the saturation lines. Judging from these JOIDES results as well as

TABLE 4

Chemical analysis of pore water extracted from a sediment core from the Antarctic (60°S 126°E)

Depth cm	Ba <sup>++</sup> μg/kg	pH	ΣCO <sub>2</sub> m mol/kg	SO <sub>4</sub> <sup>=</sup> ‰	Cl <sup>-</sup> ‰
0-7	—	7.40 ± 0.02	2.76 ± 0.01	2.68 ± 0.1	18.4 ± 0.1
14-21	40.2 ± 0.5	7.51	—	2.70	18.4
21-28	26.3	7.42	—	—	18.5
28-35	26.8	7.36	2.99	2.96	18.4
70-77	39.9	7.59	—	2.72	18.8
112-119	23.9	7.58	3.10	2.84	18.9
168-175	34.0	7.47	3.32	—	18.6
196-203	24.0	7.44	2.99	2.80	18.9
224-231	32.8	7.10	3.08	2.88	18.9
280-291	283.0	7.47	3.15	2.98	18.6
411-418	271.0	7.58	3.21	2.90	18.8
468-475	249.0	7.60	3.24	2.70	18.9
577-581	185.0	7.50	3.27	2.62	18.9

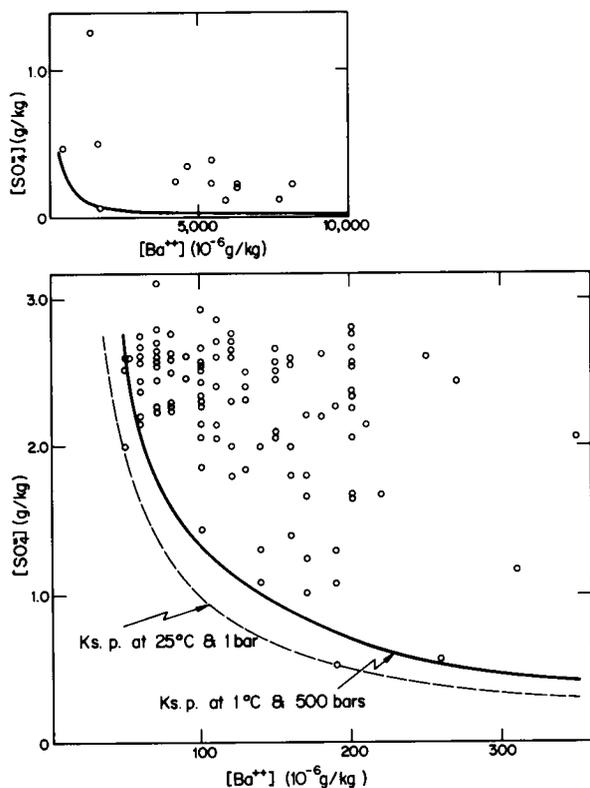


Fig. 5. Plot of  $[Ba^{++}]$  versus  $[SO_4^{=}]$  from JOIDES results [30]. The solid and dotted lines are the solubility product of barite at 1°C and 500 bars and at 25°C and 1 bar respectively.

our pore water data, we concur with the hypothesis [11] that complex formation between Ba and organic species as shown by Dasai et al. [31] must be considered in the study of the dissolved interstitial Ba distributions.

Higher Ba concentration in pore fluids as compared to that in the bottom water should lead to diffusive fluxes of Ba from sediments to the sea. Our pore water data and that by Church and Wolgemuth [11] indicate that a concentration gradient of at least about 1.5 to 2.0 μg Ba/kg/cm exists near the water-sediment interface. According to Li and Gregory [32], the diffusion coefficient of Ba in red clay with 50% water content by weight should be about  $2.2 \times 10^{-6}$  cm<sup>2</sup>/sec at 0°C and 500 bars. Thus the upward flux of Ba from the sediments to the overlying seawater is on the order of 0.1 μg Ba/cm<sup>2</sup>/yr, which is relatively insignificant as compared to the particulate flux and input from rivers (fig. 4A). In contrast, 99% of the Ra input into the ocean is derived from the sediments (fig. 4B).

#### Acknowledgements

The Physical Oceanography group at Lamont helped in collecting the samples during *Eltanin* cruise 35 under NSF Grant GA-1309. We are grateful to Drs. F.T. Bonner, W.S. Broecker and H. Craig for

discussions and comments. The research was supported by NSF Grants GA-13895, GX-33292, and the Petroleum Research Fund, administered by the American Chemical Society.

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