

C.M. 1980/C:23

The biogeochemical cycle of barium in the open ocean
An evaluation

F. DEHAIRS

Laboratorium voor Analytische Scheikunde
Vrije Universiteit Brussel, Belgium

The biogeochemical cycle of barium in the open ocean

An evaluation

F. DEHAIRS

Laboratorium voor Analytische Scheikunde
Vrije Universiteit Brussel, Belgium

Abstract

This study constitutes our contribution to the international oceanographical GEOSECS program (Geochemical Ocean Sections). The Ba content of suspended particulate matter was studied by neutron activation analysis. Analyses with the electron microscope and electron microprobe equipment have allowed the identification of the mineral barite as the main carrier of Ba in oceanic suspensions. Strong evidence is offered for a biological formation of these barite microcrystals. An estimation of the amount of Ba introduced into the deep ocean by dissolution of the barite crystals was possible. Finally, our results enabled a modelling of the general biogeochemical cycle of Ba in the ocean.

Introduction

The distribution of several trace elements, such as Cd, Zn, Cu, ... in the oceanic watercolumn and the sediments is influenced by processes depending on the biological activity in the surface water (Boyle et al., 1976 and 1977; Bruland et al., 1978). Such processes can be : adsorption and/or incorporation on/by phyto- and zooplankton ; ingestion of biogenic particulate material, as well as abiogenic material, by zooplankton; sedimentation of dead organisms and fecal material to the deep sea; partial decomposition and/or dissolution of this sedimenting material; sedimentation of the undecomposed fraction.

Furthermore, the impact of the biological processes upon the geochemistry or more accurately the biogeochemistry of trace elements, can

result in the sustainment in seawater of systems out of thermodynamic equilibrium.

This work concerns the biogeochemistry of the trace element Ba. Biological activity governs to a large extent the distribution of this element in the watercolumn and produces the Ba-mineral barite, which should not occur in seawater from a purely thermodynamical point of view.

During the past twenty years, several dissolved Ba profiles have been measured throughout the World Ocean (Chan *et al.*, 1977; Chow and Goldberg, 1960; Bacon and Edmond, 1972; Wolgemuth and Broecker, 1970).

These profiles are characterized by low dissolved Ba concentrations in the surface water ($< 7 \mu\text{g Ba/kg SW}$). In general concentrations increase, with increasing depth, towards an asymptotic value at mid-depth (world average value of $\sim 16 \mu\text{g Ba/kg SW}$). The general shape of such a profile suggests a biological control : ● consumption of dissolved Ba in surface waters during biological activity and concentration of this Ba in the particulate phase ; ● input of dissolved Ba in the deep sea as a result of decomposition and dissolution of the sedimenting biogenic Ba-carriers.

Up to recently, it were essentially the diatoms which were considered to be the organisms controlling the dissolved Ba distribution in the watercolumn (Bacon and Edmond, 1972; Li *et al.*, 1973). This conclusion was drawn from the observation that dissolved Ba and Si did correlate well. However, more recently it was shown that the correlation between dissolved Si and Ba was not always as good as observed earlier, (Chan *et al.*, 1977). Furthermore, dissolved Ba correlated also well with alkalinity (Chan *et al.*, 1977). The only conclusion which could be drawn from these observations was that the dissolved Ba profile was more likely to result from the settling and dissolution of slowly dissolving biogenic structures, such as opal and aragonite, calcite than from the decomposition of the more labile tissue components, (Chan *et al.*, 1977). It is clear that the high correlations observed between dissolved Ba, Si and alkalinity do not necessarily imply these elements to cohabit the same particulate biogenic phase.

We studied the occurrence of Ba in the oceanic suspended matter. Particulate matter suspended in seawater constitutes a field in oceanography which up to recently has been but poorly investigated.

Methods

The experimental techniques are described in detail elsewhere (Dehairs, 1979; Dehairs et al., 1980). A short description is given hereafter. Most samples of suspended matter studied here were collected during the GEOSECS cruises in the Atlantic and Pacific Ocean, resp. between 1972 - 1973 and 1973-1974 (Table 1). Some samples were collected during several

Table 1
Geographical position of stations and investigated depth intervals

Stations	Positions	Investigated depth interval (in m)		
Atlantic Ocean				
GEOSECS ST 17	74°56'N-01°07'W	992 to 3439	x	+
5	56°54'N-42°47'W	363 2464	x	
3	51°01'N-43°01'W	28 3660	x	+
27	42°00'N-41°59'W	1441 4858	x	
120	33°15'N-56°34'W	900 3187		+
115	28°04'N-25°54'W	1145 3732		+
31	27°00'N-53°31'W	1 5500		+
37	12°01'N-51°00'W	949 1940		+
58	27°02'S-37°00'W	197 4422	x	+
67	44°58'S-51°10'W	40 5580	x	+
91	49°36'S-11°37'E	486 3074	x	+
82	56°15'S-57°38'W	1 5202	x	+
ATLANTIS II				
ST 715	52°56'N-36°13'W	2000	x	
2111	33°41'N-57°38'W	954 2195	x	+
HARMATAN 1971				
ST 6	04°30'N-19°35'W	2000 3000	x	
15	00°00' -05°30'W	1000 4000	x	+
MIDLANTE 1974				
ST Madcap	28°40'N-25°25'W	1075 5043		+
9	24°03'N-28°56'W	910 2265		+
50	34°43'N-29°34'W	985 3510		+
TRANSAT 1975				
ST 17	34°06'N-61°17'W	5 4380		+
37	14°48'N-74°12'W	1000		+
Pacific Ocean				
GEOSECS ST 257	10°10'S-170°00'W	1263 5182	x	+
263	16°36'S-167°05'W	676	x	
269	23°59'S-174°26'W	1253 6348	x	+
310	26°55'S-157°11'W	1557 4789	x	+
282	57°35'S-169°36'E	2131 5187	x	+

x Inspected for BaSO₄ presence by SEM-EMP

+ Analysed for total Ba_p by INAA

French cruises in the North and Equatorial Atlantic between 1972 and 1977 (Table 1). Samples were taken with 30 litre Niskin bottles. Of this seawater volume 10 litre were filtered under pressure on 47 mm Nuclepore membrane filters of 0.4 μm pore size. The analysis of the suspended matter was carried out by : 1) Scanning Electron Microscope and Electron Microprobe (SEM-EMP) to collect qualitative and semi-quantitative data on the morphology and the elemental composition of single particles. Both, wavelength and energy dispersive spectrometers were used. This part of the study was carried out at the Laboratoire de Géochimie (Université Libre de Bruxelles); 2) Instrumental Neutron Activation Analysis (INAA) for the quantitative analysis of particulate Ba. This part of the study was carried out at the Centre des Faibles Radioactivités (CNRS, Gif sur Yvette, France) using the facilities of the Pierre Sûe Activation Analysis Laboratory (Commissariat à l'Energie Atomique, Saclay, France).

Results and discussion

1.- MEASUREMENT OF TOTAL PARTICULATE Ba

A total of 20 profiles of particulate Ba were measured for the Atlantic and Pacific Oceans (Dehairs, 1979; Dehairs et al., 1980). In figure 1 we reproduce the particulate Ba profiles measured for 9 GEOSECS stations in the Atlantic and Pacific Oceans as well as 3 profiles measured for Atlantic stations visited during French cruises. For the remaining profiles no sufficient data were obtained to establish vertical profiles. The general features of the particulate Ba profiles for which sufficient data were obtained are : ● minimal concentrations in the first 100 m ; ● increase of the concentration towards a max. located generally at less than 100 to 1000 m depth ; ● decrease of the concentration down to mid-depth ; ● relatively constant or more slowly decreasing concentrations down to the bottom water ; ● occasionally a sharp increase of the concentration in bottom waters, when a nepheloid layer is present. Such characteristics suggest that the following processes occur in the water column : ● a production of particulate Ba at some depth below the surface but generally outside the euphotic layer ; ● a dissolution of the particulate phase(s) with increasing depth ; ● an input of sedimentary Ba , close to the sea

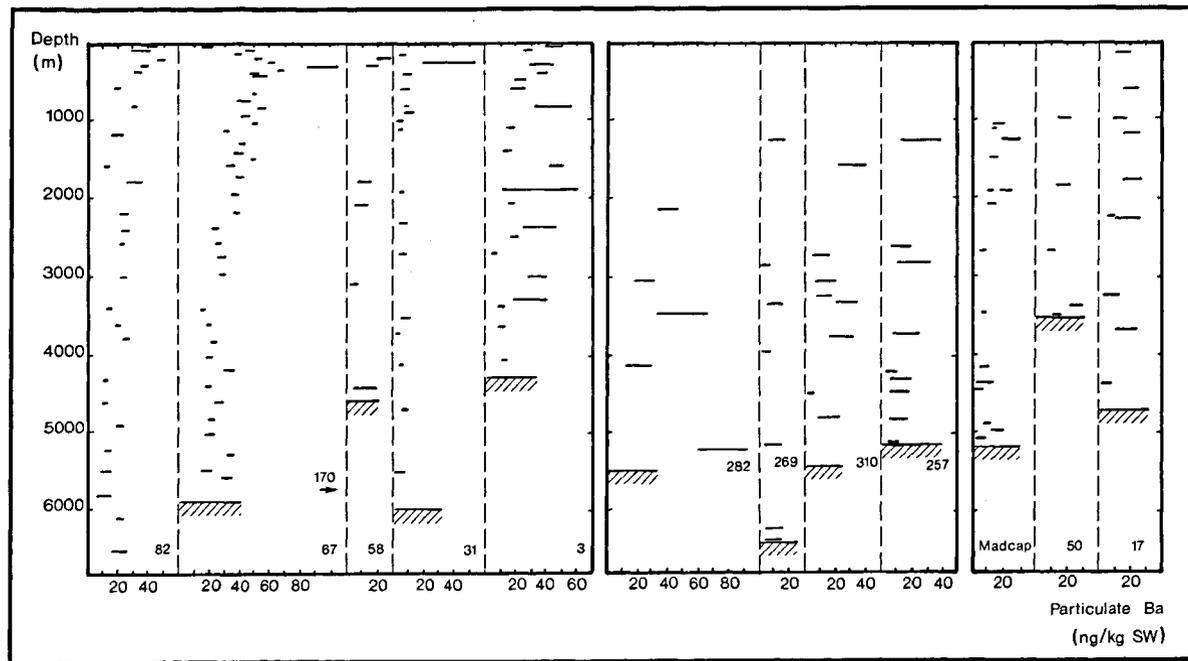


fig. 1.

Profiles of particulate Ba measured by INAA. GEOSECS Atlantic stations 82, 67, 58, 31, 3; GEOSECS Pacific stations 282, 269, 310, 257; MIDLANTE Atlantic stations Madcap, 50; TRANSAT Atlantic stations 17. For geographical location, see table 1. The depths of the watercolumns are indicated by a hatched line; at station 82 this depth is 7873 m.

floor in regions with a nepheloid layer. Furthermore, our study has shown that for the fine particulate load advective movement of the watermasses in which the particles are occluded will in part define the shape of the vertical profile (Dehairs, 1979 ; Dehairs et al., 1980).

Our measurements revealed a geometric mean particulate Ba value of 20 ng/kg seawater. No systematic differences in concentrations appeared between Pacific and Atlantic profiles.

2.- POSSIBLE Ba - CARRIERS

2.1.- Ba in POM, SiO₂ and CaCO₃

When looking for possible carriers of the particulate Ba, one can consider in the first place those particulate phases which constitute the main fraction of the total suspended matter. These are : - particulate organic matter ; - silica and carbonate skeletons ; - terrigenous aluminosilicate material.

In Table 2 we estimate the contribution of each of these phases to the total particulate Ba content. To obtain these data we have proceeded as follows (see also Dehairs, 1979 ; Dehairs et al., 1980).

1° The total suspended matter (TSM) content was deduced gravimetrically (Brewer et al., 1976).

2° The particulate organic matter (POM) content of TSM was deduced from literature data concerning the Atlantic and Indian Ocean (Krishnaswami et al., 1976 ; Copin-Montegut and Copin-Montegut, 1972 and 1978). The Ba content of this fraction (60 ppm on a dry weight basis) was deduced from literature data for cultures of skeleton-free plankton (Riley and Roth, 1971).

3° The SiO₂ content of TSM was deduced from literature data concerning the Atlantic and Indian Ocean (Krishnaswami et al., 1976 ; Copin-Montegut and Copin-Montegut, 1972 and 1978). The Ba content of this fraction (120 ppm) which is mainly composed of diatom frustules was deduced from *in vitro* Ba uptake studies we performed on two common open sea diatom species (Dehairs, 1979; Dehairs et al., 1980). These data were concordant with literature data concerning composite, diatom-rich open sea phytoplankton samples (Martin and Knauer, 1973).

Table 2

Contribution of siliceous and calcareous tests, POM and aluminosilicates
to the total barium content of suspended matter

Section of the watercolumn	A	B		C		D		E		F
	Total Ba _p (1) ng/kg SW	Ba carried by SiO ₂ tests (2) $\frac{\text{ng}}{\text{kg SW}}$ % of Ba _{p total}		Ba carried by CaCO ₃ tests (3) $\frac{\text{ng}}{\text{kg SW}}$ % of Ba _{p total}		Ba carried by POM (4) $\frac{\text{ng}}{\text{kg SW}}$ % of Ba _{p total}		Ba carried by aluminosilic. (5) $\frac{\text{ng}}{\text{kg SW}}$ % of Ba _{p total}		Fraction of total Ba _p carried by non-barite phases %
<i>Surface water</i>										
High latitudes	27	2.4	9	2.4	9	7.2	27		5	50
Low latitudes (between 45°N and 45°S)	11	0.6	5.5	0.6	5.5	1.8	16.5	1.3	12	39.5
<i>Intermediate and deep water</i>										
High latitudes	27		1		1		3.5		3	8.5
Low latitudes (between 45°N and 45°S)	10	0.3	3	0.3	3	0.9	9	0.8	8	23
<i>Bottom water</i> (nepheloid layer)	14	0.3	2	0.3	2	0.9	6.5	2.7	19	29.5

(1) Dehairs (1979) ; Dehairs et al. (1980).

(2) SiO₂ tests contain 120 ppm of Ba ; Dehairs (1979) ; Dehairs et al. (1980).

(3) CaCO₃ tests contain a max. of 200 ppm Ba ; from Church (1970).

(4) POM contains 60 ppm of Ba ; from Martin and Knauer (1973) ; Riley and Roth (1971).

(5) aluminosilicates contain 600 ppm of Ba ; from Turekian (1968) and Turekian and Wedepohl (1961).

4° The CaCO_3 content of TSM was deduced from our data on particulate Ca, as measured by INAA, for the same samples analyzed for Ba. The Ba content of the biogenic CaCO_3 phase (200 ppm) in suspension was taken from the literature (Church, 1970).

5° The aluminosilicate content of TSM was deduced from our data on particulate Al, as measured by INAA for the same samples analyzed for Ba. The Ba content of the aluminosilicate material in suspension (600 ppm) was taken from literature data concerning the Ba content of shales (Turekian, 1968 ; Turekian and Wedepohl, 1961). Indeed, since the Al content of aluminosilicate material suspended in seawater was observed to be similar to the Al content of shales (Lambert, 1979 ; Arrhenius, 1963 ; Buat-Menard and Chesselet, 1979), this was assumed to hold also for the Ba content of suspended aluminosilicate material (Dehairs, 1979 ; Dehairs et al., 1980).

In Table 2 we compare the average Ba contribution of these different phases with our average total particulate Ba values (only Atlantic Ocean values were considered) for surface water (first 300 m), intermediate and deep water (300 + 3000 m) and bottom water (3000 m + sea floor). On the basis of the TSM content in the Atlantic Ocean (Brewer et al., 1976) a distinction was made between high and low latitudes (i.e. between latitudes north and south of resp. 45°N and 45°S and latitudes between 45°N and 45°S) for the surface water and the intermediate + deep water boxes. The higher TSM contents at high latitudes are the result of a greater productivity in these waters (Brewer et al., 1976). No such regional differentiation of the TSM content exists for the bottom water box (Brewer et al., 1976).

From Table 2 it appears that the main fraction of total particulate Ba is carried by one or more non identified carrier(s).

2.2.- Ba as barite

The investigation of the suspended matter samples with the SEM-EMP revealed the presence of discrete micron-sized particles, containing Ba and S (Plate I). These particles occurred in any investigated sample at any depth (Table 1). Therefore, they can be considered as an ubiquitous component of oceanic suspended matter.

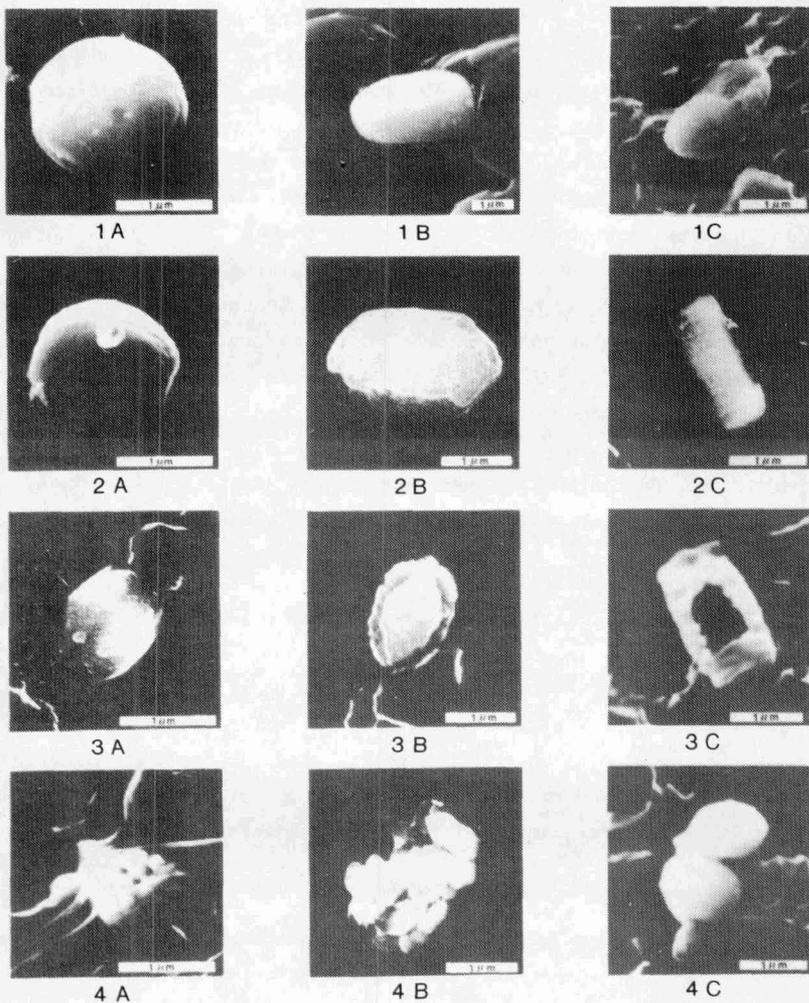


Plate I

Morphological types of barite particles in suspension in seawater

- 1) Ellipsoidal or spherical particles : A = GEOSECS station 67, 1499 m; B = GEOSECS station 3, 28 m; C = GEOSECS station 82, 832 m.
- 2) Particles with a crystalline habit : euhedral, automorphic particles : A, B, C = GEOSECS station 67, 658 m, 2982 m, 2992 m.
- 3) Irregularly shaped particles, probably affected by dissolution: A, B, C = GEOSECS station 67, 2932 m, 2193 m, 5599 m.
- 4) Aggregates of very small particles with or without a crystalline habit : A, B : GEOSECS station 67, 62 m, 4424 m; C = GEOSECS station 3, 105 m.

Besides the presence of Ba and S as major components, what suggests that they consist of $BaSO_4$, the occasional presence of Sr and K was observed. Most of these particles exhibit traces of a dissolution process; some are still clearly euhedral. Aggregates of sub-micron prisms do also occur. Electron diffraction analyses upon some of these particles revealed that they consisted of the mineral barite. Therefore we can conclude that barite is an ubiquitous component of suspended matter.

In order to deduce the contribution of the barite crystals as Ba-carriers, we systematically measured their sizes by using the SEM. From these particle-size measurements we deduced the particle volumes and the particle masses as Ba. As a result we could estimate what fraction of the total particulate Ba amount was carried by these barite crystals.

From this SEM-EMP study it appeared that up to 70% and more of the total particulate Ba content, as measured for the *same* filters by INAA, was accounted for by the suspended barite particles (Dehairs, 1979; Dehairs et al., 1980).

3.- ORIGIN OF THE $BaSO_4$ CRYSTALS IN OCEANIC SUSPENDED MATTER

The possibility of an authigenic formation of barite, by precipitation in an oversaturated seawater environment can be excluded, since the entire watercolumn is shown to be undersaturated with respect to $BaSO_4$ (Church, 1970 and 1979; Church and Wolgemuth, 1972). $BaSO_4$ saturation conditions are present only in interstitial waters of the sediments (Church, 1970 and 1979; Church and Wolgemuth, 1972). However, a theoretical study suggests that a solid solution of $BaSO_4$ with $SrSO_4$ could be stable in seawater (Hanor, 1969). We have observed minor amounts of Sr in the suspended barite crystals. Nevertheless, the observation of highly variable Sr/Ba ratios for such particles in the *same* sample is inconsistent with their authigenic formation in a single parcel of seawater, considered as a given physico-chemical environment.

There is much more evidence that the production of these barite crystals is controlled by a biological process. The particulate Ba content in the upper part of the watercolumn is positively related with the primary productivity (Figure 2). The data in Figure 2 were obtained as follows. Particulate Ba data represent average values for the first 1000 m of the watercolumn.

This depth interval was chosen, since it is between these limits that the particulate Ba maximum is generally observed (see above). The organic production data were taken from the paper of Koblentz (Mishke et al., 1970) and apply to the general vicinity in which GEOSECS stations are located. Since we have shown that it is barite which accounts for most of the total particulate Ba. The relationship in figure 2 holds also between organic productivity and *barite* content.

As concerns the mechanism of barite formation by the biological activity, 3 possibilities can be considered :

- 1° Formation of barite crystals in biological detritus, such as fecal pellets. Detritus can represent a microenvironment with specific physico-chemical

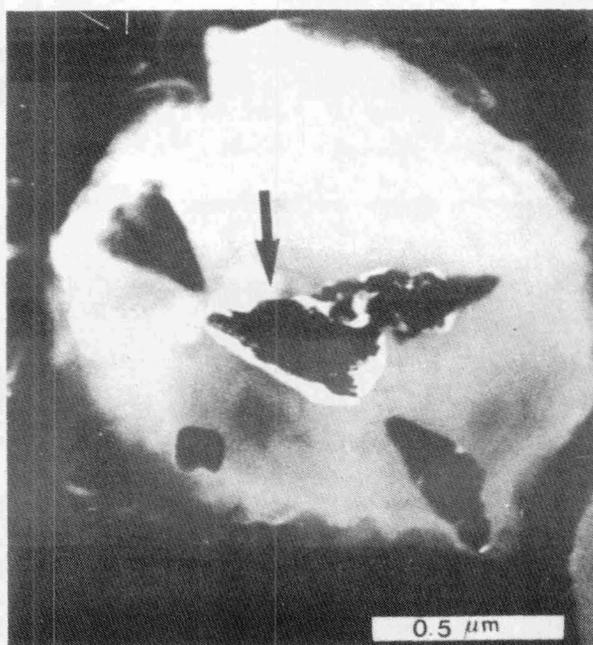


Plate II

Dark-field micrograph obtained with a 1 MeV transmission electron microscope of a barite grain (indicated by the arrow) inside an organic pellet, collected at 1860 m at GEOSECS Pacific station 306. [From J. Klossa, Laboratoire "R. Bernas", Orsay and Centre des faibles Radioactivités, Gif-sur-Yvette.]

properties, different from those present in the surrounding seawater. In fact we observed barite crystals inside particles giving no elemental signal when inspected by EMP and consisting of a low density material (Plate II). We suppose such particles to represent organic detritus, with barite having precipitated within it.

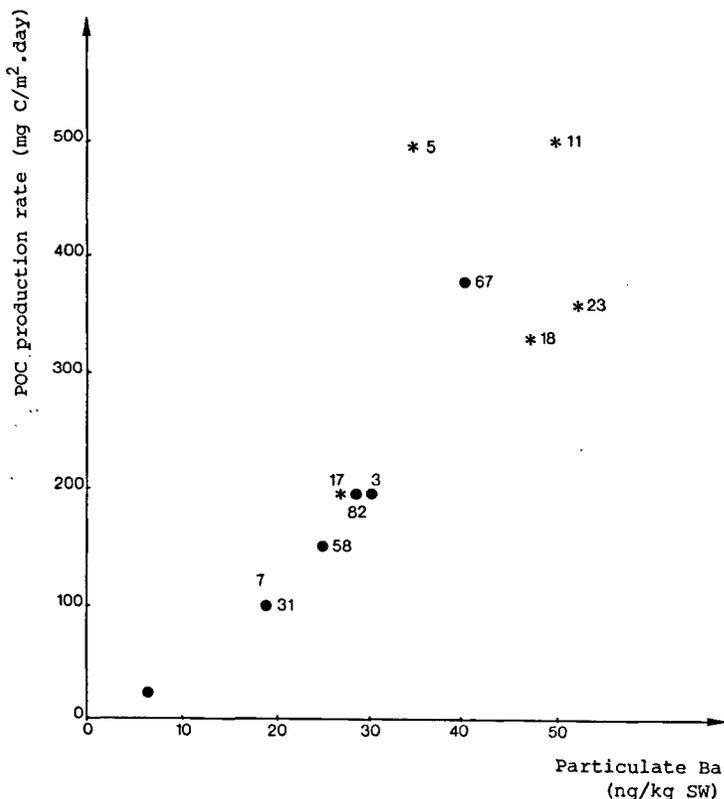


fig. 2.

Relationship between the average particulate Ba content in the first 1000 m of the watercolumn and the organic C production rate. Numbers refer to station numbers (see table 1), all stations in Atlantic Ocean.

● : own data for particulate Ba.

* : data of P. Brewer (GEOSECS unpublished results).

Organic C production rate data as given in Koblentz-Mishke (1970) for the same general vicinity of the station locations.

- 2° Formation of barite crystals through the intermediary of *Acantharia*. *Acantharia* are *Radiolaria* with a celestite (SrSO_4) skeleton. They are an ubiquitous component of oceanic plankton (Botazzi and Schreiber, 1971). At the death of such organisms, the SrSO_4 skeleton will dissolve in the sea water. Celestite is much more soluble than barite, but Ba might substitute for Sr in the celestite crystal lattice, in a tendency to produce a mineral more stable in seawater (Church, pers. comm., 1979). The endpoint of such a continuous substitution would be barite which itself, however, is undersaturated in the watercolumn (Church, 1970 and 1979; Church and Wolgemuth, 1972).
- 3° The direct formation of barite crystals by the living cell. Several observations stress the importance of the latter mechanism :
- ♦ *Xenophyophora*, which are benthic protozoa of the *Rhizopoda classis*, were observed to contain barite crystals inside vacuoles (Tendal, 1972).
 - ♦ The central capsuls of some species of the collosphaerid *Radiolaria* contain crystals which were tentatively identified by Haeckel as barite and/or celestite crystals (Haeckel, 1862). To our knowledge no further reports of such crystals were done since that early observation.
 - ♦ Marine chromophytes of the *Pavlovales ordo* were observed to carry barite crystals inside their vacuole (Gayral and Fresnel, 1979; Fresnel et al., 1979).

These three mechanisms of biological barite formation might actually occur together. They could induce the particulate Ba maximum which is observed in surface waters, generally below the euphotic zone. Indeed, the occluded barite crystals will only be liberated into the seawater, at the death of the barite producing organisms, when these start to decompose.

4.- THE FATE OF THE BARITE CRYSTALS IN THE WATERCOLUMN

Our observations with the SEM clearly showed that most of the suspended barite crystals are affected by dissolution. This is consistent with the fact that the watercolumn is undersaturated with respect to BaSO_4 (Church,

1970 and 1979; Church and Wolgemuth, 1972). Our data on the barite particle size distributions allowed us to estimate the amount of Ba dissolving per unit time in the deep ocean.

The amount J of material which is dissolving per unit time is given by (see also Lal and Lerman, 1973 and 1975) :

$$J = \frac{dM}{dt} = \frac{\pi}{6} \rho \frac{d(ND^3)}{dt} \quad (1)$$

where $\frac{dM}{dt}$ is the amount of $BaSO_4$ dissolving per unit time, ρ is the specific weight of $BaSO_4$, N is the particle number, D is the particle diameter.

By assuming that particles settle according to the Stokes sedimentation law and that the particle flux remains constant, equation (1) can be worked out

$$J = \frac{1}{3} \rho N D^2 k \quad (2)$$

where k is the barite dissolution rate constant which is dependent on the state of undersaturation of $BaSO_4$ in seawater. All terms on the right hand side of equation (2) are known with the exception of k .

By applying a Stokes settling and dissolution rate model to the size distribution data obtained for successive samples taken inside a same deep watermass it was possible to deduce k for the deep sea (Dehairs, 1979; Dehairs et al., 1980). The k value obtained ($0.04 \mu\text{m}/\text{yr}$) is consistent with the state of undersaturation of deep Atlantic Ocean water, when considering the barite dissolution to obey a second order reaction as observed *in vitro* for other sulphate phases ($PbSO_4$, $CaSO_4 \cdot 2H_2O$, $SrSO_4$) and for the crystallisation of $BaSO_4$, $PbSO_4$ and $CaSO_4 \cdot 2H_2O$ (Campbell and Nancollas, 1969; Nancollas, 1968; Nancollas and Purdie, 1963).

As a result we could deduce an average deep-ocean J_{Ba} value of $0.4 \mu\text{g Ba}/\text{cm}^2 \cdot \text{yr}$ (see figure 3).

However, it is important to verify the input of dissolved Ba in the deep sea as resulting from the dissolution of SiO_2 and $CaCO_3$ skeletal phases. Indeed, although the latter were observed to contain but minor amounts of Ba, the fact that their turn-over rate is faster than the one of barite, may finally result in an important additional input of dissolved Ba in the deep sea.

Biogenic production of particulate Ba

CaCO_3 : 0.24
 SiO_2 : 0.31
 BaSO_4 : 0.8

Total production rate : 1.35

Fast settling of fecal material flux
 0.03 - 0.7

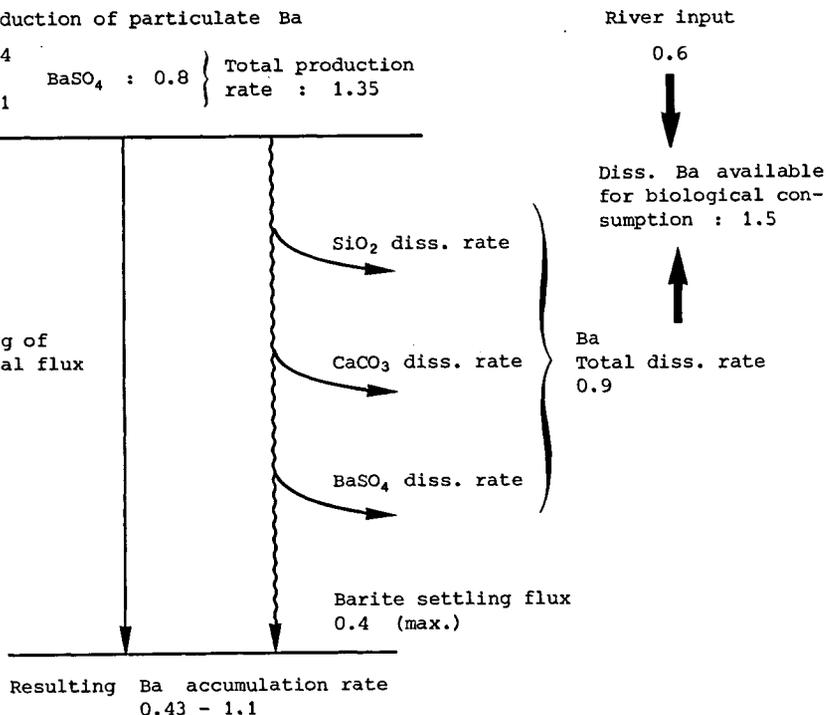


fig. 3.

Numerical values for the components of the oceanic barium cycle
 All values in $\mu\text{g Ba/cm}^2\cdot\text{yr}$

The estimation of the amounts of SiO_2 and CaCO_3 dissolving in the deep sea is based on mass balance computations of Wollast (1974) and Berger (1970).

In order to estimate the amount of dissolved Ba introduced in the deep sea as a result of the dissolution of the SiO_2 and CaCO_3 carriers, we have calculated in the first place the production rate of Ba as associated with the production of SiO_2 and CaCO_3 . From the following relationship :

$$\frac{(A)}{(\text{POC})} \times \text{POC prod. rate},$$

where A is the SiO_2 or CaCO_3 content of TSM (see discussion of table 2); POC is the particulate organic carbon; POC production rate = $7 \text{ mg C/cm}^2\cdot\text{yr}$

is an average value for the open ocean (Koblentz-Mishke et al., 1970) and from the knowledge of the Ba content in opal and carbonate phases (see discussion of the data in table 2), we obtained a Ba production rate associated with the production of SiO_2 or CaCO_3 , as given by

$$\text{prod. rate A} \times (\text{Ba})_A$$

in which $(\text{Ba})_A$ is the Ba content of the SiO_2 or CaCO_3 phase.

These values are given in figure 3. As concerns POM we have assumed that at its decomposition, which occurs almost entirely in the upper part of the watercolumn (Menzel, 1974) all the Ba is redistributed into barite. Some of the possible mechanisms of that process have been described above (see origin of BaSO_4 crystals in oceanic suspended matter). Literature data show that between 80 and 90 % of the produced amounts of SiO_2 and CaCO_3 will dissolve in the deep sea before reaching the sediments (Wollast, 1974; Berger, 1970). As a result, it was possible to deduce the contributions of dissolving SiO_2 and CaCO_3 phases to J_{Ba} -total. Together, these two phases account for about 55 % of the overall J_{Ba} value (figure 3).

The total amount of dissolved Ba introduced by this way into the deep sea will eventually be reintroduced into the surface water by vertical advection. This flux, $0.9 \mu\text{g}/\text{cm}^2.\text{yr}$, together with the average annual dissolved Ba input by rivers [$0.6 \mu\text{g Ba}/\text{cm}^2.\text{yr}$ (Chan et al., 1976)] results in a total flux of dissolved Ba to surface waters of $1.5 \mu\text{g}/\text{cm}^2.\text{yr}$ which is of the same magnitude as the consumption requirements of Ba by biological activity ($1.35 \mu\text{g}/\text{cm}^2.\text{yr}$, figure 3).

Not all of the settling particulate Ba dissolves in the deep sea. Part of it can be incorporated into the sediments. The flux of settling barite crystals to the sediments was estimated by assuming Stokes law to be obeyed. We have calculated this flux from our data for the barite size-distributions for samples closest to the ocean floor. These bottom water particles were assumed not to be affected any further by dissolution before their incorporation in the sediments. A max. $0.4 \mu\text{g Ba}/\text{cm}^2.\text{yr}$ was deduced for the particulate Ba flux of the sediments (figure 3). This flux is supplemented by the one resulting from the fast settling of large particles such as fecal pellets and foraminifera. Due to their scarcity such large particles are not sampled quantitatively by conventional small volume

sampling systems (30 litre), such as used during the GEOSECS cruises. Although they represent but a very small fraction of the biogenic suspended matter stock, such large particles are important in terms of fluxes.

Several analyses of sediment trap materials from the deep ocean have allowed to deduce a vertical flux for SiO_2 , CaCO_3 and POM (Bishop et al., 1977 and 1979) resulting mainly from the fast settling of large particles. Again, by knowing the Ba content of each of these three phases, it was possible to deduce the associated Ba flux. A range of 0.03 to $0.7 \mu\text{g Ba/cm}^2\cdot\text{yr}$ was calculated. Supplemented by the barite crystal flux (max. $0.4 \mu\text{g Ba/cm}^2\cdot\text{yr}$) a total flux of 0.43 to $1.1 \mu\text{g Ba/cm}^2\cdot\text{yr}$ is deduced (Dehairs, 1979; Dehairs et al., 1980). This value compares well with known average Ba accumulation rates (as barite) in the sediments [$0.8 \mu\text{g/cm}^2\cdot\text{yr}$, range $0.16-4 \mu\text{g/cm}^2\cdot\text{yr}$ (Dehairs, 1979; Dehairs et al., 1980; Turekian and Tausch, 1964; Hanor, 1972; Boström et al., 1973)]. This Ba accumulating in the sediments is known to be present essentially as barite (Church, 1970 and 1979; Church and Wolgemuth, 1972). Therefore part of the particulate Ba settling onto the sea floor must be redistributed into barite.

To conclude, our study has shown that particulate Ba in oceanic suspended matter is present mainly as the biogenic mineral barite. The biological production of barite in surface water and the subsequent dissolution of those crystals in the deep sea are important parts of the overall oceanic Ba cycle. It is shown that most of the Ba consumed in surface waters (60 %) is accounted for by the cyclic component.

Acknowledgments

This work was carried out under the promotorship of Prof. R. Chesselet, Prof. J. Jedwab and Prof. I. Elskens. It could not have been achieved without the kind assistance of C.E. Lambert, P. Buat-Menard and J. Klossa. This work was supported by a GEOSECS - NSF grant.

References

- ARRHENIUS, G. (1963). *Pelagic sediments*, in *The Sea*, N.N. Hill (Editor), Wiley-Interscience, N.Y., 3, 655.
- BACON, M.P. and EDMOND, J.M. (1972). Barium at GEOSECS III in the south-east Pacific. *Earth Planet. Sci. Letters*, 16, 66.

- BERGER, W.H. (1970). Biogenous deep-sea sediments ; fractionation by deep-sea circulation. *Geol. Soc. Am. Bull.*, 81, 1385.
- BISHOP, J.K., EDMOND, J.M., KETTEN, D.R., BACON, M.P. and SILKER, W.B. (1977). The chemistry, biology and vertical flux of particulate matter from the upper 400 m of the Equatorial Atlantic Ocean. *Deep-Sea Res.*, 24, 511.
- BISHOP, J.K.B., KETTEN, D.R. and EDMOND, J.M. (1979). The chemistry, biology and vertical flux of particulate matter from the upper 400 m of the Cape Basin in the south-east Atlantic Ocean. *Deep-Sea Res.*, 25, 1121.
- BOSTRÖM, K., JOENSUU, O., MOORE, C., BOSTRÖM, B., DALZIEL, M. and HOROWITZ, A. (1973). Geochemistry of barium in pelagic sediments. *Lithos*, 6, 159.
- BOTAZZI, E.M. and SCHREIBER, B. (1971). Acantharia in the Atlantic Ocean, their abundance and preservation. *Limnol. Oceanogr.*, 16, 677.
- BOYLE, E.A., SCLATER, F. and EDMOND, J.M. (1976). On the marine geochemistry of cadmium. *Nature*, 263, 42.
- BOYLE, E.A., SCLATER, F.R. and EDMOND, J.M. (1977). The distribution of dissolved copper in the Pacific. *Earth Planet. Sci. Letters*, 37, 38.
- BREWER, P.G., SPENCER, D.W., BISCAYE, P.E., HANLEY, A., SACHS, P.L., SMITH, C.L., KADAR, S. and FREDERICKS, J. (1976). The distribution of particulate matter in the Atlantic Ocean. *Earth Planet. Sci. Letters*, 32, 393.
- BRUN-COTTAN, J.C. (1976). *Contribution à l'étude de la granulométrie et de la cinétique des particules marines*. Thèse de Doctorat ès Sci. Phys., Paris 6.
- BRUN-COTTAN, J.C. (1976). Stokes settling and dissolution rate model for marine particles as a function of size distribution. *J. Geophys. Res.*, 81, 1601.
- BRULAND, K.W., KNAUER, G.A. and MARTIN, J.H. (1978). Zinc in north-east Pacific water. *Nature*, 271, 741.
- BUAT-MENARD, P. and CHESSELET, R. (1979). Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. *Earth Planet. Sci. Letters*, 42, 399.
- CAMPBELL, J.R. and NANCOLLAS, G.H. (1969). The crystallization and dissolution of strontium sulfate in aqueous solution. *J. Phys. Chem.*, 73, 1735.
- CHAN, L.H., DRUMMOND, D., EDMOND, J.M. and GRANT, B. (1977). On the barium data from the Atlantic GEOSECS expedition. *Deep-Sea Res.*, 24, 613.
- CHAN, L.H., EDMOND, J.M., STALLARD, R.F., BROECKER, W.S., CHUNG, Y.C., WEISS, R.F. and KU, T.L. (1976). Radium and barium at GEOSECS stations in the Atlantic and Pacific. *Earth Planet. Sci. Letters*, 32, 258.
- CHOW, T.J. and GOLDBERG, E.D. (1960). On the marine geochemistry of barium. *Geochim. Cosmochim. Acta*, 20, 192.
- CHURCH, T.M. (1970). *Marine barite*. Ph. D. Thesis, Univ. of California.
- CHURCH, T.M. (1979). *Marine barite*, in *Marine Minerals*, R.G. Burns (Editor), Min. Soc. Am., short course notes, 6, 175.

- CHURCH, T.M. and WOLGEMUTH, K. (1972). Marine barite saturation. *Earth Planet. Sci. Letters*, 15, 35.
- COPIN-MONTEGUT, C. and COPIN-MONTEGUT, G. (1972). Chemical analysis of suspended particulate matter collected in the north-east Atlantic. *Deep-Sea Res.*, 19, 445.
- COPIN-MONTEGUT, C. and COPIN-MONTEGUT, G. (1978). The chemistry of particulate organic matter from the south Indian and Antarctic Ocean. *Deep-Sea Res.*, 25, 911.
- DEHAIRS, F. (1979). *Discrete suspended particles of barite and the barium cycle in the open ocean*. Doctoral thesis in science, Vrije Universiteit Brussel.
- DEHAIRS, F., CHESSELET, R. and JEDWAB, J. (1980). Discrete suspended particles of barite and the barium cycle in the open ocean. *Earth Planet. Sci. Letters*, GEOSECS collected papers volume, September issue, in press.
- FRESNEL, J., GALLE, P. et GAYRAL, P. (1979). Résultats de la microanalyse des cristaux vacuolaires chez deux chromophytes unicellulaires marines : *Exanthemachrysis gayraliae*, Pavlova sp. (Prymnésiophycées, Pavlovacées). *C.R. Acad. Sci. Paris*, D288, 823.
- GAYRAL, P. et FRESNEL, J. (1979). *Exanthemachrysis gayraliae* Lepalleur (Prymnesiophyceae, Pavlovales) : ultra-structure et discussion taxinomique. *Protistologica*, 15, 271.
- HAECKEL, E. (1862). *Radiolarien (Rhizopoda Radiolaria)*, eine Monographie, G. Reimer Verlag, Berlin.
- HANOR, J.S. (1969). Barite saturation in sea water. *Geochim. Cosmoch. Acta*, 33, 894.
- HANOR, J.S. (1972). Rates of barium accumulation in the Equatorial Pacific. *Geol. Soc. Am.*, Abstracts with Programs, 4, 526.
- KOBLENZ-MISHKE, O.J., VOLKOVINSKY, V.V. and KABANOVA, J.G. (1970). Plankton primary production of the world ocean, in *Scientific Exploration of the South Pacific*, W.S. Wooster (Editor), U.S. Natl. Acad. Sci., Washington D.C., 183.
- KRISHNASWAMI, S., LAL, D. and SOMAYAJULU, B.L.K. (1976). Investigations of gram quantities of Atlantic and Pacific surface particulates. *Earth Planet. Sci. Letters*, 32, 403.
- LAL, D. and LERMAN, A. (1973). Dissolution and behaviour of particulate biogenic matter in the ocean : some theoretical considerations. *J. Geophys. Res.*, 78, 7100.
- LAL, D. and LERMAN, A. (1975). Size spectra of biogenic particles in ocean water and sediments. *J. Geophys. Res.*, 80, 423.
- LAMBERT, C.E. (1979). *Contribution à l'étude du fer et de l'aluminium particulaires dans l'océan*. Thèse de diplôme d'Etudes Supérieures, Univ. Picardie, France.
- LI, Y.H., KU, T.L., MATHIEU, G.G. and WOLGEMUTH, K. (1973). Barium in the Antarctic Ocean and implications regarding the marine geochemistry of Ba and Ra²²⁶. *Earth Planet. Sci. Letters*, 19, 352.

- MARTIN, J. and KNAUER, G.A. (1973). The chemical composition of plankton. *Geochim. Cosmochim. Acta*, 37, 1639.
- MENZEL, D.W. (1974). Primary productivity, dissolved and particulate organic matter and the sites of oxidation of organic matter, in *The Sea*, E.D. Goldberg (Editor), Wiley Interscience, N.Y., 659.
- NANCOLLAS, G.H. (1968). Kinetics of crystal growth from solution. *J. Cryst. Growth*, 3-4, 335.
- NANCOLLAS, G.H. and PURDIE, N. (1963). Crystallization of barium sulphate in aqueous solution. *Trans. Far. Soc.*, 59, 735.
- RILEY, J.P. and ROTH, I. (1971). The distribution of trace elements in some species of phytoplankton grown in culture. *J. Mar. Biol. Ass. U.K.*, 51, 63.
- TENDAL, O.S. (1972). A monograph of the *Xenophyophoria*, Galathea Report, 12, 8.
- TUREKIAN, K.K. (1968). Deep-sea deposition of barium, cobalt and silver. *Geochim. Cosmochim. Acta*, 32, 603.
- TUREKIAN, K.K. and TAUSCH, E.H. (1964). Barium in deep-sea sediments of the Atlantic Ocean. *Nature*, 201, 696.
- TUREKIAN, K.K. and WEDEPOHL, K.H. (1961). Distribution of the elements in some major units of the Earth's crust. *Geol. Soc. Am. Bull.*, 72, 175.
- WOLGEMUTH, K. and BROECKER, W.S. (1970). Barium in sea water, *Earth Planet. Sci. Letters*, 8, 372.
- WOLLAST, R. (1974). *The silica problem*, in *The Sea*, E.D. Goldberg (Editor), Wiley, N.Y., 5, 659.