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The biological production of marine suspended barite and the barium cycle in the Western Mediterranean Sea

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Abstract. Suspended particulate barium was measured in the Western Mediterranean along 4 profiles sampled during the PHYCEMED 1 cruise in 1981. The non-terrigenous fraction of particulate barium (i.e. excess Ba; Ba_{xs}) can account for up to 96% of total barium. This fraction follows the barite settling and dissolution rate model we described earlier for the Atlantic Ocean, confirming barite as the carrier of excess barium. We propose that these Ba_{xs} concentrations, which are higher in the Western Mediterranean than in the overall Atlantic, may represent an adaptation of the microplankton to the high densities and density gradients of surface Mediterranean waters.

A mass-balance for Ba in the Mediterranean Sea shows: (1) that the atmospheric source must be much more important than previously reported: (2) that contrary to the Atlantic situation, the internal recycling of barium is of little importance compared to the flow of barium through the system.

1. Introduction

Barite microcrystals are an ubiquitous component of oceanic suspended matter and their production in the surface waters and subsequent dissolution with depth plays a major role in the oceanic Ba cycle (Dehairs et al. 1980). These microcrystals are formed out of thermodynamic equilibrium in the seawater (Church and Wolgemuth 1972; Church 1979). Evidence that pelagic production of barite is biologically mediated was found by several authors (Chow and Goldberg 1960; Turekian 1968). On an oceanic scale it has been shown that barite production is related to primary productivity (Dehairs et al. 1980; Dymond 1986).

In this paper we study the impact of the specific conditions prevailing in the Mediterranean Sea on the local biogeochemistry of Ba. As compared to the open ocean, Mediterranean surface waters are reported to be enriched in those trace elements that exhibit a biogeochemical cycle closely related to the one of nutrients (Spivack et al. 1983; Laumond et al. 1984; Boyle et al. 1985). Boyle et al. (1985) explain this peculiar situation as the result of a less frequent recycling of the nutrients in the Mediterranean watercolumn as compared to the open ocean. For other trace elements (Al: Hydes 1983; Hydes 1985; REE: Elderfield and Greaves 1982; Greaves et al. 1986) the Mediterranean outflow waters exhibit clear enrichments as compared to the inflowing Atlantic waters. This is

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also the case for Ba (Bernat et al. 1972; Chan et al. 1977). Both for Al and REE, Mediterranean surface water enrichment is suggested to be maintained by desorption from eolian particles so that, while the Mediterranean is receiving Atlantic surface waters relatively depleted in trace metals, it can still export enriched deep waters. The balance must be made by the sum of sources to the Mediterranean. Furthermore, the deficit of freshwater input compared to evaporation creates strong density gradients in the Mediterranean surface waters. In the following we check (1) the effect of the seawater densities and the high dissolved Ba concentrations on the planktonic production of barite and (2) how these high dissolved Ba concentrations are maintained.

2. Experimental

2.1. Sampling and analytical methods

Sampling and analytical methods have been extensively described elsewhere (Buat-Menard et al. 1980; Lambert 1981; Risler 1984). Sea water samples were collected with (1) 10 l. Go-Flo bottles, in surface waters and (2) 30 l. Niskin bottles, fitted with teflon coated stainless steel springs, in deep waters. During the PHYCEMED I cruise, a new stainless steel grease-free hydrowire was used. Seawater was filtered under pressure on acid-washed pre-weighed, 0.45 μm pore size, 47 mm diameter Nuclepore membranes, using ultra-clean procedures (Risler 1984). Sediment samples were taken using a Reineck corer. The filters and sediment samples were analysed for elemental composition by Instrumental Neutron Activation Analysis. Following an irradiation of 1 hour under a thermal neutron flux of 1×10^{14} n. $cm^{-1}.s^{-1}$ (OSIRIS reactor, CEN, Saclay), the samples were counted on a 25% efficiency Ge(Li) detector. The complete set of data as well as the discussion of analytical uncertainties can be found in Risler (1984). The average precision (counting uncertainties plus the contribution from the procedural blank filter) is 3% for Sc and 15% for Ba.

2.2. Calculation of excess barium

It has been shown by Risler (1984) that there is a constant ratio between particulate Al and Sc in Mediterranean waters: both elements can be used as tracers of the detritic fraction as they were used in the Atlantic Ocean (Buat-Menard 1979; Buat-Menard and Chesselet 1979). The "excess particulate barium" (Ba_{xs}) fraction is given by:

$$Ba_{xs} = 1 - \frac{(Ba/Sc)_{crust} \times (Sc)_{sample}}{(Ba)_{sample}} \qquad (1)$$

in which the (Ba/Sc) crustal ratio is taken from Bowen (1979).

3. Results

Particulate suspended matter was studied at 4 stations in the Western Mediterranean (R.V. "Suroit"; PHYCEMED I cruise, 1981; Fig. 1). Total particulate Ba_p), excess Ba (Ba_{xs}) and Sc data are given in Table 1. In Fig. 2, Ba_{xs} profiles are shown together with salinity and potential temperature data. The Ba_{xs} profiles show a maximum within a few hundred meters from the surface, followed by a decrease with a depth. For stations GYW-2 and GYL-1 there is an increase of Ba_{xs} content close to the seafloor. These profiles are very similar to those observed for the Atlantic Ocean (Dehairs 1979). As in the Atlantic, they reflect production in surface waters, dissolution with depth and resuspension in the bottom layer. For station SRS in the Sardinia Strait, and SRG2 in the Alboran Sea, the maxima coincide with the salinity maximum between 400 m and 600 m which is associated with an intermediate water mass advecting from the oriental basin (Lacombe and Tchermia 1971). At station GYW-2, in the Algero-Provencal Basin, Two Ba_p maxima exist. The shallow maximum is associated with the basis of the thermocline, while the deep maximum (500 m) is located just below the salinity maximum associated with the advecting oriental water mass. At station GYL-1 in the Ligurian Sea, the Ba_p maximum at 50 m coincides with the thermocline. Deeper maxima (500 and 1150 m) do not appear related to the advecting oriental water mass.

Ba ans Sc in sediments (Table 2) have been measured at stations "M" located

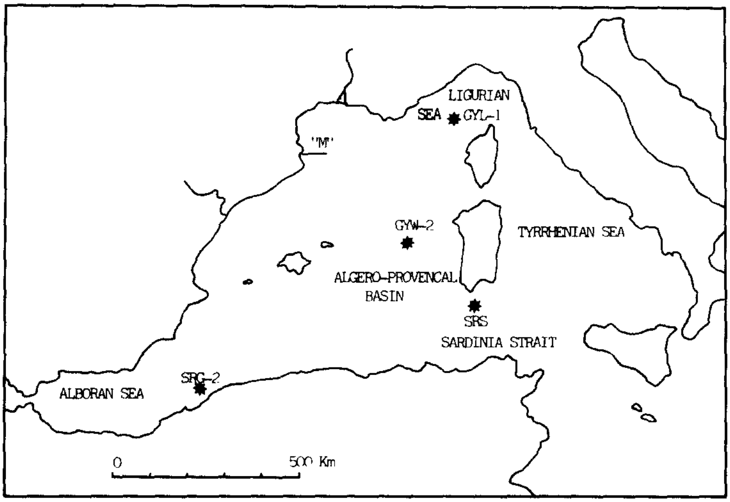

Fig. 1. Sampling stations for TSM during the PHYCEMED 1 cruise in the Western Mediterranean Basin (1981); sediment sampling transect "M" (1983) is also indicated. GYW2: 40°37′N–07°10′E; 2790 m. GYL: 46°06′N–07°56′E; 2575 m. SRS: 38°36′N–09°51′E; 1945 m. SRG2: 36°17′N–00°06′W; 2500 m.

Table 1. Vertical profiles of total particulate Ba, Sc, excess particulate Ba and σ-t at stations. SRS, SRG 2, GYW 2 and GYL 1. * = not measured

Station	Depth	Sc		Ba total (A)		Ba excess (B)	B/A	σ-t
	m	ng.l^{-1}	µg.g^{-1}	ng.l^{-1}	µg.g^{-1}	ng.l^{-1}	%	
SRS	10	0.082	1.93	19.2	450	16.6	87	27.73
	50	0.190	1.89	*	*			
	125	0.063	2.55	45.7	1850	43.7	96	28.85
	250	0.109	3.77	63.7	2200	60.3	95	
	400	0.110	4.47	69.7	2830	66.3	95	29.02
	500	0.127	5.28	88.5	3670	84.5	96	29.07
	650	0.129	5.58	49.2	2120	45.2	92	29.08
	900	0.100	7.92	25.4	2020	22.3	88	
	1200	0.124	8.47	22.5	1530	18.6	83	
	1600	0.192	10.40	18.9	1020	12.9	68	
	1845	0.197	9.50	24.1	1170	17.9	74	
	1920	0.213	10.20	13.9	666	7.2	52	
	1925	0.243	11.60	*	*			
	1940	0.205	9.48	*	*			
	1940	0.271	9.99	*	*			
	1944	0.248	10.80	*	*			
SRG2	10	0.074	3.01	*	*			26.85
	20	0.098	3.39	*	*			26.95
	100	0.013	1.81	*	*			28.10
	150	0.101	4.03	49.8	1830	46.6	94	
	200	0.082	3.82	68.1	3170	65.5	96	
	250	0.125	4.80	97.7	3750	93.4	96	28.97
	400	0.276	6.86	66.3	1650	57.7	87	
	500	0.344	10.20	50.5	1540	40.0	79	29.06
	1000	0.235	9.76	28.9	1200	21.5	75	
	1600	0.142	5.60	21.4	841	17.0	79	
	2000	0.161	10.00	18.2	1130	13.2	72	
	2400	0.400	12.50	21.9	684	9.4	43	
	2480	0.384	11.60	16.2	490	4.2	26	
	2495	0.297	11.50	*	*			
	2499	0.326	10.50	28.6	924	18.4	64	
GYW2	10	0.390	2.48	*	*			28.41
	50	0.101	2.91	75.4	2170	72.2	96	28.79
	120	0.114	3.53	93.9	2910	90.3	96	29.04
	250	0.110	5.86	85.6	4580	82.2	96	
	400	0.159	9.55	63.9	3830	58.9	92	
	500	0.161	7.15	111.0	4940	106.0	95	29.09
	800	0.110	6.90	61.9	3870	58.5	94	
	1200	0.106	8.13	41.8	3210	38.5	92	
	1650	0.092	7.61	23.1	1910	20.2	88	
	2200	0.157	12.3	17.2	1350	12.3	71	
	2600	0.297	11.2	40.1	1510	30.8	77	
	2690	1.09	13.3	71.2	873	37.1	52	
	2740	1.39	13.1	43.9	413	0.9	1	
	2770	1.60	13.1	56.4	462	6.3	11	
	2785	1.87	13.1	92.2	647	33.7	37	
	2789	1.97	12.7	86.6	557	24.9	29	

Table 1. (Continued)

Station	Depth	Sc		Ba total (A)		Ba excess (B)	B/A	σ-t
	m	ng.l^{-1}	μg.g^{-1}	ng.l^{-1}	μg.g^{-1}	ng.l^{-1}	%	
GYL1	10	0.296	1.04	*	*			
	50	0.233	3.08	168.0	2220	160.7	96	28.69
	100	0.156	5.87	42.1	1590	37.2	88	28.97
	300	0.104	4.63	61.1	2710	57.8	95	29.06
	500	0.140	4.37	98.4	3070	94.0	96	29.10
	1000	0.103	5.64	69.3	3790	66.1	95	
	1150	0.101	5.11	87.0	4420	83.8	96	
	1500	0.115	5.16	64.0	2880	60.4	94	
	2000	0.234	8.06	24.5	844	17.2	70	
	2200	0.253	5.03	*	*			
	2500	0.374	6.13	45.8	751	34.1	74	
	2560	3.03	10.5	134.0	465	39.2	29	
	2570	2.62	10.6	95.1	385	13.1	14	

on a transect across the continental slope (42°20′N–03°20′E to 04°E; R.V. "Georges Petit", 1983) and at stations SRG-2 and SRS (R.V. "Suroit", PHYCEMED I cruise, 1981; (Fig. 1). It is seen from Table 2 that for all stations the Ba$_{xs}$ fraction in sediments is small as compared to the suspended matter.

Table 2. Ba and Sc content in NW Mediterranean sediment cores

Station	Watercolumn depth, m	Core section cm	Ba μg.g^{-1}	Sc μg.g^{-1}	Ba/Sc	Ba$_{xs}$ μg.g^{-1}
MO3A	468	0–4	412	12.3	33	31
		4–8	391	10.6	37	62
		8–13	396	9.8	40	92
		13–19	326	9.7	34	25
		19–22	369	9.7	38	68
MO6A	585	0–2	482	11.7	41	119
		2–4	441	12.5	35	53
MO2A	826	0–0.5	358	9.2	39	73
		0.5–1	421	10.4	40	99
		1–2	461	11.2	41	114
		2–3	355	10.0	35	45
MO5A	1292	0–1	399	9.3	43	111
		1–2	401	9.8	41	97
		2–3	326	9.4	35	35
		3–4	291	9.1	32	9
SRG2	2600	0–4	282	13.0	22	0
SRS	2094	0–2	214	8.4	23	0
		2–4	281	8.2	30	27
Mean			367	10.2	36	59

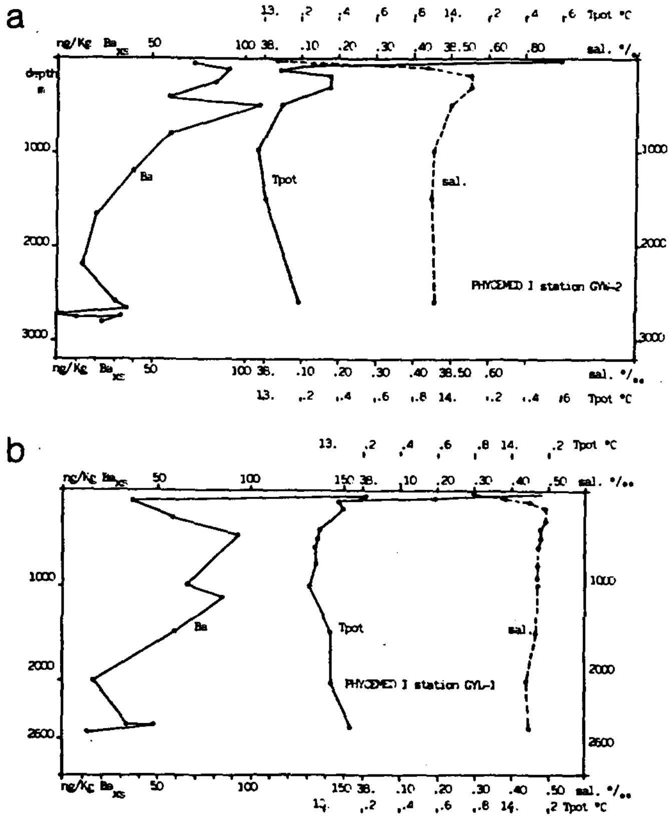

Fig. 2. Profiles of excess particulate Ba, potential temperature and salinity for PHYCEMED 1 stations SRS, SRG2, GYL1, GYW2.

4. Discussion

4.1. The excess barium as barite

For surface and mid-depth waters, the main fraction (i.e. over 90%) of total Ba is excess Ba which is not associated with a detritic alumino-silicate phase (Table 1). For the Atlantic this Ba_{xs} was shown to be essentially accounted for by barite microcrystals which dissolve in the watercolumn (Dehairs et al. 1980). Such crystals were also identified in Mediterranean suspended matter (Dehairs 1979). To conclude that the Mediterranean Ba_{xs} values are also accounted for by barite microcrystals, we can calculate if the dissolution rate of Ba_{xs} corresponds to the dissolution of barite crystals.

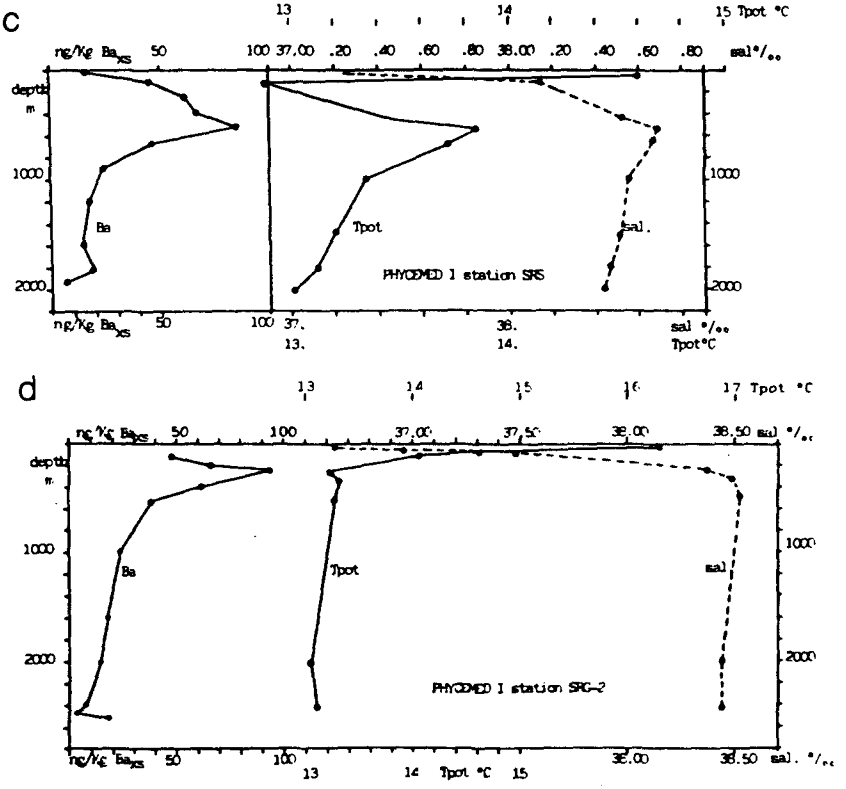

Fig. 2

4.2. *Dissolution of barite*

In the following, we test if the observed decrease of Ba$_{xs}$ fits the barite settling and dissolution rate model elaborated for the Atlantic (Dehairs 1979; Dehairs et al. 1980) This cannot be studied from a one dimensional approach, since horizontal and vertical advective input of particles at depth certainly affects the particle size distribution. For instance, an additional input of barite particles will mask the effect of vertical settling and dissolution on the original particle population produced in the local surface waters. This can result in smaller dissolution rates at depth than expected from surface water particle population characteristics. Therefore, dissolution can only be studied within specific depth intervals. For any given depth interval we calculate the barium quantity that dissolves between the upper and lower boundaries. We use the dissolution model described in Dehairs et al (1980), (see equations in appendix 1). The measured Ba$_{xs}$ concentration at the upper boundary is considered to be entirely carried by barite crystals. Using the barite dissolution rate constant $k = 0.075 \times 10^{-4}$ cm.y^{-1} obtained from the GEOSECS Atlantic data, we can calculate here the particle size decrease between an upper and lower boundary, and thus the residual barite-Ba concentration at the lower boundary. This latter value is compared with the measured Ba_{xs} at the lower boundary, allowing to check the validity of the model. Due to the lack of data on size distributions, we consider these crystal populations to have uniform sizes, similar to the median values observed for the Atlantic barite populations: the best fit of the data has to be obtained using median sizes comprised between 0.8×10^{-4} and 1.8×10^{-4} cm (Dehairs 1979). In Table 3 we compare, for the 4 profiles, the calculated residual barium as barite (column A) with the measured Ba_{xs} (column B). A is found equal to B with a maximum deviation of 10% indicating that for the Western Mediterranean waters the data fit the general barite settling and dissolution rate model. In columns C and D of Table 3 we present the calculated dissolution rates (J_{Ba}) for all depth intervals, using the formulation for J given in Appendix 2.

The total J_{Ba} is seen to range between 0.14 and 0.31 μg.cm^{-2}.y^{-1}. This is of the same order of magnitude as the average J observed for the Atlantic Ocean (J_{Ba}Atl = 0.4 μg.cm^{-2}.y^{-1}). In the Western Mediterranean Sea we can calculate the increase with depth, between 500 m and the bottom, of dissolved Ba (Ba_d) due to barite dissolution using an estimate of the deep water residence time. The residence time is comprised between 15 to 30 years (Bethoux and Copin-Montegut, 1984, based on water and salt circulation and fluxes; Merlivat, pers. comm., based on tritium data), and 100 years (Delibrias 1982; Broecker and Gerard 1969). This yields a very small concentration increase in dissolved barium, as shown by the following calculation:

$$\Delta C = \frac{J_{Ba}}{V} \times T = \frac{0.34 \times 30(100)}{150} = 0.07\text{–}0.2\,\mu g.l^{-1} \qquad (2)$$

with ΔC = concentration increase (μg.l^{-1}); T = residence time of deep water in the western basin, taken as 30–100 years; V = average volume per cm^2 of sea surface, taken as 150 l. (average depth: 1500 m).

This computed ΔC falls within the range of error for current dissolved barium measurements.

4.3. *Possible origins of Ba_{xs} in the Western Mediterranean*

Barite crystals were identified as protoplasm-inclusions of benthic Xenophyophorida [Schulze and Thierfelder 1905; Arrhenius and Bonatti 1965: Tendal 1972; Gooday and Nott 1982]. More recently, vacuolar microcrystals of barite were identified in unicellular marine chromophytes (Fresnel et al. 1979; Gayral and Fresnel 1979). Freshwater microalgae (desmids) were also shown to contain vacuolar barite microcrystals (Brook et al. 1980) as were spyrogyra (Kreger and Boere 1969). Barite production occurs in lacustrine ciliates (Loxodes) as well (Hubert et al. 1975; Rieder et al. 1982; Finlay et al. 1983). Fenchel and Finlay (1984) offer evidence for barite crystals, inside the Müller body of the ciliate Loxodes, to act as gravity sensors. These observations suggest that barite production by living cells is a rather common process in aquatic environments.

The observed positive relationship between Ba_{xs} and primary production for the Atlantic (Fig. 3) (Dehairs et al. 1980) is consistent with the production of barite by a wide variety of aquatic microorganisms. This relationship does not necessarily imply that barite is produced only by phototrophic plankton. Indeed, barite production by heterotrophic organisms, feeding on organic detritus, will also result in a positive relation between barite content and primary production.

For our Mediterranean data we have no indications that barite is produced either by algae or microzooplankton such as ciliates. However, the presence of Ba_{xs} maxima at depths below the euphotic zone indicates that barite might be rather produced by heterotrophic organisms.

In Fig. 3 the depth-weighed average Ba_{xs} is plotted against primary production for the watercolumn taken between the surface and the deepest Ba_{xs} maximum. The Atlantic data are from Dehairs et al. (1980). For our Mediterranean data we used a primary production range from 200 to 300 $mgC.m^{-2}.d^{-1}$ (Minas 1970; Jacques 1970; Sournia, 1973; Copin 1974; Coste et al. 1977; Licot 1985). These primary production data concern mainly the NW Mediterranean, and their applicability to the areas of stations SRS and SRG2 (Sardinia Strait and Alboran Sea) may be questioned.

From Fig. 3 it appears that the Western Mediterranean has a higher Ba_{xs} content, relative to the given primary production data, than expected from the relationship observed in the Atlantic. How can these high Ba_{xs} values in the Mediterranean be explained? We can make two hypotheses.

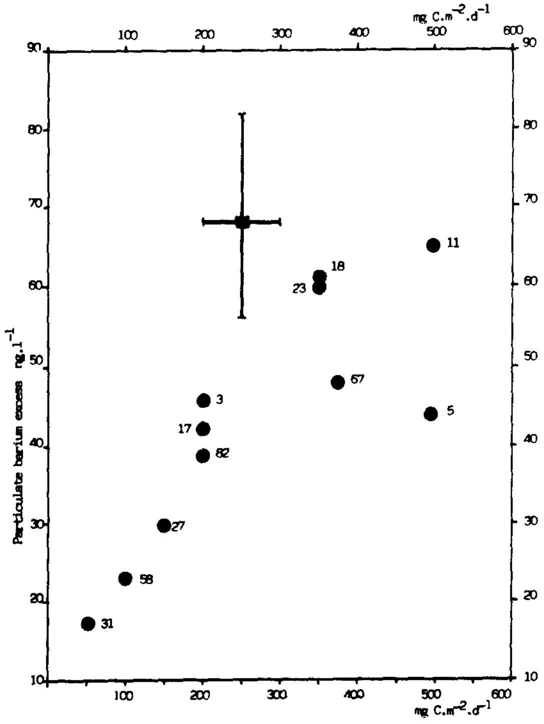

Fig. 3. Depth weighed average Ba_{xs}(in $ng.l^{-1}$) versus primary production (in mg $C.m^{-2}.d^{-1}$) in the watercolumn taken between the surface and the deepest Ba_{xs} maximum. ● GEOSECS Atlantic stations with station numbers; ■ Mediterranean Sea stations, with bars indicating ranges of values.

Table 3. Results of the barite settling and dissolution rate model applied to the Western Mediterranean. See text and appendix for calculation mode; Z_0: upper boundary of considered depth interval; D_{z_0}: particle diameter at upper boundary; Z: lower boundary of considered depth interval; D_z: particle diameter at lower boundary. Column A: calculated residual Ba as barite; Column B: measured excess Ba; column C: dissolution rate J; Column D: integrated dissolution rate J

Station	Zo m	DZo cm × 10^{-4}	Z m	Dz cm × 10^{-4}	Number of particles $N.l^{-1}$ (*)	A $ng.l^{-1}$	B $ng.l^{-1}$	A/B	C $ng.l^{-1}.y^{-1}$	D $ng.cm^{-2}y^{-1}$
SRG2	250	1.15			26,060		93.4		3.9	39
			400	0.99		60	57.7	1.04	2.9	36
			500	0.86		39	40.0	0.98	2.2	66
	1000	2.00			1,140					
							21.5		0.5	28
			1600	1.80		16	17.0	0.94	0.4	20
			2000	1.64		12	13.2	0.91	0.3	12
										Σ201
SRS	500	1.00			35,860		84.5		4.0	50
			650	0.77		45	45.2	0.99	2.4	48
	900	1.80			1,640		22.3		0.6	16
			1200	1.640		18	18.6	0.97	0.5	17
			1600	1.50		13	12.9	1.01	0.4	13
										Σ144

GYL1	500	1.70								
							94.0		2.6	91
			1000	1.46	8,120	60	66.1	0.91	1.9	62
	1150	1.57			9,190		83.8		2.5	62
			1500	1.38		57	60.4	0.94	2.0	65
			2000	0.94		18	17.2	1.05	0.9	32
										Σ312
GYW2	500	1.33					106.0		3.8	76
			800	1.09	19,120	58	58.5	0.99	2.6	91
	1200	1.48			5,040					
							38.5		1.2	51
			1650	1.18		20	20.2	0.99	0.8	32
										Σ250

(*) for a particle population with uniform particle size, the original number of particles at Z_o is maintained at Z.

(1) The Ba_{xs} content is dependent on the dissolved Ba concentration.. The dissolved Ba concentration in Mediterranean surface waters is about 11 μg.l^{-1} (Bernat et al. 1972). This is twice as high as observed in the Atlantic surface waters between 74°N and 40°S (Chan et al. 1977; Broecker and Peng 1982). Thus, increased contents of dissolved Ba could lead to a larger uptake of Ba and a higher production of barite by the plankton. This was indeed observed for in vitro cultures of freshwater algae (Brook et al. 1980). However, at GEOSECS station 82, located 56°15′S, within the Circumpolar Water, the high Ba_d concentration in surface waters (11 μg.l^{-1} f) (Chan et al. 1977) does not appear to have an impact on the local ratio of Ba_{xs} over primary production. This ratio is similar to the one observed for the rest of the Atlantic GEOSECS stations (Fig. 3). The hypothesis that an increased barite production is triggered solely by an increase in Ba_d concentration is therefore not entirely sustained.

(2) The gravitropism hypothesis. Other authors have discussed the possibility for biologically produced barite to have a role in gravitropism. Rhizoid cells of *Chara fragilis* have statolith vacuoles filled with barite crystallites (Schroter et al. 1975; Sievers and Volkmann 1979). Some authors have extrapolated these observations to the aquatic environment and suggested barite microcrystals to have also a role in gravitropism (Brook et al. 1980; Finlay et al. 1983; Fenchel and Finlay 1984).

We likewise suggest here that the barite microcrystals in the oceanic environment may represent a ballast helping the living cell in locating itself in that environment which provides optimum growth conditions (light penetration, nutrient availability . . .). When upward movement is required, these barite crystals may be excreted out of the cell to form the population of discrete crystals we observe in oceanic suspended matter.

If gravitropism is the real reason for biological barite production, the depths of Ba_{xs} maxima will rather reflect local conditions of optimal food supply. For the Mediterranean these can eventually be associated with the advecting oriental water mass. The higher Ba_{xs}/ primary production ratio in the Mediterranean can thus possibly result from an adaptation of the Mediterranean plankton to higher seawater densities. The fact that the lower sigma-t values of surface waters at stations SRS and SRG2 coincide with lower Ba_{xs} values, as compared to stations GYW2 and GYL1 (Table 4), points in this direction. Additional information for the oriental basin, characterized by even higher seawater densities, would be most valuable here to confirm this hypothesis.

This situation is probably not unique for the Mediterranean, but in the open

Table 4. Depth weighed Ba_{xs} and σ_t ranges at stations SRG2, SRS and GYL1, GYW2

Station	Depth range m	σ_t range	Depth weighed Ba_{xs} μg.l^{-1}
SRG2	10–250	26.85–28.97	56
SRS	10–500	27.73–29.07	58
GYL1	10–500	28.69–29.09	76
GYW2	10–500	28.41–29.08	82

Atlantic Ocean, characterized by lower seawater densities, the primary production effect can overwhelm the density effect.

4.4. A mass balance for barium in the Mediterranean

The simple two-boxes steady state model described here is similar to those used previously for other elements in the Mediterranean by Boyle et al. (1985), Laumond et al. (1984) and Bethoux (1980a). The model requires information on (1) the balance between Atlantic inflow and Mediterranean outflow; (2) the different sources of Ba: rivers, atmosphere, the Black Sea; (3) the flux of Ba to the sediment and the dissolution of barite in the watercolumn.

4.4.1. Flows through the Strait of Gibraltar

The inflow of Atlantic water and outflow of Mediterranean water are rather well known. Reasonably close estimations are given by Lacombe et al. (1981), Bethoux (1980b), Boyle et al., (1985). We will use here the flow rates proposed by Boyle et al. (1985); flux in: 4.1 × 10^{16} l.y^{-1}; flux out: 3.9 × 10^{16} l.y^{-1}. The model is not severely affected by the choice of the Gibralter flow rates, with the values given by Bethoux (1980b) (flux in: 5.3 × 10^{16} l.y^{-1}; flux out: 5.05 × 10^{16} l.y^{-1}) producing the largest difference between Ba influx and outflux. The calculated range of source strength will still match these requirements. The dissolved Ba concentration in the inflowing Atlantic water is taken as 5.8 μg.l^{-1} which is the concentration given by Chan et al. (1977) for surface waters at the closest-by GEOSECS station (station 115 in the NE-Atlantic at 25°15′N–26°00′W). The concentration of dissolved barium in outflowing deep Mediterranean waters is taken as 11.5 μg.l^{-1} (Bernat et al. 1972). This yields a Ba inflow of 23.8 × 10^{16} μg.y^{-1} and an outflow of 44.9 10^{16} μg.y^{-1}. However, vertical mixing in the Alboran Sea is calculated to reduce by 17% the phosphorus outflow to the Atlantic (Bethoux 1980a). If a similar reduction in Ba outflow is considered, 7.6 × 10^{16} μg.y^{-1} of Ba are returned to the Mediterranean Sea, increasing the total inflow to 31.4 × 10^{16} μg.y^{-1}. This still leaves a deficit of 30% in the Ba mass balance to be explained and requires a strong source of dissolved Ba.

4.4.2. Rivers

No data for dissolved Ba in rivers entering the Mediterranean Sea are available. From available data for other rivers (Amazon: Moore and Edmond (1984); Zaire: Edmond et al. (1978); Mississippi: Hanor and Chan (1977); Hudson: Li and Chan (1979)) an average "effectively" dissolved Ba concentration in river waters of 51 μg.l^{-1} is calculated. This "effective" concentration includes the Ba desorbed during estuarine mixing. We assume this value to apply also to rivers entering the Mediterranean. River discharge to the Mediterranean is taken as

$2 \times 10^{14} l.y^{-1}$ (UNESCO, 1971–1974). The Ba input by river discharge would therefore amount to $1 \times 10^{16} \mu g.y^{-1}$.

4.4.3. Input from the Black Sea

No data on dissolved Ba of Black Sea waters are available to our knowledge. However, Black Sea output to the Mediterranean must balance input.

$$V_{bs}\,(Ba)_{bs} = V_{ms}\,(Ba)_{ms} + V_r\,(Ba)_r - S(Ba) \qquad (3)$$

where: $V_{bs}(Ba)_{bs}$ and $V_{ms}\,(Ba)_{ms}$ are resp. the Ba flow from the Black Sea to the Mediterranean and vice-versa; $V_r(Ba)_r$ is the Ba flow from rivers into the Black Sea and S(Ba) is the Ba_{xs} sedimenting in the Black Sea.
with:

$$V_{ms}(Ba)_{ms} = 0.2 \times 10^{16} \mu g.y^{-1}$$

from,

$$V_{ms} = 2 \times 10^{14} l.y^{-1} \text{ (Dietrich et al. 1975; Grasshoff 1975)}$$

and,

$$(Ba)_{ms} = 11.5 \mu g.l^{-1} \text{ (Bernat et al. 1972)}$$

$$V_r\,(Ba)_r = 1.6 \times 10^{16} \mu g.y^{-1}$$

from

$$V^r = 3.2 \times 10^{14} l.y^{-1} \text{ (UNESCO 1971; 1974)}$$

and,

$$(Ba)_r = 51 \mu g.l^{-1} \text{ (see above)}$$

S: from the Al (6.8%) and Ba (330 ppm) contents in Black Sea sediments, given by Hirst (1974) and from the Ba/Al ratio in crust (Bowen 1979), we calculate there is no excess Ba for Black Sea sediments; so S must not be considered here. Then $V_{bs}(Ba)_{bs}$ the Black Sea output to the Mediterranean amounts to $1.8 \times 10^{16} \mu g.y^{-1}$.

The two sources mentioned in sections 4.4.2. and 4.4.3 amount to 2.8×10^{16} $\mu g.y^{-1}$. While this value is only indicative of their order of magnitude, it is unlikely that it would be much larger and reach the required amount of $13.5 \times 10^{16} \mu g.y^{-1}$. So, there still is a missing source that amounts to: $13.5 \times 10^{16} - 2.8 \times 10^{16} = 10.7 \times 10^{16} \mu g.y^{-1}$.

4.4.4. Atmospheric deposition.

We deal here with two different questions: (A) what is the fraction of the eolian input that dissolves in seawater? and (B) what is the deposition flux of total Ba to the sea surface?

(A) The fraction of eolian input that dissolves in seawater can be estimated in two different ways:

1. By analogy with the quantity of particulate Ba in rivers that is desorbed with the salinity shock during estuarine mixing. Desorption of Ba is a known phenomenon (Li and Chan 1979) and is observed by the increase of dissolved Ba in estuaries. We observed a 50% decrease in the Ba/Al ratio of suspended matter collected between 0 and 33 per mil salinity in the Scheldt estuary. Li and Chan (1979) observed the concentration of exchangeable Ba ion in sediments from the freshwater zone in the Hudson river to amount to 142 $\mu g.g^{-1}$ of dry sediment. Since we observe about 400 μg of Ba per g of dry suspended matter in the freshwater zone of the estuary, some 200 μg of this amount would represent exchangeable Ba, a value similar to the one given by Li and Chan (1979). Thus, for terrigenic particles, a 50% desorption of the original Ba load may indeed occur worldwide, during estuarine mixing. This data is only indicative, since the nature of the particles settling in the Mediterranean is probably quite different from the one of river sediments and suspensions.

2. Assuming all the detritic material of the sediment in the open Mediterranean comes from the atmosphere, we can calculate the loss of Ba in seawater by comparing Ba/Sc ratios in the atmosphere and in the sediments. Ba/Sc ratios are shown in Table 5.

One measurement of particles filtered from a Mediterranean rain sample immediately after sampling (Dulac 1986), suggests that the desorption of Ba from atmospheric particles could occur in rain. Indeed, data shows 6,500 $ng.l^{-1}$ of particulate Ba and 164 $ng.l^{-1}$ of particulate Sc. The Ba/Sc ratio of 39.6 indicates that most of the desorption probably occured in rain, as this ratio is 160 in Mediterranean aerosols (Table 5).

From the data in Table 5, it appears that: (i) Mediterranean aerosol and Saharan eolian dust is much more enriched in Ba than the average crust; (ii) the Mediterranean sediment shows low Ba/Sc ratios, similar to the crustal ratio; (iii) data from one rain sample (Dulac 1986) show that an important fraction of the Ba from Mediterranean aerosol is already dissolved in rain; (iv) the fraction of Ba lost to the dissolved phase amounts to: $1 - (36/160) = 0.77$.

These two approaches converge, indicating that a dissolution range of 50% to 77% for terrigenous Ba reaching seawater, either by river run-off or atmospheric deposition, is likely.

Table 5. Ba/Sc ratios in different source materials and Mediterranean sediments

Sample	Ba/Sc	Reference
Crust	31	Bowen (1979)
Saharan dust over Atlantic	100	Rahn et al. (1977)
Mediterranean aerosols	160	Arnold (1985)
Particles in rain	40	Dulac (1986)
Mediterranean sediments	36	see Table 2

(B) The deposition flux of total Ba to the sea surface. The published eolian fluxes of particulate Ba to the Western Mediterranean surface (1.3×10^{16}km^2) range from 0.25×10^{16} to 1.07×10^{16} μg.y^{-1} (Arnold et al. 1982; Arnold 1985). For the whole Mediterranean (surface 2.5×10^6km^2), this amounts from 0.48×10^{16} to $2.06 \times 10^{16}$$\mu$g.y^{-1}. These results are based on average concentrations measured during several cruises and a mean aerosol settling velocity of 1 to 3 cm/s taking into account wet and dry deposition. However, the authors point out that despite the fact that such fluxes are much higher than observed for the Atlantic, they still may be largely underestimated. Indeed, these fluxes correspond to a background level of dust and do not take into account the high inputs during episodic dust storms that occur over the Mediterranean (Prodi and Fea 1979; Arnold 1985; Ganor and Mamane 1982). These last authors assume a dust storm input from 160 to 320μg.cm^{-2}.y^{-1} of Al. Considering a Ba/Al ratio of 2×10^{-2} for Saharan dust (from a Ba/Sc ratio for Saharan dust of 100 (Table 5) and a crustal Al/Sc ratio of 5125 (Bowen 1979)), this is equivalent to a Ba-flux from 8×10^{16} to 16×10^{16} μg.y^{-1}. If we consider that 50 to 77% of this amount desorbs when dust particles enter seawater (see A.2 above), a dissolved Ba input from 4×10^{16} to 12×10^{16} μg.y^{-1} is obtained. The missing flux to be accounted for in the mass balance calculation is 10.7×10^{16} μg.y^{-1} (section 4.4.3), what is similar to the values we calculated here for desorption.

We can check the validity of these data if we assume here that the sedimentary record better integrates the overall atmospheric input . We can estimate the accumulation rate of Ba in the sediments, and assuming that sedimentary Ba represents 23% of the atmospheric input (using the $(Ba/Sc)_{Sedim}/(Ba/Sc)_{atm}$ ratio discussed above in A.2), we can calculate the loss range. The sedimentation rate for four cores taken in the western and eastern basin ranges between 4.5 and 30 cm. (1000 y)$^{-1}$ (Vergnaud-Grazzini 1975). Using a sediment density of 2, a porosity of 0.5 and a Ba content of 370 ppm (Table 2), we obtain a sedimentation rate of total Ba ranging between:

$$4.5 \times 2 \times 0.5 \times 370\ 10^{-6}\text{g.}(1000\,\text{y})^{-1} = 1.7\,\mu\text{g.cm}^{-2}.\text{y}^{-1} \text{ and}$$

$$30 \times 2 \times 0.5 \times 370\ 10^{-6}\text{g.}(1000\,\text{y})^{-1} = 11.1\,\mu\text{g.cm}^{-2}.\text{y}^{-1}. \qquad (4)$$

This is equivalent to 4.3×10^{16} and 28×10^{16} μg.y^{-1} and yields from 14.4×10^{16} to 94×10^{16} μg.y^{-1} of dissolved Ba (i.e. 77% of the atmospheric input to the whole Mediterranean). The lower value is consistent with the calculated missing dissolved Ba flux of 10.7×10^{16} μg.y^{-1}.

4.5. Internal cycling

The flux of dissolved Ba from barite dissolution (0.14 to 0.31 μg.cm^{-2}.y^{-1}; see section 4.2) represents an average of $0.6 \times 10^{16}$$\mu$g.y^{-1} for the whole Mediterranean. This flux is at least ten times smaller than the excess Mediterranean outflow, stressing the fact that Ba transport in the Mediterranean is mainly advective.

The production of barite is estimated in two different ways.

First, we assume all Ba_{xs} accumulating in the sediments (i.e. between 0.7×10^{16} and $4.4 \times 10^{16} \mu g.y^{-1}$; from section 4.4.4. B. and the data in Table 2) to be carried by barite. Adding this amount to the release of Ba by dissolution of barite crystals (from 0.4×10^{16} to 0.8×10^{16} $\mu g.y^{-1}$) gives a range for barite production in surface waters from 1.1×10^{16} to $5.2 \times 10^{16} \mu g.y^{-1}$.

Second, we assume suspended barite distributions to obey steady state conditions. Then the magnitude of the vertical flux due to Stokes settling in surface waters should be equal to production. The vertical flux in the Ba_{xs} maximum depth region, using a uniform barite population of 1.5×10^{-4}cm particle size and 100 ng $Ba_{xs}.l^{-1}$, is: $2.3 \times 10^{16} \mu g.y^{-1}$. Thus, barite production should at least match this rate and is therefore consistent with the range obtained previously, using Ba_{xs} data in sediments. The global budget of Ba in the Mediterranean is shown in Fig. 4.

5. Conclusions

1. Vertical profiles of excess particulate Ba in the Western Mediterranean are consistent with a settling and dissolution rate model elaborated previously for the Atlantic; this confirms the fact that Mediterranean Ba_{xs} is also carried by barite microcrystals.

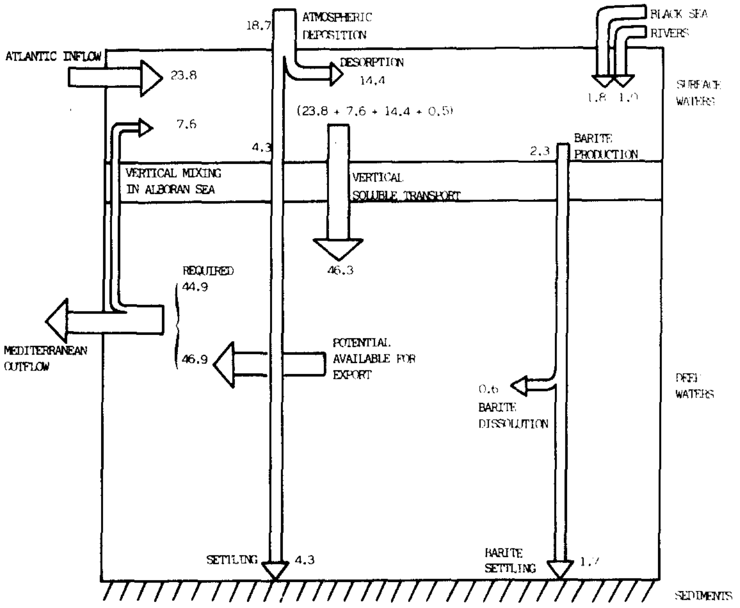

Fig. 4. The Ba budget in the Mediterranean; all fluxes in $\mu g.y^{-1}$. The value for atmospheric deposition is deduced from the sedimentation rate (minimum value, see text).

2. While our previous data for the Atlantic showed the barite content in the upper watercolumn to be positively related to primary production, our present Mediterranean data allow in addition to shed some light on the role of biological barite production in the marine environment. The hypothesis of barite having a role in gravitropism, proposed by others, is sustained here. However, additional data, especially concerning the more saline oriental basin of the Mediterranean, would be most useful to further verify this hypothesis.

3. Excess outflow of dissolved Ba over inflow through the Strait of Gibraltar is accounted for 20% by river discharge and Black Sea outflow. the remaining 80% must be provided through eolian input. The two independent approaches used to estimate the magnitude of eolian Ba input provide evidence that atmospheric deposition can indeed account for the deficit, but stress the important contribution of episodic dust storms.

4. Internal cycling of Ba, through production and dissolution of barite is of minor importance as compared to the fluxes through the system.

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Appendix 1

The change of particle size, inside a given depth interval, due to particle settling (Stokes settling is assumed) and dissolution can be written:

$$D_0 = D\left(1 + \frac{k'.(z - z_0)}{C.D^3}\right)^{1/3} \qquad (1)$$

[from Brun-Cottan, 1976a,b,; Dehairs, 1979 and partially based on theories described in Lal and Lerman, 1973; Wollast, 1974; Lal, 1977].

D_o = particle diameter at the upper boundary z_o

D = particle diameter at the lower boundary z

$k' = (-6/\pi)k$ = dissolution rate constant

$= 0.075 \times 10^{-4}$cm.y^{-1}for barite [Dehairs et al., 1980; Dehairs, 1979].

$$C = \text{Stokes' law constant} = \frac{1.g(\varrho_p - \varrho_w)}{18.\eta} \qquad (2)$$

with

η = seawater viscosity, taken as 1.5×10^{-2}g.cm^{-2}.s^{-1}

g = gravitational acceleration

ϱ_p = barite density = 4.5

ϱ_w = seawater density, taken as 1.02

Appendix 2

J, the amount of matter entering solution per unit volume and unit time can be written:

$$J = (1/3).\varrho_p.N.D^2. \qquad (1)$$

[from Lal and Lerman, 1973; Brun-Cottan, 1976a,b; Dehairs, 1979; Dehairs et al., 1980].

ϱ_p = particle density

N = particle number per unit volume

D = particle diameter

k = dissolution rate constant (see appendix 1)