

The barite-opal-organic carbon association in oceanic particulate matter

James K. B. Bishop

Lamont-Doherty Geological Observatory of Columbia University, Palisades, New York 10964, USA

Barite particles 0.5–5 μm in size are ubiquitous in the ocean and their formation, sinking and dissolution is a major part of the marine barium cycle^{1,2}. Barite formation appears to be caused by biological activity in the upper water column, but the exact mechanism is unknown. Analysis of 1–53 μm and >53 μm sized particles obtained by large volume *in situ* filtration in the Atlantic suggests that barites are formed in the >53 μm fraction in near-surface waters and released into the 1–53 μm fraction at depths below the euphotic zone. Scanning electron microscopy and energy dispersive X-ray fluorescence analysis of both size fractions shows first, that barites are formed almost exclusively in microenvironments containing decaying organic matter and the remains of siliceous plankton, and second that barites do not appear to be actively formed by the planktonic organism sampled. This explains the origin of suspended barite, and the similarity of dissolved Si and Ba distributions in the ocean. Suspended and sedimented barite may indicate the intensity of organic matter regeneration in the water column.

Barium has been extensively mapped in the world's oceans because of its surrogate role as a stable isotope of radium-226, a radioactive tracer of ocean circulation^{3–5}. A stable form is required as ²²⁶Ra is heavily involved in the biogeochemical cycle^{3,5,6}. In sediments, Ba occurs mainly as barite (BaSO_4) and is strongly enriched below equatorial zones of high biological productivity^{7,8}. A secondary source of sedimentary barite may be hydrothermal activity near mid-ocean ridges⁹. Recently, barite distributions in sediment cores have been proposed as an index of palaeoproductivity^{10,11}. Such applications require a better understanding of how Ba is involved in the biogeochemical cycle.

There has been much controversy about the mechanism by which biological activity causes barium to be transformed from dissolved into particulate form. Hypotheses include: (1) formation of barite in microenvironments enriched with sulphate from decaying organic matter; (2) incorporation of barium into the skeletons of siliceous plankton; and (3) active precipitation of

barite by other planktonic organisms. The first was based on seawater being undersaturated with respect to barite^{3,12}, and is supported by observations of barite in faecal debris¹. The second was suggested by the similarity of dissolved Ba profiles to those of the nutrient element Si⁶; by strong Ba enrichment in Black Sea plankton samples dominated by the diatom *Rhizosolenia*^{13,14}; and by the covariation of Ba and Si in estuaries¹⁵. This hypothesis was disfavoured when plankton samples from the Pacific Ocean¹⁶ were found to be 10–100 times lower in Ba than Black Sea plankton, and cultures of *Rhizosolenia* showed similarly low levels¹. A phytoplankton source was also ruled out as many particulate Ba profiles exhibit maxima at 100–200 metres, well below the euphotic zone^{1,2}. The third hypothesis^{1,17} was based mainly on the correlation between suspended barite concentration and primary productivity, and on the possible existence of planktonic protozoa related to the benthic protozoan *Xenophyophora*¹⁸, a known barite precipitator. Support also came from the discovery of the dominant role of the protozoan *Loxodes* in the freshwater barium cycle¹⁹. But a comparison of the freshwater *Loxodes* with its close marine relative *Remanella* showed that the marine form precipitated celestite and not barite²⁰. A planktonic barite precipitator has yet to be identified. This study seeks to clarify the mechanism of barite precipitation in seawater.

Particulate matter samples, divided into 1–53 and >53 μm size fractions, were collected by large volume *in situ* filtration²¹ from the upper 1,000 m of the northwestern Atlantic²². The >53 μm particle size fraction was not adequately sampled previously^{1,17} because samples were obtained by filtration of seawater collected by 30-litre Niskin bottles^{23,24}. Large volume filtration overcomes this bias as 1,000 times more water is filtered and samples are collected *in situ*. The 1–53 μm size fraction collected by large volume *in situ* filtration is comparable to the slowly sinking particle population sampled by the Niskin filtration method²³.

Most 1–53 μm Ba profiles showed the lowest concentrations in the euphotic zone (maximum depth, 70 m) and a large increase to high values by 100–200 m (Fig. 1a–d). Concentrations were lowest in waters of Sargasso Sea origin (Fig. 1c) and highest in the Slope Water (Fig. 1d), consistent with the biological productivity of these waters. This agrees with previous findings¹.

In contrast, >53 μm Ba was generally highest in the euphotic zone and decreased to uniform levels by 200 m. In some near surface samples, over 90% of the total Ba was in the >53 μm fraction. Replicate profiles taken one week apart (Fig. 1a and b) in the same water mass show that partitioning of Ba between 1–53 and >53 μm fractions can vary significantly in surface

Fig. 1 Particulate barium distribution in 1–53 μm (small symbols) and >53 μm (large symbols) size fractions in the core waters of Warm-Core Ring (WCR) 82B on a, 18 June and b, 24 June 1982; c, newly formed WCR 82H, representative of the Sargasso Sea, 7 October 1982; and d, Slope Water, 15 October 1982. Although data from WCR is used in 3 of 4 examples, these profiles are a representative selection of those collected by large volume *in situ* filtration from the Slope Water, Gulf Stream and Sargasso Sea in the north-west Atlantic. Barium was extracted from filter subsamples in 0.6M HCl overnight at 60 °C and the resulting solutions were analysed by graphite furnace atomic absorption spectroscopy (J.K.B.B. manuscript in preparation). Blank corrections were minor. Relaching of leached samples demonstrated that barium extraction was complete. Error bars indicate the precision of each data point, which in most cases is smaller than the symbol.

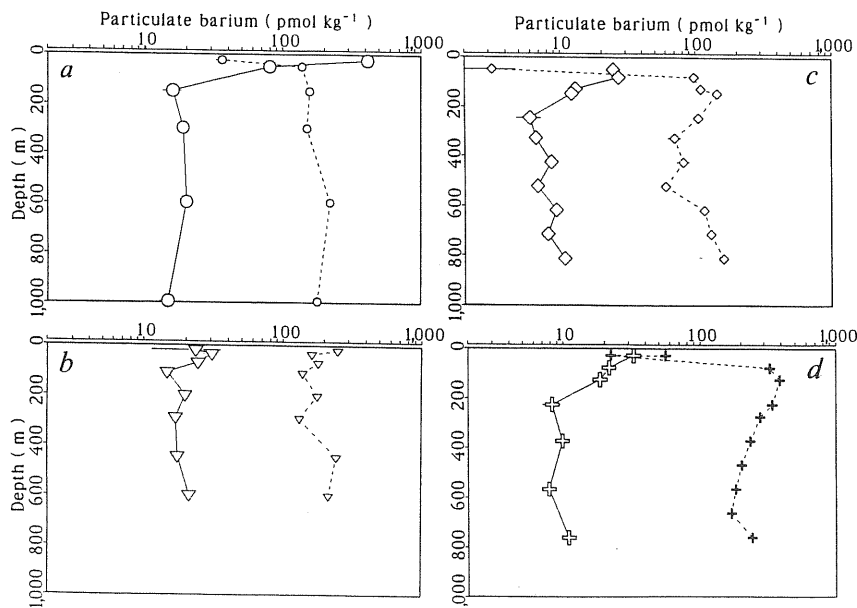
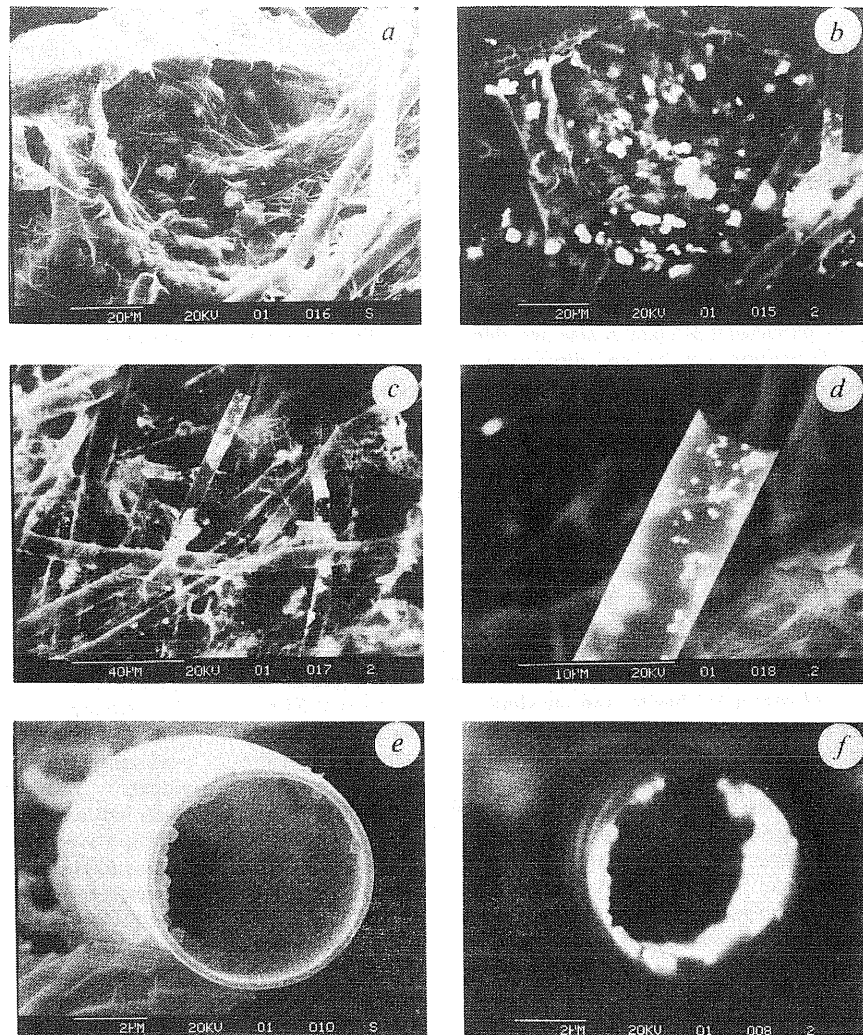


Fig. 2 *a*, Secondary electron (SE) image $\times 1,000$ of barites beneath organic matter in the presence of opal. $>53 \mu\text{m}$ sample from 24 m (Fig. 1*a*). *b*, Backscattered electron (BSE) image of the same organic-silica rich environment. Barites here range from sub-micron to $5 \mu\text{m}$ in size. Barite particles appear bright against the organic carbon and silica of the sample as BSE intensity is determined by atomic number (z) of the sample. This greatly facilitated the search for Ba ($z = 56$) in samples dominated by elements C, O, Si and Ca (z ranging from 6–20). *c*, BSE image $\times 650$ showing the barites in degraded *Rhizosolenia* frustules but a lack of barite in intact members of the same species. *d*, BSE image. Transverse view of broken *Rhizosolenia* frustule at $\times 2,000$. *e*, Axial view (SE image) of same *Rhizosolenia* frustule $\times 10,000$. *f*, BSE image corresponding to *e*. Sample was carbon coated and analysed using a Cambridge SEM, beam energy 20 kV, with KEVEX energy dispersive X-ray fluorescence analysis system. Scale bars: *a*, *b*, $20 \mu\text{m}$; *c*, $40 \mu\text{m}$; *d*, $10 \mu\text{m}$; *e*, *f*, $2 \mu\text{m}$.



waters. All profiles (not just those shown) suggest that Ba is formed in $>53 \mu\text{m}$ size fraction in shallow waters and released to the $1\text{--}53 \mu\text{m}$ fraction by 100–200 m. The Ba formation process appears to occur episodically.

Examination by scanning electron microscopy (SEM) and energy dispersive X-ray fluorescence (EDXRF) of several $1\text{--}53 \mu\text{m}$ samples from the 100–200 m Ba maximum showed mainly individual barite particles ranging from $0.5\text{--}5 \mu\text{m}$ in size. A small proportion of the barites contained minor amounts of strontium (Ba: Sr > 5), but most contained only Ba and S, again in agreement with Dehairs *et al.*¹. No barite was found in any intact organism.

The $>53 \mu\text{m}$ sample from 24 m (Fig. 1*a*) was dominated by the diatom *Rhizosolenia* (uncountable because they occurred in dense mats in the sample) and the dinoflagellate *Ornithocercus* (850 per litre), and contained the highest amount of Ba. Barites occurred as clumps beneath organic and siliceous material (Fig. 2*a* and *b*) and also as clumps or strings of crystals inside broken *Rhizosolenia* (Fig. 2*c* and *f*). Individual members of such clusters were chemically and morphologically similar to individual barite particles found in the $1\text{--}53 \mu\text{m}$ fraction and to those described previously¹. Barites were not found in any structurally intact *Rhizosolenia*, or in association with broken or intact *Acantharia*, or with any of the numerous dinoflagellates in the same sample. Analysis of another Ba-rich $>53 \mu\text{m}$ sample from 20 m in the Slope Water also showed the barite-opal-organic matter association.

The SEM/EDXRF study of barite-particle associations was extended to include some $>53 \mu\text{m}$ samples collected from the southeastern Atlantic^{25,26}. The Ba results²⁵, although giving con-

sistent profiles, showed little consistency with plankton group abundances or chemistry of the same samples. Sample selection was based on highest amount of Ba in the profile or on enrichment of specific organism groups. Like the North Atlantic zone, the $>53 \mu\text{m}$ Ba maxima were found in the euphotic zone. Samples were: C115-5-39N (R V *Chain* 115, Sta. 5, 40 m; Ba = 900 pmol kg^{-1}) dominated by *Acantharia* and dinoflagellates; C115-5-44N (88 m; Ba = 80 pmol kg^{-1}), Foraminifera, broken and dissolving *Acantharia*; C115-6-47N (52 m; Ba = 123 pmol kg^{-1}), *Rhizosolenia*; C115-8-55N (20 m; Ba = $1,450 \text{ pmol kg}^{-1}$), centrate diatoms. No intact organism contained barites in any of these samples. Once again, barites dominantly occurred as clusters in association with organic matter and the remains of siliceous plankton.

The high concentration of barite in the *Rhizosolenia*-rich sample from the North Atlantic provides renewed credibility for the old Black Sea plankton data¹³. Also, plankton tows from the Pacific¹⁶ off Oregon described as “practically pure phytoplankton detritus” may have been misidentified *Rhizosolenia* mats containing comparable quantities of barite. The samples left a white precipitate (said to be SrSO_4) insoluble in concentrated HNO_3 , HCl and HF (ref. 16) after sample extraction. Barite matches the chemical properties of the white precipitate better than SrSO_4 as the latter is easily soluble in the HNO_3 and HCl and barite is relatively insoluble. These samples were the most Ba-rich of all Pacific samples reported¹⁶ (320 p.p.m. Ba) and, when reanalysed later (J. Martin, personal communication), were twelve times more concentrated ($3,800 \text{ p.p.m. Ba}$) than originally thought.

The occurrence of barite in broken *Rhizosolenia* and not in

intact members of the same species reconciles the high Ba content in *Rhizosolenia*-rich plankton samples¹³ with low Ba content in actively growing cultures of this species¹. The consistent barite-opal association explains the observed first-order covariation of dissolved Ba and Si in the ocean and estuaries. The fact that secondary differences exist in profile systematics of these two elements^{2,6}, especially in the upper several hundred metres, suggests: (1) that some (but not all) siliceous plankton are important in the oceanic barium cycle and (2) that barite is formed in microenvironments rich in decaying organic matter and opal. This also explains why plankton group abundances and Ba are not well correlated in the water column.

These results support the hypothesis that barite precipitation in the water column occurs in microenvironments enriched in sulphate from decaying organic matter³. How much organically bound sulphur is required to react to form the observed barite? On a molar basis, diatom C:Si is about 2:1 and C:S is about 100:1, which yields a Si:S ratio of about 50:1. Because dissolved Si and Ba covary in a ratio of 1,300:1, the reaction of organically bound S to form barite in microenvironments needs to be only 4% efficient if diatoms are the only sulphur source. As other

plankton groups contribute to the particulate sulphur pool, the 4% estimate is an upper limit. The remains of siliceous organisms also appear to catalyse barite formation. Fresh silica surfaces may adsorb cations such as Ba better than other biogenic inorganic phases (J. Martin, personal communication), or diatom frustules may form better microenvironments than other plankton groups. Thus, it is concluded that conditions favouring barite formation (decaying organic matter and silica) are found in recently dead siliceous plankton and large aggregate particles, such as faecal material²⁶ and marine snow²⁷.

No support was found for the hypothesis that marine plankton (large or small) actively form barite. The use of barite as an indicator of organic matter regeneration intensity in the water column and sediments warrants further development. The diverse morphologies of suspended barite¹ could provide clues as to the mode of organic matter regeneration.

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