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An Experimental Investigation of Barite Formation in Seawater

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Abstract—We report results from time-series decay and sequential leaching experiments of laboratory cultured and coastal plankton to elucidate the mechanisms controlling barite formation in seawater. Batch-cultured diatoms (*Stephanopyxis palmerina*) and coccolithophorids (*Emiliania huxleyi*) were let to decay in the dark for 8–10 weeks, suspended in aerated seawater. The development of barite crystals was monitored by Scanning Electron Microscopy (SEM). A similar experiment was conducted with plankton collected during the spring-bloom in Vineyard Sound (MA). In addition to SEM, suspended particles were sequentially leached for Ba (distilled water rinse; 10% (v/v) HNO_3 rinse at room temperature; 30% (v/v) HCl at 80°C overnight; 50% (v/v) HNO_3 at 80°C overnight) immediately after collection, and after 10-week decay in seawater, in seawater poisoned with $HgCl_2$, and in seawater spiked with ^{135}Ba.

Both experiments showed an increase in the number of barite crystals during decay. The spring-bloom plankton had initially a large pool of labile Ba, soluble in distilled water and cold dilute HNO_3 that was lost from the plankton after 10-week decay in both axenic and nonaxenic conditions. In contrast, Ba in the decayed plankton samples was predominantly in forms extracted by hot HCl and hot HNO_3 acids, which were attributed to presence of barite Ba and refractory organic Ba respectively. The increase in barite crystal counts under a Scanning Electron Microscope (SEM), the increase in HCl extractable Ba relative to organic carbon, and the loss of a large fraction of Ba during plankton decay suggest that living plankton consists of a relatively large pool of labile Ba, which is rapidly released during plankton decomposition and acts as the main source of Ba for barite formation in supersaturated microenvironments. Since mass balance indicates that only a small proportion (2 to 4%) of the labile-Ba pool is converted to barite, the availability of microenvironments that could locally concentrate Ba released by plankton decay seems to be the main limiting factor in barite precipitation. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

Barite formation in seawater and its flux to the seafloor appear linked to surface productivity (Goldberg and Arrhenius, 1958; Church, 1979; Bishop, 1988; Dehairs et al., 1987, 1990, 1992; Paytan et al., 1996). Barite fluxes estimated from the sedimentary record could thus potentially provide quantitative information on past changes in primary production (e.g., Schmitz, 1987; Shimmield 1992; Gingele and Dahmke, 1994; Paytan et al., 1996; Ganeshram et al., 1995; Francois et al., 1997; Ganeshram and Pedersen, 1998). Fluxes of organic carbon and Ba measured with sediment traps in different oceanic regions have been used to develop preliminary algorithms that link excess Ba rain rate (i.e., the flux of barium in excess to the contribution from crustal material) to export production (Dymond et al., 1992; Francois et al., 1995; Nurnberg et al., 1997). However, seasonal (Dymond and Collier, 1996) and geographic (Dymond et al., 1992; Francois et al., 1995) variations in the relationship between carbon and barium fluxes indicate that additional factors modulate the relationship. Before developing a truly reliable paleoproductivity algorithm, these factors must thus be identified, and one important step in that direction is elucidating the exact mechanism of barite formation in seawater.

The presence of barite crystals throughout the water column has been a long-standing puzzle, mainly because seawater is largely undersaturated with respect to barite (Monin et al., 1999). Barite formation thus requires either direct biologic mediation or abiotic precipitation within supersaturated microenvironments. Although the presence of barite crystals in the cytoplasm of specific groups of freshwater planktonic organisms has been reported (Brook et al., 1980), their occurrence in marine species has not yet been documented and appears much too rare to explain the ubiquitous presence of barite in seawater. Instead, mechanisms invoking indirect biologic mediation and abiotic precipitation from supersaturated microenvironments within settling particles have retained the most attention. The clear association of barite crystals with fecal pellets and decaying diatom aggregates, documented by scanning electron microscopy (Dehairs et al., 1980; Bishop, 1988), supports this general view. Two mechanisms that could produce barite supersaturation within microenvironments of settling particles have been proposed. One mechanism invokes the degradation and oxidation of organic sulfur to produce sulfate (Chow and Goldberg, 1960; Dehairs, 1980; Bishop, 1988), while the other rely on the release of both Ba and sulfate from the dissolution of Ba-enriched celestite ($SrSO_4$) (Bernstein et al., 1992), a mineral produced by acantharians that readily dissolves in seawater. The importance of either of these two mechanisms, however, has not yet been unambiguously demonstrated. Another possibly important factor that has been largely overlooked so far is the release of Ba from decaying organic matter. Stecher and Kogut (1998) have recently documented a dramatic

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decrease in dissolved Ba concentration at the end of the spring bloom in the Delaware estuary, and a rapid regeneration during the following month. Although it was not clear whether the decrease in dissolved Ba concentration was due to direct biologic uptake or abiotic adsorption on planktonic surfaces, this observation points to the potential of phytoplankton as a vector for locally concentrating Ba and promoting the formation of supersaturated microenvironments for barite precipitation.

Elucidating the sources of S and Ba and the exact mechanism of barite formation would have important implications for the potential of barite as a paleoproductivity indicator. If it can be demonstrated that celestite is a prerequisite or an important contributor to barite formation, then its potential would be lessened, since barite formation would reflect the presence of acantharia rather than export production. On the other hand, if planktonic organic matter is the primary source of Ba and/or sulfate that produces supersaturation in microenvironments, the prospect for developing a quantitative Ba-based paleoproductivity proxy would improve, pending identification of the extraneous factors that may be affecting barite formation (e.g., catalytic effect of opal surfaces; Bishop, 1988; aggregation and fecal pellet formation; Dehairs et al., 1980) and better constraints on the diagenetic processes regulating its preservation in marine sediments (McManus et al., 1998).

We present here the results from two sets of laboratory decay experiments. The first experiment demonstrates that barite is rapidly produced in suspensions of decaying phytoplankton grown in non-axenic cultures and that acantharia, opal surfaces, and fecal pellets formation are not prerequisites, although they may modulate barite formation in the environment. The second experiment suggests that barite precipitation occurs mainly as a result of Ba release from plankton in surface waters. Ba associated with plankton is very labile and readily released into the surrounding water during the early stages of organic decay. A small fraction of this Ba precipitates as barite, presumably in microenvironments that became supersaturated due to the rapid release of labile Ba. These results are consistent with the ubiquity of barite in seawater and are encouraging for the eventual development of a quantitative Ba-based paleoproductivity proxy.

2. MATERIAL AND METHODS

2.1. Decay Experiment with Laboratory Cultures of Phytoplankton

Stephanopyxis palmerina (diatom) and *Emiliania huxleyi* (coccolithophorid) were grown by batch cultures in 12L acid leached glass carboys in filtered (0.8 μm) and autoclaved natural seawater medium using methods and materials reported in Goldman et al. (1992). At the end of the logarithmic growth phase (*S. palmerina*: 94 cells/mL; *E. huxleyi*: 160 cells/mL) the carboy was moved to the dark to start the decay process. The cultures were kept aerated at room temperature and gently suspended by bubbling air filtered through a 0.2 μm teflon filter. Aliquots of 200 mL of suspension were sampled after gentle mixing at different time intervals and filtered through acid-cleaned 0.45 μm 12 mm diameter nucleopore filters. The particulate material collected on the filters was rinsed with ultrapure double distilled de-ionized water (DDW), and dried in an oven at 60°C before SEM investigation.

2.2. Decay Experiment with a Natural Population of Coastal Plankton

4 × 30L samples (A, B, C, D) of coastal seawater were collected in Vineyard Sound (MA) on May 5, 1999 in acid-cleaned PE carboys. Samples were taken from a pole upstream of a rubber boat to avoid contamination during sampling. Upon return to the laboratory, one carboy (A) was gently shaken. An aliquot of 12.3 kg was immediately filtered on 0.45 μm 37 mm diameter Nucleopore filters for subsequent Ba leaching and dissolved Ba measurement. Another 7.05 kg aliquot was filtered on 0.8 μm 47 mm diameter precombusted GFF filters for POC measurements. In addition, 50 mL were also filtered through a separate 12 mm diameter, 0.45 μm Nucleopore filter for Scanning Electron Microscopy. Initial screening of this filter revealed the presence of large numbers of broken diatom frustules consistent with the notion that diatoms dominate plankton assemblages in Vineyard Sound. The remainder of sample A was then covered in a black plastic bag to stop photosynthesis and aliquots were taken after gentle resuspension at the end of the decay experiment to monitor the growth of barite in the particulate phase by SEM. It was then assumed that the other 3 carboys (B, C and D) had the same initial conditions as the first one (A). One was left as is (B), another was spiked with ^{135}Ba increasing dissolved Ba concentration by 50.7 nmoles/kg but keeping Ba concentrations well below saturation (Monnin et al., 1999; Rushdi et al., 2000) (C), and the last was poisoned with 200 μl of saturated $HgCl_2$ solution for every liter of seawater (D). The three carboys were then immediately closed, covered in a black plastic bag and left to decay for 10 weeks. We did not sample these carboys during the course of the experiments to avoid Ba contamination. At the end of the experiment the samples were shaken and large aliquots (ca 5 to 15 kg) were filtered on several 0.45 μm 37 mm diameter Nucleopore filters for sequential Ba leaching and dissolved Ba analysis, and on precombusted GFF (0.8 μm 47 mm diameter) for POC analysis. The two unspiked samples (B and D) were analyzed for Ba concentration, while the spiked sample (C) was used to measure Ba isotopic ratios ($^{135}Ba/^{138}Ba$). Procedural blanks consisted of manipulating and leaching blank filters in parallel with the sample filters.

2.3. Leaching Procedure

The filters (and filter blanks) from the initial sample A and the final samples B, C and D were subjected to the following sequential leaching steps:

1. Water: Deionized water was first used to rinse dissolved Ba associated with residual seawater. This step also extracts weakly sorbed Ba and Ba in the cytoplasm released during cell lysis.
2. Dilute nitric acid: The samples were added to 10% (v/v) HNO_3 (*Seastar Ultra-pure*) at room temperature for a few minutes to remove readily exchangeable and easily hydrolyzable organic-bound Ba.
3. Hot hydrochloric acid: HCl 30% (v/v) (*Seastar Ultra-pure*) was kept at 80ºC overnight to mainly dissolve barite. Barite is relatively insoluble in HNO_3 but very soluble in hot HCl (Paytan, 1995). This property was also verified by a dissolution experiment that was conducted with barite produced in the laboratory by adding $BaCl_2$ to seawater. No weight loss of laboratory-produced barite was observed after rinsing with dilute nitric acid but complete dissolution was achieved with hot HCl within five hours. SEM examination confirmed the absence of barite after hot HCl treatment.
4. Hot nitric acid: 50% (v/v) HNO_3 was kept at 80ºC overnight to oxidize refractory organic matter and release the associated Ba.

2.4. Analytical Methods

Dissolved Ba was measured by high-resolution ICP-MS (Element; MAT-Finnigan) at the Wood Hole Oceanographic Institution using methods described in Rodushkin and Ruth (1997). The instrument was calibrated with standard solutions (*Spex CertiPrep, Inc*) and indium as an internal standard. Certified seawater NASS-5 (NRC-Canada) was routinely run with seawater samples to cross check the accuracy of the measurements. Seawater samples were diluted 10-fold and acidified with 5% (v/v) HCl (*Seastar Ultra-pure*) before analysis. The leachates were similarly diluted to appropriate concentrations and acidified if required before analysis. The samples were aspirated into the plasma using a Meinhardt nebulizer and the analysis required ca. 2ml of solution. The analytical precision for Ba determinations was better than ± 5%. Ba isotopic ratios (experiment C) were also measured on the

HR-ICPMS. Repetitive analysis of seawater (natural abundance) did not reveal mass biases during isotope ratio determinations on the ICP-MS within the precision of our isotope ratio measurements (± 2%). POC were determined by flash-combustion gas chromatography (Carlo-Erba NA 1500) as described by Verardo et al. (1990). Analytical precision was ± 1.25% for total carbon. All precision estimates are reported as 1σ Relative Standard Deviation. For barite crystal identification, the oven dried Nucleopore filters were carbon-coated in a vacuum evaporator for scanning under a SEM. The analyses were performed in an Etec Autoscan, Model U-1, SEM; a Kevex 7000 energy dispersive X-ray spectrometer (EDS) employing methods and materials described in Commeau et al., (1992).

3. RESULTS AND DISCUSSION

3.1. Decay of Cultured Phytoplankton

In both decay-experiments conducted with cultured phytoplankton, barite was not detected before the initiation of the decay in the dark. With *E. huxleyi*, eight barite crystals per liter were counted after one week in the dark, and the number increased linearly to 80 per liter after 8 weeks of incubation (Fig. 1). The size (~2 μm) and morphology of the crystals (Fig. 2) were similar to those collected from seawater (Dehairs et al., 1980; Bishop, 1988). Taking a mean volume of 4 μm^3 per crystals, 80 crystals per kg of seawater would correspond to: 320 μm^3/kg × 4.5 10^{-3} ng/μm^3 × 0.59 ≈ 1 ng Ba/kg. Although this is lower than the particulate Ba concentration typically found in surface waters (15–20 ng Ba/kg; Bishop, 1988), one must consider that only a small fraction (e.g., 1.6% in a sample from coastal surface water; see below) of particulate Ba present in surface water is barite, so that the level of barite formation in the culture is not dramatically different from natural samples.

The number of barite crystals produced by the decay of the diatom culture was slightly less, increasing from 0 to 40 crystals/L over a ten-week period. This may reflect the lower cell counts in the diatom culture (94 cell/mL vs. 160 cell/mL for *E. huxleyi*) or undersampling of suspended barite. Diatoms tend to form aggregates and sink while decaying. The larger scatter in the barite counts in the diatom experiment reflects the greater difficulty in obtaining representative aliquots of suspension in the presence of aggregated particles.

Since barite was absent in the cultures of living cells, this experiment unambiguously demonstrates that barite precipitation occurs during phytoplankton decay. In addition, as barite was produced in the absence of acantharia and opal (in the *E. huxleyi* culture), and without fecal pellet packaging, we conclude that these factors are not prerequisite for barite formation.

3.2. Decay of Coastal Plankton

Initial POC concentration (34.4 $\mu g\ C_{org}$/kg) was measured in one of the four duplicate carboys (Sample A; T_0). After 10 weeks of incubation in the dark, POC dropped by 31–42% in the un-poisoned samples (B and C) and by 24% in the sample poisoned with $HgCl_2$ (Table 1; T_f).

In contrast to the experiment with cultures, SEM clearly identified the presence of barite in the initial sample (Fig. 2). After 10 weeks of incubation in the dark the number of barite crystals appeared to have increased by ~ 30% (Table 1).

Sequential leaching documents a large drop in the total Ba/POC of the suspended particles during incubation and large differences in the chemical forms of Ba present in the initial and final samples (Table 2; Fig. 3). The bulk (>90%) of particulate Ba in the initial sample (Sample A, T_0) consisted of very labile Ba that could be leached by de-ionized water and cold dilute HNO_3. Release of Ba by deionized water (ca. 20% of total leachable particulate Ba) could result from residual seawater adhering to particles after filtration, desorption of weakly sorbed Ba^{++} and Ba release from cell lysis as a result of changing osmotic pressure. Ba released by a brief rinsing with dilute nitric acid (ca. 70% of the total leachable particulate Ba) could result from ion exchange or hydrolysis of labile organic matter.

This labile Ba fraction was reduced from 350 ng/kg (90% of the initial total leachable particulate Ba) to <5 ng/kg (10% of the final total leachable Ba) after 10 weeks in the dark, independently of the presence of $HgCl_2$ to stop bacterial decomposition (Table 2; Fig. 3). Likewise, the "labile Ba"/POC ratio dropped from 10.2 ng/μg before decay to <0.2 ng/μg (Table 2). Since very little Ba could be released from the decayed

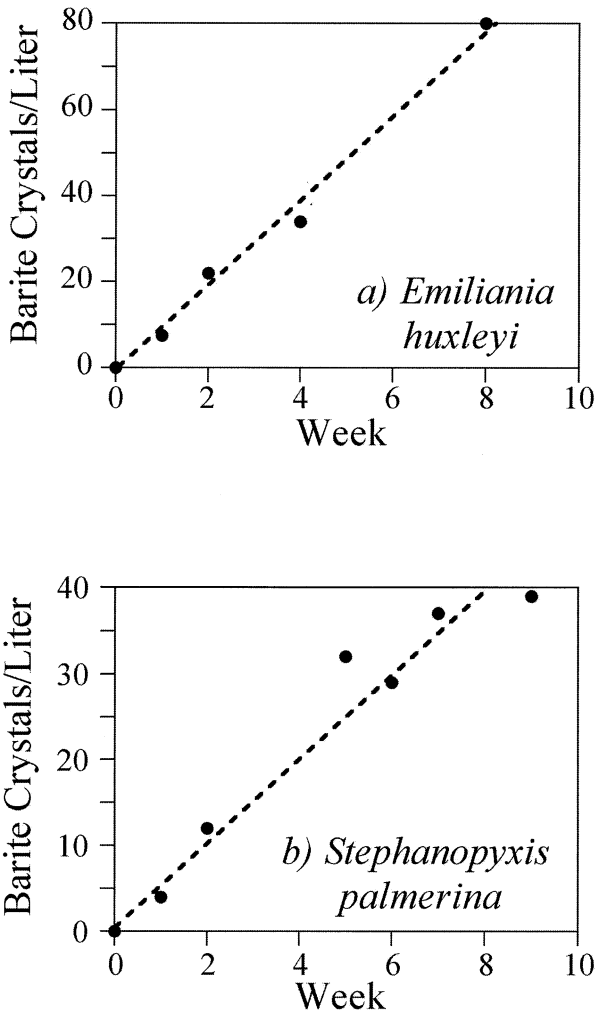

Fig. 1. Results from incubation experiments of batch cultured *Emiliania huxleyi (upper) Stephanopyxis palmerina (lower)*. Plots show the increase in the number of barite crystals in the suspension of decaying phytoplankton with time. Note that no barite crystal was identified at the beginning of the decay experiments in the plankton cultures.

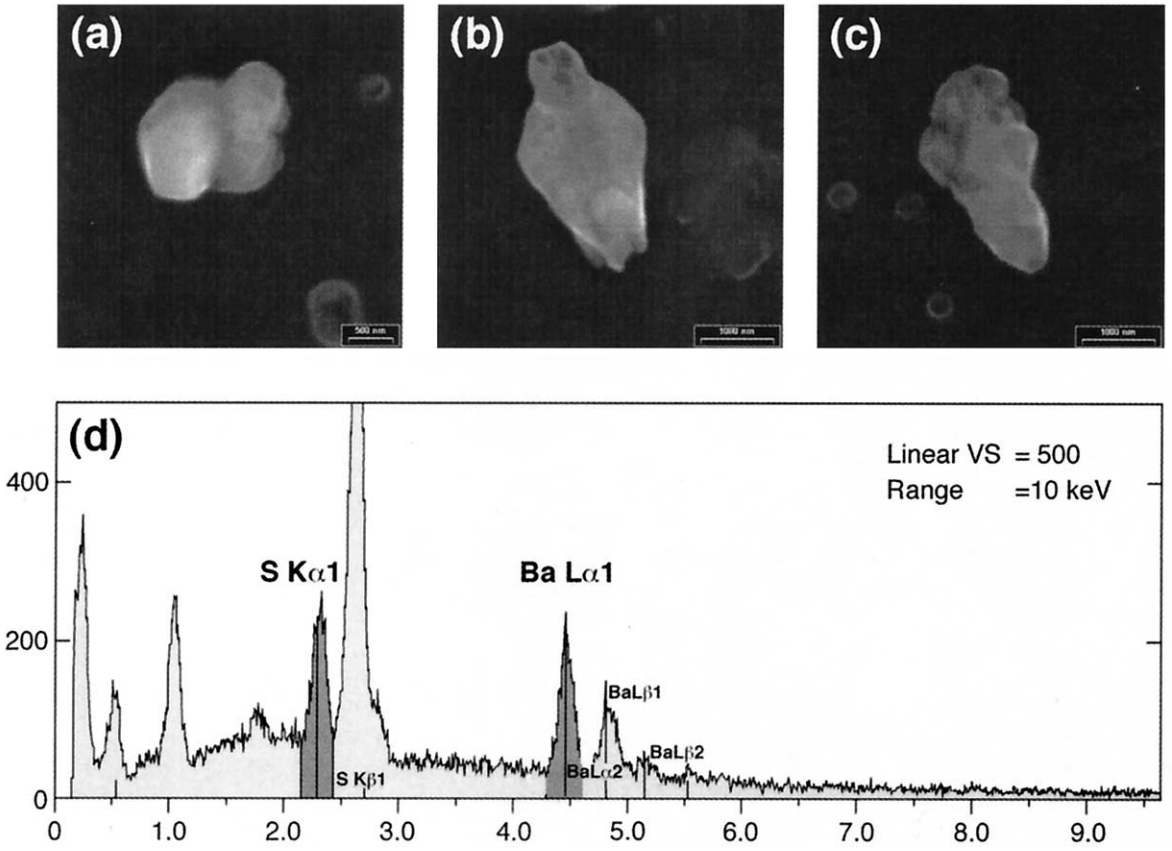

Fig. 2. SEM micrographs obtained during phytoplankton decay experiment. (*a&b*) Barite crystals identified after 8-week decay of *E. huxleyi* (Right Panel in Fig. 1). (*c*) Barite crystal observed after the natural population of coastal plankton was left to decay in the dark for 10 weeks. The scale bars are 500 *nm* in micrograph *a* and 1000 *nm* in *b&c*. (*d*) EDXA spectra of barite particles isolated after 10-week decay of coastal plankton highlighting the Ba and S peaks.

samples with deionized water, cell lysis or desorption must be the main source of water-leachable Ba in the initial samples, since residual seawater would have similarly affected the postincubation samples. Likewise, Ba released by dilute acid decreased dramatically (from 275 ng/kg to <5 ng/kg; Table 2; Fig. 3). The ion-exchange sites or the hydrolyzable organic matter and associated Ba have been removed from the decaying particles, either by oxidation or solubilization. Considering that little difference was observed between the poisoned and unpoisoned sample (B vs D) and assuming that $HgCl_2$ was effective at stopping microbial decomposition, abiotic solubilization would seem to be the main agent for the release of this labile fraction of particulate Ba. Of possible significance for this pool of Ba is the recent recognition of the pervasiveness of transparent exopolymer particles (TEP), apparently produced by metal bridging between soluble polysaccharides exuded by phytoplankton and bacteria (Alldredge et al., 1993). This substrate could provide ion-exchange sites for Ba (Stecher and Kogut, 1998), from which it could be readily displaced by a mild acid treatment. Highly ordered polysaccharides associated with the cell walls (Kloareg and Quatrano, 1988) could also provide ion-exchange sites for Ba.

Table 1. The POC concentration and the barite crystal counts of the coastal plankton sample before (Sample A) and after (Sample B, C, D) incubation in the dark for 10 weeks.

Carboy	POC (μg/kg seawater)	barite (crystals/Liter)
Sample A (T_0)	34.4	2640
Sample B (T_f): unspiked, not poisoned	19.8	3480
Sample C (T_f): ^{135}Ba-spiked, not poisoned	23.7	n.a.
Sample D (T_f): unspiked, poisoned	26.1	n.a.

Leaching with hot HCl (30% v/v) confirms SEM observations of the presence of barite (6 ng Ba/kg) at the start of the experiment. Our leaching protocol indicates however that barite amounts to only a small fraction (1.6%) of the total leachable Ba present in the initial sample (Table 2; Fig. 3). After decay, the hot HCl-soluble particulate Ba increased two to three-fold and became a major component of particulate Ba (40% of the total leachable Ba), whether or not $HgCl_2$ was present (Fig. 3; Table 2).

A small fraction of the total particulate Ba present in the initial sample (~ 8%) required oxidation by hot nitric acid (50%) for its solubilization. It decreased only slightly during the incubation, by 45% without $HgCl_2$ and by 24% in the

Table 2. Ba phase transformation during decay.

	Sample A (T_0)	Sample B (T_f) not poisoned	Sample D (T_f) poisoned
	ng Ba/kg (%ΣBa_p)		
Seawater	8070	9080	9070
DDW	75 (19.4%)	0.3 (1.0%)	0.3 (0.6%)
HNO_3 cold 10% (v/v)	275 (71.2%)	2.5 (8.3%)	4.5 (9.6%)
HCl. hot 30% (v/v)	6 (1.6%)	12 (40.0%)	20 (42.6%)
HNO_3 hot 50% (v/v)	30 (7.8%)	16 (53.3%)	22 (46.8%)
Total	386 (100%)	30 (100%)	47 (100%)
	(ng/μg)		
Labile Ba/POC	10.2	0.14	0.18
HCl soluble Ba/POC	0.17	0.59	0.76
Refractory Ba/POC	0.87	0.81	0.84
Total Ba/POC	11.2	1.6	1.8

Ba concentration (absolute; ng Ba/kg and relative to POC) in seawater and in successive chemical leachings in the sample at the start of the dark 10-week incubation (Sample A; T_0); after incubation without $HgCl_2$ (Sample B; T_f); after incubation with $HgCl_2$ (Sample D; T_f). Numbers in brackets represent the percentage of total particulate Ba present in each leachate.

poisoned sample, in concert with POC (Table 2), and became the predominant ($\sim$ 50%) particulate Ba fraction after decay (B, D, T_f; Fig. 3; Table 2), reflecting its preferential accumulation as a result of its slower rate of remineralization (Fig. 3).

The total leachable particulate Ba decreased by about 350 ng/kg during the incubation, but the concomitant increase in dissolved Ba was much larger (1000 $\pm$ 30 ng/kg; Table 2). This disparity is attributed to experimental errors, mainly linked to the difficulty of obtaining representative samples from suspensions, which resulted in undersampling particles that had a tendency to settle. Although this undersampling does not affect conclusions derived from the relative proportion of the different chemical forms of particulate Ba (Table 2), it may affect those derived from temporal changes in particulate Ba concentration. In particular, while it is clear that the relative proportion of HCl-soluble Ba increased from $<$2% to $>$40% of the total leachable Ba during decay, it is possible that higher HCl-soluble Ba concentrations measured after decay (12 & 20 ng/kg at T_f vs 6 ng/kg at T_0) may be sampling artifacts rather than reflecting barite formation. To circumvent this difficulty, we normalized the different fractions of Ba to POC (Table 2). Although the POC and Ba had to be measured on two different filters, both were filtered from the same aliquot and therefore subjected to similar sampling biases. HCl-leachable Ba/POC increased by a factor of 3.5 in sample B (un-poisoned) and 4.5 in sample D (poisoned). Since POC decreased by $\sim$42% in sample B and $\sim$24% in samples D (Table 1), the ratios indicate an absolute increase in HCl-leachable Ba and formation of barite during decay resulting in a two-fold (sample B; 3.5 $\times$ 0.58) and three-fold (sample D; 4.5 $\times$ 0.76) increase in barite concentration at the end of the decay experiment (Table 2). The conversion from labile particulate Ba into barite is thus relatively inefficient. Of the $\sim$ 350 ng/kg of labile Ba released, only 6 to 12 ng/kg (2–4%) were converted to barite (Table 2). Most of the labile Ba is returned to the dissolved Ba pool and the total Ba/POC drops sharply (from 11.3 ng/μg to 1.6–1.8 ng/μg). These ratios are much lower than what is typically found in the material collected in deep-sea moored sediment traps (typically 20–50 ng/μg; Francois et al., 1995). The difference is mainly due to the degradation of organic carbon as particles settle through the water column. Extensive organic matter remineralization ($>$90%) is taking place within the upper 1000 m of the water column in deep-sea settings (Suess, 1980; Martin et al., 1987). This remineralization must mainly reflect trophic processing of organic matter, which is not replicated in our decay experiments, where POC dropped only by 31–42% in the unpoisoned samples (B and C) and by 24% in the sample poisoned with $HgCl_2$ (Table 1; T_f).

A several-fold increase in barite during the incubation is not quantitatively consistent, however, with the SEM analysis of sample A and B (Table 1). The increase in barite derived from this approach is much lower (30% increase). We attribute this discrepancy to the small size of the aliquots taken for SEM analysis (50ml) that exacerbated the sampling problem. SEM counts are thus not regarded as quantitative.

Formation of barite during incubation in the dark is also confirmed by the isotope tracer experiment (Sample C). A natural plankton sample (with natural Ba isotopic ratio) was let to decay in seawater spiked with ^{135}Ba to drop its $^{138}Ba/^{135}Ba$ ratio from natural abundance (10.9) to 0.70. The $^{138}Ba/^{135}Ba$ ratios obtained by sequential leaching of Sample C gradually evolves from a nearly pure spiked seawater end-member in the labile Ba fraction leached with DDW to a nearly pure natural abundance end-member in the refractory Ba fraction (Table 3). Barite-Ba, dissolved in hot HCl, had an intermediate isotopic composition.

The isotopic ratio measured in the small residual pools of labile Ba still present in the decayed samples are taken to reflect residual seawater (water leached) and residual ion-exchange sites (acid leached). On the other hand, the isotopic composition of the refractory Ba fraction remained close to natural abundance, indicating neither formation nor isotopic exchange with seawater during the incubation.$^{138}Ba/^{135}Ba$ in the HCl-soluble fraction indicates that 25% of the HCl-leachable Ba at the end of the incubation originated from the spiked seawater (Table 3). This barite could only have been formed after spiking at the start of the incubation and is another clear indication that barite was produced during decay.

Our initial goal for the Ba tracer experiment was to establish whether Ba in the barite fraction originates from seawater or phytoplankton. Here the results are not as definite. We have established that barite concentration doubled (Sample A to B)

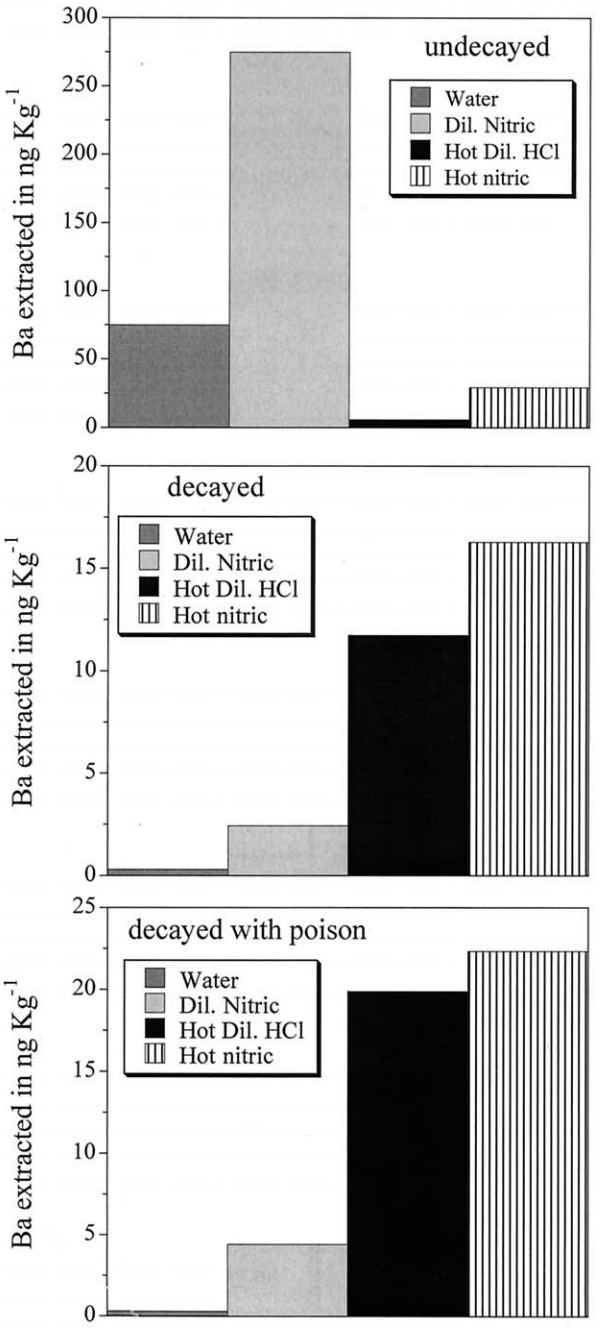

Fig. 3. Results from the sequential leach procedure. (*Upper*) Undecayed sample (A, T_0); (*Middle*) after decaying 10 weeks in the dark without poisoning (sample B, T_f); and (*lower*) after decaying 10 weeks in the dark with $HgCl_2$ to stop bacterial activity (sample D, T_f).

or tripled (Sample A to D) during the incubation. Should all the newly formed barite originate from unlabelled plankton, the isotopic ratio of the HCl-soluble particulate Ba fraction should have remained close to 10.9, as for the refractory fraction. On the other hand, if Ba were coming from the (spiked) surrounding water, its isotopic ratio would have been 5.8 (if barite doubled during incubation) or 4.1 (if barite tripled). The $^{138}Ba/^{135}Ba$ ratio recorded is intermediate between these extremes (8.49; Table 3), suggesting contributions from both potential

Table 3. Result from isotopic analysis in the spiked decay experiment: a surface water sample collected during a coastal spring bloom was incubated in seawater spiked with ^{135}Ba for 10 weeks in the dark. Isotopic ratios were measured in successive leachates.

	$^{138}Ba/^{135}Ba$ ($\pm$ 2%; 1σRSD)	% Ba from spiked seawater
Natural Seawater	10.9	0
Spiked Seawater	0.70	100
DDW	0.97	97
HNO_3 cold 10% (v/v)	1.83	89
HCl. hot 30% (v/v)	8.49	25
HNO_3 hot 50% (v/v)	10.76	2

sources. Given that the HCl-leachable Ba doubled (Sample A to B) and tripled (Sample A to D), 50 to 65% of the barite formed during incubation must have been produced from Ba originated from unlabeled coastal plankton [8.49permil = ((1−A) × 10.9permil) + (A × ((f × 10.9permil) + ((1−f) × 0.7permil))); where A is the proportion of barite formed during the dark incubation and f is the proportion of newly formed barite produced with a natural Ba isotopic ratio)]. This calculation ascertains that at least a significant fraction of barite-Ba originates from the plankton. The remainder may have come from spiked seawater that was present in the microenvironments at the beginning of the incubation before the release of labile-Ba from plankton decay.

4. PROPOSED MECHANISM FOR BARITE FORMATION IN SEAWATER

Results with cultures unambiguously demonstrate that barite is produced during the laboratory decay of phytoplankton in undersaturated seawater. Results from sequential leaching of a coastal plankton sample collected during the spring-bloom and let to decay in the dark shows that a large fraction of particulate Ba in surface waters is very labile and readily released during decay under both axenic and non-axenic conditions. While most of the barium is released into the surrounding waters, a small fraction is converted to barite. These findings suggest the following mechanism for barite formation in seawater:

1. Biologic uptake of dissolved Ba by plankton or abiotic adsorption on organic matter, resulting in high particulate Ba concentration in surface water that is mostly very labile.
2. Rapid release of dissolved Ba from labile particulate Ba during the early stages of plankton decomposition either by cell lysis or decay of labile organic matter.
3. Most of the released Ba is returned to the dissolved Ba pool in surrounding water, but a small fraction (2–4% in our experiments) precipitates as barite in supersaturated microenvironments created as a result of the rapid Ba release.
4. Barite and Ba bound to more refractory organic matter are removed to the deep sea with large sinking particles.

5. PROSPECT FOR THE DEVELOPMENT OF A PALEOPRODUCTIVITY PROXY

The mechanism underlined above, advocating a plankton source for Ba leading to barite formation, bodes well for the eventual development of a quantitative Ba-based paleoproductivity proxy, but much remains to be done to evaluate the role

of environmental factors that may affect the quantitative relationship between the export fluxes of carbon and barite. The observation that only a small fraction of labile Ba is converted to barite indicates that the availability of dissolved Ba is not the main limiting factor in barite formation. Instead, barite formation is likely to be controlled by the availability of microenvironments that could effectively retain Ba released from plankton decomposition. Thus, trophic processing, fecal-pellet packaging, particle aggregation, and possibly catalytic surfaces, although not prerequisite for barite formation, as indicated by our experiments, are likely to enhance barite precipitation. The role of these factors in controlling barite flux to the deep sea remains to be established.

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