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## **Morphological and compositional evidence for biotic precipitation of marine barite**

by Miriam A. Bertram<sup>1</sup> and James P. Cowen<sup>1</sup>

### **ABSTRACT**

Barite formation in the surface oceans is generally assumed to be dominated by abiotic precipitation. Acceptance of this pathway is largely the result of the absence of a pelagic marine organism known to precipitate the ovoid to rounded-rectangular barite crystals typically observed in marine waters and sediments.

Barite crystals observed in net-tow particles and on substrates retrieved from the seafloor (both in the central North Pacific) were examined by scanning electron microscopy and energy dispersive X-ray spectrometry. Three distinct crystalline forms of barite were observed: ovoid and hexagonal crystals several microns in diameter, and aggregates of submicron-sized crystals. Ovoid and hexagonal-type crystals contained between 0 and 26 mole percent SrSO<sub>4</sub>. The microcrystalline barite contained no detectable Sr (<0.05 percent). Hexagonal-type crystals were precipitated by an unusual benthic foraminifera. Comparison of the morphology and composition of the barite crystals observed in this study to crystals precipitated by a variety of biotic and abiotic processes suggests a biotic origin for the ovoid barite crystals, the most common form of barite observed in this region.

### **1. Introduction**

Barite (BaSO<sub>4</sub>) preserved in marine sediments has been used as a tracer for paleoproductivity and for reconstructing the paleocomposition of seawater (e.g. Paytan *et al.*, 1993). In the modern ocean, rates of barium accumulation in sediments underlying high productivity regions of the oceans are 20 times higher than those observed under lower-productivity waters (Goldberg and Arrhenius, 1958; Murray and Leinen, 1993). As a result, high levels of barite in sediment cores are thought to represent periods of high paleoproductivity (e.g. Schmitz, 1987; Gingele and Dahmke, 1994). Barite crystals precipitated in seawater also contain coprecipitated elements (i.e. Sr) with isotopic ratios that may reflect the chemical signature of the seawater from which they are formed. Thus the Sr-isotopic composition of sedimentary barite may be a useful means of reconstructing the paleoceanographic Sr-isotopic ratio of seawater (e.g. Paytan *et al.*, 1993; Martin *et al.*, 1995), a parameter that varies with the relative volume of seawater circulating through mid-ocean ridges and with rates of river runoff (Holland, 1984 and references therein). However, interpretations of barite abundance and chemical composition data are hampered by a lack of fundamental

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knowledge of the processes producing marine barite, and of the processes affecting its preservation in the sedimentary record.

Barite crystals are found throughout the water column in the worlds' oceans, most commonly as single, rounded rhombohedral crystals (Dehairs, 1979). Because surface ocean waters are highly undersaturated with respect to barite, two pathways have been proposed to explain their presence: abiotic formation within microenvironments saturated with respect to barite (e.g. Chow and Goldberg, 1960; Bishop, 1988), and direct biological precipitation, where an organism provides an environment suitable for crystal formation. The second pathway, biological precipitation, has generally been discounted because no pelagic marine organism has been found that directly precipitates the ovoid to rectangular barite crystals that are commonly observed in marine sediments. Abiotic precipitation has been proposed to occur when the degradation of organic matter within an isolated solution creates a microenvironment suitable for barite precipitation. Such microenvironments are hypothesized to exist within aggregated organic-rich particles (Chow and Goldberg, 1960; Dehairs *et al.*, 1980; Bishop, 1988) or within the guts of zooplankton (Bernstein *et al.*, 1992).

There are a number of organisms known to precipitate barite, including benthic marine protozoans (i.e. certain foraminifera, Dugolinsky *et al.*, 1977), pelagic freshwater protozoans (i.e. *Loxodes* spp., Finlay *et al.*, 1983) and freshwater algae (i.e. desmids, Wilcock *et al.*, 1989). Crystals produced by these organisms exhibit a range of morphologies, from clusters of submicron-sized crystals (*Loxodes* spp.) to large well-formed crystals (desmids), both of which are similar to barite crystals commonly observed in pelagic marine waters. The existence of such barite-precipitating organisms in other environments suggests that biotic sources for pelagic marine barite should also be considered.

In this study we examined the morphology and elemental composition of marine barite from surface waters in the central North Pacific, and of crystals found on substrates recovered from the ocean floor in the same region. While our focus was on characterizing barite crystals that are likely to contribute to the sedimentary record, we also observed and discuss results for a class of barite crystals that appear to be restricted to solid substrates. The morphology and composition of barite crystals precipitated by foraminifera found attached to surfaces are of interest both because of their known biological origin in the marine environment, and for their potential use in stratigraphic interpretations of the Sr and Ba content of ferromanganese-oxide deposits.

## 2. Methods

*a. Sampling and sample preparation.* Oblique plankton tows (63  $\mu\text{m}$  mesh) were conducted in the surface waters (0–30 m), to depths below the mixed layer (200 m), and to 450 m at station ALOHA in the central North Pacific (22°45'N, 158W). Three net-tows were done in surface waters, one to 200 m, and one to 450 m in each of February and August 1994. Net-tows were designed to sample roughly equivalent volumes of water at the maximum depth range, and to minimize the material collected during transit to and

from the target depth. Immediately after collection, material was divided into two subsamples using a plankton splitter. One subsample was frozen for future analyses and one was preserved in a sodium-borate buffered 2% formaldehyde-seawater solution. Homogenized aliquots of the preserved particles were filtered through 0.2  $\mu\text{m}$  Nuclepore filters, rinsed with deionized water, and dried overnight in a desiccator or 60°C oven. Filters were then cut into quarters, glued to aluminum stubs, and carbon-coated in preparation for examination by scanning electron microscopy and energy dispersive X-ray fluorescence spectrometry (SEM/EDS).

Particles deposited and precipitated on artificial and natural substrates were collected as part of an experiment investigating the role of microbiota in the accumulation of minerals on the seafloor (Bertram and Cowen, 1994). The study site consisted of a series of stations on Cross Seamount (18°40'N, 158°17'W) at depths of 800, 975, 1285 or 1985 meters. Artificial substrates (surface area approximately 4 cm<sup>2</sup>) were constructed of fine-grained minerals embedded in a polyester resin and affixed to a plastic base plate. Naturally occurring ferromanganese-oxide (dredged), rhodochrosite (Ward's Geology), and basalt (dredged) samples were ground to obtain materials for these substrate types. Three different calcium carbonate substrates were constructed using ground Iceland Spar (Ward's Geology), laboratory grade powder (Matheson), and liths of cultured coccolithophores. Forty to sixty artificial substrates were mounted on fiberglass frames (arrays) and deployed and recovered (1 to 42 months later) by the PISCES V submersible. Four to fifteen samples from each array were analyzed for barite. In addition, samples of natural substrates (ferromanganese-oxide encrusted basalt) were collected from Cross Seamount during the submersible dives. Both the artificial substrates and subsamples of natural substrates (approximately 4–8 cm<sup>2</sup>) were rinsed with distilled water or preserved in a buffered 2% formaldehyde solution. In the laboratory, these artificial and natural substrates were oven dried at 60°C and carbon coated for analysis by SEM/EDS.

*b. Scanning electron microscopy and elemental analysis (SEM/EDS).* Samples were placed in a Zeiss DSM 962 scanning electron microscope (SEM) interfaced to an Oxford Instruments Inc. energy dispersive X-ray fluorescence spectrometer (EDS). A backscattered electron (BSE) detector was used for imaging, facilitating discrimination between barite crystals and particles with different elemental compositions (e.g. organic matter, diatom and radiolarian SiO<sub>2</sub>, foraminiferal CaCO<sub>3</sub>, and substrate minerals). Once located, barite crystals were imaged and crystals not significantly obstructed by other particles were analyzed for elemental composition. The ultra-thin window of the EDS detects all elements with atomic number >4, at concentrations greater than approximately 0.05%. The atomic percent of each element in the whole-mounted samples was approximated using the software procedure SEMquant (Link, Oxford Instruments, Inc.). Reliability of abundance estimates was verified by analysis of resin-mounted samples of known elemental composition (calcite-CaCO<sub>3</sub> and rhodochrosite-MnCO<sub>3</sub>). Particles containing approximately equimolar concentrations of Ba and S were classified as barite (BaSO<sub>4</sub>), and mole percent

Table 1. Barite particles observed in net-tow samples from the central North Pacific.

Number of net-tows	Number of samples analyzed‡	Microcrystalline aggregates†		Ovoid		Irregularly shaped		Depth sampled (meters)
		#	#/sample	#	#/sample	#	#/sample	
6	13	5	0.4	1 (0)††	0.08	4	0.3	0–30
2	5	1	0.2	10 (4)	2	1	0.2	0–200
2	3	0	0	6 (1)	2	3	1.0	0–450

†Microcrystalline aggregates generally occurred as many clusters of similar size in one location. Each group of clusters is tabulated as a single aggregate.

††( ) indicates number of crystals surrounded by an organic envelope and attached to a crustacean.

‡More surface water samples than deeper samples were analyzed in order to verify the rare occurrence of ovoid crystals in the shallow samples.

$\text{SrSO}_4$  was calculated assuming that Sr and Ba were the only solid-solution components of barite.

### 3. Results

*a. Net-tow barite.* Barite crystals were found in net tow samples from both cruises (February and August) and from all three sampled depth ranges (0–30 m, 0–200 m and 0–450 m). Three distinct forms of barite were observed: ovoid crystals, microcrystalline aggregates, and irregularly shaped crystals. The most common form of barite observed were ovoid crystals of between 1 and 5  $\mu\text{m}$  maximum dimension (Table 1, Fig. 1). This form was most abundant in samples obtained from 0–200 m and 0–450 m and was very rare in surface water samples (Table 1). Five of the seventeen ovoid crystals were encased in an organic envelope that was itself attached to a crustacean carapace (Plate 1). Ovoid crystals observed in net-tow samples contained from 0 to 19 mole percent  $\text{SrSO}_4$  (Fig. 2).

Aggregated microcrystalline barite was observed in samples from both February and August in the 0–30 m and 0–250 m samples. This form was generally observed as several to many clumps of particles found in association with either a diatom skeleton (Plate 2) or affixed to organic surfaces. Individual clumps within an observed aggregate were from 1 to 5.5  $\mu\text{m}$  in diameter (Fig. 1). Each clump was composed of approximately spherical euhedral subunits of less than 0.5  $\mu\text{m}$  diameter (Plate 2), or of fine powdery subunits  $\ll 0.5 \mu\text{m}$  in diameter. Reliable elemental analyses were possible on only two of the six, both of which were associated with a diatom. These microcrystalline aggregates contained no detectable Sr. Results of the elemental analysis of the other four Ba-S aggregates were questionable because of severe topographic interferences from other particles in the sample.

Finally, irregularly shaped barite particles larger than 1  $\mu\text{m}$  in diameter were observed in net-tow samples from both the February and August cruises and from all three depth ranges (Table 1). All but two of these particles were less than 3  $\mu\text{m}$  in maximum dimension (Fig. 1). Irregularly shaped particles found in samples from near-surface waters (0–30 m) contained no detectable Sr; those observed in samples obtained from deeper waters contained between 2 and 6 mole percent  $\text{SrSO}_4$  (Fig. 2).

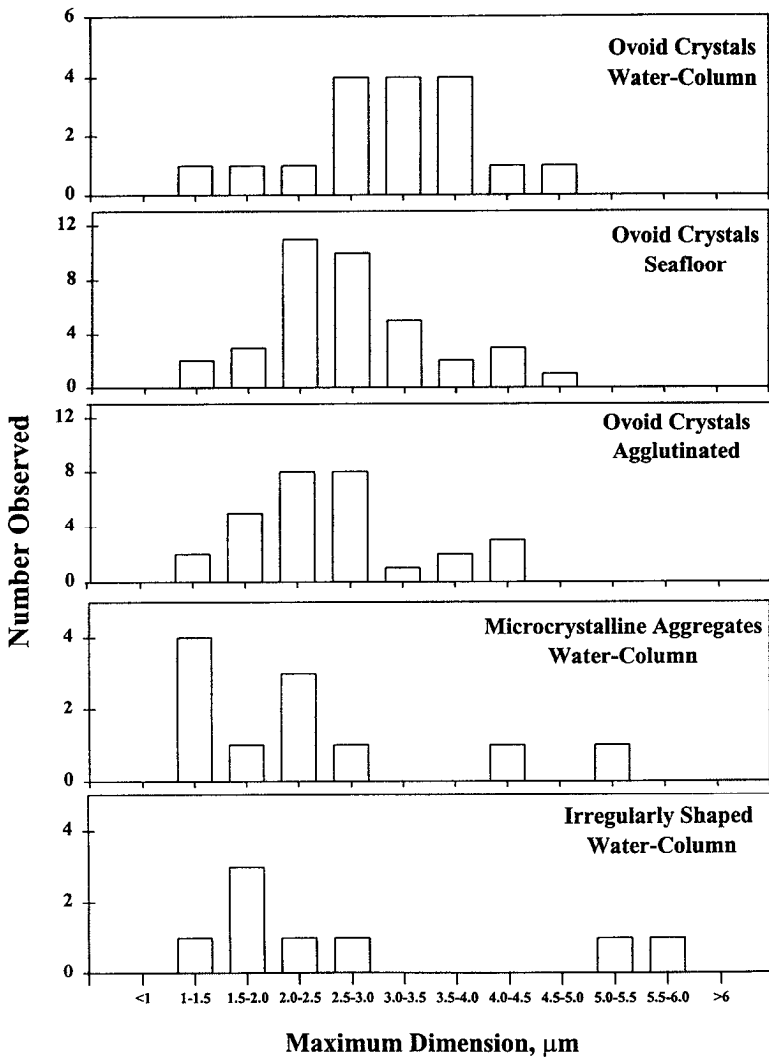


Figure 1. Size distribution of barite crystals observed in this study. Average maximum diameter of ovoid crystals observed in the water column is larger than that of crystals observed on the artificial substrates ( $T = 1.74$ ,  $p = 0.088$ ,  $t$ -test assuming equal variance). Maximum dimension for microcrystalline aggregates refers to "cluster" diameter. Crystalline subunits making up clusters were  $\ll 0.5$  to  $0.5 \mu\text{m}$  in diameter. See text for details.

*b. Seafloor barite.* Barite crystals were found on both natural and artificial substrates as single or clustered crystals, as detrital crystals incorporated into the tests of agglutinating foraminifera, and as crystals precipitated to form discrete portions of foraminiferal tests.

Single crystals were found on all substrates and appeared to be randomly dispersed on the substrate surfaces. In contrast, clusters occurred as patchy deposits covering approximately circular areas. Clusters contained tens to hundreds of single crystals (Plate 3a).

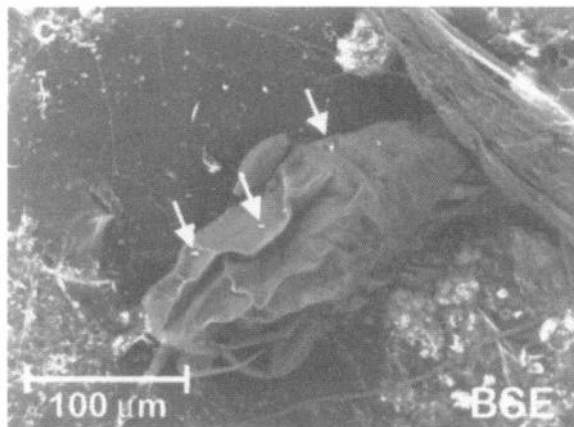
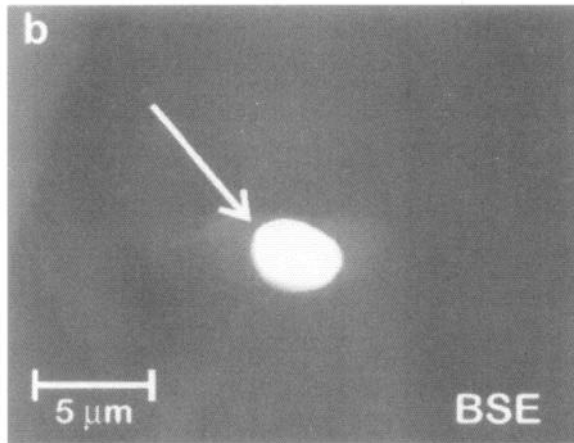
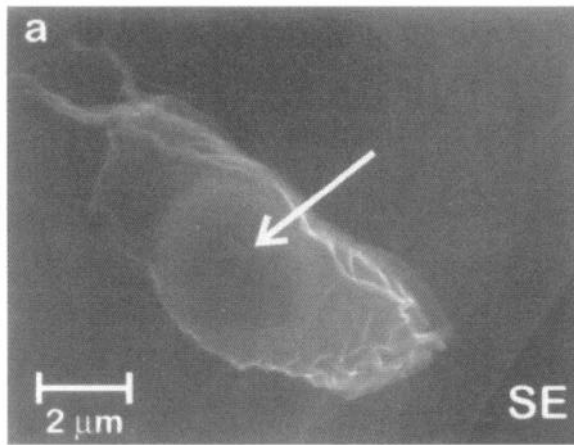


Plate 1. Ovoid barite crystals attached to an unidentified crustacean carapace. (a) Scanning electron (SE) and (b) backscattered electron (BSE) image of an ovoid barite crystal (bright white area) in an organic envelope. In (a) the point of attachment between the organic envelope and crustacean is seen at the upper left corner of the image. The organic envelope appears shriveled because of sample dehydration. Arrow in (a) shows point where X-ray analysis created a hole in the organic membrane. In (b) the bright area indicated by the arrow is the barite crystal. (c) BSE image of an unidentified barite-bearing crustacean. Arrows indicate three organically enveloped barite crystals (small, bright white particles).

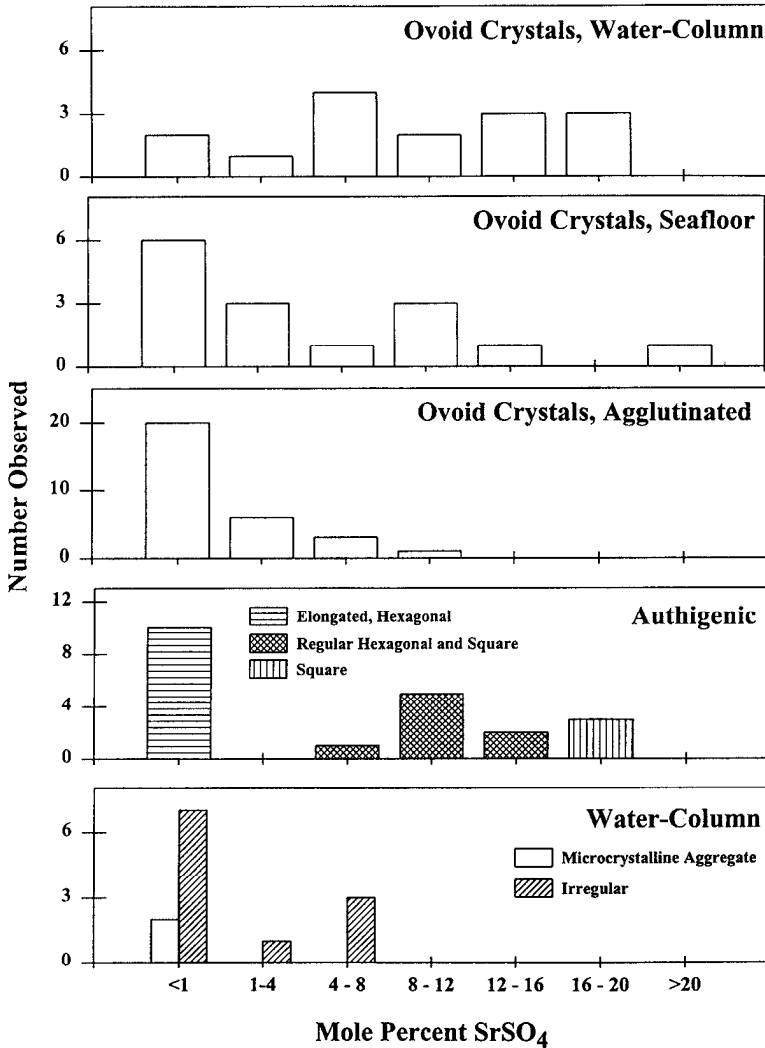


Figure 2. Mole percent SrSO<sub>4</sub> in barite crystals from this study.

Clusters of barite were observed on substrates from all depths sampled, but were absent on plates deployed for less than one year. Isolated crystals and crystals observed in clusters, were round, ovoid or rectangular, often with rough surfaces (Plate 3b). These crystals were from 1.5 to 5.5 μm in maximum dimension, with these values distributed approximately normally about an average diameter of 2.7 μm (Fig. 1). Six of the fifteen crystals analyzed contained <1 mole percent SrSO<sub>4</sub>; the remaining nine contained variable Sr concentrations ranging from 1 to 25 mole percent SrSO<sub>4</sub> (Fig. 2). Morphologically and compositionally, these crystals were very similar to ovoid crystals sampled in the water column.

Barite crystals were also found incorporated into the tests of agglutinated benthic



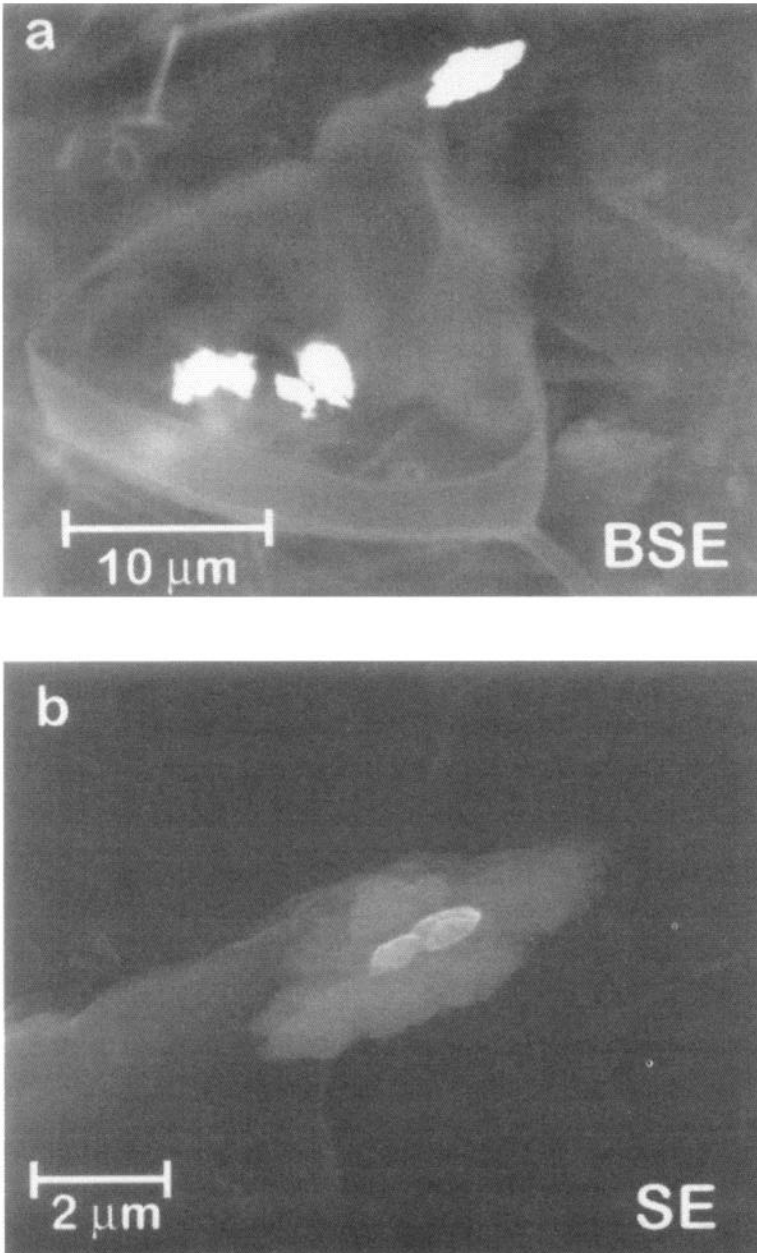


Plate 2. Microcrystalline aggregates from the February 0–200 m net-tow. (a) BSE image of broken diatom frustule containing 3 clusters of microcrystals. (b) Enlarged view of the upper right cluster in (a). Each of the crystals in the cluster is  $< 1 \mu\text{m}$  in size.

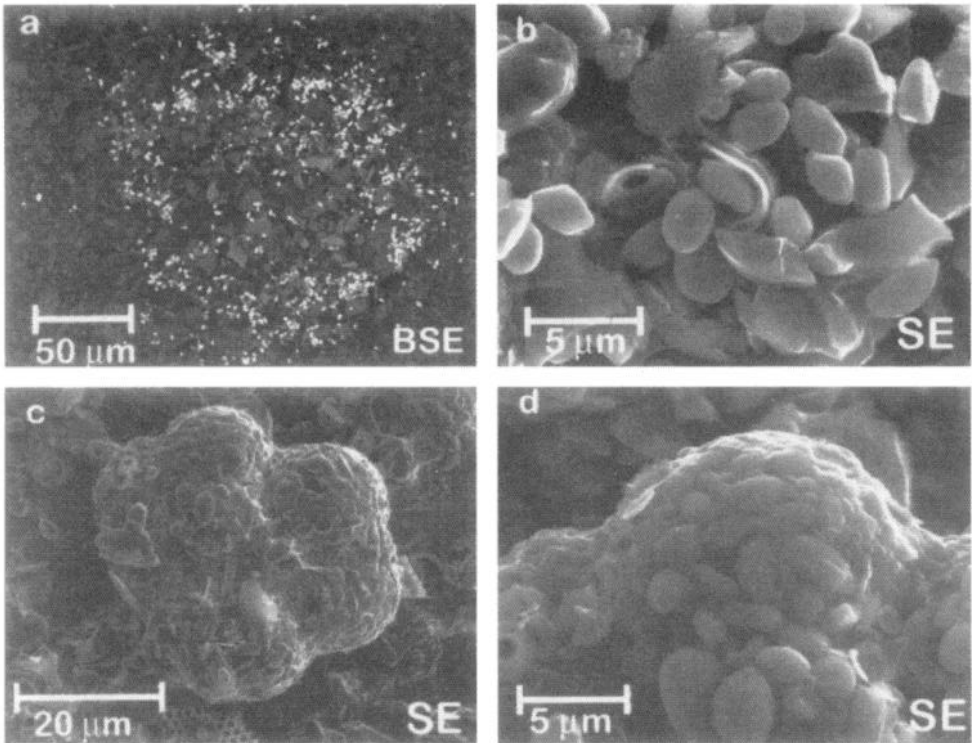


Plate 3. Ovoid barite crystals observed on artificial substrates. (a) BSE image of several hundred ovoid crystals (bright white) on a basalt substrate at 975 m. (b) Enlargement of barite crystals in (a). (c) Ovoid crystals agglutinated within a benthic foraminifera found on a rhodochrosite substrate (SE image). (d) Enlarged view of foraminiferal test in (c).

foraminifera on artificial and natural substrates from all sampled depths (800, 975, 1285 and 1985 m). Benthic foraminifera with chamber walls composed almost entirely of agglutinated barite (Plate 3c) are similar to those classified as Trochamminacea (Brönnimann and Whittaker, 1988). These foraminifera are motile, scavenging the seafloor for food. The incorporated crystals, like the crystals described above, were ovoid in shape and between 1 and 4.5  $\mu\text{m}$  in maximum dimension (Fig. 1, Plate 3c,d). Twenty of the twenty-nine agglutinated barite crystals analyzed from two different trochamminaceous foraminifera contained less than 1 mole percent  $\text{SrSO}_4$  (Fig. 2). The remaining agglutinated crystals contain variable Sr concentrations ranging from 1 to 11 mole percent  $\text{SrSO}_4$ .

Barite crystals precipitated by benthic foraminifera were observed only rarely on artificial substrates (4 foraminifera on substrates from the 975 m, 42 month deployment) but were commonly observed on natural ferromanganese-oxide crust surfaces from 975 m. Precipitated crystals were found only in a specific test morphology consisting of a hemispherical proloculus (first chamber) followed by a tubular second chamber (Plate 4). Where precipitated barite was observed, the walls of the proloculus were composed

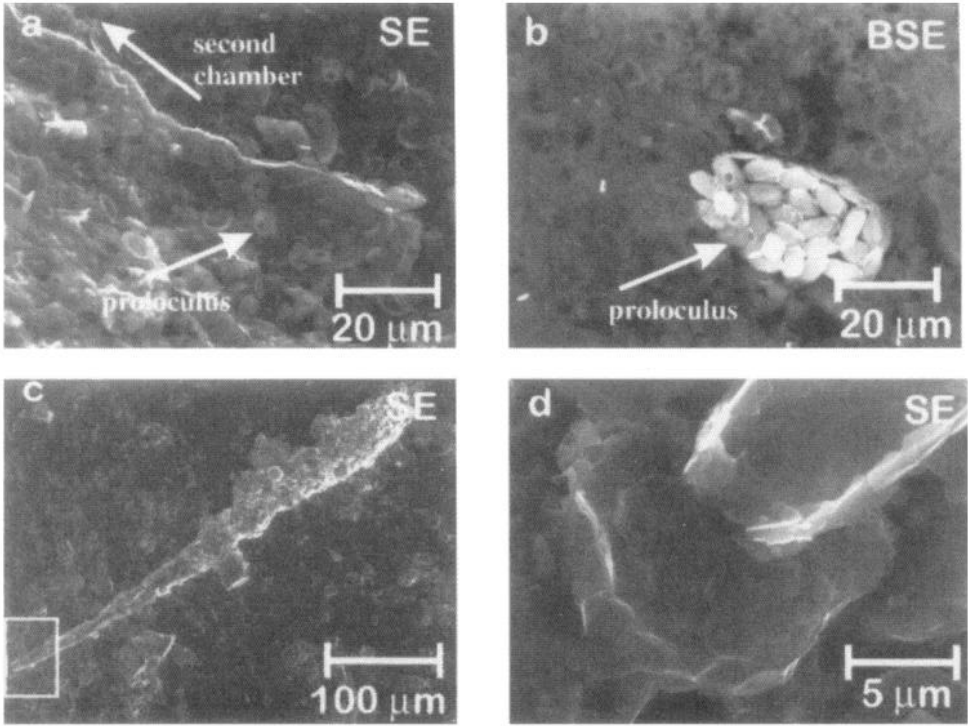


Plate 4. Authigenic foraminiferal barite. (a) SE and (b) BSE of a benthic foraminifera found on a natural ferromanganese-oxide crust at 975 m. Overlapping elongated hexagonal barite crystals form the walls of the proloculus. The second chamber does not contain this type of barite crystal, although agglutinated ovoid crystals are occasionally seen. (c) A 2-chambered foraminifera observed on a rhodochrosite substrate at 975 m. (d) Enlarged view of area shown in box at lower left of (c). Thin, regular hexagonal barite crystals form the proloculus and a segment of the second chamber wall. Agglutinated detrital particles form the remainder of the second chamber wall (not shown).

entirely of interlocking barite crystals, while the tubular second chamber was composed primarily of detrital particles (coccoliths and other fine grained minerals). Authigenic barite crystals were less than 20 nm thick (i.e. the thickness of the proloculus wall), with exposed crystal faces between 2 and 6  $\mu\text{m}$  in largest dimension. Three distinct crystal forms were observed: elongated hexagonal, regular hexagonal, and square, although within a single foraminiferal test, precipitated crystals were uniform in size and shape (Plates 4 and 5). Elongated hexagonal crystals were 6  $\mu\text{m}$ , regular hexagonal crystals 2  $\mu\text{m}$  and square crystals 5  $\mu\text{m}$  in length. The Sr-content of barite crystals within each test were also unique and appeared to be correlated with crystal shape. Elongated hexagonal crystals contained no detectable Sr, regular hexagonal crystals contained moderate Sr concentrations (9 to 13 mole percent  $\text{SrSO}_4$ ), and square crystals contained moderate to high Sr concentrations (8 to 20 mole percent  $\text{SrSO}_4$ ).

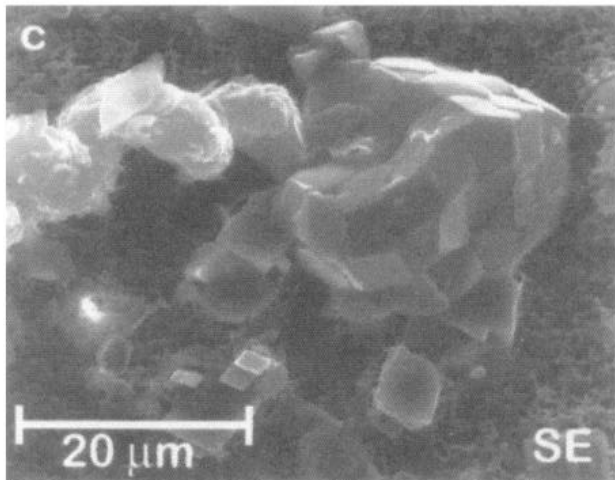
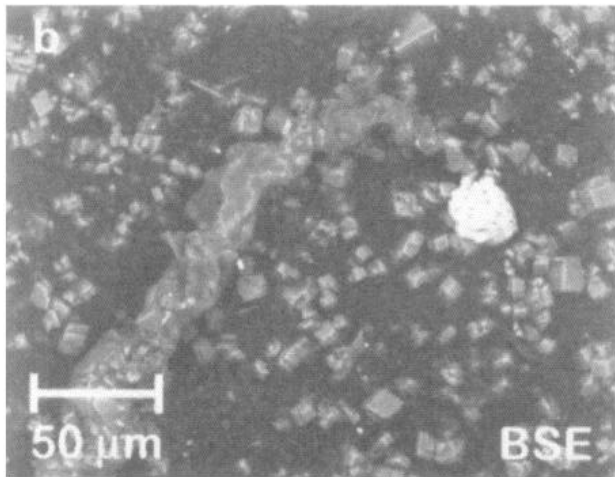
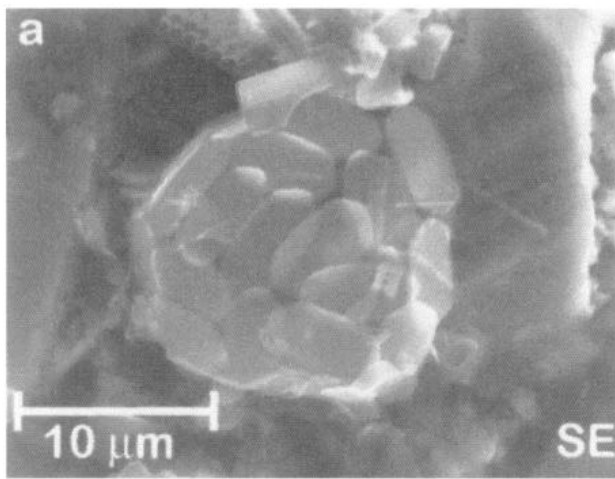


Plate 5. Authigenic foraminiferal barite, continued. (a) SE image of elongated hexagonal barite crystals that form a single foraminiferal chamber on a rhodochrosite substrate at 975 m. (b) BSE image of a 2-chambered foraminifera on a calcite substrate from 975 m. Bright white area is the first chamber (proloculus). (c) Enlarged view of the overlapping, square barite crystals in the first chamber of the foraminifera shown in (b).


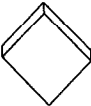
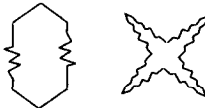

#### 4. Discussion

A number of morphologically and compositionally distinct forms of barite crystals were observed in this study. Several are clearly associated with a biological source but are unlikely to contribute to sedimentary barite (i.e. barite crystals precipitated by benthic foraminifera). Others (ovoid crystals observed in net-tow samples and free and agglutinated crystals found on seafloor substrates) cannot be directly linked to a known biotic source, but morphological and compositional results suggest that a biotic source is at least reasonable, and perhaps probable. The benthic ovoid crystals have a surface water origin, and the Sr content of crystals observed in the surface particles and those on the benthic substrates, suggest that these barite crystals preferentially lose Sr during exposure to seawater. Another form (microcrystalline aggregates) may precipitate abiotically, but appears to dissolve in the surface waters and therefore does not contribute to the flux of barite to the seafloor. These ideas are developed in the following discussion, followed by a discussion of the implications of these data to paleoceanographic studies.

*a. Crystal morphology.* Barite crystal morphology is affected by a number of factors, including the chemical and physical environment of precipitation. Laboratory studies have shown that when temperature is held constant and no physical constraints are imposed, crystal form is controlled primarily by precipitation rate, which in turn is a function of saturation state. Highly supersaturated solutions ( $>100$  times saturation) promote the spontaneous and extremely rapid formation of clusters of submicron-sized crystals very similar to the microcrystalline deposits found within diatom skeletons and attached to the surface of large organic particles (Walton, 1967; Bishop, 1988; Williams, 1989). Similar masses of crystals form the gravity sensors of *Loxodes* spp., suggesting that this crystal form can also be precipitated biologically. At lower degrees of supersaturation ( $\ll 100$  times saturation) micron-sized crystals precipitate relatively slowly, producing the equilibrium-crystal forms predicted by crystal theory (Table 2). Thus, the rhombic and hexagonal barite crystals observed within desmids and in the proloculi of benthic foraminifera are likely the result of biologically maintained solution compositions (Wilcock *et al.*, 1989). Analogously, the presence of abundant, well-formed ovoid barite crystals in the surface ocean suggests a consistent environment of formation between crystals, as well as one that is maintained for sufficient time to produce crystals several microns in diameter. Such an environment seems far more likely to be associated with a biologically-controlled process than with a passive microenvironment.

Morphology can also be used to infer a linkage between the ovoid barite crystals found in surface-ocean waters and crystals observed free and agglutinated on the seafloor. The most abundant surface-water and seafloor crystals share a nearly identical ovoid shape. The only significant difference is the rougher surfaces observed on seafloor crystals, a feature consistent with partial dissolution of these crystals. Crystal size is also consistent with this interpretation; mean maximum dimension of ovoid crystals decreases from the water column to the seafloor, i.e. with increased age of the crystals. Ovoid crystals formed in the

Table 2. Morphology and conditions of precipitation of barite crystals.

	Crystal morphology	Chemical conditions of formation	Occurrence in nature
Increasing precipitation rate and increasing solution saturation state with respect to BaSO <sub>4</sub>	 Ovoid, typically 2–5 μm in length.	Vesicle-limited growth. Similar in morphology to inorganic laboratory precipitates when diphosphonates added to solution (Black <i>et al.</i> , 1991).	1. Desmids, freshwater algae (Wilcock <i>et al.</i> , 1989). 2. Sediments and sediment traps.
	 Rhombic, and related geometric forms.	Slow growth rate controlled by surface transport. Precipitation from solution of constant composition.	1. Desmids, freshwater algae (Wilcock <i>et al.</i> , 1989). 2. Benthic foraminifera (Dugolinsky <i>et al.</i> , 1977). 3. Hydrothermal precipitates (Feely <i>et al.</i> , 1987; Shikazono, 1994).
	 Irregular crystal forms with rough edges.	Rapid growth rate limited by diffusion of ions to crystal surface. (Williams 1989; Shikazono 1994).	None.
	 Mass of small crystals, individual crystallites < 1 μm diameter.	Rapid and uncontrolled nucleation and growth rate (Williams, 1989).	1. <i>Loxodes</i> spp, a freshwater protozoan (Finlay <i>et al.</i> , 1983). 2. Surface ocean (Dehairs <i>et al.</i> , 1980; Bishop 1988). 3. Black Sea sediment trap samples (Falkner <i>et al.</i> , 1991).

water column, observed loose on the seafloor and agglutinated within the chamber walls of benthic foraminifera had an average length of 3.1 μm, 2.7 μm, and 2.5 μm, respectively (Fig. 1). After formation, barite crystals are exposed to seawater that is significantly undersaturated with respect to barite (Church and Wolgemuth, 1972; Bernstein *et al.*, 1992). Subsequent dissolution would produce both a decrease in size and roughened surfaces. By comparison, the high surface area to volume ratio of the microcrystalline barite would predispose this form to rapid dissolution. Thus, dissolution can explain both the weathered appearance of ovoid crystals on the seafloor (loose and agglutinated) and the absence of microcrystalline barite, both in the net-tow material from 450 m, and on artificial and natural substrates recovered from the seafloor.

The irregularly shaped crystals, intermediate in form between that of the microcrystalline and ovoid barite, could be related to either form. Irregular shapes may be formed by weathering of ovoid or other regularly shaped particles or by the recrystallization of

microcrystalline aggregates within a suitable environment. Morphology alone cannot distinguish between these two possibilities.

*b. Crystal composition.* The strontium content of barite crystals recovered from different environments is also a useful tool for understanding the possible relationships between the crystal forms observed in this study.

Biotic microenvironments may facilitate barite precipitation, as well as control the resulting mineral composition. Biotic control over mineral composition is illustrated by the benthic foraminifera, all from 975 meters on Cross Seamount, that precipitated barite of variable Sr concentration.

Seawater Sr:Ba ratios may also influence the Sr content of barite. The nutrient-like profiles of Sr and Ba, and Sr depletion during blooms of biomineralizing plankton (e.g. SrSO<sub>4</sub>-producing acantharia), can produce variations in the Sr:Ba ratio of surface waters (Bernstein *et al.*, 1987). The variable Sr concentrations seen in ovoid barite crystals from the upper water column may reflect these differences in seawater composition. Alternatively, like the barite precipitated by benthic foraminifera, this compositional variability can be biologically controlled.

The original Sr content of barite can be altered during exposure to seawater. Seawater is highly undersaturated with respect to both SrSO<sub>4</sub> and BaSO<sub>4</sub> (Bernstein *et al.*, 1992), but celestite (SrSO<sub>4</sub>) dissolves much faster than barite and is absent in deep water sediment traps (Bernstein *et al.*, 1992). Ovoid barite crystals from net-tow particles contained more Sr than did those on the seafloor (Fig. 2). This trend indicates that these two pools of barite are different in age. The older, seafloor barite is depleted in SrSO<sub>4</sub>. Also, the measurable but low Sr content of the irregular barite crystals suggests that their origin is more likely associated with dissolution of Sr-containing barite than with recrystallization from microcrystals of undetectable Sr content.

*c. Implications.* Both morphological and composition evidence suggest that surface waters contain a biotic source for the barite observed on the seafloor. This argument is strengthened by the frequent association of ovoid barite crystals with crustacean carapaces. The implications of a biotic source of barite that preferentially loses Sr in the water column are briefly discussed below.

The association of barite with certain particle size fractions has been used to argue for an abiotic source of marine barite (Bishop, 1988). In the upper 800–1000 m of the Sargasso Sea the abundance of particulate Ba (pBa) in the 1–53 μm size fraction increased below 100–200 m. This increase of fine pBa was accompanied by a concurrent decrease in the pBa in the >53 μm size fraction (Bishop, 1988). SEM analyses of surface water particles revealed an abundance of microcrystalline barite in association with diatom skeletons. These data suggested that marine barite originates as the microcrystalline form, supporting the hypothesis of abiotic microenvironment precipitation in association with other marine particles (Bishop, 1988). However, the association of microcrystalline aggregates with

large organic particles, and of ovoid crystals with the bodies of crustaceans (as observed in our samples), would place both forms of barite in a large (i.e.  $>53\ \mu\text{m}$ ) particle size fraction. Release of ovoid crystals from crustacean carapaces and dissolution of microcrystalline aggregates with depth would also lead to a roughly inverse relationship between pBa abundances in large and small particle size fractions. Thus, the pBa profiles obtained in the Sargasso Sea could also be produced by dissolution of microcrystalline barite and release of ovoid crystals below the euphotic zone.

Ovoid and irregular barite crystals are likely to dominate the sedimentary record, and authigenic crystals may be encapsulated into ferromanganese-oxide crusts. While differential dissolution appears to affect the overall concentration of Sr in ovoid and irregular crystals, dissolution in the water column is unlikely to effect their  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio. Therefore not only do sedimentary barite crystals retain the isotopic ratio of seawater (Paytan *et al.*, 1993; Martin *et al.*, 1995), but the biotic host indiscriminantly incorporates both isotopes during barite precipitation. If this is also true of benthic foraminifera, the authigenic seafloor barite and the ovoid water-column crystals should contain the same  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic ratio (oceans are well mixed with respect to Sr). Thus, barite crystals precipitated in the oceans and buried within oxic sedimentary deposits, are likely to preserve paleoceanographic Sr isotopic ratios (Paytan *et al.*, 1993; Martin *et al.*, 1995).

Finally, barite distributions observed in this study suggest that spatial and temporal variability in barite fluxes may be significant. Such variability can be the result of both production and transport processes. In particular, the majority of the crystals observed on seafloor substrates occurred in roughly circular patches containing tens to hundreds of crystals. This pattern suggests crystal transport through the water column in concentrated clumps, presumably via sinking detrital aggregates. Detrital aggregates have been shown to be important in enhancing overall particulate flux, but aggregate formation and flux appears to be highly variable in both space and time (Deuser, 1986; Fowler and Knauer, 1986; Riebesell, 1992). Variable depth and extent of formation of barite-rich aggregates would produce variability in the ratio of pBa to particulate organic carbon (pBa:POC) observed in sediment trap data within a single geographic location (Francois *et al.*, 1995). Sediment trap data also show geographic variability in the pBa:POC flux. For example, the pBa:POC flux ratio is greater in the Pacific and north Atlantic than it is in the western Atlantic and Panama Basin (Dymond *et al.*, 1992; Francois *et al.*, 1995). Such regional variability may reflect differences in the activity of the biota responsible for barite production in the surface oceans.

## 5. Summary and conclusions

Three distinct crystalline forms of barite, each with a unique elemental signature, were observed in the samples analyzed in this study. Microcrystalline aggregates contained no detectable Sr, while ovoid and hexagonal-type crystals contained variable and sometimes high Sr concentrations. Available evidence suggests that microcrystalline aggregates may be passively formed within abiotic microenvironments, while certain hexagonal-type



crystals are clearly precipitated by benthic foraminifera. Ovoid crystals, the most common form of barite observed in these samples, seem likely to be biologically precipitated. Size and Sr concentration both decline from surface water to seafloor ovoid barite crystals, suggesting that particles observed on the seafloor originate in surface waters and undergo partial dissolution, including preferential dissolution of SrSO<sub>4</sub> after formation. Microcrystalline barite appears to undergo dissolution before reaching the seafloor, thus barite preserved in the sedimentary record is likely to be dominated by biotic surface-water sources.

*Acknowledgments.* We gratefully acknowledge the critical comments of D. Hoover, Y. H. Li and J. Resing. We also thank R. Arvidson, J. Bishop, R. Collier, J. Dymond and K. K. Falkner for their valuable contributions to the ideas presented. This research was supported in part by grants from NSF (OCE 9217514), a cooperative agreement from the National Oceanic and Atmospheric Administration, project #R/OM-6, sponsored by the University of Hawaii Sea Grant College Program, Institutional Grant No. NA36RG0507, and the State of Hawaii's Department of Business and Economic Development. This is SeaGrant Publication UNIH-SEAGRANT-JC-97-11 and SOEST publication no. 4179.

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