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#### Notes

# Precipitation of barite by marine bacteria: A possible mechanism for marine barite formation

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## ABSTRACT

**Barite (BaSO<sub>4</sub>) is found throughout the ocean, yet seawater is undersaturated with respect to barite, and organisms that could account for the abundance of barite have not yet been identified. The mechanism for barite formation in seawater is not fully understood. Here we show that marine bacteria have the ability to precipitate barite through a metabolically mediated biomineralization process. We precipitated barite in laboratory experiments in the presence of several strains of marine bacteria grown on yeast media enriched with barium (Ba); barite did not precipitate under identical conditions in killed-bacteria controls. The crystals develop from amorphous, phosphorous-rich spherical precursors with fibrous internal textures, common in bacterial mineral precipitation. Bacterial mediation of barite precipitation can explain the distribution of barite in the water column and the occurrence of barite crystals in organic-rich sinking aggregates where bacteria are concentrated. This finding has implications for the use of barite and Ba proxies in paleoceanographic research.**

## INTRODUCTION

The mineral barite (barium sulfate, BaSO<sub>4</sub>) is ubiquitous in marine sediments underlying areas of high biological productivity, and is found throughout the oceanic water column in association with decaying organic matter and biogenic debris (Dymond et al., 1992; Dehairs et al., 2000). Several major (e.g., S, Sr, Ca) and trace (e.g., Ba, Ra, Pb, Nd) elements in seawater are incorporated into barite and have been used for reconstructing the chemistry of the solutions from which barite precipitated (e.g., Paytan et al., 1993, 2002; Griffith and Paytan, 2012). The accumulation rate of marine barite in oxic pelagic sediments has also been used to reconstruct changes in ocean export production (e.g., Paytan and Griffith, 2007). Thus, it is important to understand the mechanisms for barite precipitation in order to best utilize its potential as an archive of seawater chemistry, as well as for reconstructing changes in ocean productivity. Seawater is largely undersaturated with respect to barite (e.g., Church and Wolgemuth, 1972; Monnin et al., 1999; Rushdi et al., 2000), yet barite is ubiquitous in seawater, and marine barite is regionally dispersed in deep-sea sediments (Church, 1970; Paytan et al., 1996; Paytan and Griffith, 2007). In the water column, barite crystals are most abundant at depths of 500–1500 m, where most of the organic matter is regenerated (Dehairs et al., 1980; Bishop, 1988). It is, however, unclear how barite forms in undersaturated waters, and it has been suggested that barite may be precipitated by organisms. Certain protozoa and algae are thought to precipitate barite intracellularly to serve as statoliths to maintain orientation and depth (Tendal, 1972; Gooday and Nott, 1982; Swinbanks and Shirayama, 1986). In the marine environment, barite crystals have been found inside of the cells of the benthic protozoan *Xenophyophores* (deposit feeders), but it is not clear if these organisms actively precipitate barite or selectively retain it in their cells during filter feeding (Fresnel et al., 1979; Gooday and Nott, 1982). Bertram and Cowen (1997) described various organisms that contain barite crystals within their tests or covering their tests; however, these

organisms are mostly benthic and are not abundant in the ocean. So far no abundant living marine planktonic organism with intracellular barite crystals has been identified, thus formation of barite in the water column by direct biological precipitation in living organisms (i.e., biogenic rather than authigenic barite) is thought to be negligible.

The undersaturated seawater and the minor role protozoans and algae assume in direct barite precipitation led to the suggestion that Ba released during degradation of organic material can create microenvironments in the water column that are supersaturated with respect to barite, inducing authigenic precipitation of barite (Goldberg and Arrhenius, 1958; Bishop, 1988; Ganeshram et al., 2003). The Ba content of many marine organisms is considerably higher than seawater concentrations (Fisher et al., 1991), providing a potential source of Ba to the microenvironments in which marine barite then precipitates.

Acantharia (protozoan zooplankton) have specifically been proposed as mediators of marine barite formation (Bernstein et al., 1992, 1998; Bertram and Cowen, 1997). Using the noncarbonate Sr content in suspended particles to track the presence of Acantharia, van Beek et al. (2007) suggested that acantharian dissolution contributes to barite formation in the upper 500 m of the water column. However, the lack of a clear correlation between barite abundance in the water column or in marine sediment and acantharian distribution indicates that these organisms are not required for the formation of barite in the ocean (Bertram and Cowen, 1997). Moreover, mesocosm decay experiments with natural coastal plankton and pure diatoms or coccolithophorids cultures that were allowed to decompose in dark oxic conditions induced barite formation (Ganeshram et al., 2003). These experiments provided direct evidence to support the water column microenvironment mechanism of marine barite formation and to verify that barite can form in the absence of Acantharia as long as some source of organic matter is present.

Bacterially induced barite precipitation was documented by González-Muñoz et al. (2003). This work was done with bacterial cultures using the heterotrophic soil bacterium *Myxococcus xanthus*. Glamoclija et al. (2004), Sanchez-Moral et al. (2004), Senko et al. (2004), Bonny and Jones (2007), and Tazaki et al. (1997) reported barite precipitation in natural terrestrial environments where microbes may have played a role in precipitation by oxidizing sulfur compounds to generate sulfate, providing biofilms favoring biomineralization, or bioaccumulating Ba in extracellular polymeric substances (EPS). Dehairs et al. (2008) demonstrated that higher mesopelagic particulate Ba concentrations in seawater coincided with higher bacterial activity, and suggested a potential relation. However, the role of marine bacteria in directly or indirectly mediating barite crystallization has not been confirmed. We demonstrate here that marine bacteria can mediate the precipitation of barite by providing nucleation sites and enhancing crystal growth.

## METHODS

Several strains of marine bacteria including *Idiomarina* (gram negative  $\gamma$ -Proteobacteria) from different habitats, *Idiomarina loihiensis*, *I. baltica*, *I. abyssalis*, *I. fontislapidosi*, and *I. ramblicola*, as well as the gram negative ( $\gamma$ -Proteobacteria) bacterium *Marinobacter hydrocarbonoclasticus* and the gram positive (Firmicutes) bacterium *Planomicrobium*

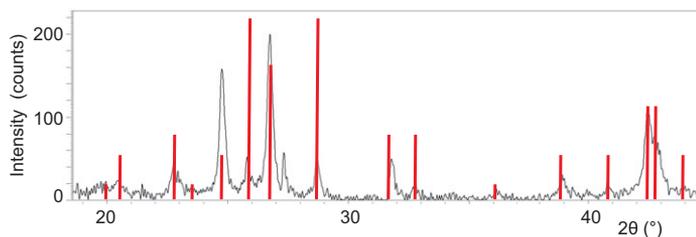
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*oceanokoite* were used for our experiments. These bacteria were selected because they are abundant in seawater; they live in different marine habitats and correspond to phylogenetically diverse species. Dead bacteria cells (prepared by autoclaving at 120 °C for 20 min or by ultraviolet light) were used as controls. Living and dead cells were inoculated on two different solid culture media enriched with Ba: (1) CM-Ba1: 0.4% yeast extract, 2 mM  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , 0.7% NaCl, 2% purified Difco agar-agar in distilled water (pH 7); and (2) CM-Ba2: 0.4% yeast extract, 2 mM  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , 3.5% NaCl, 2% purified Difco agar-agar in distilled water (pH 7). These two media contained different NaCl concentrations, one providing the minimum necessary NaCl concentration for marine bacterial growth and another close to seawater salinity, in order to check any potential salinity effect on bacterial growth and precipitation. It is important to note that the media used in the experiment initially contained no free sulfate, to avoid inorganic precipitation of barite; thus the entire sulfate in the barite was produced through bacterial metabolism and was released into the media. The inocula were prepared by cultivating bacteria in Difco-marine broth medium for 48 h at 28 °C. In both living-cell and dead-cell experiments, 50  $\mu\text{L}$  aliquots of the inocula were deposited on the solid media. Petri dishes were incubated at 28 °C and 5 °C for 30 days (to cover a wide range of seawater temperatures).

X-ray diffraction (XRD) was used for mineral identification. Representative portions of the cultures were dried at 37 °C for 24–48 h without microwave treatment to melt and remove the agar, in order to avoid any effect of melting on the nature of mineral phases. Subsequently, for detailed morphological analyses, precipitates were recovered by melting the solid medium in a microwave oven (600 W for 50 s) followed by washing with distilled water to eliminate culture medium remains and cellular debris. XRD analyses were done using a Panalytical diffractometer. For diffractogram interpretations, X Powder software (<http://www.xpowder.com>; Martin, 2004) was used. As halite precipitation resulted from drying out the media, this mineral was subtracted from the XRD diffractograms by using the X Powder software, which enabled better identification of barite phases. Precipitate compositions and morphologies were analyzed by scanning electron microscopy (SEM; LEO Carl Zeiss GEMINI-1530 and LEO GEMINI 1430-VP, coupled with energy-dispersive X-ray [EDX] microanalysis, QX, 2000 Link, at 20 kV).

## RESULTS

The Petri dishes were observed once a day under light microscopy to detect the presence of precipitates. Precipitates appeared in bacterial colonies after 3 days of incubation when incubated at 28 °C, and after 7 days when incubated at 5 °C; crystals were abundant and easily detectable in all living-cell experiments after 15 days. The final-stage pH was ~8 in the living-cell experiments. No precipitates were observed in the kill controls. XRD analyses show that barite is the only mineral phase present (Fig. 1), other than halite, which formed from media desiccation. XRD diffractograms obtained from precipitates at different stages of incubation show an evolution from poorly crystallized phases at early stages to increased

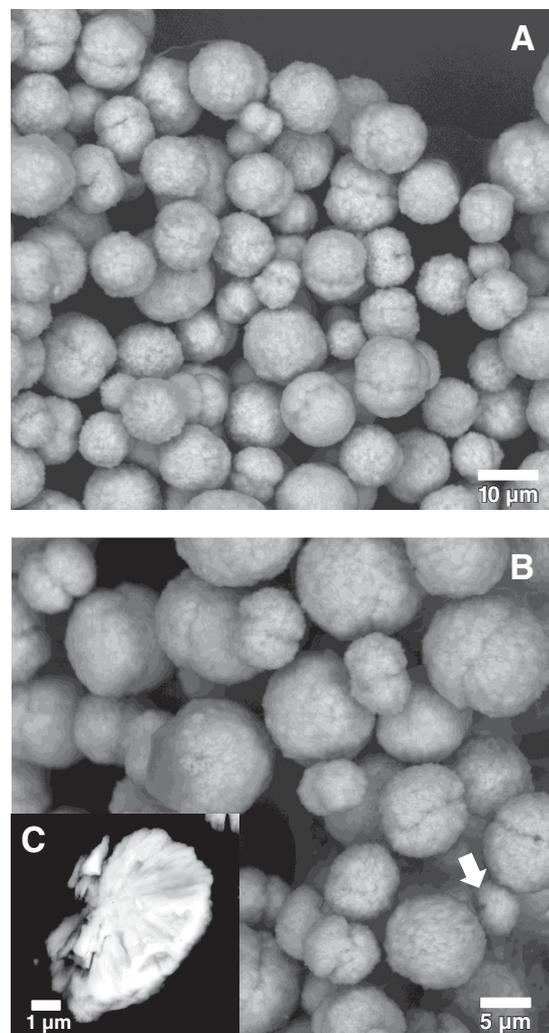


**Figure 1.** X-ray diffraction diagram of precipitates formed in culture experiments; barite peaks are indicated with red bars. Mineral halite peaks have been subtracted because halite precipitation results from desiccating media. All assayed bacteria produced similar precipitates.

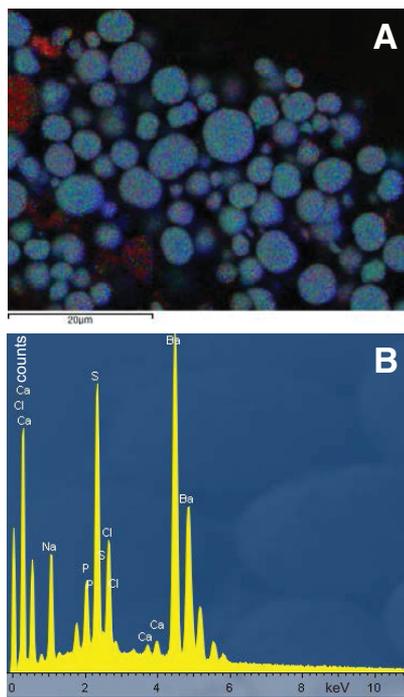
crystallinity with time. Crystal morphology as determined by SEM observations shows similarity of barite crystals in all experiments where they were seen. Barite habits were mostly spherulitic, with occasional dumbbell-shaped structures (Fig. 2). When visible, the internal textures of the barite crystals show fibroradial features (Fig. 2C). EDX analyses of the newly formed barite showed enrichment in P at the initial phases of crystallization, which became less prominent with time as barite precipitates became more crystalline (Fig. 3).

## DISCUSSION

Laboratory experiments (Bonny and Jones, 2008) and field observations (Bonny and Jones, 2007, and references therein) reveal that barite crystals of various shapes, morphology, and size can precipitate in association with bacteria. The crystal morphology depends on the presence of EPS or cell surfaces, whether the barite forms from addition of sulfate to a Ba-rich solution or vice versa. Solution viscosity, amino acid content, and other variables also exert control on morphology (e.g., Braissant et al., 2003). In our experiments, the barite morphologies seen (e.g., spherulitic and dumbbell habit) are similar to those observed in many other microbially



**Figure 2.** Scanning electron microscopy photographs showing morphologies of barite precipitates (*Idiomarina loihiensis* incubated at 28 °C). A, B: Spherulitic and dumbbells shapes. Arrow in B indicates analyzed point corresponding to energy-dispersive X-ray spectroscopy (EDS) analysis shown in Figure 3B. C: Backscattered image showing detail of fibrous internal textures.



**Figure 3. Energy-dispersive X-ray spectroscopy (EDS) micro-analytical data of barite precipitates. A: Phase map showing P (in red), S (green), and Ba (blue) distributions. B: EDS spectrum corresponding to analyzed point indicated with arrow in Figure 2B, which shows P-rich phases at initial stages of crystallization.**

precipitated mineral phases, and have been linked specifically to bacterial mineral precipitation (e.g., Braissant et al., 2003; González-Muñoz et al., 2003). These morphologies may differ from marine barite crystals found in natural environments (e.g., in the oceanic water column and sediments) (Bishop, 1988; Paytan et al., 2002) because of the range of factors controlling crystal habit and morphologies. Furthermore, crystallization rates may also be different in natural environments. However, the small size and rounded to elliptical morphologies seen in natural marine barite in the water column and in sediments underlying areas of high biological productivity (Bishop, 1988; Paytan et al., 2002) may be related to bacterial precipitation. Specifically, Bishop (1988) found barite microcrystals of similar size range, morphology, and varying degrees of crystallinity in oceanic sinking particulate matter.

The presence of high P levels in the initial crystals is also consistent with bacterial crystallization. The presence of a P-rich precursor seems to be a common step in microbial mineral precipitation; nucleation of an amorphous phosphate phase has also been reported for microbial aragonite precipitation and for bacterial biomineralization of apatite and iron oxides in laboratory conditions and also in natural environments (Rivadeneira et al., 2010, and references therein). This initial amorphous or poorly crystalline P-rich precursor phase suggests that phosphoryl groups in structural polymers (e.g., cell membranes or EPS) may act as sorbent constituents during the precipitation process. With the deprotonation of these groups, complexation sites are provided for metals in solution to bind. Because  $\text{Ba}^{2+}$  is a large cation, it would be particularly favored by  $\text{PO}_4^{3-}$  ligands. It is likely that cellular surfaces provide sites for the nucleation of Ba phosphate as Ba binds to the phosphate group of the cytoplasmic and/or outer membranes; following this, sulfate from the media binds to the Ba to form barite. XRD analyses are consistent with this process, showing increasing crystallinity over time as Ba and sulfate contents increase and the relative abundance of P decreases. The phosphate-sulfate transfer is a common process in natural environments specifically during crystallization (e.g., Van der Sluis et al., 1986). In fact, enzymatic reactions that promote the exchange of phosphate groups by sulfate groups play important roles in metabolism (e.g., Cleland and Hengge, 2006), and seem to be common in bacterial mineral precipitation, as also observed in microbial carbonate precipitation experiments (e.g., Gonzalez-Muñoz et al., 2008). Our results indicate that in our experimental setup bacteria play both an active and an

indirect passive role in the precipitation of barite. First they provide the necessary binding sites for Ba (EPS and cell walls), locally increasing its concentration and allowing for crystal nucleation and growth. Second, bacteria in the experiment were responsible for forming sulfate for mineral precipitation (our media did not contain free sulfate) and increasing the pH. Notably, in the ocean sulfate release is not important because of the high sulfate content in seawater. The EPS, in addition to functioning as a chelator for cations, may also provide a template for crystal nucleation.

Because the bacteria strains we used are common in the ocean in different habitats, it is likely that the processes we observe in cultures are occurring commonly in the ocean. The mechanisms for barite formation we propose here, i.e., Ba binding to phosphate groups on bacteria cells and EPS, which locally increases Ba concentrations, followed by replacement of phosphate by sulfate from seawater and barite crystal nucleation and growth, are consistent with all of the observations made regarding Ba and barite distribution in the ocean.

Bacteria in the water column are responsible for organic matter degradation and are more abundant where organic matter is plentiful, such as in organic-rich sinking particulate matter, biogenic debris, and sinking organic aggregates, which is where much of the barite in seawater has been observed (e.g., Bishop, 1988). Thus, while bacterial activity serves as an intermediate linking organic carbon export (e.g., export production) and barite formation, the empirical relation observed between barite concentrations in seawater and marine sediments and export productivity should be valid as long as bacterial activity is related in a consistent manner to available organic carbon. If, however, bacterial production varies from one region to another without maintaining a relatively constant relation to export production, and if this variability in bacterial production affects how much barite precipitates, this may introduce error to algorithms linking barite accumulation rates to export production.

The presence of specific binding sites for cations during barite formation may imply that trace element substitutions in the barite crystal structure could deviate from the expected theoretical inorganic distribution coefficient. For example, the calculated equilibrium Sr content in barite is ~13 mol%, while observations indicate that the actual Sr content in marine barite is typically <0.5 mol% (Averyt and Paytan, 2004). Moreover, if bacterial activity that forms the phosphorous compounds that mediate Ba binding is sensitive to temperature, as expected for bacterial metabolism (Hall et al., 2008), the temperature dependence of distribution coefficients may deviate from that expected from theoretical considerations. The bacterial involvement in barite precipitation may also explain the deviation of observed isotopic fractionation compared to those calculated from first-principles lattice dynamical modeling (Griffith et al., 2008). This suggests that for paleoceanographic applications, determining distribution coefficients empirically may be more useful than relying on theoretical inorganic chemical calculations, and that care should be taken when considering such chemical parameters when using barite for reconstructing ocean chemistry.

## CONCLUSIONS

Culture experiments with marine bacteria have served to demonstrate that bacteria have the capability to precipitate barite by providing nucleation sites and enhancing crystal growth. Bacterial precipitation is also supported by initial amorphous or poorly crystalline P-rich precursor phases that evolved to barite. The bacteria strains we used for our experiments are common in different ocean habitats, and therefore suggest that processes observed in culture are also likely occurring in the ocean. Hence, the role of bacteria in barite precipitation should be considered when using barite for paleoproductivity as well ocean chemistry reconstructions.

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