Quantitative visual analysis of marine barite microcrystals: Insights into precipitation and dissolution dynamics

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Abstract

The accumulation rate of authigenic barite (BaSO₄) in marine sediments is a promising proxy for reconstructing marine export production, but many aspects of barite precipitation and dissolution in the water column remain unknown. Here, we collected, imaged, and quantitatively analyzed 5481 barite microcrystals in bottle casts from the Eastern Pacific water column to gain a better understanding of in situ barite dynamics. Barite crystal abundance increases rapidly between the surface and 500 m in depth and then declines to predominantly low abundances below ~ 1000 m. The falloff in barite abundance between the oxygen minimum zone (OMZ) and the ocean interior suggests 60% ± 20% loss of barite by dissolution, nearly all of which is complete by water depths of 1000 m. However, there are occasional samples, as deep as 1250 m, with unusually high barite abundance that may represent marine snow deposition events. We found that microcrystals associated with organic matter substrates were smaller and less solid than free crystals, which suggests ongoing barite precipitation toward larger, more regularly shaped microcrystals within organic matter aggregates. Trends in barite microcrystal size with depth suggest that organic matter aggregates also play a role in shielding barite microcrystals from dissolution. In addition, our extensive data set raises new questions regarding marine barite nucleation and spatial heterogeneity. By helping bridge the gap between hypothesized barite dynamics and in situ observations of barite microcrystals, this study advances our understanding of water column Ba processes and the utility of sediment barite as an export production proxy.

Introduction

Export production, or the downward flux of organic carbon out of the surface ocean, plays an important role in regulating atmospheric carbon dioxide concentrations and thus global climate on a range of time scales (e.g., DeVries et al. 2012; Martinez-García et al. 2014; Gottschalk et al. 2019). Reliable proxies for export production in the geologic past are necessary to constrain the effect of climate on export production and vice versa. While various export production proxies have been employed, these proxies all present their own limitations (Hain et al. 2014).

The accumulation rate of the mineral barite (BaSO₄) in marine sediments and related sediment parameters are particularly promising proxies for reconstructing export production (Paytan and Griffith 2007; Griffith and Paytan 2012; Carter et al. 2020). The ocean is largely undersaturated with respect to barite (Monnin et al. 1999), but barite microcrystals are observed throughout the water column (e.g., Dehairs et al. 1980; Bishop 1988). Marine sediments that underlay more productive regions have been observed, since the mid-20th century, to contain elevated Ba concentrations (Chow and Goldberg 1960; Turekian and Tausch 1964). Extensive evidence has explained this correlation by barite precipitation within microenvironments created by sinking organic matter aggregates in the water column (e.g. Bertram and Cowen 1997; Ganeshram et al. 2003; Horner et al. 2015).

Recent work has helped illuminate the exact processes by which this barite precipitation occurs. Laboratory experiments and in situ observations suggest that bacterial biofilms, and in particular extracellular polymeric substances (EPS), mediate authigenic barite precipitation by concentrating Ba via amorphous, P-rich barite precursors (Martínez-Ruiz et al. 2018, 2019, 2020). Several strains of bacteria have also been shown to facilitate barite precipitation in the laboratory (González-Muñoz et al. 2003, 2012; Torres-Crespo et al. 2015). However, many aspects of marine barite precipitation remain elusive, in part due to the relative scarcity of direct observations of barite microcrystals in the water column.

The extent of barite dissolution in the water column is also poorly constrained (Carter et al. 2020). Approximately, 70% of authigenic barite deposited at the sediment water interface is thought to dissolve before incorporation into the sediment
record (Paytan and Kastner 1996). Qualitative morphological evidence of microcrystal etching and dissolution pits suggests that barite dissolution is also widespread in the water column (Sun et al. 2015). However, organic matter aggregates may play an important role in protecting barite microcrystals from dissolution (Carter et al. 2020).

A robust understanding of the factors that control water column barite precipitation and dissolution in the water column is crucial to our ability to reliably use sediment Ba proxies to reconstruct past particulate matter. Seawater (3–5 L) was filtered through polycarbonate filters with a diameter of 47 mm and a pore diameter of 12 μm. Subsamples of coarsely filtered water (1–2 L) were then filtered through polycarbonate filters with a diameter of 47 mm and a pore diameter of 0.22 μm. All filters were rinsed with 30 mL of deionized water to remove salts. Filters were dried in a fume hood and stored in airtight sample bags until later analysis. Filtration of all samples was completed within 6 h of collection.

**Methods**

**Sample collection**

Barite microcrystals were collected during a cruise of the R/V Sally Ride from 13 January 2020 to 21 January 2020 along the Fieberling-Guadalupe Seamount Chain in the Eastern Pacific (Fig. 1). This relatively oligotrophic ocean region experiences large-scale flows associated with the eastern rim of the subtropical gyre, southward surface flow associated with the California current, and northwestern currents from the equator (Roden 1991). The study site is 800 km from the nearest-known active hydrothermal vent, the White Point vent off the coast of Southern California (Beaulieu and Szafrański 2020).

Sampling was conducted using Niskin bottles attached to a conductivity-temperature-depth (CTD) rosette sampling system at five sites along the seamount chain, including one deep water site (Table 1). Continuous measurements of water temperature, salinity, and oxygen concentrations were recorded during each cast using a Sea-bird Electronics 911plus CTD (Fig. 2, Supporting Information S1). Continuous transmission measurements were recorded using a C-Star Transmissometer (Supporting Information S1).

Seawater from each depth was sampled via Niskin bottle spigot and sequentially filtered to collect suspended particulate matter. Seawater (3–5 L) was filtered through polycarbonate filters with a diameter of 47 mm and a pore diameter of 12 μm. Subsamples of coarsely filtered water (1–2 L) were then filtered through polycarbonate filters with a diameter of 47 mm and a pore diameter of 0.22 μm. All filters were rinsed with 30 mL of deionized water to remove salts. Filters were dried in a fume hood and stored in air-tight sample bags until later analysis. Filtration of all samples was completed within 6 h of collection.

**Barite analysis**

Barite microcrystals on each filter with 0.22-μm pores were imaged via scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDS). Approximately one quarter of each filter was mounted on an aluminum stub with carbon tape for analysis. Analyses were conducted on a Phenom Desktop SEM with an accelerating voltage of 15 kV, vacuum of 1 Pa, and working distance of 9–10 mm. For each filter sample, a random number generator was used to randomly select a field (0.65–0.81 mm² in area) for analysis. A backscatter electron detector was used to systematically identify all potential barite microcrystals within the field by their high atomic number. Identification was confirmed by EDS, and all barite microcrystals were imaged. Additional point(s) were analyzed as necessary to determine if microcrystals were associated with organic matter substrates, which appeared visually distinct from the flat surface of the polycarbonate filter. This process was repeated for two additional randomly selected fields for each filter. Smaller areas (0.2–0.4 mm²) were analyzed for two filters with extremely high barite microcrystal densities (S4 100 m and S5 1250 m). A total of 5481 barite microcrystals were imaged from 54 bottles sampled at 5 sites.

Images were quantitatively analyzed using the FIJI distribution of ImageJ (Schindelin 2012; Schindelin et al. 2015). Scaling parameters were extracted from the metadata of each image. Barite particles were distinguished from the filter background and surrounding particles using the Trainable Weka Segmentation plugin (Arganda-Carreras et al. 2017). The resulting binary image was smoothed to retain 10% of available Fourier descriptors using the Shape Smoothing plugin. Barite microcrystal abundance for each field was calculated as follows:

\[
A_b = \frac{n_b \cdot A_f}{A_u \cdot V},
\]

**Fig. 1.** Locations of sampling sites S1–S5 in the Eastern Pacific. Bathymetry is from the global multiresolution topography (GMRT) synthesis (Ryan 2009).
Table 1. Sampling locations and depths. In total, 54 samples were collected across 5 sites.

| Site | Latitude  | Longitude  | Seamount      | Maximum water depth (m) | Water depths sampled (m) |
|------|-----------|------------|---------------|-------------------------|--------------------------|
| S1   | 32.434°N  | 127.801°W  | Fieberling     | 544                     | 50, 100, 150, 200, 300, 400, 500 |
| S2   | 32.261°N  | 127.233°W  | Fieberling 2   | 1407                    | 50, 100, 150, 200, 300, 400, 500, 750, 1000, 1250, 1400 |
| S3   | 32.086°N  | 126.906°W  | Hoke          | 1044                    | 50, 100, 150, 200, 300, 400, 500, 750, 1000 |
| S4   | 31.916°N  | 126.561°W  | N/A           | 4274                    | 50, 100, 150, 200, 300, 400, 500, 750, 1000, 1250, 1500, 2000, 2500, 3000, 3500, 4000, 4200 |
| S5   | 31.765°N  | 126.249°W  | Stoddard      | 1579                    | 50, 100, 150, 200, 300, 500, 750, 1000, 1250, 1500 |

Fig. 2. (A) Abundances of all barite microcrystals, (B) dissolved oxygen concentrations, (C) abundances of clusters of adjoined barite microcrystals, and (D) temperature with depth in the water column. Abundance points indicate average abundance ± standard error across the three filter fields analyzed for each sampling depth and site. Vertical lines and text labels indicate average abundance ± standard error for each water layer. Outlying abundance values ± standard error are shown in the middle panel. Dissolved oxygen and temperature profiles were acquired during CTD down casts and were smoothed via boxcar averaging with a step size of 10 m.
where \( A_b \) is barite microcrystal abundance, \( n_p \) is number of barite particles observed in a given field, \( A_f \) is area of the filter, \( A_s \) is area of the field analyzed, and \( V \) is the volume of seawater filtered through the corresponding filter. Area, solidity, aspect ratio, and circularity were calculated for each smoothed particle using the ImageJ’s Analyze Particle plugin (Supporting Information S2–S5). Solidity was calculated as a quantitative measure of morphology—specifically of the regularity of the outline of each microcrystal—according to the equation:

\[
S = \frac{A}{A_C},
\]

where \( S \) is solidity, \( A \) is the area of the particle, and \( A_C \) is the area of the convex hull, or the smallest convex polygon that encloses the particle’s outline (Supporting Information S2). Images were also visually analyzed to determine if each barite microcrystal was associated with organic matter and/or occurred in a cluster with other barite microcrystals. Barite particles greater than 8 \( \mu m \) in diameter were identified as potentially hydrothermal in origin and excluded from statistical analyses.

**Statistical analyses**

The abundance and features of barite microcrystals were statistically compared for three layers in the water column: surface (0–200 m), OMZ (201–1000 m), and deep (> 1001 m). These layers were consistent with observed \( O_2 \) profiles during sampling (Supporting Information S1). We calculated barite particle and microcrystal cluster loss from the OMZ to the deep water layer according to the equation:

\[
L = 1 - \frac{A_{\text{Deep}}}{A_{\text{OMZ}}},
\]

where \( L \) is loss, \( A_{\text{Deep}} \) is the abundance of barite particles/clusters in the deep water layer, and \( A_{\text{OMZ}} \) is the abundance of barite particles/clusters in the OMZ layer. One-way ANOVAs with a posteriori Tukey’s honestly significant difference (HSD) tests were used to compare barite microcrystal abundance and microcrystal cluster abundance between layers, treating layer as a fixed variable and filter as a random variable. Filters S4 100 m and S5 1250 m were identified as statistical outliers according the protocol described by Zuur et al. (2010) and thus excluded from abundance statistics.

One-way ANOVAs with a posteriori Tukey’s HSD tests were used to compare microcrystal area and solidity per particle between layers. Two-way ANOVAs were conducted to examine the interaction of association with organic matter and layer on particle area and solidity. Post hoc simple effects comparisons were conducted to determine the influence of association with organic matter on area and solidity within each layer. A chi-squared test of independence was used to compare frequency of organic matter association between clusters and individual particles. Abundance values were square root transformed and area and solidity values were log transformed for all statistical analyses to meet assumptions of normality and homogeneity of variances.

All analyses were performed in R: A Language and Environment for Statistical Computing, Version 3.6.3 (R Core Team 2020). Tidyverse was used for data processing (Wickham et al. 2019), lme4 was used to fit linear mixed effects models for statistical analyses (Bates et al. 2015), and ggplot2 was used for data visualization (Wickham 2016).

**Results**

**Barite microcrystal abundance and size**

Barite microcrystal abundance increased rapidly between the surface and ~ 500 m depth before steadily decreasing until ~ 1000 m depth (Fig. 2A). Barite microcrystal abundance was higher in the OMZ (45.0 ± 4.1 particles mL\(^{-1}\)) than in the surface (23.9 ± 3.0 particles mL\(^{-1}\)) or deep (18.8 ± 2.2 particles mL\(^{-1}\)) water layers (\( p = 0.004 \), Fig. 2A). Barite was observed on 52 out of 54 filters analyzed; only filters S1 50 m and S5 50 m contained no visible microcrystals in the fields randomly selected for analysis.

Of 5481 barite particles imaged, 971 were present as clusters of submicron barite microcrystals (e.g., Fig. 3D,K). Clusters were observed on 48 out of 54 filters analyzed. The distribution of microcrystal clusters largely mirrored that of barite particles as a whole (Fig. 2B). Cluster abundance was higher in surface (4.4 ± 0.9 clusters mL\(^{-1}\)) and OMZ (5.5 ± 0.7 clusters mL\(^{-1}\)) layers than in the deep (1.6 ± 0.6 clusters mL\(^{-1}\)) layer (\( p = 0.036 \), Fig. 2B).

Barite microcrystal abundance was more than 3 times higher and microcrystal cluster abundance was more than 10 times higher for filters S4 100 m and S5 1250 m than for any other filter (Fig. 2). With the exception of these outliers, microcrystal and microcrystal cluster abundance patterns were similar across all five sites.

Most barite microcrystals were between 0.25 and 1.75 \( \mu m \) in length (Supporting Information S3). Barite microcrystals were larger in the OMZ (0.90 ± 0.03 \( \mu m^2 \)) than in surface (0.81 ± 0.03 \( \mu m^2 \)) or deep (0.74 ± 0.04 \( \mu m^2 \)) layers (\( p = 0.002 \), Fig. 4). Average barite microcrystal size increased below 3000 m (1.12 ± 0.10 \( \mu m^2 \)), but relatively few (\( n = 183 \)) microcrystals were analyzed for these depths. There was a significant interaction between layer and association with organic matter on microcrystal size (\( p < 0.001 \), Fig. 5A). In post hoc comparisons, particles associated with organic matter were smaller than particles not associated with organic matter in surface (\( p < 0.001 \)) and OMZ layers (\( p < 0.001 \), but no significant difference was observed in the deep layer (Fig. 5A). Clusters of barite microcrystals were ~ 50% larger by area than individual barite particles, but since each cluster contained from at least 4 to more than 20 microcrystals, microcrystals within clusters
Fig. 3. Representative barite microcrystals displaying a range of morphologies. (A) Large, platy barite microcrystal potentially hydrothermal in origin. (B) Barrel-shaped barite microcrystal in association with organic matter. (C) Barrel-shaped barite microcrystal displaying etch pits and signs of dissolution. (D) Cluster of submicron, barrel-shaped barite microcrystals. (E) Barrel-shaped barite microcrystal. (F) Circular barite microcrystal. (G) Hexagonal barite microcrystal. (H) Double-headed arrow barite microcrystal showing signs of dissolution along edges. (I) Irregularly shaped barite microcrystal. (J) Irregularly shaped barite microcrystal in association with organic matter. (K) Cluster of submicron barite microcrystals with diverse morphologies and sizes. (L) Hexagonal barite microcrystal with an etch pit in the center.
were, on average, much smaller than barite particles that were not in clusters (Fig. 3). No systematic differences in barite microcrystal area were observed between sites.

Five barite microcrystals had diameters greater than 8 μm and were thus characterized as potentially hydrothermal in origin. These five microcrystals resembled the hydrothermal barite particles displayed in Paytan et al. 2002 and exhibited platy morphologies visually distinct from the other barite microcrystals observed in the water column (e.g., Fig. 3A). Two of these likely hydrothermal barite particles were from S4 100 m water depth, two were from S5 400 m water depth, and one was from S5 1250 m water depth.

**Barite microcrystal morphology**

A wide range of barite morphologies were observed across all five study sites (Fig. 3, Supporting Information S3). Most microcrystals were ovoid or barrel shaped (e.g., Fig. 3B–E), but many microcrystals also displayed rectangular or hexagonal morphologies (e.g., Fig. 3G). Several circular (e.g., Fig. 3F) and double-headed arrow (e.g., Fig. 3H) morphologies were also observed. Many microcrystals also displayed irregular or amorphous morphologies (e.g., Fig. 3I,J). Most microcrystal clusters contained microcrystals displaying similar sizes and morphologies within the cluster (e.g., Fig. 3D), but some displayed more heterogeneous microcrystal sizes (e.g., Fig. 3K). Nearly 50% of particles were visibly associated with organic matter substrates (e.g., Fig. 3B,J). There was no significant difference in association with organic matter between individual microcrystal and microcrystal clusters. Approximately, 10% of microcrystals (e.g., Fig. 3C,L) displayed visible signs of dissolution such as etch pits or inner cavities (Dunn et al. 1999).

Microcrystal solidity ranged from 0.5 to 1, which means that particle outlines ranged from very concave and irregular to perfectly solid, such as in the case of a perfect ellipse or polygon. Barite microcrystals displayed higher solidity, or had more regularly shaped outlines, in the OMZ (0.921 ± 0.002)
than in surface (0.945 ± 0.001) or deep (0.927 ± 0.002) layers
($p < 0.001$, Fig. 4). There was a significant interaction between
layer and association with organic matter on microcrystal
solidity ($p = 0.039$, Fig. 5B). In post hoc comparisons, particles
associated with organic matter displayed lower solidity than
particles not associated with organic matter in the surface
layer ($p = 0.012$), but no significant difference was observed in
OMZ and deep layers (Fig. 5A). No systematic differences
in solidity were observed between sites.

Discussion

Potential allogenic barite sources

The distinctive morphology and relatively large size of five
barite microcrystals suggest that they are in a different class
than the authigenic marine barite microcrystals that dominate
our sample, and for this reason we excluded them from our
statistical analyses. Nonetheless, the origins of these micro-
crystals are speculative given the local nature of our sample
set, and hence we can only suggest possible sources. First,
the large microcrystals may have come from a hydrothermal
source north of the study region. Our samples were collected
in the western limb of the California Current, where flow is to
the southeast with a mean velocity of 3–5 cm s$^{-1}$ (Centurioni
et al. 2008). Since there is no known near-surface source area
for hydrothermal barite to the northwest of our study area,
the microcrystals may have been advected offshore by coastal
jets within the California Current System (Centurioni
et al. 2008; Matthews and Emery 2009). The nearest-known
active hydrothermal vents (Beaulieu and Szafrański 2020) are,
respectively, 800 km to the east and 1000 km to the north of
Study Sites S4 and S5, raising the possibility of long distance,
offshore transport.

A second possibility is that these particles may be diagenetic
barite locally derived by advection off the tops or flanks of the
Fieberling Seamount chain. However, we consider a local source
unlikely because the unusually large barite microcrystals were distributed
throughout the water column and the CTD profiles we
collected with our bottle casts suggest that localized upwelling
was not occurring during our cruise (Figs. 2, S1). A third possibili-
ty is that the large barite microcrystals might reach our site via
dust transport from the Southwestern deserts; Santa Ana winds
transport large amounts of dust and soot offshore into the Eastern
Pacific (e.g., Jardine et al. 2021). This possible origin is made more
plausible by observations that the large barite microcrystals are on
the small end of the grain-size spectrum for loess deposited on
the Channel Islands, where the mean grain size is about 35 μm
(Muhls et al. 2007). In addition, authigenic barite is observed in
paleosols in Southern Nevada (Brock-Hon et al. 2012; Robins
et al. 2012). However, barite has not been reported in loess from
the California deserts or islands, suggesting that if it is present, it
is a rare accessory mineral.

Barite precipitation in organic matter aggregates

Barite microcrystal abundance patterns provide evidence
for barite precipitation in association with organic matter
remineralization (Fig. 2). The rapid increase in barite microcrystal
abundance between the surface and 500 m depth is consistent
with carbon remineralization rate profiles in the Eastern Pacific
(Feely et al. 2004). These mesopelagic increases in microcrystal
abundance are consistent with mesopelagic particulate Ba peaks
reported in previously studies (Dehairs et al. 1980, 1991;
Martínez-Ruiz et al. 2020) and implied by dissolved Ba and Ba
isotope profiles (Horne et al. 2015; Hsieh and Henderson 2017;
Bridgestock et al. 2018). The presence of barite microcrystals at
all sample sites below 50 m depth also indicates that widespread
authigenic barite precipitation begins in the euphotic zone, as
does organic matter remineralization (Abell et al. 2000).

Barite microcrystal area and solidity data also highlight the
link between organic matter aggregates and barite precipitation.
Marine barite particles are thought to begin as amorphous pre-
cursors and precipitate toward more regularly shaped micro-
crystals (Martínez-Ruiz et al. 2019). Thus, the small size and
low solidity of microcrystals observed in association with
organic matter substrates compared to free crystals suggest that
crystals within aggregates represent snapshots of ongoing barite
precipitation (Fig. 5). The microenvironments created by these
aggregates likely facilitate precipitation toward larger microcrys-
tals with more regular, that is, solid, morphologies. Disintegra-
tion of these aggregates over time then leaves behind barite
microcrystals not associated with organic matter. Ongoing pre-
cipitation toward larger, more solid particles also helps explain
crystal solidity and area patterns with depth; microcrystals were
smaller and less solid in surface waters relative to more mature
barite microcrystals in the OMZ (Figs. 4 and 6).

Together, these findings constitute novel lines of evidence
for recently proposed pathways for barite precipitation. While
precise characterization of the organic matter substrates
observed here is outside the scope of this study, our extensive
observations of barite microcrystals associated with organic
matter are consistent with the proposed link between barite
precipitation and EPS suggested by Martínez-Ruiz et al. (2019).
Our findings of ongoing precipitation toward more solid barite
microcrystals may also be evidence of barite precipitation via
sulfate substitution for phosphate in amorphous Ba-rich inter-
mediaries (Martínez-Ruiz et al. 2018). A range in crystal shapes
during early crystallization may also explain the wide range in
morphologies we observed among barite microcrystals (Fig. 3,
Supporting Information S3).

Water column barite dissolution dynamics

Barite microcrystal abundance profiles indicate an increase
in water column barite dissolution relative to precipitation
between depths of 500 and 1000 m (Fig. 2). The falloff in bar-
ite abundance between the OMZ and the ocean interior below
1000 m is consistent with 60% ± 20% loss by dissolution for
all barite particles and 70% ± 40% loss for microcrystal clusters in particular. This decline may reflect an absolute increase in barite dissolution below 500 m. Alternatively, since organic matter remineralization is expected to decrease below depths of 500 m, this decline in barite microcrystal abundance may be the result of fairly consistent rates of barite dissolution in the upper 1000 m accompanied with a decrease in barite precipitation below 500 m.

Microcrystal size and morphology are consistent with water column barite dissolution, particularly in the lower OMZ. Barite microcrystals were smaller and less solid in deep water relative to the OMZ (Figs. 4 and 6). We also observed qualitative evidence of barite microcrystal dissolution in the form of etching and dissolution pits, similar to that reported by Sun et al. (2015), in approximately 10% of barite microcrystals analyzed throughout the water column (Fig. 3).

The abundance of marine barite microcrystals appears to be fairly constant below 1000 m in depth, which suggests that rates of barite dissolution are relatively low in deep waters (Fig. 2). This may be partly due to the shielding of barite microcrystals from dissolution by organic matter aggregates. Microcrystals that are associated with organic matter are smaller and less solid than microcrystals that are not associated with organic matter in the surface layer (Fig. 5). However, in the deep layer mean area and solidity are equivalent for microcrystals that are and are not associated with organic matter (Fig. 5). In the case of microcrystal area, this convergence is largely driven by a reduction in area for microcrystals that are not associated with organic matter. This suggests that dissolution is less pronounced within the microenvironments made by flocs of sinking organic matter. This organic matter shielding effect likely occurs throughout the water column, but its importance for marine barite cycling is most pronounced in deep waters, where barite microcrystal abundances are low. The shielding effect of organic matter aggregates may also play a significant role in facilitating barite preservation long enough to reach marine sediments.

The size distribution of the water column barite microcrystals we analyzed here was skewed toward smaller particles relative to the barite microcrystal size distribution reported for Central North Pacific marine sediment in Robin et al. 2003. This likely indicates that most submicron barite microcrystals in the water column dissolve at the sediment–water interface before incorporation into the sediment record. The increase we observed in average barite microcrystal size below 3000 m depth may similarly indicate the complete dissolution of smaller barite microcrystals in the deep water column (Fig. 4). However, we did not observe a continued decrease in microcrystal abundance at these depths, and significant deep-water precipitation to offset dissolution and maintain constant barite abundances is unlikely because of continued destruction of sinking organic flocs.

**Barite microcrystal clusters**

The prevalence of submicron barite microcrystal clusters suggests that clusters may provide clues to authigenic barite formation mechanisms. Barite clusters imply that relatively large numbers of distinct barite nucleation points can exist in close proximity to one another within organic matter aggregates. The formation of larger barite microcrystals may be impeded by growth competition within microcrystal clusters, as has been shown to occur when other minerals precipitate from multiple nucleation sites in close proximity to one another (e.g., Yang et al. 2014). Moreover, the range of microcrystal size and shape within some clusters (e.g., Fig. 3K) implies that a range of barite precipitation rates can occur within individual organic matter aggregates. This points to the complexity of barite precipitation mechanisms and the likelihood of Ba-rich intermediary phases.

Submicron microcrystal clusters themselves could serve as precursors to larger barite particles. Clusters are particularly abundant in the surface layer and on filters with very high barite microcrystal abundance (Fig. 2), which suggests that clusters may form early in the barite precipitation process. In addition, the combination of submicron microcrystals into larger particles may explain the irregularly shaped barite microcrystals observed here (e.g. Fig. 3L,J) and described in other studies (Dehairs et al. 1980; Sun et al. 2015). However, we find that microcrystal clusters were not significantly more likely to be associated with organic matter than individual particles. Since our other data indicate that microcrystals within organic matter aggregates represent snapshots of ongoing barite precipitation, this undermines the hypothesis of microcrystal clusters as precursors of larger particles. Further research is needed to determine the role submicron microcrystal clusters play in the broader context of authigenic barite precipitation.

**Spatial variability and authigenic barite hotspots**

We did not observe systematic differences in barite microcrystal abundance or properties along the study site transect or between our deep water site and the sites overlying seamounts (Figs. 2, 4, and 6). However, we did observe considerable variability between individual sites and depths. Downward organic carbon flux is largely driven by relatively large and rare organic matter aggregates (Alldredge and Silver 1988; Honjo et al. 2008). Since barite precipitation is thought to occur in association with organic matter aggregates, it thus follows that barite distribution in the water column is heterogeneous and somewhat stochastic. By sampling small water volumes, our investigation likely captured this spatial heterogeneity.

Two filters in particular, S4 100 m and S5 1250 m, showed exceptionally high barite microcrystal abundances (Fig. 2). Transmission data and other water parameters showed no discontinuities at these depths (Supporting Information S1), so
these peaks are likely not due to oceanographic perturbations such as sediment advected off the seamounts or hydrographic transitions in water properties at these depths. Rather, they may be remnants of large organic matter aggregates that just happened to be sampled by the Niskin Bottle. Alternatively, these peaks may track events of mass production of organic matter flocs near the surface and their sedimentation into the ocean interior.

The samples with very high barite microcrystal abundance suggest that sediment barite accumulation may be dominated by localized barite precipitation events. Apart from the aforementioned overrepresentation of clusters, microcrystals at these depths were similar to those observed elsewhere in the water column. This suggests that they precipitated through similar mechanisms, but additional research is necessary to constrain the drivers for and implications of barite heterogeneity in the water column.

**Conclusions**

Our quantitative visual analysis of thousands of barite microcrystals provides a novel line of evidence for authigenic barite precipitation in association with organic matter aggregates and suggests that these aggregates help protect barite microcrystals from dissolution. We can also quantify the steep loss of barite microcrystals below ~500 m water depth, presumably due to the dissolution of 60% ± 20% of particles formed shallower in the water column. This large-scale data set is the first of its kind and opens up new avenues for research regarding submicron microcrystal clusters and spatial heterogeneity of barite in the water column. While the accumulation rate of barite in marine sediments is a common export production proxy, direct observations of in situ barite microcrystals are limited and significant questions remain regarding the factors that influence marine barite precipitation and preservation, both within the water column and at the sediment–water interface. By providing insight into water column barite dynamics, our findings help contextualize the sediment barite record and serve as a crucial intermediary step in developing Ba sediment proxies to their full potential.

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Conflict of Interest
None declared.