

# Unravelling organic-mediated pathways in barium phosphate formation: insights into marine barite nucleation

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## INTRODUCTION

The biogeochemical role of barium (and barite,  $\text{BaSO}_4$ ) in ocean chemistry and regulating the global carbon cycle has been broadly demonstrated (DeVries, 2022). Consequently, Ba proxies have proven to be valuable tools for reconstructing past export production in the ocean, due to the relationship between particulate organic carbon and Ba fluxes (Martinez-Ruiz et al., 2018). However, much of the research on marine barite leaved several unknowns regarding the nucleation and precipitation process of this mineral in marine environments (Paytan and Griffith, 2007) and crucial aspects, such as the formation mechanisms and the role of organics in barite precipitation, limiting its effective use as a biogeochemical proxy (Light et al., 2023). In this context, previous studies suggest that marine barite formation follows a two-step process, with a barium phosphate precursor (Ba-P) playing a key role in concentrating Ba for subsequent barite formation (Martinez-Ruiz et al., 2019). To the best of our knowledge, this critical phase has not been studied in detail, increasing the gaps in understanding the marine barite precipitation process and, consequently, its application as a paleo-productivity proxy.

In this work, we performed a series of controlled precipitation experiments to characterize and investigate the formation mechanisms of the Ba-P precursor phase and assess the impact of organic additives on its nucleation and stability. By using  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{NaH}_2\text{PO}_4$  as phosphate sources and introducing various organic compounds (i.e., soy phospholipids, sodium formate, ascorbic acid, and pyromellitic acid), we aimed to elucidate the conditions that favor Ba-P formation. Our findings contribute to understanding how organics influence precursor pathways and offer insights into the early stages of marine barite precipitation.

## MATERIALS AND METHODS

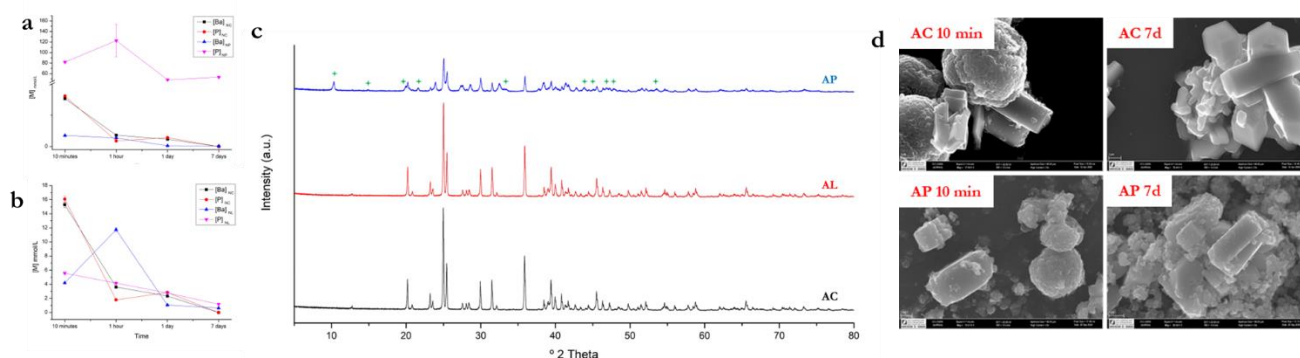
**Experimental Setup:** Two experimental setups were conducted: (i) barium chloride dihydrate (0.1 M) was mixed with either di-ammonium phosphate (0.1 M) or (ii) sodium phosphate (0.1 M) to examine the influence of the phosphate source. To assess the impact of organics, each experiment was run independently with soy phospholipids (200 ppm), L-ascorbic acid (0.1 M), sodium formate (0.1 M), and pyromellitic acid (50 mM), selected for their roles in mineral morphology and biogeochemical cycles. Reactions were conducted at room temperature with 50 mL of ultrapure Milli-Q water, sampled at four intervals. Solids were filtered, ethanol-washed, and dried.

**Analytical Techniques:** Solution pH was measured with a glass electrode, and Ba and P concentrations were analyzed by ICP-OES. XRD with Cu  $K\alpha$  radiation characterized crystalline precipitates, and Rietveld analysis was performed using TOPAS 5.0 to match Ba-P lattice parameters with PDF4 database peaks. ATR-FTIR provided structural, organic, and hydration information, and FE-SEM with EDS and TEM-EDS enabled morphological and compositional studies.

## RESULTS AND DISCUSSION

Control solutions showed a progressive decrease, up to zero, of both ions (e.g., Ba and P) over time in the same ratio (Fig. 1a). However, in solutions containing organics, particularly acids, a discrepancy in P concentration relative to Ba was observed, with P even increasing over time in some cases, while Ba continued to decrease (Fig. 1a). These results suggest that Ba-containing phases depleted in P precipitated in the system. This pattern was not seen in

solutions with phospholipids (Fig. 1b), where both ions followed a similar trend, indicating that for each Ba precipitated, a P ion was also incorporated into the phase.



**Fig 1.** Ba and P concentration in solution in control experiments with  $(\text{NH}_4)_2\text{HPO}_4$  (AC) and (a) pyromellitic acid (AP) and (b) soy phospholipids (AL). (c) XRD patterns of AC, AL and AP after 7 days of experiment. (d) FESEM micrographs of AC and AP after 10 min and 7 days.

In the XRD analyses (Fig. 1c), our results revealed diffraction peaks corresponding to  $\text{BaHPO}_4$  (BHP), along with a substantial background that decreased over time, indicating a reduction in the amorphous content. These findings challenge previous assumptions about this phase, demonstrating that the Ba-P precipitate was not entirely amorphous but contained a substantial crystalline component. These results are crucial, as they shift the current understanding of the transformation from this precursor to barite. Previously, it was believed that this transformation occurred from an amorphous BaP to a crystalline barite. However, the kinetics and transformation dynamics between two crystalline materials differ fundamentally, impacting the final properties of the resulting sulfate. Additionally, XRD results showed that BHP was the only crystalline phase identified in the control experiments, whereas in organic acid solutions, other Ba-containing phases were detected (e.g., Ba-pyromellitic in pyromellitic acid solutions, green stars in Fig. 1c), and confirmed by FT-IR analyses. This indicates that the variations in the Ba/P ratio in solution were influenced by Ba interacting with organics to precipitate as organic complexes. Rietveld results revealed a d-spacing decrease with time in control experiments, typical from a time-resolved crystallization pathway. However, two key differences were observed in experiments with organics: (i) an increase in d-spacing, primarily in the a- and c-axes, with a reduction in the b-axis compared to control experiments, suggesting the occlusion of organics within the BHP unit cell, and (ii) a further increase in d-spacing in BHP precipitated from organic acid solutions, indicating a rise in organic content within the unit cell over time. Finally, FESEM micrographs (Fig. 1d) confirmed an increase in crystalline material in the control samples, showing more well-formed crystals after 7 days, while in pyromellitic solutions, an increase in a nanogranular phase was observed at the end of the experiments, demonstrating the coexistence of both Ba-containing phases.

Our findings reveal that, contrary to previous assumptions, the transformation from BaP to barite is not straightforward and is heavily influenced by kinetics and the dynamics of transitioning from one crystalline phase to another. Furthermore, these results underscore the presence of organic complexes with Ba, adding complexity to the system and the subsequent formation of barite from these phases.

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