

## Kinetic study of bio-barite preservation in deep-sea sediments

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Relationships between barite (BaSO<sub>4</sub>) microcrystals production in the water column (bio-barite) and ocean productivity are now clearly established, although formation mechanisms are still poorly understood. As such quantitative information might be preserved in sedimentary records, barium (or more precisely bio-barite) has been proposed as a proxy to reconstruct paleoproductivity (Dymond et al., 1992; François *et al.*, 1995). Recently, Robin *et al.* (submitted) proposed a new method for quantifying directly biobarite concentrations in deep-sea sediments that allows low level detections. Additional studies aimed at validating the use of bio-barite as a proxy are still needed. As an example, the preservation of biobarite within sediments in relationship with pore water and sediment compositions has to be better understood.

In this work, we investigate sediment reactivity with respect to pore-water barium concentrations. As a first attempt, we utilize bulk sediments from the North Tropical Atlantic Ocean (EUMELI IV cruise, 3104 m water depth) and stirred micro-reactors. Experiments are designed to extract apparent solubility and dissolution/precipitation reaction rates. Preliminary solubility value for bulk sediments supports the hypothesis of a control of pore water barium concentrations by nearly pure barite precipitation. This result will be compared to that obtained with chemically separated bio-barite (van Beek and Reyss, 2001).

## Geomicrobial Mechanisms of Carbonate Precipitation: Novel Insights from Laminated Structures

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Carbonates, including CaMg(CO<sub>3</sub>)<sub>2</sub> and CaCO<sub>3</sub>, are common features in sedimentary systems. Recently, several models for dolomite (Vasconcelos and McKenzie 1995) and aragonite (Reid et al. 2000) formation have been postulated.

Laminated sedimentary biofilms (e.g., microbial mats) are structures in which microbes live in close proximity, resulting in tight cycling of major elements (C, N, S, etc.). As with all elements, C cycling requires additional redox species to function: For example, electron donor for C fixation can be O (H<sub>2</sub>O) or S (HS<sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, etc.) and respiration of organic C is facilitated by O<sub>2</sub> or SO<sub>4</sub><sup>2-</sup> (SO<sub>3</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, etc.). The C cycle is primarily an energy-transfer mechanism, in which reductive and oxidative processes are balanced. However, decoupling of these processes in time and/or space may result in permanent biogenic signatures: When respiration prevails, carbonates can be formed as a permanent signature.

We observed in various laminated sediment systems (Mexico, Bahamas, and Brazil) that a simple balance between oxygenic photosynthesis and aerobic respiration does not explain precipitation. Instead, S cycling needs to be considered: Spatial and temporal decoupling of SO<sub>4</sub><sup>2-</sup> reduction and HS<sup>-</sup> oxidation and metabolic diversity of organisms involved in S cycling are fundamental phenomena that determine whether precipitation or dissolution occurs. The laminated organization of populations, processes and products makes such contemporary structures very useful in understanding mechanisms of carbonate precipitation.

### References

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