

Barite Formation Experiments

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The ultimate burial of particulate organic carbon (POC) represents a climatically significant sink of the CO₂ drawn down by photosynthetic organisms in the sunlit surface ocean. However, quantification of marine export production and POC burial in the sediments, and its ultimate effects on global climate, has remained a delicate problem described by a handful of proxies, each with caveats. Marine barites have emerged as one powerful proxy option based on the barite formation pathway currently invoked in the literature. Despite this potential, controls on the formation of barite in the water column are greatly understudied. Currently, consensus does not exist as to the mechanism of barite formation (Chow & Goldberg 1960, Van Beek et al 2007, Gonzalez-Muñoz et al 2012) or the depth of barite formation in the water column (Van Beek et al 2007, Horner et al 2015). Although pelagic surface waters are under saturated with respect to barite, microcrystalline barite appears throughout the water column. To overcome this apparent paradox, much of the current literature invokes the microenvironment model: Barite precipitation occurs exclusively within locally supersaturated microenvironments contained within sinking POM, of which POC is a fraction. Supersaturation occurs through the release of dissolved barium during the microbial degradation of POM. To Investigate the controls on this precipitation mechanism, incubation experiments using a stable ¹³⁵Ba tracer were carried out during the SAMW 2020 cruise.

Barite formation experiments were initiated at the same stations as the Balch/Morton nutrient amendment incubations (Stations 05, 18, 28, 56) and coincided with productivity and trace metal casts. From the main CTD casts, water samples from the fluorescence peak, maximum increase in beam transmission (region of decreasing particle load), and oxygen minimum were used to target areas with high phytoplankton growth, particle degradation, and microbial action, respectively. Samples were first spiked with ¹³⁵Ba to $\Omega_{\text{barite}} \approx 1$ to allow tracing of new barite precipitation during the course of the experiment. Notably, homogenous barite precipitation occurs where $\Omega_{\text{barite}} > 8$ (Nancollas & Purdie 1963). We explored the influence of particulate availability (microenvironments) and microbial action at each of these depths. Four conditions were carried out at each depth: 1) Unadulterated water, 2) Filtered to 0.2μm (no particulates/microenvironments), 3) poisoned with mercuric chloride (no microbial action), 4) filtered to 0.2μm and poisoned (control). Three time points were taken over the course of one week, with replicates performed for the latter two time points. The particulate fraction was saved for shore-side analysis. Pre-cruise experiments show that the uptake of ¹³⁵Ba into the particulate fraction can be observed over this time period. All analytical measurements for these experiments will be carried out at the Woods Hole Oceanographic Institution (WHOI) ICP Facility.

Additionally, dissolved barium samples (0.4μm Isopore polycarbonate track-etch filter) were collected from every depth of the trace metal cast. Dissolved barium samples were also

collected were collected from the A & C replicates of all nutrient amendment incubations, throughout the full time period of each experiment. Dissolved samples will be measured post cruise for barium concentration and barium isotopes at the WHOI ICP Facility.

Inventory of barite formation experiments (5 samples per line, for 3 time points)

Stn #	Niskin #	Depth (m)	Depth name	<i>In-situ</i> temp (C)	Goal [Ba]
5	2	21.7	Fluorescence max.	16.3	189
5	14	38.3	Max ▽ transmission	14.9	182
5	18	750	O2 min. (cast)	4.8	127
18	12	84	Fluorescence max.	18.2	200
18	10	93	Max ▽ transmission	17.6	196
18	2	750	O2 min. (cast)	7.4	141
28	14	32	Fluorescence max.	14.3	178
28	12	41	Max ▽ transmission	13.8	175
28	4	450	O2 min. (cast)	11.2	161
56	16	70	Fluorescence max.	14.3	178
56	14	83	Max ▽ transmission	13.8	175
56	2	751	O2 min. (cast)	11.2	161