Barium isotope tracer experiment results from barite–fluid laboratory equilibration experiments

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Project
» The Speed, Signature, and Significance of Barium Transformations in Seawater (The Three S's)

Contributors	Affiliation	Role
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Abstract
These data are from laboratory barite–fluid equilibration experiments conducted with synthetic barite and artificial seawater under marine-relevant conditions. Experiments were performed in duplicate 1 liter reactors at three initial leverage values and measured the temporal evolution of the 137Ba:135Ba ratio in filtered fluid samples and recovered barite from 135Ba tracer experiments. Artificial seawater was prepared to salinity 35 ± 0.5 and approximately pH 8.1, and experiments were carried out at ambient temperature of 20 ± 2 degrees Celsius. Tracer experiments were initiated at slightly supersaturated conditions of Ωbarite = 1.3. Fluid subsamples were collected through time and filtered through 0.22 micrometer polyethersulfone membrane filters. Filtered samples were diluted and analyzed for 137Ba:135Ba by quadrupole inductively coupled plasma mass spectrometry at the Woods Hole Oceanographic Institution Plasma Facility. A control reactor without seed barite was used to assess adsorption to reactor walls. These data were collected to evaluate barium isotope exchange between barite and fluid under chemical equilibrium conditions.

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Methods & Sampling

Laboratory barite–fluid equilibration experiments were conducted in the NIRVANA Labs at the Woods Hole Oceanographic Institution using trace metal clean procedures. Labware was cleaned with hydrochloric acid and nitric acid, ultra-pure reagents were used, and critical solution handling was carried out in laminar flow workbenches. Experiments used synthetic barite and artificial seawater as a marine analogue system. The barite seed material was 99.998 weight percent pure barium sulfate (Puratronic, Alfa Aesar, Lot 24177) with a nominal grain diameter of 3 micrometers. A 25 liter stock of artificial seawater with salinity 35 ± 0.5 was prepared following Smith and Chanley (1975) and adjusted to approximately pH 8.1 with concentrated potassium hydroxide. The artificial seawater stock contained a background dissolved barium concentration of 26 ± 0.8 nanomoles per liter from the reagent salts. All reactions were carried out at ambient temperature of 20 ± 2 degrees Celsius.

For the isotope-tracer experiments, most dissolved barium in solution was supplied as dissolved 135Ba,

whereas solid-phase barium in the seed barite possessed natural abundances. Dissolved 135Ba was derived from 135BaCO3 powder that was dissolved in hydrochloric acid and reconstituted in ultra-high purity water before addition to experiments. Experiments were carried out in duplicate in 1 liter acid-washed high-density polyethylene reactors at three initial leverage values. The amount of 135Ba spike added was adjusted based on temperature, salinity, and preexisting dissolved barium in the artificial seawater to achieve an initial barite saturation state of Ωbarite = 1.3. Reactors were agitated continuously on a New Brunswick Scientific Innova 2100 orbital shaker table. Reactors were removed from the shaker table 10 minutes before sampling to allow settling of the solid phase. Fluid aliquots of 2 milliliters were collected through time and immediately filtered through acid-cleaned 0.22 micrometer polyethersulfone membrane disc filters. A control reactor without seed barite was run under the same conditions to assess adsorption of barium to reactor walls.

Recovered barite samples were dissolved by alkaline conversion to barium carbonate using a modification of the method of Breit et al. (1985). Briefly, recovered solid-phase material was reacted in perfluoroalkoxy alkane vials with 1 molar sodium carbonate solution, followed by sonication, heating at 80 degrees Celsius, repeated decantation, rinsing with 18.2 megaohm-centimeter water, and final dissolution in 2 molar hydrochloric acid.

For isotope ratio analysis, filtered samples were diluted with 2 percent nitric acid and indium was added as an internal standard to a final concentration of 1 nanogram per milliliter. Samples were diluted and measured at salinity 1.75 to minimize non-spectral matrix effects. Filtered samples were analyzed for 137Ba:135Ba at the Woods Hole Oceanographic Institution Plasma Facility.

Data Processing Description

For isotope-tracer experiments, filtered samples were diluted with 2 percent nitric acid, indium was added as an internal standard, and 137Ba:135Ba was measured on a quadrupole inductively coupled plasma mass spectrometer. Samples were measured at salinity 1.75 to reduce non-spectral matrix effects. Precision of the tracer ratio measurement was estimated from repeat analysis of barite samples as 4 percent relative standard deviation. The submitted tracer file reports measured 137Ba:135Ba values and associated ±2 standard error values from the publication table.

The tracer file contains time-series filtered fluid samples together with recovered barite rows from the tracer experiments. Estimated dissolved barium values discussed in the paper were derived separately from blank-corrected ion beam intensities and are not the primary measurements reported in this tracer dataset. Modeled rate calculations from the reactor model are not included in this submission.

BCO-DMO Processing Description

- Loaded table BCO-DMO_Tracer.xlsx,treating "" and "nd" as missing values
- Renamed table bco-dmo_tracer-1 to 1004723_v1_bariumisotopes

Problem Description

A control reactor without seed barite was used to assess adsorption of barium to reactor walls, and the paper reports no significant loss of dissolved barium to reactor walls during this experiment. One low-leverage duplicate tracer experiment, LB-135(2), was harvested before chemical equilibrium was attained. Recovered solid barite rows are included where applicable.

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Related Publications

Bates, S. L., Hendry, K. R., Pryer, H. V., Kinsley, C. W., Pyle, K. M., Woodward, E. M. S., & Horner, T. J. (2017). Barium isotopes reveal role of ocean circulation on barium cycling in the Atlantic. Geochimica et Cosmochimica Acta, 204, 286–299. doi:10.1016/j.gca.2017.01.043
Methods

Breit, G. N., Simmons, E. C., & Goldhaber, M. B. (1985). Dissolution of barite for the analysis of strontium

isotopes and other chemical and isotopic variations using aqueous sodium carbonate. Chemical Geology: Isotope Geoscience Section, 52(3–4), 333–336. https://doi.org/10.1016/0168-9622(85)90043-0
Methods

Middleton, J. T., Hong, W.-L., Paytan, A., Auro, M. E., Griffith, E. M., & Horner, T. J. (2023). Barium isotope fractionation in barite–fluid systems at chemical equilibrium. Chemical Geology, 627, 121453. https://doi.org/10.1016/j.chemgeo.2023.121453
Results

Smith, W. L., & Chanley, M. H. (Eds.). (1975). Culture of Marine Invertebrate Animals. Springer US. https://doi.org/10.1007/978-1-4615-8714-9
Methods

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Related Datasets

IsRelatedTo

Horner, T. J., Middleton, J. (2026) **Barium isotope tracer experiment results from natural and synthetic barite–fluid laboratory equilibration experiments in artificial and filtered seawater.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2026-08-12 http://lod.bco-dmo.org/id/dataset/1004882 [view at BCO-DMO]
Relationship Description: Same experiment series

Horner, T. J., Middleton, J. (2026) **Mass-dependent barium isotope and dissolved barium concentration results from barite–fluid laboratory equilibration experiments.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2026-08-13 http://lod.bco-dmo.org/id/dataset/1005137 [view at BCO-DMO]
Relationship Description: Same experiment series

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Parameters

Parameter	Description	Units
experiment_id	Identifier for the experiment group in the tracer dataset	unitless
l_barite_initial	Initial fraction of total barium present in the solid barite phase at the start of the experiment	unitless
replicate_id	Replicate identifier for duplicate experiments	unitless
sample_type	Sample type category for the row	unitless
time_h	Elapsed time since the start of the experiment	hours
ba137_ba135_ratio	Measured 137Ba:135Ba ratio for the sample	unitless
ba137_ba135_2se	Analytical uncertainty of the measured 137Ba:135Ba ratio reported as plus or minus 2 standard error	unitless

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Instruments

Dataset-specific Instrument Name	Thermo Fisher Scientific iCAP Q quadrupole inductively coupled plasma mass spectrometer
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	Thermo Fisher Scientific iCAP Q quadrupole inductively coupled plasma mass spectrometer, Woods Hole Oceanographic Institution Plasma Facility, used for 137Ba:135Ba measurements in isotope-tracer experiments.
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset-specific Instrument Name	New Brunswick Scientific Innova 2100 orbital shaker table
Generic Instrument Name	Shaker
Dataset-specific Description	New Brunswick Scientific Innova 2100 orbital shaker table, used for continuous agitation of experimental reactors.
Generic Instrument Description	A Shaker is a piece of lab equipment used to mix, blend, or to agitate substances in tube(s) or flask(s) by shaking them, which is mainly used in the fields of chemistry and biology. A shaker contains an oscillating board which is used to place the flasks, beakers, test tubes, etc.

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Project Information

The Speed, Signature, and Significance of Barium Transformations in Seawater (The Three S's)

Coverage: Eastern Tropical Pacific, Subtropical South Pacific, Sub-Antarctic Pacific, and Southern Oceans

NSF Award Abstract:
The biological cycling of carbon in the oceans entrains many other elements, some directly (like nutrients that are essential for life) and some indirectly, as they become chemically involved in the processes that are affecting carbon. One such element is barium (Ba). Particles of the mineral barite (barium sulfate) have been found to form in association with microbial consumption of organic material in the ocean’s “twilight zone.” These particles settle to the ocean floor, and their presence in sediments has been used to infer changes in the conditions in the ocean back in time. Both the amount of barite in sediments and the isotope composition of Ba in barite are potentially sensitive to processes occurring in the twilight zone. However, several long-standing questions remain about Ba cycling in the oceans, which complicates the interpretation of barium-based proxy records. Examples of remaining questions include how much barium enters the oceans at mid-ocean ridge hydrothermal sites, and what controls the precipitation and dissolution of barite in the water column. This project seeks to tackle these questions using new approaches, on three scheduled research expeditions in the Pacific and Southern Oceans. In doing so, this project will support the education, training, and career

development of a graduate student, postdoctoral researcher, and junior investigator. Undergraduate students from underrepresented groups will be recruited to conduct complementary shore-based experiments.

This proposal seeks to answer four questions central to the utility of barium-based proxies in oceanography: What are the major inputs of new Ba to the ocean? What are their isotopic compositions? What controls the amount of pelagic barite precipitated during the remineralization of organic matter? What influences its isotopic composition? These questions will be addressed using a field-centric approach combining: in situ and shipboard tracer-incubation experiments, AUV-led adaptive sampling of Ba cycling ‘hotpots’, and section-based surveying of the surrounding oceanographic features. This multi-pronged approach will be used to investigate: the flux and isotopic composition of Ba released from the largest hydrothermal fields in the ocean, the Southern East Pacific Rise, with a focus on low-temperature venting; rates and signatures of pelagic barite precipitation associated with different phytoplankton assemblages in the Southern Ocean; and, the importance of environmental conditions, such as low ambient oxygen concentrations, in setting the efficiency of barite precipitation in the Eastern Tropical Pacific. The significance of each transformation will be assessed, which may lead to ruling out the importance of certain processes, or identifying new dependencies that could form the basis of new proxies.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-2023456

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