Mass-dependent barium isotope and dissolved barium concentration 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 dissolved barium concentration, mass-dependent barium isotope composition, and associated analytical uncertainties in filtered fluid samples, together with final barite and initial endmember values. 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. No additional dissolved barium was added to these reactors, which were initiated under barite-undersaturated conditions of Ωbarite ≈ 0.1. Fluid subsamples were filtered through 0.22 micrometer polyethersulfone membrane filters, acidified to 0.024 molar hydrochloric acid, and stored before analysis. Mass-dependent barium isotope measurements were made by multi-collector inductively coupled plasma mass spectrometry at the Woods Hole Oceanographic Institution Plasma Facility following double-spike equilibration and ion-exchange purification. These data were collected to evaluate the evolution of dissolved barium concentrations and barium isotope compositios during barite–fluid equilibration under chemical equilibrium conditions.

Table of Contents

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.

Mass-dependent isotope experiments were conducted in duplicate in 1 liter acid-washed high-density polyethylene reactors at three initial leverage values. All barium in these experiments possessed natural abundances, and no additional dissolved barium was added. Reactors were initiated under barite-undersaturated conditions corresponding to Ωbarite ≈ 0.1, with initial dissolved barium concentration of 26 ± 0.8 nanomoles per liter. Reactors were agitated continuously on an orbital shaker table. Prior to sampling, reactors were removed from the shaker table for 10 minutes to allow settling of the solid phase. Fluid aliquots of 2 milliliters were collected periodically and immediately filtered through acid-cleaned 0.22 micrometer polyethersulfone membrane disc filters. After collection, filtrates were acidified to 0.024 molar hydrochloric acid, at pH less than or equal to 2, and stored for several weeks before analysis. Experiments were incubated under constant agitation for up to 429 hours, and one duplicate from each leverage set was terminated at an intermediate time to allow analysis of the solid phase.

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.

Mass-dependent barium isotope analyses followed Bates et al. (2017). Dissolved samples were equilibrated with a 135Ba–136Ba double spike, pre-concentrated from 5 milliliters of seawater matrix by barium–calcium carbonate co-precipitation, dissolved in hydrochloric acid, and purified by passing samples twice through AG 50W-X8 cation-exchange resin before analysis by multi-collector inductively coupled plasma mass spectrometry.

Data Processing Description

For mass-dependent isotope experiments, barium isotope compositions were calculated using the three-dimensional geometric interpretation of the double-spike problem with corrections for isobaric interferences from xenon, cerium, and lanthanum. Concentration- and spike-matched aliquots of NIST SRM 3104a were analyzed after every four samples, and sample isotope compositions were calculated relative to the average of the nearest four standard measurements. Dissolved barium concentration data were corrected for procedural blanks. No blank correction was applied to the barium isotope data because blank contributions were low and the isotopic composition of the blank was poorly constrained. Reported isotope uncertainties are either pooled 2 standard error from replicate analyses or the long-term method uncertainty of ±0.03 per mil, whichever was greater. Samples were analyzed with two, three, or four replicates depending on sample barium concentration. Accuracy was monitored using NBS-127 and SAFe D1 reference materials processed alongside samples.

The submitted file reports measured dissolved barium concentrations, mass-dependent barium isotope compositions, and associated uncertainties from the publication table, together with final solid-phase and initial endmember values. Modeled rate calculations from the reactor model are not included in this submission.

Problem Description

One low-leverage duplicate mass-dependent experiment, LB-iso(2), was harvested before chemical equilibrium was attained. Dissolved barium concentration is not reported for solid-phase endmember rows because it is not applicable to those samples.

[table of contents | back to top]

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

[table of contents | back to top]

Related Datasets

IsRelatedTo

Horner, T. J., Middleton, J. (2026) **Barium isotope tracer experiment results from barite–fluid laboratory equilibration experiments.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2026-08-12 http://lod.bco-dmo.org/id/dataset/1004723 [view at BCO-DMO]
Relationship Description: Same experiment series

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

[table of contents | back to top]

Parameters

Parameter	Description	Units
experiment_id	Identifier for the experiment group in the mass-dependent isotope 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
ba_concentration_nmol_l	Measured dissolved barium concentration in the sample.	nanomoles per liter
ba_concentration_2se_nmol_l	Analytical uncertainty of the measured dissolved barium concentration reported as plus or minus 2 standard error.	nanomoles per liter
d138Ba_permil	Measured mass-dependent barium isotope composition of the sample, reported as delta 138Ba relative to NIST SRM 3104a.	per mil
d138Ba_2se_permil	Analytical uncertainty of the measured delta 138Ba value reported as plus or minus 2 standard error.	per mil

[table of contents | back to top]

Instruments

Dataset-specific Instrument Name	ThermoFinnigan Neptune
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	ThermoFinnigan Neptune multi-collector inductively coupled plasma mass spectrometer, Woods Hole Oceanographic Institution Plasma Facility, used for mass-dependent barium isotope measurements. Samples were introduced using a perfluoroalkoxy alkane micro-concentric nebulizer and CETAC Aridus II desolvation system.
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 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.

[table of contents | back to top]

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.

[table of contents | back to top]

Funding

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

[table of contents | back to top]