Barium stable isotopes from seawater and sediment core samples collected during the R/V Falkor 160115 and R/V Thomas G. Thompson TT013 cruises in the Equatorial Pacific in 2016 and 1992

Website: https://www.bco-dmo.org/dataset/1005542
Data Type: Other Field Results
Version: 1
Version Date: 2026-08-19

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

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Abstract
Barium isotopes have proven to be a powerful tool for understanding barium cycling on unprecedented spatial and temporal scales in the modern ocean. This dataset contains profiles of barium isotopes for samples collected from the sediment-water interface to 40 cm in cores collected during cruises on the R/V Falkor and R/V Thomas G. Thompson. The R/V Falkor cores were collected during cruise 160115 in the Central Pacific during 2016 as part of the ProteOMZ project, while the R/V Thomas G. Thompson cores were collected during cruise TT013 in the Equatorial Pacific in 1992 during the U.S. JGOFS Equatorial Pacific (EqPac) project.

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Coverage

Location: Equatorial Pacific
Spatial Extent: **N**:4.0413 **E**:-139.735 **S**:-4.9738 **W**:-140
Temporal Extent: 1992-10-30 - 1996-02-11

Methods & Sampling

Pore-water sampling. Pore-waters were extracted from the upper N 30 cm of sediments along an Equatorial Pacific transect at 14O”W, from 12% to 9”N, at a water depth of approximately 4300 m (JGOFS-

EqPac, Leg TTO13, November 1993); sample locations and water depths are listed in Table 1. Sediments were collected using a multi-corer. All cores had a well-preserved sediment-water interface with an occasional fluff of phyto-detritus, overlain by clear bottom seawater. Thus, sediment disturbance seems to have been minimal during the coring and recovery operations. Sub-cores were transferred within minutes of arrival on board into a cold room of 2”C, where they were sectioned into 0.5, 1 and 2 cm intervals in a nitrogen atmosphere glove bag and centrifuged at 700010,000 rpm. The pore-waters obtained were passed through pre-washed Nucleopore 0.45 km filters in a nitrogen atmosphere, acidified to a pH of 2 with distilled HNO3, and stored in acid-cleaned polypropylene bottles at 2°C. The pore-water sampling procedure was usually completed within less than 24 h of core recovery. Two cores from each latitude were processed in order to identify spatial variability. All the equipment used for sample processing was thoroughly pre-cleaned with 8 N HNO3, in order to reduce the blank.

Pore fluid sampling methods: Paytan et al., 1996 (see related publications).

Barite and seawater sampling. Dissolved seawater samples were collected on the ProteOMZ FK150116 expedition (Jan-Feb 2016) using a 12-bottle trace metal clean rosette equipped with 8 L X-Niskin bottles (Ocean Test Equipment), a titanium frame, and a Kevlar cable, as described in (Cutter and Bruland 2012). Seawater from the Go-Flo bottles was subsampled in a trace metal clean plastic "bubble" equipped with HEPA filters providing positive air pressure. Dissolved Ba subsamples were filtered using a 142 mm polycarbonate plastic sandwich filter (Geotech Environmental Equipment) equipped with a 0.2 um Supor membrane filter (Pall Corporation) and stored until analysis in the laboratory in a 60 mL HDPE bottle (Nalgene) that had been soaked for ~1 week in Citranox, an acidic detergent, rinsed with Milli-Q water (Millipore), soaked for ~2 weeks in 10% trace metal grade HCl (Optima), and rinsed with lightly acidic Milli-Q water (<0.1% HCl). Samples were stored at 4ºC.

Data Processing Description

Barite processing. Barite samples were dissolved through an alkaline dissolution in perfluoroalkane vials by addition of 1 M Na2CO3 solution to form (Ba,Ca)CO3 as in Breit et al. (1985). The Na2CO3 solution was added to achieve BaSO4:Na2CO3 of 1:10 by mass, then 18.2 M water was added such that there was 10 mg of BaSO4 per 2 mL of solution. Samples were then sonicated for 60 minutes at room temperature and then heated to 80◦C for ≥16 h. After cooling, the fluid was decanted and two further rounds of Na2CO3 addition, sonication, heating, and decantation were performed. Samples were rinsed with 18.2 M water and the remaining solid, BaCO3, dissolved with 2 M HCl. An aliquot of this solution was equilibrated with a 135Ba–136Ba double spike of known concentration to achieve a spike- to sample-derived [Ba] ratio of between 1–2 and reconstituted in 250 µL of 2 M HCl ready for ion-exchange chromatography.

Porewater and seawater processing. Porewater and seawater samples were prepared for Ba isotope analysis following the procedure outlined in Bates et al. (2017).

Briefly, dissolved samples were equilibrated with the double spike and then co-precipitated into (Ba,Ca)CO3 by drop-wise addition of 1 M Na2CO3. The precipitate was then dissolved in 250 µL of 2 M HCl for chromatography. Barium was purified from matrix elements by passing all samples twice through 500 µL of AG 50W-X8 (200–400 mesh) cation-exchange resin (Bio-Rad), following the protocol described by Horner et al. (2015).

Isotope analysis. Full barium isotope measurement methods can be found in: Middleton et al., 2023. (see related publications).

Purified Ba was analyzed for Ba isotopes using a ThermoFinnigan Neptune multi-collector inductively coupled plasma mass spectrometer in the WHOI Plasma Facility. Isotope compositions were calculated using the three-dimensional geometric interpretation of the double-spike problem (Siebert et al., 2001) with additional processing for isobaric corrections (136Xe and 136Ce on 136Ba, 138Ce and 138La on 138Ba; Horner et al., 2015). Barium isotope compositions were calculated relative to NIST by standard-sample bracketing. Four procedural blanks were found to range from 305 to 489 pg, below the long-term average NIRVANA Labs procedural blank (692 pg). A further four analytical blanks were found to range from 14 to 301 pg. The contribution of the highest blank to the sample with the lowest [Ba] was < 3%. Given the low blank contribution and poor constraints on the true Ba isotope blank value, no blank correction was applied. Barium isotope compositions are reported as deviations in the 138Ba/134Ba ratio in a sample relative to the NIST SRM 3104a standard, hereafter ‘NIST’: $\delta^{138}Ba(\text{ }) = [(^{138}Ba/^{134}Ba)_{sample}/(^{138}Ba/^{134}Ba)_{NIST}-1]\times1000$. Uncertainties are reported as either a long-term measurement of uncertainty (±2 SD about the mean; ± 0.03 , Horner et al., 2015) or pooled 2 SE from n sample analyses, whichever was greater. Accuracy of isotope measurements was

monitored by processing two internal reference materials alongside samples: the Alfa Aesar BaSO4 powder and GEOTRACES SAFe D1 (northeast Pacific seawater; 1,000 m). The BaSO4 and SAFe D1 possessed δ138Ba = −0.02 ± 0.03 and +0.33 ± 0.04 , in agreement with previous measurements of −0.04 ± 0.07 (n = 7, ±2SE; T.J. Horner pers. comm.) and +0.31 ± 0.03 (Cao et al., 2020; Geyman et al., 2019; Hsieh and Henderson, 2017), respectively.

BCO-DMO Processing Description

CURATION ACTIONS PERFORMED ON DATA
approved by submitter

* Two Excel source files, 2022-11-17_JGOFS_manuscript_DataTables_BCODMO.xlsx and 2022-11-17_ProteOMZ_manuscript_DataTables_BCODMO.xlsx
* blanks, nd, and NaN were set as missing-value markers
* The two source tables were concatenated into a single table, following fields were merged: Core_id & Stn_id, Ba_conc_err & Ba_conc_2SE, 138Ba_iso_err & 138Ba_iso_2SE, depth_water_m & Depth_m
* Sample_type was standardized so that records with Cruise_id = FK160115 were classified as Seawater; existing Sample_type values were retained for all other records.
* fields were renamed: 138Ba_iso → Ba138_iso, 138Ba_iso_err → Ba138_iso_err, , Core_id (from Stn_id) → Sample_id,Long → Lon, depth_core → Depth_core, and depth_water_m → Depth_water_m.
* The concatenated table was renamed 1005542_v1_bariumisotopes.

CURATION ACTIONS PERFORMED ON METADATA
approved by submitter

* Merged metadata entries from 2 submission
* Added standardized instruments

ISSUES POTENTIALLY IMPACTING REUSE

* no measurement specific sampling date provided

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Related Publications

Middleton, J. T., Paytan, A., Auro, M., Saito, M. A., & Horner, T. J. (2023). Barium isotope signatures of barite–fluid ion exchange in Equatorial Pacific sediments. Earth and Planetary Science Letters, 612, 118150. https://doi.org/10.1016/j.epsl.2023.118150
Results

Paytan, A. (1996). Benthic Ba fluxes in the central Equatorial Pacific, implications for the oceanic Ba cycle. Earth and Planetary Science Letters, 142(3-4), 439–450. https://doi.org/10.1016/0012-821x(96)00120-3
https://doi.org/10.1016/0012-821X(96)00120-3
Methods

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Parameters

Parameter	Description	Units
Cruise_id	Cruise identifier	unitless
Sample_type	Pore fluid, barite, bottom water or seawater	unitless
Sample_id	Core ID number	unitless
Lat	Latitude	decimal degrees
Lon	Longitude	decimal degrees
Depth_core	Depth below sediment water interface, where 0cm refers to measurements of the overlying bottom water	cm
Depth_water_m	Depth in water column	meters (m)
Ba_conc	Barium concentration	nmol L-1
Ba_conc_err	2SE uncertainty of barium concentration	nmol L-1
Ba138_iso	Barium stable isotope value	‰
Ba138_iso_err	2SE uncertainty of barium stable isotope value	‰

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Instruments

Dataset-specific Instrument Name	Trace metal clean rosette
Generic Instrument Name	CTD - profiler
Dataset-specific Description	12-bottle trace metal clean rosette with 8 L X-Niskin bottles, a titanium frame, and a Kevlar cable
Generic Instrument Description	The Conductivity, Temperature, Depth (CTD) unit is an integrated instrument package designed to measure the conductivity, temperature, and pressure (depth) of the water column. The instrument is lowered via cable through the water column. It permits scientists to observe the physical properties in real-time via a conducting cable, which is typically connected to a CTD to a deck unit and computer on a ship. The CTD is often configured with additional optional sensors including fluorometers, transmissometers and/or radiometers. It is often combined with a Rosette of water sampling bottles (e.g. Niskin, GO-FLO) for collecting discrete water samples during the cast. This term applies to profiling CTDs. For fixed CTDs, see https://www.bco-dmo.org/instrument/869934.

Dataset-specific Instrument Name	multi-corer
Generic Instrument Name	Multi Corer
Dataset-specific Description	Sediments were collected using a multi-corer. All cores had a well-preserved sediment-water interface with an occasional fluff of phyto-detritus, overlain by clear bottom seawater.
Generic Instrument Description	The Multi Corer is a benthic coring device used to collect multiple, simultaneous, undisturbed sediment/water samples from the seafloor. Multiple coring tubes with varying sampling capacity depending on tube dimensions are mounted in a frame designed to sample the deep ocean seafloor. For more information, see Barnett et al. (1984) in Oceanologica Acta, 7, pp. 399-408.

Dataset-specific Instrument Name	ThermoFinnigan Neptune
Generic Instrument Name	Thermo Finnigan Neptune inductively coupled plasma mass spectrometer
Dataset-specific Description	Purified Ba was analyzed for Ba isotopes using a ThermoFinnigan Neptune multi-collector inductively coupled plasma mass spectrometer in the WHOI Plasma Facility.
Generic Instrument Description	A laboratory high mass resolution inductively coupled plasma mass spectrometer (ICP-MS) designed for elemental and isotopic analysis. The instrument is based on a multicollector platform, comprising eight moveable collector supports and one fixed center channel equipped with a Faraday cup and, optionally, an ion counter with or without a retardation lens. The Faraday cup is connected to a current amplifier, whose signal is digitized by a high linearity voltage to frequency converter. The instrument was originally manufactured by Thermo Finnigan, which has since been replaced by Thermo Scientific (part of Thermo Fisher Scientific). This model is no longer in production.

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Deployments

FK160115

Website	https://www.bco-dmo.org/deployment/708387
Platform	R/V Falkor
Report	https://service.rvdata.us/data/cruise/FK160115/doc/FK160115_OfficialCruiseReport_Saito_v3.pdf
Start Date	2016-01-16
End Date	2016-02-11
Description	Project: Using Proteomics to Understand Oxygen Minimum Zones (ProteOMZ) More information is available from the ship operator at https://schmidtocean.org/cruise/investigating-life-without-oxygen-in-the... Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/FK160115

TT013

Website	https://www.bco-dmo.org/deployment/57732
Platform	R/V Thomas G. Thompson
Start Date	1992-10-30
End Date	1992-12-13
Description	Purpose: Benthic Survey, 12°N-12°S at 140°W TT013 was one of five cruises conducted in 1992 in support of the U.S. Equatorial Pacific (EqPac) Process Study. The five EqPac cruises aboard R/V Thomas G. Thompson included two repeat meridional sections (12°N - 12°S), 2 equatorial surveys, and a benthic survey (all at 140° W). The scientific objectives of this study were to observe the processes in the Equatorial Pacific controlling the fluxes of carbon and related elements between the atmosphere, euphotic zone, and deep ocean. As luck would have it, the survey window coincided with an El Nino event. A bonus for the research team.

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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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