# Barium isotope ratios ( $\delta$ 138Ba) in small size fraction particles from Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1815) on R/V Roger Revelle from Oct-Nov 2018

Website: https://www.bco-dmo.org/dataset/834066

**Data Type**: Cruise Results

Version: 2

Version Date: 2021-06-22

## **Project**

» US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)

» U.S. GEOTRACES Pacific Meridional Transect: Tracing Basin-scale Nutrient Cycling and Carbon Export with Dissolved and Particulate Barium-isotopic Distributions (GEOTRACES PMT Barium)

## **Program**

» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
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### **Abstract**

This dataset reports barium isotope ratios ( $\delta$ 138Ba) in small size fraction particles Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1815) on R/V Roger Revelle from October to November 2018.

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# Coverage

**Spatial Extent**: N:17.5 **E**:-151.969217 **S**:-20 **W**:-152.0288

Temporal Extent: 2018-10-27 - 2018-11-23

# Methods & Sampling

The sampling procedure is similar to what was used in the previous U.S. GEOTRACES cruises (GA03 and GP16). Particles were sampled using *in sit*u battery-powered pumps (McLane WTS-LV) that were set up with two "mini-MULVFS" filter holders (QMA and PES; Bishop et al., 2012). Each filter holder contained a 142 mm diameter, 51  $\mu$ m pore-size polyester pre-filter, and a pair of quartz fiber Whatman QMA filters ('QMA side') or a pair of 0.8  $\mu$ m pore-size Supor brand polyethersulfone filters ('PES side') downstream of the pre-filter. (Note that only the top PES filter was processed for Ba isotope analysis.)

All filters were acid-leached in a HEPA-filtered clean environment prior to the cruise, and assembled onto the filter holders in a HEPA-filtered trace-metal clean bubble on board. Pumps were deployed on a metal-free hydrowire (Hytreljacketed Vectran) and operated for 4 h, pumping seawater *in situ* through both filter holders in parallel. The pumping

speed was initially programmed as 8 L/min. Typically 1,000–1,200 L (median: 1091 L) of seawater passed through the QMA side, and 350–450 L (median: 403 L) through the Supor side flowpaths. Two complete sets of blank filters ("QMA" set and "Supor" set) were deployed with pumps in each cast. The dipped blank filters were processed identically to samples.

Immediately upon recovery of the pumps, the sample holders were brought into the clean bubble, and the filters were cut using a ceramic rotary blade (Cadence Inc.). For the small size fraction (SSF, 0.8–51  $\mu$ m), Supor filters from the Supor side filter holder were cut into 1/16 or 1/8 wedges. SSF filter wedges were then dried at room temperature on acid-leached polystyrene "eggcrate" grids in a laminar flow bench and then stored in particle-free cleanroom polyethylene bags (KNF Flexpak).

Filter wedges were prepared for analysis by leaching in 40 mL of 0.6 M HCl (hydrochloric acid) at 80 °C for 16 h. (Note that particulate samples from St. 29 and 39 of GP15 were dissolved using the protocols developed in Phoebe Lam's lab, and thus differ slightly from those used at the other stations. Given that both methods achieve near-quantitative yields for particulate Ba (e.g., Bishop et al., 2012; Planquette & Sherrell, 2012), we do not expect any systematic offsets arising from these different pre-treatments.) In both cases, the leachate was dried and reconstituted in 1 M HCl, from which an aliquot containing ~10 % of the sample was taken for multi-element analysis. The aliquot was reconstituted in 2 % HNO3, spiked with indium to achieve a final [In] of ~1 ng/mL and analyzed using a ThermoFisher iCAP reverse quadrupole ICP-MS (inductively coupled plasma mass spectrometer) at the WHOI Plasma Facility. Quantification was achieved by comparing indium- and blank-corrected ion beam intensities measured in samples to those of a reference curve constructed from serial dilutions of a reference standard containing known element concentrations. These values were used to calculate particulate trace metal concentrations in seawater, and guide spiking for Ba isotope analysis.

Samples containing sufficient Ba for isotope analysis were spiked with an appropriate quantity of  $^{135}$ Ba- $^{136}$ Ba double spike to achieve a spike:sample ratio of between 1-2. Following spiking, samples were dried, fluxed overnight in a 1 mL of mixture containing equal parts concentrated nitric acid and hydrogen peroxide, dried, and reconstituted in 2 M HCl for ion-exchange chromatography. Chromatography protocols are detailed in Horner et al. (2015). Following purification, samples were reconstituted in 2 % nitric acid and analyzed for  $\delta^{138}$ Ba (Ba isotope compositions) using a ThermoFinnigan Neptune multicollector ICP-MS, also situated at the WHOI Plasma Facility. Samples were aspirated at 140 µL/min, desolvated using an Aridus II, and introduced into the instrument using 1 L/min Ar carrier gas containing 2-5 mL/min admixed nitrogen. Samples are measured in low-resolution mode relative to concentration- and spike:sample-matched aliquots of NIST SRM 3108 ( $\equiv 0$  %). Samples are analyzed between 2-4 times, and Ba-isotopic compositions calculated using an iterative, geometric-based deconvolution of spike-sample mixtures. Resultant  $\delta^{138}$ Ba are normalized to a moving average of the nearest four analyses of NIST SRM 3108. The accuracy of the NIST normalization is monitored using a secondary standard, analyzed in place of every 11th sample. Typical  $2\sigma$  precision for the complete protocol is  $\pm 0.03$  % for samples containing >40 ng of Ba, which is an appropriate level of uncertainty given replicate analyses of filters conducted during the course of this study.

# **Data Processing Description**

### Quality Flags:

SeaDataNet quality flags have been assigned. More information on SeaDataNet quality flags is available from GEOTRACES at <a href="https://www.geotraces.org/geotraces-quality-flag-policy/">https://www.geotraces.org/geotraces-quality-flag-policy/</a> and from SeaDataNet at <a href="https://www.seadatanet.org/Standards/Data-Quality-Control">https://www.seadatanet.org/Standards/Data-Quality-Control</a>. In summary:

0 = no quality control;

1 = good value;

2 = probably good value;

3 = probably bad value;

4 = bad value;

5 = changed value;

6 = value below detection;

7 =value in excess;

8 = interpolated value;

9 = missing value;

A =value phenomenon uncertain.

# **BCO-DMO Processing:**

- renamed fields:
- added date/time field in ISO8601 format.

Version history:

2021-06-22 (v2) - renamed columns.

2020-12-17 (v1) - version 1 processed by BCO-DMO.

### **Related Publications**

Bishop, J. K. B., Lam, P. J., & Wood, T. J. (2012). Getting good particles: Accurate sampling of particles by large volume in-situ filtration. Limnology and Oceanography: Methods, 10(9), 681–710. doi:10.4319/lom.2012.10.681

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Horner, T. J., Kinsley, C. W., & Nielsen, S. G. (2015). Barium-isotopic fractionation in seawater mediated by barite cycling and oceanic circulation. Earth and Planetary Science Letters, 430, 511–522. doi:10.1016/j.epsl.2015.07.027 Methods

Planquette, H., & Sherrell, R. M. (2012). Sampling for particulate trace element determination using water sampling bottles: methodology and comparison to in situ pumps. Limnology and Oceanography: Methods, 10(5), 367–388. doi:10.4319/lom.2012.10.367

Methods

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# **Related Datasets**

## **Continues**

Horner, T. J. (2021) Barium isotope ratios (δ138Ba) in small size fraction particles from Leg 1 (Seattle, WA to Hilo, HI) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1814) on R/V Roger Revelle from September to October 2018. Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 2) Version Date 2021-06-22 doi:10.26008/1912/bco-dmo.834052.2 [view at BCO-DMO] Relationship Description: GP15 was made up of two cruise legs, RR1814 (Leg 1) and RR1815 (Leg 2)

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# **Parameters**

Parameter	Description	Units
Station_ID	Station number	unitless
Start_Date_UTC	Date (UTC) at start of sample collection; format: MM/DD/YYYY	unitless
Start_Time_UTC	Time (UTC) at start of sample collection; format: hh:mm	unitless
Start_ISO_DateTime_UTC	Date and time (UTC) at start of sample collection; formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	unitless
End_Date_UTC	Date (UTC) at end of sample collection	unitless
End_Time_UTC	Time (UTC) at end of sample collection	unitless
Start_Latitude	Latitude at start of sample collection	degrees North
Start_Longitude	Longitude at start of sample collection	degrees East
End_Latitude	Latitude at end of sample collection	degrees North
End_Longitude	Longitude at end of sample collection	degrees East
Event_ID	Event number	unitless
Sample_ID	GEOTRACES sample number	unitless
Sample_Depth	Sample depth	meters (m)
Ba_138_134_SPL_DELTA_PUMP_ernqes	delta138Ba; Atom ratio of dissolved Ba isotopes expressed in conventional DELTA notation referenced to {NIST 3104a} in small size fraction particles	per mil
SD1_Ba_138_134_SPL_DELTA_PUMP_ernqes	One standard deviation of Ba_138_134_SPL_DELTA_PUMP_ernqes	per mil
Flag_Ba_138_134_SPL_DELTA_PUMP_ernqes	Quality flag for Ba_138_134_SPL_DELTA_PUMP_ernqes	unitless

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# Instruments

Dataset- specific Instrument Name	ThermoFinnigan Neptune multicollector ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
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	ThermoFisher iCAP reverse quadrupole ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
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	McLane WTS-LV
Generic Instrument Name	McLane Large Volume Pumping System WTS-LV
Generic Instrument Description	The WTS-LV is a Water Transfer System (WTS) Large Volume (LV) pumping instrument designed and manufactured by McLane Research Labs (Falmouth, MA, USA). It is a large-volume, single-event sampler that collects suspended and dissolved particulate samples in situ. Ambient water is drawn through a modular filter holder onto a 142-millimeter (mm) membrane without passing through the pump. The standard two-tier filter holder provides prefiltering and size fractioning. Collection targets include chlorophyll maximum, particulate trace metals, and phytoplankton. It features different flow rates and filter porosity to support a range of specimen collection. Sampling can be programmed to start at a scheduled time or begin with a countdown delay. It also features a dynamic pump speed algorithm that adjusts flow to protect the sample as material accumulates on the filter. Several pump options range from 0.5 to 30 liters per minute, with a max volume of 2,500 to 36,000 liters depending on the pump and battery pack used. The standard model is depth rated to 5,500 meters, with a deeper 7,000-meter option available. The operating temperature is -4 to 35 degrees Celsius. The WTS-LV is available in four different configurations: Standard, Upright, Bore Hole, and Dual Filter Sampler. The high-capacity upright WTS-LV model provides three times the battery life of the standard model. The Bore-Hole WTS-LV is designed to fit through a narrow opening such as a 30-centimeter borehole. The dual filter WTS-LV features two vertical intake 142 mm filter holders to allow simultaneous filtering using two different porosities.

Dataset- specific Instrument Name	"mini-MULVFS"
Generic Instrument Name	Multiple Unit Large Volume Filtration System
Description	The Multiple Unit Large Volume Filtration System (MULVFS) was first described in Bishop et al., 1985 (doi: 10.1021/ba-1985-0209.ch009). The MULVFS consists of multiple (commonly 12) specialized particulate matter pumps, mounted in a frame and tethered to the ship by a cable (Bishop et al., 1985; Bishop and Wood, 2008). The MULVFS filters particulates from large volumes of seawater, although the exact protocols followed will vary for each project.

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# **Deployments**

# RR1815

Website	https://www.bco-dmo.org/deployment/776917
Platform	R/V Roger Revelle
Report	https://datadocs.bco-dmo.org/docs/geotraces/GEOTRACES_PMT/casciotti/data_docs/GP15_Cruise_Report_with_ODF_Report.pdf
Start Date	2018-10-24
End Date	2018-11-24
Description	Additional cruise information is available from the Rolling Deck to Repository (R2R): <a href="https://www.rvdata.us/search/cruise/RR1815">https://www.rvdata.us/search/cruise/RR1815</a>

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# **Project Information**

US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)

Website: http://www.geotraces.org/

Coverage: Pacific Meridional Transect along 152W (GP15)

A 60-day research cruise took place in 2018 along a transect form Alaska to Tahiti at 152° W. A description of the project titled "Collaborative Research: Management and implementation of the US GEOTRACES Pacific Meridional Transect", funded by NSF, is below. Further project information is available on the US GEOTRACES website and on the cruise blog. A detailed cruise report is also available as a PDF.

## Description from NSF award abstract:

GEOTRACES is a global effort in the field of Chemical Oceanography in which the United States plays a major role. The goal of the GEOTRACES program is to understand the distributions of many elements and their isotopes in the ocean. Until quite recently, these elements could not be measured at a global scale. Understanding the distributions of these elements and isotopes will increase the understanding of processes that shape their distributions and also the processes that depend on these elements. For example, many "trace elements" (elements that are present in very low amounts) are also important for life, and their presence or absence can play a vital role in the population of marine ecosystems. This project will launch the next major U.S. GEOTRACES expedition in the Pacific Ocean between Alaska and Tahiti. The award made here would support all of the major infrastructure for this expedition, including the research vessel, the sampling equipment, and some of the core oceanographic measurements. This project will also support the personnel needed to lead the expedition and collect the samples.

This project would support the essential sampling operations and infrastructure for the U.S. GEOTRACES Pacific Meridional Transect along 152° W to support a large variety of individual science projects on trace element and isotope (TEI) biogeochemistry that will follow. Thus, the major objectives of this management proposal are: (1) plan and coordinate a 60 day research cruise in 2018; (2) obtain representative samples for a wide variety of TEIs using a conventional CTD/rosette, GEOTRACES Trace Element Sampling Systems, and in situ pumps; (3) acquire conventional CTD hydrographic data along with discrete samples for salinity, dissolved oxygen, algal pigments, and dissolved nutrients at micro- and nanomolar levels; (4) ensure that proper QA/QC protocols are followed and reported, as well as fulfilling all GEOTRACES intercalibration protocols; (5) prepare and deliver all hydrographic data to the GEOTRACES Data Assembly Centre (via the US BCO-DMO data center): and (6) coordinate all cruise communications between investigators, including preparation of a hydrographic report/publication. This project would also provide baseline measurements of TEIs in the Clarion-Clipperton fracture zone (~7.5°N-17°N, ~155°W-115°W) where large-scale deep sea mining is planned. Environmental impact assessments are underway in partnership with the mining industry, but the effect of mining activities on TEIs in the water column is one that could be uniquely assessed by the GEOTRACES community. In support of efforts to communicate the science to a wide audience the investigators will recruit an early career freelance science journalist with interests in marine science and oceanography to participate on the cruise and do public outreach, photography and/or videography, and social media from the ship, as well as to submit articles about the research to national media. The project would also support several graduate students.

# U.S. GEOTRACES Pacific Meridional Transect: Tracing Basin-scale Nutrient Cycling and Carbon Export with Dissolved and Particulate Barium-isotopic Distributions (GEOTRACES PMT Barium)

# NSF Award Abstract:

The goal of the international GEOTRACES program is to understand the distributions of trace chemical elements and their isotopes in the oceans. This project would measure stable isotopes of barium on a 2018 U.S. GEOTRACES expedition in the Pacific Ocean. Barium is a trace element whose distribution is relevant to all three themes of the GEOTRACES program, as barium can be used to: study chemical cycling within the oceans; trace exchanges of elements at ocean boundaries; and infer past environmental conditions. The data collected here will be the first of their kind for barium isotopes and will illuminate the geochemical cycle of this element. Moreover, conducting this work as part of the GEOTRACES program will maximize the return on investment in the barium isotope data by providing a rich interpretative framework.

This project seeks to understand how the interplay between internal cycling and boundary processes sets basin-scale barium concentration and isotopic distributions in the Pacific Ocean. Despite possessing a nutrient-like dissolved profile, marine barium cycling has a fundamentally different boundary condition to the major algal nutrients: barium cycling is not driven by production of organic matter but rather by its remineralization. Respiration of sinking organic matter in the ocean's 'twilight zone' releases carbon dioxide, mineralizes nutrients, and promotes precipitation of micron-size crystals of barite. Since barite is the major vector of particulate barium in seawater, the abundance and isotopic composition of barium in the oceans is tied to global carbon and nutrient cycling at the 'dark end' of the biological carbon pump. The data collected here will be used to test hypotheses across an unprecedented range of oceanographic conditions regarding: the formation, export, and regeneration of particulate material and the connection to seafloor processes; the importance of boundary sources to regional and global trace element and

isotope budgets; the formation of putative soft-metal sulfides in oxygen-minimum zones; and the origin of enigmatic suspended particles in the deep open ocean. This proposal will contribute to education by training undergraduate research fellows and through presentation of seminars and guest lectures to regional science educators through collaboration with a regional conservation organization.

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# **Program Information**

U.S. GEOTRACES (U.S. GEOTRACES)

Website: <a href="http://www.geotraces.org/">http://www.geotraces.org/</a>

Coverage: Global

**GEOTRACES** is a <u>SCOR</u> sponsored program; and funding for program infrastructure development is provided by the U.S. National Science Foundation.

GEOTRACES gained momentum following a special symposium, S02: Biogeochemical cycling of trace elements and isotopes in the ocean and applications to constrain contemporary marine processes (GEOSECS II), at a 2003 Goldschmidt meeting convened in Japan. The GEOSECS II acronym referred to the Geochemical Ocean Section Studies To determine full water column distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form, along a sufficient number of sections in each ocean basin to establish the principal relationships between these distributions and with more traditional hydrographic parameters;

- \* To evaluate the sources, sinks, and internal cycling of these species and thereby characterize more completely the physical, chemical and biological processes regulating their distributions, and the sensitivity of these processes to global change; and
- \* To understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

GEOTRACES will be global in scope, consisting of ocean sections complemented by regional process studies. Sections and process studies will combine fieldwork, laboratory experiments and modelling. Beyond realizing the scientific objectives identified above, a natural outcome of this work will be to build a community of marine scientists who understand the processes regulating trace element cycles sufficiently well to exploit this knowledge reliably in future interdisciplinary studies.

Expand "Projects" below for information about and data resulting from individual US GEOTRACES research projects.

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# **Funding**

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1736949

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