

Particulate multi-element geochemical concentrations, dissolved barium concentrations and barium-isotopic data collected during the R/V Blue Heron cruise BH15-11 in Lake Superior during August 2015

Website: <https://www.bco-dmo.org/dataset/680091>

Data Type: Cruise Results

Version:

Version Date: 2017-03-24

Project

» [EAGER - Introducing Early Career Scientists to Research on the Great Lakes](#) (Early Career Great Lakes research)

» [Calibration of a Novel Nutrient Paleoproxy in the Southern Ocean](#) (Novel Nutrient Paleoproxy)

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Coverage

Spatial Extent: N:47.331611 E:-89.821389 S:46.998528 W:-91.24625

Temporal Extent: 2015-08-26 - 2015-08-27

Dataset Description

This dataset includes geochemical profiles of water samples collected in August 2015 at two stations in the western arm of Lake Superior.

These data were published in:

Tristan J. Horner, Helena V. Pryer, Sune G. Nielsen, Peter W. Crockford, Julia M. Gauglitz, Boswell A. Wing & Richard D. Ricketts (2017) Pelagic barite precipitation at micromolar ambient sulfate. Nature Communications 8, Article number: 1342 (2017) doi:10.1038/s41467-017-01229-5

Other relevant files and publications:

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.

Methods & Sampling

Sampling was performed aboard the RV Blue Heron during cruise BH15-11, which sailed from Duluth MN to Duluth MN during August 2015. Best-practice metal-clean protocols were followed to the greatest extent possible before, during, and after the cruise using only acid-washed sample containers, filters, labware, etc. Particulate sampling comprised one cast at FWM and two casts at WM. The first water drawn from each Niskin was used to fill a 20 mL high-density polyethylene bottle for analysis of total dissolvable barium concentrations and barium-isotopic compositions; the remaining water (~8 L) was transferred to 10 L low-density polyethylene cubitainers to be taken below deck for filtration.

Samples were filtered immediately after collection using negative pressure from a central vacuum line. Each sample was drawn across a polyethersulphone filter membrane (0.45 μm cutoff) from a collapsible cubitainer. Filters were held in place using acid-cleaned Swinnex filter holders (EMD Millipore) and connected to the tubing lines with Luer taper fittings; filters were stored before and after use in sealed polycarbonate petri slide holders and manipulated using plastic forceps. Filtration proceeded for a minimum of three hours or until the filters clogged, at which point the filters were removed from their holders, stored, and the water level recorded; filtered volumes ranged from 0.5-3 L.

Particulate samples were prepared for analysis by leaching in 0.6 M hydrochloric acid at 80 °C for ≥ 16 hours. Total dissolvable (i.e. unfiltered) samples were weighed and acidified with hydrochloric acid to a concentration of 0.01 M. Samples were left to equilibrate for several months before any sample processing took place.

Following multi-element geochemical analyses—but before ion-exchange chromatography—all samples were dried and spiked with an appropriate amount of barium double spike to ensure the ratio of spike- to sample-derived barium was between one and two. Samples were additionally fluxed in a 1:1 mixture of concentrated hydrogen peroxide and nitric acid for ≥ 16 hours at 135 °C to oxidize any organic matter in the sample that could interfere with column chemistry or mass spectrometry.

Problem report:

Two minor issues to note:

- The shallowest particulate samples contained insufficient barium to perform a precise isotopic measurement. As such, samples from these depths were 'pooled' to yield a depth-integrated value; the depth noted for these pooled samples reflects the average depth of the pooled sample, weighted by the fractional contribution to the total (measured) barium present in each pooled sample. This pooling does not apply to the multi-element geochemical data as these measurements were performed on separate aliquots.
- One sample yielded an anomalous total particulate titanium concentration (002.02.12) and one sample yielded an anomalous total particulate aluminum concentration (002.02.10); these have been listed as 'nd'.

Data Processing Description

Elemental quantification in sample solutions was achieved via comparison of blank-corrected ion beam intensities to those of a reference curve constructed from measurement of eight standards with known concentrations (seven serially diluted standards plus origin). Ion beam intensities of barium, cadmium, and yttrium were measured in low-mass resolution mode whereas aluminum, calcium, iron, manganese, phosphorus, strontium, titanium, and vanadium were measured in medium-mass resolution mode; In was monitored in both modes and internal normalization was performed separately for low- and medium-mass resolution elements. Analytical uncertainties from ICP-MS analysis refer to the propagated uncertainties from ion counting statistics, In normalization, and from the goodness-of-fit of the standard reference curve. Measured concentrations were converted to Lake Superior particulate concentrations by subtracting the blank from the leachate and then normalizing by the measured volume of water passed through each filter.

Barium-isotopic data reduction was performed using baseline-corrected ion beams corresponding to m/z 131 (Xe, xenon), 135 (Ba), 136 (Xe; Ba; Ce, cerium), 137 (Ba), 138 (Ba; La, lanthanum; Ce), 139 (La) and 140 (Ce), which were measured simultaneously. Barium-isotopic compositions were calculated using the three-dimensional geometric interpretation of the double spike problem, with data reported in parts per one thousand deviations (‰) relative to NIST SRM 3104a.

BCO-DMO Processing Notes:

- added conventional header with dataset name, PI name, version date
- modified parameter names to conform with BCO-DMO naming conventions

Data Files

File
geochem.csv (Comma Separated Values (.csv), 7.15 KB) MD5:95fa5a05fb480bb3dd488799ddaa764f
Primary data file for dataset ID 680091

Parameters

Parameter	Description	Units
ISO_DateTime_UTC	collection date and time; ISO formatted: yyyy-mm-ddThh:mm:ss.sss [UTC]	unitless
lat	latitude; north is positive	decimal degrees
lon	longitude; east is positive	decimal degrees
depth_w	depth of the water; bottom depth	meters
sta	station identifier	unitless
sample	sample identifier	unitless
Rosette_Position	bottle position on rosette	unitless
depth	sample depth	meters
CTDTMP	water temperature	degrees Celcius
Ba_TD_CONC_BOTTLE	total dissolvable barium concentration	nanomoles per liter
Ba_TD_CONC_BOTTLE_stdev	total dissolvable barium concentration standard deviation	nanomoles per liter
Ba_138_TD_DELTA_BOTTLE	total dissolvable barium-isotopic compositions	per mil relative to NIST SRM 3104a
Ba_138_TD_DELTA_BOTTLE_stdev	total dissolvable barium-isotopic compositions standard deviation	per mil relative to NIST SRM 3104a
Al_TP_CONC_BOTTLE	total particulate aluminum concentration	picomoles per liter
Al_TP_CONC_BOTTLE_stdev	total particulate aluminum concentration standard deviation	picomoles per liter
Ba_TP_CONC_BOTTLE	total particulate barium concentration	picomoles per liter
Ba_TP_CONC_BOTTLE_stdev	total particulate barium concentration standard deviation	picomoles per liter
Ca_TP_CONC_BOTTLE	total particulate calcium concentration	picomoles per liter
Ca_TP_CONC_BOTTLE_stdev	total particulate calcium concentration standard deviation	picomoles per liter
Cd_TP_CONC_BOTTLE	total particulate cadmium concentration	picomoles per liter
Cd_TP_CONC_BOTTLE_stdev	total particulate cadmium concentration standard deviation	picomoles per liter
Fe_TP_CONC_BOTTLE	total particulate iron concentration	picomoles per liter
Fe_TP_CONC_BOTTLE_stdev	total particulate iron concentration standard deviation	picomoles per liter

Mn_TP_CONC_BOTTLE	total particulate manganese concentration	picomoles per liter
Mn_TP_CONC_BOTTLE_stdev	total particulate manganese concentration standard deviation	picomoles per liter
P_TP_CONC_BOTTLE	total particulate phosphorus concentration	picomoles per liter
P_TP_CONC_BOTTLE_stdev	total particulate phosphorus concentration standard deviation	picomoles per liter
Sr_TP_CONC_BOTTLE	total particulate strontium concentration	picomoles per liter
Sr_TP_CONC_BOTTLE_stdev	total particulate strontium concentration standard deviation	picomoles per liter
Ti_TP_CONC_BOTTLE	total particulate titanium concentration	picomoles per liter
Ti_TP_CONC_BOTTLE_stdev	total particulate titanium concentration standard deviation	picomoles per liter
V_TP_CONC_BOTTLE	total particulate vanadium concentration	picomoles per liter
V_TP_CONC_BOTTLE_stdev	total particulate vanadium concentration standard deviation	picomoles per liter
Y_TP_CONC_BOTTLE	total particulate yttrium concentration	picomoles per liter
Y_TP_CONC_BOTTLE_stdev	total particulate yttrium concentration standard deviation	picomoles per liter
Ba_138_TP_DELTA_BOTTLE	total particulate barium-isotopic compositions	per mil relative to NIST SRM 3104a
Ba_138_TP_DELTA_BOTTLE_stdev	total particulate barium-isotopic compositions standard deviation	per mil relative to NIST SRM 3104a

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Instruments

Dataset-specific Instrument Name	ThermoFisher ELEMENT 2 ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	Sample leachates were analyzed for their multi-element geochemical compositions
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 Neptune multi-collector ICP-MS at the WHOI Plasma Facility
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	Used for Barium-isotopic analyses.
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	
Generic Instrument Name	Niskin bottle
Dataset-specific Description	For sample collection
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

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Deployments

BH15-11

Website	https://www.bco-dmo.org/deployment/685923
Platform	R/V Blue Heron
Start Date	2015-08-26
End Date	2015-08-28

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Project Information

EAGER - Introducing Early Career Scientists to Research on the Great Lakes (Early Career Great Lakes research)

Coverage: Great Lakes

NSF Award Abstract:

This proposal to fund a research training cruise on the University of Minnesota's R/V Blue Heron for early career scientists from the Great Lakes basin. The proposed work will have two goals: 1) teach early career lacustrine scientists how to acquire, plan for, and manage cruises aboard UNOLS ships, possibly having some impact on the long-term decrease in requests for ship time on UNOLS ships in general; and 2) expose members of the Great Lakes scientific community, which has an abysmally low submittal rate of proposals to NSF requesting UNOLS ships, to UNOLS and the academic fleet. This project mirrors the successful Chief Scientist training program that Dr. Claire Reimers at Oregon State University has run on ocean-going ships such as the R/V Wecoma, New Horizon and Endeavor.

Intellectual Merit :

The training cruise envisioned herein will allow early career scientists to collect seed data and test hypotheses for future proposals to NSF.

Broader Impacts :

This proposal intends to educate the next generation of researchers about the capabilities of UNOLS. This type of outreach between UNOLS and potential users is not only important for the broader scientific community, but doubly important for the Great Lakes community which seems resistant to using assets like the UNOLS fleet.

Calibration of a Novel Nutrient Paleoproxy in the Southern Ocean (Novel Nutrient Paleoproxy)

Coverage: Southern Ocean

NSF Award Abstract:

Human observations of Earth's climate span only a narrow window of Earth History. Understanding how and why Earth's climate changed before human observations can be overcome through the measurement and interpretation of the chemical composition of marine sediments. Accurate interpretation of these records -- also known as "proxy" records, because they stand in for direct measurements of environmental conditions in the past -- first requires that the behavior of the proxy be properly calibrated against direct observations in modern environments. This project will develop a novel proxy for marine nutrient utilization based on a comprehensive characterization of the chemical composition of particulate organic matter in the Southern Ocean. The formation and export of organic matter in the ocean requires nutrients, consumes carbon, and can influence the global air-sea balance of carbon dioxide. New proxies and calibrations offer novel ways of looking at Earth's climate history and can potentially illuminate interactions within marine ecosystems.

The efficiency of the biological carbon pump depends critically on the availability and utilization of marine nutrients, particularly in the Southern Ocean. However, ambiguity in, and disagreement between current nutrient utilization paleoproxies renders reconstruction of past nutrient regimes uncertain. Cadmium -- a known proxy for phosphate -- offers a means to circumvent many of the known limitations of existing nutrient proxies, but requires a full isotopic characterization before its application. In this project, researchers will trace the stable isotopic composition of cadmium recorded in organic matter using multiple collector inductively coupled plasma mass spectrometry. The researchers will make isotopic measurements across numerous surface nutrient regimes in the Southern Ocean, with a focus on three critical geochemical transitions: the formation of organic carbon at the sea surface, its transit and decomposition through the ocean's interior, and its behavior during burial on the sea floor. This sea surface-to-sea floor calibration will thus comprehensively determine the utility and fidelity of a novel nutrient proxy, allowing a more accurate view of how Earth's climate was related to ocean biogeochemistry in the past.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1430015
NSF Division of Ocean Sciences (NSF OCE)	OCE-1443577

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