

Dataset: 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

Project(s): 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)

Abstract: Particles are important vectors of nutrients, carbon, and several trace metals within large bodies of water. Broadly speaking, particle distributions can be classified into three major groups on the basis of their multi-element geochemistry: biogenic (organic matter-associated phases and tests); lithogenic (highly refractory rock-derived materials); and authigenic (formed in situ below the euphotic zone). We collected particulate samples spanning the full water column of Lake Superior at Stations FWM (46.998528, -91.246250) and WM (47.331611, -89.821389) during the height of 2015 summer thermal stratification (cruise BH15-11). We analyzed particle leachates for their multi-element geochemistry using ICP-MS (inductively-coupled plasma mass spectrometry) at the Woods Hole Oceanographic Institution Plasma Facility. We report elemental concentrations in Lake Superior particulate matter in (nano or pico) moles per liter, defined by a 0.44 μm filter cutoff. Lithogenic cycles are resolved by Al, Fe, Ti, V, and Y; biogenic phases by Ca, Cd, P, and Sr; and authigenic processes by Ba, Cd, and Mn. Several elements exhibit hybrid-type distributions depending on the depth range under investigation. Also reported are stable barium-isotopic distributions for particulate and total dissolvable Ba, measured using multiple-collector ICP-MS and reported relative to NIST SRM 3104a in permill. For a complete list of measurements, refer to the supplemental document 'Field_names.pdf', and a full dataset description is included in the supplemental file 'Dataset_description.pdf'. The most current version of this dataset is available at: <http://www.bco-dmo.org/dataset/680091>

Description: Particulate multi-element geochemical concentrations - Lake Superior

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:

Horner et al. (in revision as of 3/2017). Pelagic barite precipitation at micromolar ambient sulphate.

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.

Acquisition Sampling was performed aboard the RV Blue Heron during cruise BH15-11, **Description:** 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 Nisken 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'.

Processing Elemental quantification in sample solutions was achieved via comparison of **Description:** 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

Instrument Information

Instrument	
Description	For sample collection
Generic Instrument	Niskin bottle

Name	
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.

Instrument	ThermoFisher ELEMENT 2 ICP-MS
Description	Sample leachates were analyzed for their multi-element geochemical compositions
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.

Instrument	ThermoFisher Neptune multi-collector ICP-MS at the WHOI Plasma Facility
Description	Used for Barium-isotopic analyses.
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.