# Particulate data collected on R/V Melville (MV1405, IrnBru) along the California coast in July 2014

Website: https://www.bco-dmo.org/dataset/663183

Data Type: Cruise Results

Version: 1

Version Date: 2016-10-26

#### Project

» Collaborative Research: Investigating the Ecological Importance of Iron Storage in Diatoms (Diatom Iron

Storage)

Contributors	Affiliation	Role
Twining, Benjamin	Bigelow Laboratory for Ocean Sciences	Principal Investigator
Rauschenberg, Sara	Bigelow Laboratory for Ocean Sciences	Contact
Ake, Hannah	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

#### **Abstract**

This dataset includes trace element concentrations in particles collected with GO-Flo bottles on R/V Melville (MV1405, IrnBru) along the California coast in July 2014.

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#### Coverage

Spatial Extent: N:42.866 E:-120.03 S:34.23 W:-126.75

Temporal Extent: 2014-07-06 - 2014-07-25

## **Dataset Description**

Trace element concentrations in particles collected with GO-Flo bottles and analyzed with inductively-coupled plasma mass spectrometry (ICP-MS). Concentrations of labile, refractory, and total metal fractions are reported.

#### Methods & Sampling

#### Total, refractory, and labile particulate element concentrations via ICPMS:

Labile and total suspended particulate trace elements concentrations are reported for: Al, Ba, Cd, Co, Cu, Fe, La, Mn, Ni, P, Pb, Sc, Th, Ti, V, Y, Zn. Concentrations of the labile fraction of these particulate elements are indicated as element names followed by the suffix '-Labile', refractory portions are indicated with the suffix '-Refractory', and concentrations of total particulate elements (the sum of labile and refractory) are followed by

'-Total'. Concentrations are reported in units of picomoles per liter (pmol/L).

#### Sampling Methodology:

Trace metal-clean seawater samples were collected using a sampling system consisting of Teflon-coated GO-Flo bottles and following methods described in Bruland et al (1979). Additional samples were collected from surface waters (~2 meters) using a towed 'fish' deployed by Ken Bruland's lab. Water collected with GO-Flo bottles and the 'fish' was transferred into acid-washed 4-liter (L) LDPE carboys for off-line filtration.

All filtration was conducted in a HEPA-filtered 'bubble' (temporary clean room). A filter holder containing a 25-millimeter (mm) diameter Pall Supor 0.4-micrometer (um) polyethersulfone membrane was attached to the opening at the carboy top. Carboys were pressurized with 0.2-um filtered air and inverted during filtration to ensure that all particles were captured on the membrane. Filtrate was collected to determine the volume of seawater filtered: an average of 2.1L was filtered through each membrane. After filtration, membranes were folded into quarters, placed in 1.7-milliliter (mL) polypropylene vials, and stored at -20 degrees Celsius until analysis.

#### **Analytical Methodology:**

All digestion steps were performed in a Class-100 clean room using standard clean techniques. Filters were sequentially digested, first following the protocol of Berger et al. (2008) to obtain labile particulate concentrations and then digested using a 4M HCl, 4M HNO3, and 4M HF mixture as described in Ohnemus et al. (2014) to obtain refractory particulate element concentrations.

For the labile particulate leach, a 1-milliliter solution of 25% Optima-grade acetic acid and 0.02 M hydroxylamine was added to the filter stored in a 1.7 mL polypropylene vial. Following the recommendation of Berger et al. (2008), the solution was heated to 95 degrees C in a water bath for 10 minutes and then allowed to cool to room temperature. The filter was in contact with the acetic acid leach for a total of two hours, after which the filter was removed from the polypropylene vial and placed in an acid-cleaned 22-mL PFA vial. The acetic acid/hydroxylamine leachate was centrifuged at 14,000 rpm for 10 minutes to sediment all particles. Without disturbing particles on the bottom of the tube, approximately 0.8 mL of leachate was transferred into an acid-cleaned 7 mL PFA digestion vial. Optima-grade HNO3 was added (100 uL) to the digestion vial, which was subsequently heated uncapped at 110 degrees C to near dryness. Vial contents were redissolved with 2% HNO3 (Optima grade).

Refractory particulate metals were determined by subsequent digestion of the filter. Two milliliters of a solution containing 4M HCl, 4M HNO3, and 4M HF (all Optima grade) was added to the filter which was placed in a cleaned 22-mL PFA vial. The vial was tightly capped and heated to  $110^{\circ}$ C for 4 hours. This procedure has been determined to be adequate for digestion of all particulate material, while allowing the Supor filter to remain intact (Ohnemus et al. 2014). Following heating, the acid solution in the bomb was poured into a second PFA vial, leaving the filter piece behind. To ensure complete transfer of acid, the bombs were thoroughly rinsed with  $3 \times 0.5$  mL aliquots of ultrapure water which were poured into the secondary vial. The secondary vial was then heated to dryness and the contents redissolved with 1 mL of a 50% Optima-grade HNO3 + 15% Optima-grade H2O2 (v/v of concentrated reagents) solution. This solution was again dried down and the contents redissolved with 2% HNO3.

All digests were analyzed using a Finnigan-MAT Element2 HR-ICP-MS at the University of Maine following the protocols outlined in Twining et al. (2011). The instrument is equipped with a cyclonic nebulizer, an autosampler contained under a HEPA filter, and nickel cones. Ba, Cd, La, Th, and Y were analyzed in low-resolution mode, while the remaining isotopes were analyzed in medium-resolution mode.

Quantification was performed by external calibration, and In-115 was used as an internal standard to correct for variations in instrumental sensitivity during analyses. Cs-133, spiked during the initial sample leaches, was used as a process recovery monitor, but no samples were discarded or corrected using the Cs recoveries, as typical Cs recoveries were 90-110%. Certified reference materials were digested alongside refractory sample digests. Average recoveries for each element are given in the attached supplemental file "CRMs.png".

#### **Data Processing Description**

All ICP-MS elemental concentration data were normalized to an In-115 internal standard and quantified using external standard curves. After accounting for sample dilutions due to acid digestion steps, quantities of each element per filter (pmol/filter) were calculated for each analytical run. The contribution of the 'process blank' (measured as the elements contained in an acid-washed filter through which 0.2-um filtered water was passed during the cruise) was then subtracted. Process blanks were pooled from across the cruise section. Separate

process blanks were calculated for the labile (acetic acid/hydroxylamine) and refractory (HCl/HNO3/HF) digestions. The median process blanks for each digestion scheme and each element are given in the attached supplemental file "Blanks" and DetectionLimits.png".

Following process blank correction, element concentrations (per volume of water filtered) were calculated by dividing the determined pmol/filter by the volume of water passed through each filter.

Detection limits are calculated as 3 times the standard deviation of the process blanks for the relevant digestion procedure after pooling of process blanks from across the transect.

Total element concentrations are calculated as the sum of the labile and refractory portions. Total concentrations are not reported if either the labile or refractory concentrations are below detection limits.

#### Description of data quality flags:

The standard Ocean Data View flags were used:

- 1: Good Value: Used when replicate samples were analyzed for a particular concentration.
- 2: Probably Good Value: Used when the reported value reflects analysis of a single replicate.
- 3: Probably Bad Value: Used when a value appears abnormally high or low (oceanographically inconsistent) based on adjacent depths or typical profile variability and shape using the context of relevant nearby stations.
- 6: Value Below Detection Limit: Used when value is below the detection limit for that given element. Empty values are reported rather than zero or a detection limit value.

#### **BCO-DMO Processing Description**

- reformatted column names to comply with BCO-DMO standards.
- filled in blank cells with "nd"
- added the DateTime column "ISO DateTime UTC"

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#### **Data Files**

#### **File**

**stations.csv**(Comma Separated Values (.csv), 28.21 KB)
MD5:ce0elee609375cef48cffddd524f572f

Primary data file for dataset ID 663183

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### **Supplemental Files**

#### File

**Blanks\_and\_DetectionLimits.png**(Portable Network Graphics (.png), 283.98 KB)

MD5:ea6bb11db0c5391d4cd3b369a29648ed

Supplemental file for dataset ID 663183, version 1.

CRMs.png

(Portable Network Graphics (.png), 150.50 KB) MD5:92d86b5aa7531a324619b3dd0b684220

Supplemental file for dataset ID 663183, version 1.

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#### **Related Publications**

Berger, C. J. M., Lippiatt, S. M., Lawrence, M. G., & Bruland, K. W. (2008). Application of a chemical leach technique for estimating labile particulate aluminum, iron, and manganese in the Columbia River plume and coastal waters off Oregon and Washington. Journal of Geophysical Research, 113. doi:10.1029/2007jc004703 <a href="https://doi.org/10.1029/2007JC004703">https://doi.org/10.1029/2007JC004703</a>

Methods

Bruland, K. W., Franks, R. P., Knauer, G. A., & Martin, J. H. (1979). Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water. Analytica Chimica Acta, 105, 233–245. doi:10.1016/s0003-2670(01)83754-5 <a href="https://doi.org/10.1016/S0003-2670(01)83754-5">https://doi.org/10.1016/S0003-2670(01)83754-5</a>

Methods

Ohnemus, D. C., Auro, M. E., Sherrell, R. M., Lagerström, M., Morton, P. L., Twining, B. S., ... Lam, P. J. (2014). Laboratory intercomparison of marine particulate digestions including Piranha: a novel chemical method for dissolution of polyethersulfone filters. Limnology and Oceanography: Methods, 12(8), 530–547. doi:10.4319/lom.2014.12.530

Methods

Twining, B. S., Antipova, O., Chappell, P. D., Cohen, N. R., Jacquot, J. E., Mann, E. L., ... Tagliabue, A. (2020). Taxonomic and nutrient controls on phytoplankton iron quotas in the ocean. Limnology and Oceanography Letters. doi:10.1002/lol2.10179

Results

Twining, B. S., Baines, S. B., Bozard, J. B., Vogt, S., Walker, E. A., & Nelson, D. M. (2011). Metal quotas of plankton in the equatorial Pacific Ocean. Deep Sea Research Part II: Topical Studies in Oceanography, 58(3-4), 325–341. doi:10.1016/j.dsr2.2010.08.018

Methods

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#### **Parameters**

Parameter	Description	Units
description	PI issued sample ID	unitless
station	Station where sampling occurred	unitless
depth	Depth where sampling occurred	meters
lat	Latitude; N is positive	decimal degrees
lon	Longitude; W is positive	decimal degrees
date	Date of sampling; mm/dd/yy	unitless
time_gmt	Time of sampling; HH:MM	unitless
Cd_Labile	Labile concentration of Cadmium	picomole per liter (pmol/L)
La_Labile	Labile concentration of Lanthanum	picomole per liter (pmol/L)
Y_Labile	Labile concentration of Yttrium	picomole per liter (pmol/L)
Pb_Labile	Labile concentration of Lead	picomole per liter (pmol/L)
Ba_Labile	Labile concentration of Barium	picomole per liter (pmol/L)
Th_Labile	Labile concentration of Thorium	picomole per liter (pmol/L)

Al_Labile	Labile concentration of Aluminum	picomole per liter (pmol/L)
Mn_Labile	Labile concentration of Maganese	picomole per liter (pmol/L)
Fe_Labile	Labile concentration of Iron	picomole per liter (pmol/L)
Co_Labile	Labile concentration of Cobalt	picomole per liter (pmol/L)
Cu_Labile	Labile concentration of Copper	picomole per liter (pmol/L)
Ni_Labile	Labile concentration of Nickel	picomole per liter (pmol/L)
P_Labile	Labile concentration of Phosphorus	picomole per liter (pmol/L)
Ti_Labile	Labile concentration of Titanium	picomole per liter (pmol/L)
V_Labile	Labile concentration of Vanadium	picomole per liter (pmol/L)
Zn_Labile	Labile concentration of Zinc	picomole per liter (pmol/L)
Sc_Labile	Labile concentration of Scandium	picomole per liter (pmol/L)
Cd_Refractory	Refractory concentration of Cadmium	picomole per liter (pmol/L)
La_Refractory	Refractory concentration of Lanthanum	picomole per liter (pmol/L)
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P_Refractory	Refractory concentration of Phosphorus	picomole per liter (pmol/L)
Ti_Refractory	Refractory concentration of Titanium	picomole per liter (pmol/L)

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Quality flag for Labile concentration of Iron	unitless
Quality flag for Labile concentration of Cobalt	unitless
Quality flag for Labile concentration of Copper	unitless
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Quality flag for Labile concentration of Phosphorus	unitless
Quality flag for Labile concentration of Titanium	unitless
Quality flag for Labile concentration of Vanadium	unitless
Quality flag for Labile concentration of Zinc	unitless
Quality flag for Labile concentration of Scandium	unitless
Quality flag for Refractory concentration of Cadmium	unitless
Quality flag for Refractory concentration of Lanthanum	unitless
Quality flag for Refractory concentration of Yttrium	unitless
Quality flag for Refractory concentration of Lead	unitless
Quality flag for Refractory concentration of Barium	unitless
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Quality flag for Refractory concentration of Zinc	unitless
Quality flag for Refractory concentration of Scandium	unitless
Quality flag for total particulate concentration (sum of Labile and Refractory) of Cadmium	unitless
Quality flag for total particulate concentration (sum of Labile and Refractory) of Lanthanum	unitless
Quality flag for total particulate concentration (sum of Labile and Refractory) of Yttrium	unitless
Quality flag for total particulate concentration (sum of Labile and Refractory) of Lead	unitless
Quality flag for total particulate concentration (sum of Labile and Refractory) of Barium	unitless
Quality flag for total particulate concentration (sum of Labile and Refractory) of Thorium	unitless
Quality flag for total particulate concentration (sum of Labile and Refractory) of Aluminum	unitless
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Fe_TotalFlag	Quality flag for total particulate concentration (sum of Labile and Refractory) of Iron	unitless
Co_TotalFlag	Quality flag for total particulate concentration (sum of Labile and Refractory) of Cobalt	unitless
Cu_TotalFlag	Quality flag for total particulate concentration (sum of Labile and Refractory) of Copper	unitless
Ni_TotalFlag	Quality flag for total particulate concentration (sum of Labile and Refractory) of Nickel	unitless
P_TotalFlag	Quality flag for total particulate concentration (sum of Labile and Refractory) of Phosphorus	unitless
Ti_TotalFlag	Quality flag for total particulate concentration (sum of Labile and Refractory) of Titanium	unitless
V_TotalFlag	Quality flag for total particulate concentration (sum of Labile and Refractory) of Vanadium	unitless
Zn_TotalFlag	Quality flag for total particulate concentration (sum of Labile and Refractory) of Zinc	unitless
Sc_TotalFlag	Quality flag for total particulate concentration (sum of Labile and Refractory) of Scandium	unitless
ISO_DateTime_UTC	Date/Time of sampling at station (UTC) ISO formatted	unitless

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#### Instruments

<b>Dataset-specific Instrument Name</b>	Towed fish
Generic Instrument Name	GeoFish Towed near-Surface Sampler
Dataset-specific Description	Used to collect surface seawater samples
Generic Instrument Description	The GeoFish towed sampler is a custom designed near surface (

Dataset- specific Instrument Name	Teflon-coated GO-Flo Bottle
Generic Instrument Name	GO-FLO Teflon Trace Metal Bottle
Dataset- specific Description	Used to collect trace metal-clean seawater samples
	GO-FLO Teflon-lined Trace Metal free sampling bottles are used for collecting water samples for trace metal, nutrient and pigment analysis. The GO-FLO sampling bottle is designed specifically to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

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## Deployments

#### MV1405

Website	https://www.bco-dmo.org/deployment/559966
Platform	R/V Melville
Start Date	2014-07-03
End Date	2014-07-26
Description	Deployment MV1405 on R/V Melville. Cruise took place during July 2014.

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#### **Project Information**

## Collaborative Research: Investigating the Ecological Importance of Iron Storage in Diatoms (Diatom Iron Storage)

Coverage: North Pacific, California coast and subarctic gyre

#### NSF Award Abstract:

Diatoms are responsible for a significant fraction of primary production in the ocean. They are associated with enhanced carbon export and usually dominate the response of phytoplankton to additions of the micronutrient iron in high-nutrient, low-chlorophyll (HNLC) regions. Diatoms, particularly those isolated from the open ocean, appear to have a significant capacity to store iron for later use, and in some groups of diatoms this ability is enabled by the iron storage protein ferritin. Such luxury uptake of iron has long been observed in laboratory cultures and hypothesized to provide diatoms with an ecological benefit in the low-iron waters that cover 40% of the global ocean. However iron storage has been difficult to observe in natural systems due to the methodological challenges of working with mixed plankton assemblages, and a physiological understanding of the impacts of iron on ocean diatoms is lacking. This project combines state-of-the-art high-throughput transcriptomic sequencing and single-cell element analysis with novel laboratory and field incubation experiments to quantify iron storage abilities of cultured and natural diatoms that either contain or lack ferritin and determine the ecological impacts of this process. The overall objective of this project is to examine the ecological importance of iron storage as a selective mechanism controlling the distributions of diatoms along iron gradients in marine ecosystems. The proposed research includes three specific objectives:

- A. Determine if there is a consistent physiological difference in the ability of pennate versus centric diatoms to store iron.
- B. Examine whether iron storage capacities across diverse diatom taxa consistently provide a mechanistic explanation for continued growth in the absence of iron.
- C. Determine whether enhanced iron storage provides diatoms with a competitive within natural phytoplankton assemblages in both coastal and oceanic regions.

Transcriptomic sequencing on a variety of ecologically important pennate and centric diatoms will be used to survey for the presence of ferritin-like genes in order to establish biogeographical and/or phylogenetic patterns of occurrence of diatom ferritin. Laboratory culture experiments will be used to quantify the iron storage abilities of these diatoms, as well as the number of cell divisions that can be supported by the stored iron, providing valuable physiological data to inform the understanding of plankton ecology in iron-limited coastal and HNLC systems. The laboratory experiments will be complemented by measurements of ferritin expression and iron storage in coastal and ocean diatoms sampled across gradients of iron availability on two cruises-of-opportunity to the northeast Pacific Ocean.

The NCBI bioproject page can be found <u>here</u>.

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#### **Funding**

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1334632

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