Dissolved iron-binding ligands and their respective conditional stability constants in upper water column, R/V Knorr KN192-05, S. Atlantic subtropical gyre and Benguela upwelling region, Nov. 2007 (CoFeMUG project)

Website: https://www.bco-dmo.org/dataset/3986 Version: 2 Version Date: 2016-12-02

Project

» Cobalt, Iron and Micro-organisms from the Upwelling zone to the Gyre (GAc01) (CoFeMUG)

Programs

- » Ocean Carbon and Biogeochemistry (OCB)
- » U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
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Dataset Description

Dissolved iron-binding organic ligand concentrations and conditional stability constants from CoFeMUG water column samples collected in 2007 in the Eastern South Atlantic on the R.V. Knorr, cruise KN192-05.

Samples were obtained through the CoFeMUG program, funded by NSF OCE-0452883 to Mak Saito (WHOI). Buck was funded for these analyses by the Walwyn Hughes Fund for Innovation at the Bermuda Institute of Ocean Sciences (BIOS).

These data should be considered and cited as preliminary until the public release of the GEOTRACES Intermediate Data Product in August 2017.

Methods & Sampling

Sampling and analytical methodology:

Sample collection and filtering: Water column samples were collected from a trace metal rosette outfitted with Teflon-coated X-Niskin samplers (Ocean Test Equipment) and deployed on a nonmetallic line. Samples were filtered through acid-cleaned 142-mm polycarbonate filters with a 0.4 μ m pore size (Geotech Environmental) in a laminar flow clean hood. Please see Noble et al. (2012) for detailed information on sample acquisition and processing.

Filtered seawater samples for iron speciation (organic complexation) were collected in 500 mL acid-cleaned

Nalgene narrow-mouth fluorinated high-density polyethylene (FPE) bottles that had been filled with Milli-Q for at least two weeks after acid cleaning and rinsed three times with filtered seawater prior to sample collection (Buck et al. 2012). All filtered seawater samples for dissolved iron speciation were frozen at -20 °C shipboard by the sampling team and shipped to the Bermuda Institute of Ocean Sciences for laboratory-based analyses post cruise.

Dissolved iron speciation (organic complexation) analyses: Dissolved Fe speciation (organic complexation) was analyzed using a competitive ligand exchange- adsorptive cathodic stripping voltammetry (CLE-ACSV) method with salicylaldoxime as the added competing ligand (Buck et al. 2007, 2012), modified from the original Rue and Bruland (1995) method. Dissolved Fe additions of 0 to 7.5 nM were used in the titrations, for a total of 12 points in each titration. Deposition times of 120 s were applied to the analyses. All analyses were performed on Bioanalytical Systems (BASi) Controlled Growth Mercury Electrodes (static mercury drop setting, size 14) with Epsilon e2 (BASi) electrochemical analyzers. There are no reference samples available for iron speciation/ organic complexation measurements of iron in seawater, though this method was shown to compare well with other labs and techniques in the GEOTRACES intercalibration exercises (Buck et al. 2012, 2016).

FLAG: The standard Ocean Data View qualifying flags were used (reference all flags at <u>https://www.bodc.ac.uk/data/codes_and_formats/odv_format/</u>):

1: Good Value: Good quality data value that is not part of any identified malfunction and has been verified as consistent with real phenomena during the quality control process. [Used when data were shown to be reproducible]

2: Probably Good Value: Data value that is probably consistent with real phenomena but this is unconfirmed or data value forming part of a malfunction that is considered too small to affect the overall quality of the data object of which it is a part. [Used when the reported value reflects analysis of a single or unverified replicate]

3: Probably Bad Value: Data value recognized as unusual during quality control that forms part of a feature that is probably inconsistent with real phenomena. [Not used]

4: Bad Value: An obviously erroneous data value. [Not used]

5: Changed Value: Data value adjusted during quality control. [Not used]

6: Value Below Detection Limit: The level of the measured phenomenon was too small to be quantified by the technique employed to measure it. The accompanying value is the detection limit for the technique or zero if that value is unknown. [We report "not_detected" rather than zero or a detection limit value for this case]

7: Value in Excess: The level of the measured phenomenon was too large to be quantified by the technique employed to measure it. The accompanying value is the measurement limit for the technique. [Not used]

8: Interpolated Value: This value has been derived by interpolation from other values in the data object. [Not used]

9: Missing Value: The data value is missing. Any accompanying value will be a magic number representing absent data. [Not used]

Data Processing Description

Data processing:

Dissolved Fe concentrations for each sample from the Mak Saito lab at Woods Hole Oceanographic Institution were used to calculate ligand concentrations and conditional stability constants from the titrations; see Noble et al. (2012) for details of dissolved iron analyses. Titration data was interpreted with a combination of Scatchard (Scatchard 1949) and van den Berg-Ruzic (Ruzic 1982; van den Berg 1982) linearization techniques, as has been described previously (Buck et al. 2012, 2015, 2016). An inorganic side reaction coefficient, aFe¢, of 1010 was used in the iron speciation calculations (Buck et al. 2012). Ligand concentrations and conditional stability constants determined from each linearization of a titration dataset were then combined for a final ligand concentration and conditional stability constant for each sample. When available, results from replicate titration analyses were averaged together and the average with standard deviations of all sample titrations were then reported for each parameter in the spreadsheet.

Related files and references:

Buck, K. N., L. J. A. Gerringa, and M. J. A. Rijkenberg. 2016. An intercomparison of dissolved iron speciation at the Bermuda Atlantic Time-series Station (BATS): Results from the GEOTRACES Crossover Station A. Frontiers in Marine Biogeochemistry 3: article 262.

Buck, K. N., M. C. Lohan, C. J. M. Berger, and K. W. Bruland. 2007. Dissolved iron speciation in two distinct river plumes and an estuary: Implications for riverine iron supply. Limnology and Oceanography 52: 843-855.

Buck, K. N., K. E. Selph, and K. A. Barbeau. 2010. Iron-binding ligand production and copper speciation in an incubation experiment of Antarctic Peninsula shelf waters from the Bransfield Strait, Southern Ocean. Marine Chemistry 122: 148-159.

Buck, K. N., J. W. Moffett, K. A. Barbeau, R. M. Bundy, Y. Kondo, and J. Wu. 2012. The organic complexation of iron and copper: an intercomparison of competitive ligand exchange- adsorptive cathodic stripping voltammetry (CLE-ACSV) techniques. Limnology and Oceanography: Methods 10: 496-515.

Noble, A. E., C. H. Lamborg, D. C. Ohnemus, P. J. Lam, T. J. Goepfert, C. I. Measures, C. H. Frame, K. L. Casciotti, G. R. Ditullio, J. Jennings, and M. A. Saito. 2012. Basin-scale inputs of cobalt, iron, and manganese from the Benguela-Angola front to the South Atlantic Ocean. Limnology and Oceanography 57: 989-1010.

Rue, E. L., and K. W. Bruland. 1995. Complexation of iron(III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration adsorptive cathodic stripping voltammetric method. Marine Chemistry 50: 117-138.

Ruzic, I. 1982. Theoretical aspects of the direct titration of natural waters and its information yield for trace metal speciation. Analytica Chimica Acta 140: 99-113.

Scatchard, G. 1949. The attractions of proteins for small molecules and ions. Annals of the New York Academy of Sciences 51: 660-672.

van den Berg, C. M. G. 1982. Determination of copper complexation with natural organic ligands in sea water by equilibrium with MnO2: I. Theory. Marine Chemistry 11: 307-322.

BCO-DMO Processing Notes:

- added conventional header with dataset name, PI name, version date

- column names reformatted to comply with BCO-DMO standards

- replaced blank cells with nd, 'no data'

- version 2016-12-05 replaced v2013-07-01: revised parameter names, added data columns for flags and ligand 3.

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Data Files

File	
Fe_speciation_v20161202.csv(Comma Separated Values (.csv), 6.95 K MD5:7062f6e79e27613316ffc03cbc2627c0	B)
Primary data file for dataset ID 3986	

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Parameters

Parameter	Description	Units
cruise_id	cruise identification	unitless
station	station number	unitless
date	GMT date when rosette cast was started; formatted as yyyymmdd	unitless

lat	Station latitude; north is positive: position when sampling cast was started (2 m sample = underway sample collected typically on approach to station)	decimal degrees
lon	Station longitude; east is positive; position when sampling cast was started (2 m sample = underway sample collected typically on approach to station)	decimal degrees
depth	sample collection depth below sea surface	meters
depth_w	water column depth at sampling location	meters
N_TITRATIONS	number of titrations performed for sample analyses	unitless
Fe_D_CONC_BOTTLE	Dissolved iron (Fe) concentration value used in the speciation data interpretation. Data received from Mak Saito's lab at Woods Hole Oceanography Institution; contact Saito for additional information. Units	nanomoles/liter (10^-9 M)
L1Fe_D_CONC_BOTTLE	concentration of dissolved iron-binding ligand with log K1 = 12. "not_detected" used when this parameter was not determined in sample analyses.	nanomoles/liter (10^-9 M)
L1_FLAG	L1 quality flag	unitless
L1_stdev	standard deviation of averaged results from replicate analyses; only available for samples with $n>1$ titrations. "nd = no data" used when standard deviations were not available either because of single replicate sample analyses or this ligand classes was not detected in the analyses.	nanomoles/liter (10^-9 M)
L1Fe_D_LogK_BOTTLE	log conditional stability constant of L1 complexes with iron (log). "not_detected" used when this parameter was not determined in sample analyses.	No units; K1 has units of M- 1
log_K1_FLAG	K1 quality flag	unitless
log_K1_stdev	standard deviation of averaged results from replicate analyses; only available for samples with $n>1$ titrations. "nd = no data" used when standard deviations were not available either because of single replicate sample analyses or this ligand classes was not detected in the analyses.	No units; K1 has units of M- 1
L2Fe_D_CONC_BOTTLE	concentration of dissolved iron-binding ligand with log K2 = 11-12. "not_detected" used when this parameter was not determined in sample analyses.	nanomoles/liter (10^-9 M)
L2_FLAG	L2 quality flag	unitless
L2_stdev	standard deviation of averaged results from replicate analyses; only available for samples with $n>1$ titrations. "nd = no data" used when standard deviations were not available either because of single replicate sample analyses or this ligand classes was not detected in the analyses.	nanomoles/liter (10^-9 M)
L2Fe_D_LogK_BOTTLE	log conditional stability constant of L2 complexes with iron (log). "not_detected" used when this parameter was not determined in sample analyses.	No units; K2 has units of M^-1
log_K2_FLAG	K2 quality flag	unitless
log_K2_stdev	standard deviation of averaged results from replicate analyses; only available for samples with $n>1$ titrations. "nd = no data" used when standard deviations were not available either because of single replicate sample analyses or this ligand classes was not detected in the analyses.	No units; K2 has units of M^-1
L3Fe_D_CONC_BOTTLE	concentration of dissolved iron-binding ligand with log K3 = 10-11. "not_detected" used when this parameter was not determined in sample analyses.	nanomoles/liter (10^-9 M)

L3_FLAG	L3 quality flag	unitless
L3_stdev	standard deviation of averaged results from replicate analyses; only available for samples with $n>1$ titrations. "nd = no data" used when standard deviations were not available either because of single replicate sample analyses or this ligand classes was not detected in the analyses.	nanomoles/liter (10^-9 M)
L3Fe_D_LogK_BOTTLE	log conditional stability constant of L3 complexes with iron (log). "not_detected" used when this parameter was not determined in sample analyses.	No units; K3 has units of M^-1
log_K3_FLAG	K3 quality flag	unitless
log_K3_stdev	standard deviation of averaged results from replicate titrations; only available for samples with replicate titrations. "nd = no data" used when standard deviations were not available either because of single replicate sample analyses or this ligand classes was not detected in the analyses.	No units; K3 has units of M^-1

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Instruments

Dataset- specific Instrument Name	BASi Controlled Growth Mercury Electrode
Generic Instrument Name	BASi Controlled Growth Mercury Electrode
Dataset- specific Description	http://www.basinc.com/products/ec/cgme.php
Generic Instrument Description	Bioanalytical Systems (BASi) Mercury drop electrodes are generated by the BASi Controlled Growth Mercury Electrode (CGME) in three modes: DME (Dropping Mercury Electrode) - mercury is allowed to flow freely from the reservoir down the capillary and so the growth of the mercury drop and its lifetime is controlled by gravity. (The optional 100 um capillary is recommended for this mode.) SMDE (Static Mercury Drop Electrode) - the drop size is determined by the length of time for which the fast-response capillary valve is opened, and the drop is dislodged by a drop knocker. The dispense/knock timing is microprocessor-controlled and is typically coordinated with the potential pulse or square-wave waveform. This mode can also used to generate the Hanging Mercury Drop Electrode required for stripping experiments. CGME (Controlled Growth Mercury Electrode) - the mercury drop is grown by a series of pulses that open the capillary valve. The number of pulses, their duration, and their frequency can be varied by PC control, providing great flexibility in both the drop size and its rate of growth. This CGME mode can be used for both polarographic and stripping experiments. http://www.basinc.com/products/ec/cgme.php

Dataset- specific Instrument Name	BASi EC-epsilon 2 Autoanalyzer
Generic Instrument Name	BASi EC-epsilon 2 Autoanalyzer
Dataset- specific Description	http://www.basinc.com/products/ec/epsilon/
Generic Instrument Description	The Bioanalytical Systems EC epsilon is a family of potentiostat/galvanostats for electrochemistry. The most basic epsilon instrument can be used for standard techniques, as well as chronopotentiometry for materials characterization (e.g., characterization of transition metal complexes by cyclic voltammetry and controlled potential electrolysis, or of biosensors by cyclic voltammetry and constant potential amperometry). Pulse, square wave, and stripping techniques can be added by a software upgrade, and a second channel can be added by a hardware upgrade. http://www.basinc.com/products/ec/epsilon/

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Deployments

KN192-05

Website	https://www.bco-dmo.org/deployment/57852
Platform	R/V Knorr
Report	http://bcodata.whoi.edu/CoFeMUG/CruiseReport_KN192-5.pdf
Start Date	2007-11-16
End Date	2007-12-13
Description	The South Atlantic subtropical gyre and Benguela Upwelling region were sampled for chemistry and biological properties relating to the trace metal nutrition and phytoplankton diversity and productivity. Specifically cobalt and iron dissolved seawater concentrations will be measured and related to the abundance of cyanobacteria including nitrogen fixers and eukaryotic phytoplankton. The phytoplankton of the Benguela Upwelling region were also examined to determine if their growth was iron or cobalt limited. A total of 27 station locations were occupied in the study area to collect the water chemistry and biological samples for these analyses (see cruise track). Iron and cobalt analyses will be conducted using inductively coupled plasma mass spectrometry and cathodic stripping voltammetry electrochemical methods. The sample preparation and subsequent analyses are technically demanding, but data generated from the cruise samples are being contributed beginning in mid 2009. The CoFeMUG KN192-5 cruise was supported by NSF OCE award # 0452883 A station map showing the 27 sampling locations is available as a PDF file. Original cruise data are available from the NSF R2R data catalog CoFeMUG - South Atlantic 2007 Cruise Participant List 1. Mak Saito (Chief Scientist/WHOI) 2. Abigail Noble (Saito/WHOI) 3. Alysia Cox (Saito/WHOI) 4. Whitney Krey (Delong/Saito/MIT/WHOI) 5. Carl Lamborg (clamborg AT whoi.edu/WHOI) 6. Phoebe Lam (pjlam AT whoi.edu WHOI) 7. Chad Hammerschmidt (chammerschmidt AT whoi.edu, Wright State) 8. Caitlin Frame (cframe AT whoi.edu, W HOI/Casciotti Student) 9. Tyler Goepfert (tgoepfert AT whoi.edu Web/Saito) 10. Jill Sohm (sohm AT usc.edu) 11. Maria Intermaggio 12. Jack DiTullio U. Charleston) 13. Amanda McLenan (amanda.mclennon AT gmail.com, DiTullio U. Charleston) 13. Masa (enahas AT u.washington.edu) 24. Christian Frazar (Chris, U. Washington, Morris Iab) 25. Jason Hilton (Zehr, UCSC) 26. Reserved for Angolan Observers 27. Reserved for Angolan Observers Collecting GEOTRACES-compliant samples for: 1.

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Project Information

Cobalt, Iron and Micro-organisms from the Upwelling zone to the Gyre (GAc01) (CoFeMUG)

Coverage: South Atlantic subtropical gyre and Benguela upwelling region

The geochemistries of dissolved cobalt (Co) and iron (Fe) in the oceanic water column share several characteristics such as extremely low concentrations, redox chemistry, low solubility, and utilization as micronutrients by marine microbes. Iron has been the subject of considerable research focus in recent years due to its role in limiting phytoplankton productivity in oceanic and coastal upwelling environments. Cobalt has been much less studied, but recent data show it may be important in influencing primary productivity or phytoplankton community composition in certain geographical areas.

The CoFeMUG project predated GEOTRACES, so while it is not formally recognized as a GEOTRACES section, it is considered a GEOTRACES-related project and the CoFeMUG data are GEOTRACES compliant.

State-of-the-art geochemical and molecular biological techniques were used to address biogeochemical questions in the South Atlantic, and focus especially on the two trace metals, cobalt and iron. The 27-day cruise in November and December 2007 to the South Atlantic was designed to study cobalt and iron biogeochemistry and focus on four major hypotheses.

(1) Large fluxes of labile cobalt are associated with upwelling systems even in Aeolian dominated environments.
(2) Cobalt and phosphate show correlations in (and only in) surface waters due to micronutrient utilization and rapid remineralization. The slope of the correlation is dependent on the chemical speciation of cobalt.
(3) The absence of Trichodesmium populations in the subtropical and tropical South Atlantic is caused by iron limitation.

(4) Based on work from the California and Peru Upwelling regimes, primary productivity in the Benguela upwelling regime off of South West Africa may be iron limited or iron-cobalt colimited.

A combination of geochemical and biological/molecular analyses were made across an oligotrophic-upwelling transition to examine how changing metal regimes affect the physiology and growth of the important primary producers Trichodesmium and Synechococcus.

CoFeMUG project results are published in:

Noble, Abigail E., Carl H. Lamborg, Dan C. Ohnemus, Phoebe J. Lam, Tyler J. Goepfert, Chris I. Measures, Caitlin H. Frame, Karen L. Casciotti, Giacomo R. DiTullio, Joe Jennings, and Mak A. Saito (2012) Basin-scale inputs of cobalt, iron, and manganese from the Benguela-Angola front to the South Atlantic Ocean. Limnology & Oceanography. Vol. 57(4), July 2012. pgs 989-1010. doi:10.4319/lo.2012.57.4.0989 (www.aslo.org/lo/toc/vol_57/issue_4/0989.pdf)

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Program Information

Ocean Carbon and Biogeochemistry (OCB)

Website: <u>http://us-ocb.org/</u>

Coverage: Global

The Ocean Carbon and Biogeochemistry (OCB) program focuses on the ocean's role as a component of the global Earth system, bringing together research in geochemistry, ocean physics, and ecology that inform on and advance our understanding of ocean biogeochemistry. The overall program goals are to promote, plan, and coordinate collaborative, multidisciplinary research opportunities within the U.S. research community and with international partners. Important OCB-related activities currently include: the Ocean Carbon and Climate Change (OCCC) and the North American Carbon Program (NACP); U.S. contributions to IMBER, SOLAS, CARBOOCEAN; and numerous U.S. single-investigator and medium-size research projects funded by U.S. federal agencies including NASA, NOAA, and NSF.

The scientific mission of OCB is to study the evolving role of the ocean in the global carbon cycle, in the face of environmental variability and change through studies of marine biogeochemical cycles and associated ecosystems.

The overarching OCB science themes include improved understanding and prediction of: 1) oceanic uptake and release of atmospheric CO2 and other greenhouse gases and 2) environmental sensitivities of biogeochemical cycles, marine ecosystems, and interactions between the two.

The OCB Research Priorities (updated January 2012) include: ocean acidification; terrestrial/coastal carbon fluxes and exchanges; climate sensitivities of and change in ecosystem structure and associated impacts on biogeochemical cycles; mesopelagic ecological and biogeochemical interactions; benthic-pelagic feedbacks on biogeochemical cycles; ocean carbon uptake and storage; and expanding low-oxygen conditions in the coastal and open oceans.

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

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

Coverage: Global

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

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)	<u>OCE-0452883</u>	

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