Dissolved Cobalt and Labile Cobalt 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 October to November 2018

Website: https://www.bco-dmo.org/dataset/818610
Data Type: Cruise Results
Version: 1
Version Date: 2020-07-15

Project
» US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)
» US GEOTRACES PMT: Cobalt Biogeochemical Cycling and Connections to Metalloenzymes in the Pacific Ocean (PMT Cobalt and Metalloenzymes)

Program
» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
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Abstract
Dissolved Cobalt and Labile Cobalt 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 October to November 2018.

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Coverage

Spatial Extent: **N**:18.907 **E**:-151.993 **S**:-20 **W**:-155.258
Temporal Extent: 2018-10-25 - 2018-11-22

Methods & Sampling

North and equatorial Pacific seawater samples were collected on the GP15 expedition as part of the U.S. GEOTRACES program (RR1804 and RR1805, September to November 2018). Dissolved water samples were collected along a transect that mostly followed the 152W meridian from 76N to 20S, traveling from the Gulf of Alaska to Hawaii (Leg 1), and on to Tahiti, French Polynesia (Leg 2). Sampling locations included 20 deep full-depth stations with a bottom depth of over 4000 m, 5 shallow/coastal full-depth stations, and 10 surface stations where only the surface 1000 m was sampled.

Dissolved seawater samples were collected using a 24-bottle trace metal clean rosette equipped with 12 L Go-Flo bottles (General Oceanics), a titanium frame, and a Kevlar cable, as described in (Cutter and Bruland 2012). Surface water samples were collected from a trace metal clean towfish and pump while arriving at each station. Seawater from

the Go-Flo bottles was subsampled in a trace metal clean van under positive pressure. Dissolved Co subsamples were filtered using a 0.2 um Acropack (Pall) and stored until analysis at 4 degrees C in a 60 mL LDPE bottle that had been soaked for ~1 week in Citranox, an acidic detergent, rinsed with Milli-Q water (Millipore), soaked for ~2 weeks in 10% trace metal grade HCl, and rinsed with lightly acidic Milli-Q water (<0.1% HCl). All Co values were analyzed at sea, but replicates of all samples were taken for future dCo analysis in the laboratory. Preserved samples were filled entirely with no remaining headspace, stored with one oxygen-absorbing satchel (Mitsubishi Gas Chemical, model RP-3K) per 60 mL water sample, vacuum-sealed in plastic bags, and stored at 4 degrees C.

Dissolved cobalt was determined by cathodic stripping voltammetry (CSV) as originally described by (Saito and Moffett 2001) and modified by (Saito et al. 2010; Hawco et al. 2016). Measurement occurred shipboard within a trace metal clean plastic "bubble" within one week of sample collection using the Metrohm 663 VA and uAutolabIII systems equipped with a hanging mercury drop working electrode. For total dissolved Co (dCo) analysis, 0.2 um filtered water samples were UV-irradiated in acid-washed quartz tubes for one hour using a water-cooled UV irradiation system (Metrohm 705 UV Digestor) to destroy natural ligand-bound Co complexes. For labile dissolved Co analysis (L-dCo), no UV-irradiation was performed. Then, 11 mL of sample seawater was aliquoted into 15 mL acid-washed polypropylene vials, and 33 uL of 0.1 M dimethyglyoxime (DMG, Sigma Aldrich) and 130 uL of 0.5 M N-(2-hydroxyethyl)piperazine-N-(3-propanesulfonic acid) (EPPS, Sigma Aldrich) buffer was added. The samples were then processed on an autosampler (Metrohm 858 Sample Processor), which added 8.5 mL of the sample solution and 1.5 mL of a 1.5 M $NaNO_2$ reagent (Merck) to a Teflon cup for electrochemical analysis. The mercury electrode performed a fast linear sweep from -1.4 V to -0.6 V at a rate of 5 V s^{-1}, which reduced the Co bound in the $Co(DMG)_2$ complex from Co(II) to Co(0) and produced a Co reduction peak at -1.15 V (Saito and Moffett 2001) with a height linearly proportional to the amount of dCo present in the sample. A standard curve was created with 4 additions of 25 pM $CoCl_2$ to each sample, and a linear regression of the addition standard curve allowed for the calculation of the initial amount of Co present in the sample, assuming all available Co binds to the DMG ligand. Reagent purification protocols and standard addition calculations are outlined in more detail in (Saito and Moffett 2001). Triplicate technical replicates were run on every sample to determine the precision of the method, and duplicate depths from different rosette casts were run when available.

Data Processing Description

Peak heights were determined by ElectroChemistry Data SOFTware (ECDSOFT v. 1.0.0.0).

Data were flagged using the SeaDataNet quality flag scheme. For more information on SeaDataNet flags, see: https://www.geotraces.org/geotraces-quality-flag-policy/ and https://www.seadatanet.org/Standards/Data-Quality-Control

SeaDataNet quality flag definitions:
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 columns in ISO8601 format;
- corrected erroneous year values to '2018'.

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Data Files

File
Co_Leg2.csv (Comma Separated Values (.csv), 52.64 KB) MD5:ce65e7d020fbda13a32ea272d4ae930a Primary data file for dataset ID 818610

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Related Publications

Chmiel, R., Lanning, N., Laubach, A., Lee, J.-M., Fitzsimmons, J., Hatta, M., Jenkins, W., Lam, P., McIlvin, M., Tagliabue, A., & Saito, M. (2022). Major processes of the dissolved cobalt cycle in the North and equatorial Pacific Ocean. Biogeosciences, 19(9), 2365–2395. https://doi.org/10.5194/bg-19-2365-2022
Results

Cutter, G. A., & Bruland, K. W. (2012). Rapid and noncontaminating sampling system for trace elements in global ocean surveys. Limnology and Oceanography: Methods, 10(6), 425–436. doi:10.4319/lom.2012.10.425
Methods

Hawco, N. J., Ohnemus, D. C., Resing, J. A., Twining, B. S., & Saito, M. A. (2016). A dissolved cobalt plume in the oxygen minimum zone of the eastern tropical South Pacific. Biogeosciences, 13(20), 5697–5717. doi:10.5194/bg-13-5697-2016
Methods

Saito, M. A., & Moffett, J. W. (2001). Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean work. Marine Chemistry, 75(1-2), 49–68. doi:10.1016/s0304-4203(01)00025-1
Methods

Saito, M. A., Goepfert, T. J., Noble, A. E., Bertrand, E. M., Sedwick, P. N., & DiTullio, G. R. (2010). A seasonal study of dissolved cobalt in the Ross Sea, Antarctica: micronutrient behavior, absence of scavenging, and relationships with Zn, Cd, and P. Biogeosciences, 7(12), 4059–4082. doi:10.5194/bg-7-4059-2010
Methods

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Related Datasets

Continues

Saito, M. A. (2021) **Dissolved Cobalt and Labile Cobalt 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 2021-05-05 doi:10.26008/1912/bco-dmo.818383.2 [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	Sampling start date (UTC); format: MM-DD-YY	unitless
Start_Time_UTC	Sampling start time (UTC); format: hh:mm	unitless
Start_ISO_DateTime_UTC	Sampling start date/time (UTC) formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	yyyy-MM-dd'T'HH:mm'Z'
End_Date_UTC	Sampling end date (UTC); format: MM-DD-YY	unitless

End_Time_UTC	Sampling end time (UTC); format: hh:mm	unitless
End_ISO_DateTime_UTC	Sampling end date/time (UTC) formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	unitless
Start_Latitude	Sampling start latitude	decimal degrees North
Start_Longitude	Sampling start longitude	decimal degrees East
End_Latitude	Sampling end latitude	decimal degrees North
End_Longitude	Sampling end longitude	decimal degrees East
Event_ID	GEOTRACES event number	unitless
Sample_ID	GEOTRACES sample number	unitless
Sample_Depth	Sample/sensor pressure (CTDPRS)	decibars
Co_D_CONC_BOTTLE_0vn2hs	Concentration of dissolved Co (after UV oxidation) from Niskin	picomoles per kilogram (pmol/kg)
SD1_Co_D_CONC_BOTTLE_0vn2hs	One standard deviation of Co_D_CONC_BOTTLE_0vn2hs	picomoles per kilogram (pmol/kg)
Flag_Co_D_CONC_BOTTLE_0vn2hs	Quality flag for Co_D_CONC_BOTTLE_0vn2hs	unitless
L1Co_D_CONC_BOTTLE_mgxi4u	Concentration of dissolved labile Co from Niskin	picomoles per kilogram (pmol/kg)
SD1_L1Co_D_CONC_BOTTLE_mgxi4u	One standard deviation of L1Co_D_CONC_BOTTLE_mgxi4u	picomoles per kilogram (pmol/kg)
Flag_L1Co_D_CONC_BOTTLE_mgxi4u	Quality flag for L1Co_D_CONC_BOTTLE_mgxi4u	unitless
Co_D_CONC_FISH_r17gqs	Concentration of dissolved Co (after UV oxidation) from tow fish	picomoles per kilogram (pmol/kg)
SD1_Co_D_CONC_FISH_r17gqs	One standard deviation of Co_D_CONC_FISH_r17gqs	picomoles per kilogram (pmol/kg)
Flag_Co_D_CONC_FISH_r17gqs	Quality flag for Co_D_CONC_FISH_r17gqs	unitless
L1Co_D_CONC_FISH_u2dkub	Concentration of dissolved labile Co from tow fish	picomoles per kilogram (pmol/kg)

SD1_L1Co_D_CONC_FISH_u2dkub	One standard deviation of L1Co_D_CONC_FISH_u2dkub	picomoles per kilogram (pmol/kg)
Flag_L1Co_D_CONC_FISH_u2dkub	Quality flag for L1Co_D_CONC_FISH_u2dkub	unitless

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Instruments

Dataset-specific Instrument Name	trace metal clean towfish
Generic Instrument Name	GeoFish Towed near-Surface Sampler
Dataset-specific Description	Surface water samples were collected from a trace metal clean towfish and pump while arriving at each station.
Generic Instrument Description	The GeoFish towed sampler is a custom designed near surface (2 meters or less) sampling system for the collection of trace metal clean seawater. It consists of a PVC encapsulated lead weighted torpedo and separate PVC depressor vane supporting the intake utilizing all PFA Teflon tubing connected to a deck mounted, air-driven, PFA Teflon dual-diaphragm pump which provides trace-metal clean seawater at up to 3.7L/min. The GeoFish is towed at up to 13kts off to the side of the vessel outside of the ship's wake to avoid possible contamination from the ship's hull. It was developed by Geoffrey Smith and Ken Bruland (University of California, Santa Cruz).

Dataset-specific Instrument Name	Go-Flo bottles
Generic Instrument Name	GO-FLO Teflon Trace Metal Bottle
Dataset-specific Description	Dissolved seawater samples were collected using a 24-bottle trace metal clean rosette equipped with 12 L Go-Flo bottles (General Oceanics), a titanium frame and a Kevlar cable, as described in (Cutter and Bruland 2012).
Generic Instrument Description	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.

Dataset-specific Instrument Name	Metrohm 858 Sample Processor
Generic Instrument Name	Laboratory Autosampler
Dataset-specific Description	The samples were processed on an autosampler (Metrohm 858 Sample Processor), which added 8.5 mL of the sample solution and 1.5 mL of a 1.5 M $NaNO_2$ reagent (Merck) to a Teflon cup for electrochemical analysis.
Generic Instrument Description	Laboratory apparatus that automatically introduces one or more samples with a predetermined volume or mass into an analytical instrument.

Dataset-specific Instrument Name	Metrohm 663 VA
Generic Instrument Name	Metrohm 663 VA Stand mercury electrode
Dataset-specific Description	Measurement occurred shipboard within a trace metal clean plastic "bubble" within one week of sample collection using the Metrohm 663 VA and µAutolabIII systems equipped with a hanging mercury drop working electrode.
Generic Instrument Description	The Metrohm 663 VA stand forms the wet chemical part of a polarographic and voltammetric analytical system. It features a mercury electrode, an Ag/AgCl reference electrode and a glassy carbon counter electrode. The size of the mercury drop and the stirrer speed are set manually on the VA Stand. The VA Stand can be operated in Dropping Mercury Electrode (DME), Hanging Mercury Drop Electrode (HMDE) and Static Mercury Drop Electrode (SMDE) modes. The VA Stand can be controlled by a potentiostat in conjunction with the Metrohm IME663 interface.

Dataset-specific Instrument Name	Metrohm 705 UV Digestor
Generic Instrument Name	UV Digester
Dataset-specific Description	For total dissolved Co (dCo) analysis, 0.2 um filtered water samples were UV-irradiated in acid-washed quartz tubes for one hour using a water-cooled UV irradiation system (Metrohm 705 UV Digestor) to destroy natural ligand-bound Co complexes.
Generic Instrument Description	Digestion instrument for UV photolysis of water samples

Dataset-specific Instrument Name	µAutolabIII
Generic Instrument Name	Voltammetry Analyzers
Dataset-specific Description	Measurement occurred shipboard within a trace metal clean plastic "bubble" within one week of sample collection using the Metrohm 663 VA and µAutolabIII systems equipped with a hanging mercury drop working electrode.
Generic Instrument Description	Instruments that obtain information about an analyte by applying a potential and measuring the current produced in the analyte.

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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): https://www.rvdata.us/search/cruise/RR1815

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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.

US GEOTRACES PMT: Cobalt Biogeochemical Cycling and Connections to Metalloenzymes in the Pacific Ocean (PMT Cobalt and Metalloenzymes)

Coverage: Laboratory Study and Cultures from Northeast Pacific Line P Transect 48.8167 N 128.667 W

NSF abstract:

Cobalt is important for many forms of marine life, yet it is one of the scarcest nutrients in the sea. Cobalt's oceanic abundance and distribution, along with other scarce nutrients, can influence the growth of microscopic plants (phytoplankton). This in turn can influence carbon cycles in the ocean and atmosphere. Therefore, knowledge of the controls on cobalt's abundance and chemical forms in seawater is a valuable component of our ability to understand the ocean's influence on global carbon cycling. Within phytoplankton and other marine microbes, metals such as cobalt, iron, nickel, and copper are used as critical components of enzymes responsible for key cellular reactions. Since these enzymes require metals to work, they are named metalloenzymes. Participating in a Pacific Ocean cruise from Alaska to Tahiti, this project will study the oceanic distributions of dissolved cobalt and the cellular content of a group of metalloenzymes known to influence biogeochemical cycles. The project will provide scientific impact by creating new knowledge about oceanic micronutrients in regions of economic interest with regard to fisheries and deep-sea mining. Measurement of proteins in the North Pacific will provide data of broad biological and chemical interest and will be made available through a new NSF-funded "EarthCube Ocean Protein Portal" data base. Educational impact will stem from participation of a graduate student and two young technicians, as well as the PI's development of a high school chemistry curriculum for use in two local high schools, thus allowing teachers to include real oceanic and environmental data at their first introduction to chemistry.

Cobalt has a complex biogeochemical cycle. Both its inorganic and organic forms are used by biology in the upper ocean and it is removed from solution by being scavenged in the intermediate and deep ocean. This scavenging removal results in cobalt having the smallest oceanic inventory of any biologically utilized element. Recent studies, however, have found that large dissolved cobalt plumes occur in major oxygen minimum zones due to a combination of less scavenging and additions from sedimentary and remineralization fluxes. The GP15 US GEOTRACES Pacific Meridional Transect (PMT) provides an opportunity to examine the influence of oxygen depletion on cobalt chemistry. Moreover, the study of the protein component of microbial communities using new proteomic techniques will provide evidence of how different major microorganisms respond to the chemical environment (e.g. through transporter production for specific nutrients and micronutrients) as well as the biochemical basis for metal requirements related to the use of specific metalloenzymes. Specifically, the PMT provides an opportunity to confirm that the Pacific oxygen minimum zones contain a large amount of cobalt and to test the hypotheses that simultaneous zinc scarcity could induce wide-scale biochemical substitution of cobalt for zinc in the North Pacific Ocean.

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Program Information

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

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

Coverage: Global

GEOTRACES is a SCOR 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-1736599

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