

# Copper speciation results for dissolved organic copper binding ligand concentrations, stability constants, and free copper from the U.S. GEOTRACES Equatorial Pacific cruise (R/V Thomas G. Thompson TN303) from October to December 2013

**Website:** <https://www.bco-dmo.org/dataset/740051>

**Data Type:** Cruise Results

**Version:** 2

**Version Date:** 2019-09-23

## Project

» [U.S. GEOTRACES East Pacific Zonal Transect \(GP16\)](#) (U.S. GEOTRACES EPZT)

» [US GEOTRACES Pacific Section: Measurement of the organic complexation of dissolved iron, copper and cobalt, and total dissolved cobalt](#) (EPZT Fe Cu Co)

## Program

» [U.S. GEOTRACES](#) (U.S. GEOTRACES)

Contributors	Affiliation	Role
<a href="#">Barbeau, Katherine</a>	University of California-San Diego Scripps (UCSD-SIO)	Principal Investigator
<a href="#">Rauch, Shannon</a>	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

## Abstract

Copper speciation results for dissolved organic copper binding ligand concentrations, stability constants, and free copper from the U.S. GEOTRACES Equatorial Pacific cruise (R/V Thomas G. Thompson TN303) from October to December 2013.

## Table of Contents

- [Coverage](#)
- [Dataset Description](#)
  - [Methods & Sampling](#)
  - [Data Processing Description](#)
- [Data Files](#)
- [Related Publications](#)
- [Parameters](#)
- [Instruments](#)
- [Deployments](#)
- [Project Information](#)
- [Program Information](#)
- [Funding](#)

## Coverage

**Spatial Extent:** N:-10.50017 E:-77.3761 S:-16.0005 W:-152.0385

**Temporal Extent:** 2013-10-28 - 2013-12-17

## Dataset Description

Copper speciation results for dissolved organic copper binding ligand concentrations, stability constants, and free copper for the U.S. GEOTRACES Equatorial Pacific cruise.

## Methods & Sampling

Sample bottles were cleaned according to GEOTRACES protocols found in the [GEOTRACES cookbook](#) which also provides descriptions for sample collection. After collection samples were frozen, -20 freezer, until thawed for analysis in the lab.

Speciation analysis was carried out using a competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV) described in Bundy et al, 2013, utilizing a 5uM concentration of the competing ligand salicylaldoxime with a 300 second deposition time.

## Data Processing Description

Sample processing employed a one ligand model utilizing the ProMCC software described in Omanovic et al. 2015. The software provides a 95% confidence interval for uncertainties in the fitted parameter, these uncertainties are presented for samples without a duplicate titration. Samples with duplicate titrations are presented with average values for ligand concentration, logK, and free copper values initially determined by ProMCC. Averaged values for samples with duplicate titrations are presented with a standard deviation.

Dissolved copper concentration values were provided by Claire Till and Saeed Roshan, these values were used in ProMCC for ligand and logK value determinations and provided here for reference.

## Quality flags:

The standard Ocean Data View qualifying flags were used (reference all flags at [https://www.bodc.ac.uk/data/codes\\_and\\_formats/odv\\_format/](https://www.bodc.ac.uk/data/codes_and_formats/odv_format/)):

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 for data with duplicate and with a percent error below 25%]

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 samples with duplicates have a percent error above 25%, also used for samples without duplicates]

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. [Used when [Cu] was higher than expected]

4: Bad Value: An obviously erroneous data value.

5: Changed Value: Data value adjusted during quality control.

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.

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.

8: Interpolated Value: This value has been derived by interpolation from other values in the data object.

## BCO-DMO Processing:

- modified parameter names to conform with BCO-DMO naming conventions (replaced ' symbol with "prime");

- replaced blanks (missing/no data) with "nd";
- joined to EPZT master events file;
- 23-Sept-2019: Moved data values for sample 10339 that were erroneosly in the BOTTLE columns (Cu\_Cu\_prime\_D\_CONC\_BOTTLE\_95pctn\_CI and Cu\_Cu\_prime\_D\_CONC\_BOTTLE\_95pctn\_Cl) to the corresponding FISH columns.

**Additional BCO-DMO GEOTRACES Processing:**

As was done for the GEOTRACES-NAT data, BCO-DMO added standard US GEOTRACES information, such as the US GEOTRACES event number, to each submitted dataset lacking this information. To accomplish this, BCO-DMO compiled a 'master' dataset composed of the following parameters: cruise\_id, EXPOCODE,SECT\_ID, STNNBR, CASTNO, GEOTRC\_EVENTNO, GEOTRC\_SAMPNO, GEOTRC\_INSTR, SAMPNO, GF\_NO, BTLNBR, BTLNBR\_FLAG\_W, DATE\_START\_EVENT, TIME\_START\_EVENT, ISO\_DATETIME.UTC\_START\_EVENT, EVENT\_LAT, EVENT\_LON, DEPTH\_MIN, DEPTH\_MAX, BTL\_DATE, BTL\_TIME, BTL\_ISO\_DATETIME.UTC, BTL\_LAT, BTL\_LON, ODF\_CTDPRS, SMDEPTH, FMDEPTH, BTMDEPTH, CTDPRS, CTDDEPTH.

This added information will facilitate subsequent analysis and inter comparison of the datasets.

Bottle parameters in the master file were taken from the GT-C Bottle and ODF Bottle datasets. Non-bottle parameters, including those from GeoFish tows, Aerosol sampling, and McLane Pumps, were taken from the TN303 Event Log (version 30 Oct 2014). Where applicable, pump information was taken from the PUMP\_Nuts\_Sals dataset.

A standardized BCO-DMO method (called "join") was then used to merge the missing parameters to each US GEOTRACES dataset, most often by matching on sample\_GEOTRC or on some unique combination of other parameters.

If the master parameters were included in the original data file and the values did not differ from the master file, the original data columns were retained and the names of the parameters were changed from the PI-submitted names to the standardized master names. If there were differences between the PI-supplied parameter values and those in the master file, both columns were retained. If the original data submission included all of the master parameters, no additional columns were added, but parameter names were modified to match the naming conventions of the master file.

See the dataset parameters documentation for a description of which parameters were supplied by the PI and which were added via the join method.

[ [table of contents](#) | [back to top](#) ]

**Data Files**

File
<b>copper_speciation_joined.csv</b> (Comma Separated Values (.csv), 95.51 KB) MD5:1cab553c4fc6f77973e6de18f2c30022
Primary data file for dataset ID 740051

[ [table of contents](#) | [back to top](#) ]

**Related Publications**

Bundy, R. M., Barbeau, K. A., & Buck, K. N. (2013). Sources of strong copper-binding ligands in Antarctic Peninsula surface waters. Deep Sea Research Part II: Topical Studies in Oceanography, 90, 134–146. doi:[10.1016/j.dsr2.2012.07.023](#)

*General*

Cutter, Gregory, Casciotti, Karen, Croot, Peter, Geibert, Walter, Heimbürger, Lars-Eric, Lohan, Maeve, Planquette, Hélène, van de Flierdt, Tina (2017) Sampling and Sample-handling Protocols for GEOTRACES Cruises. Version 3, August 2017. Toulouse, France, GEOTRACES International Project Office, 139pp. & Appendices. DOI: [http://dx.doi.org/10.25607/OBP-2](#)

*Methods*

Omanović, D., Garnier, C., & Pižeta, I. (2015). ProMCC: An all-in-one tool for trace metal complexation studies. Marine Chemistry, 173, 25–39. doi:[10.1016/j.marchem.2014.10.011](#)

*Methods*

[ [table of contents](#) | [back to top](#) ]

**Parameters**

Parameter	Description	Units
cruise_id	Cruise identification	unitless
STNNBR	Station number; joined from BCO-DMO EPZT master events file	unitless
GEOTRC_SAMPNO	Unique GEOTRACES sample number	unitless
Lat	Latitude; provided by PI	decimal degrees
Lon	Longitude; provided by PI	decimal degrees
Depth	Depth in water column; provided by PI	meters (m)
Cu_D_CONC_BOTTLE	Dissolved copper from bottle sample	nanomoles per kilogram (nmol/kg)
Cu_D_CONC_FISH	Dissolved copper from FISH sample	nanomoles per kilogram (nmol/kg)
L1Cu_D_CONC_FISH	[L] value from FISH sample	nanomoles per kilogram (nmol/kg)
L1Cu_D_CONC_FISH_STDV	Standard deviation from duplicates for FISH sample	nanomoles per kilogram (nmol/kg)
L1Cu_D_CONC_FISH_95pctn_CI	95% confidence interval for FISH sample	nanomoles per kilogram (nmol/kg)

L1Cu_D_CONC_BOTTLE	[L] value from bottle sample	nanomoles per kilogram (nmol/kg)
L1Cu_D_CONC_BOTTLE_STDV	Standard deviation from duplicates for bottle sample	nanomoles per kilogram (nmol/kg)
L1Cu_D_CONC_BOTTLE_95pctn_CI	95% confidence interval for bottle sample	nanomoles per kilogram (nmol/kg)
L1Cu_D_LogK_FISH	LogK for FISH sample	unitless
L1Cu_D_LogK_FISH_STDV	LogK standard deviation for FISH sample	unitless
L1Cu_D_LogK_FISH_95pctn_CI	LogK 95% confidence interval for FISH sample	unitless
L1Cu_D_LogK_BOTTLE	LogK for bottle sample	unitless
L1Cu_D_LogK_BOTTLE_STDV	LogK standard deviation for bottle sample	unitless
L1Cu_D_LogK_BOTTLE_95pctn_CI	LogK 95% confidence interval for bottle sample	unitless
Cu_Cu_prime_D_CONC_FISH	Free Cu concentration from FISH sample	femtomoles per kilogram (fmol/kg)
Cu_Cu_prime_D_CONC_FISH_STDV	Free Cu concentration standard deviation from FISH sample	femtomoles per kilogram (fmol/kg)
Cu_Cu_prime_D_CONC_FISH_96pctn_CI	Free Cu concentration 95% confidence interval from FISH sample	femtomoles per kilogram (fmol/kg)
Cu_Cu_prime_D_CONC_BOTTLE	Free Cu concentration from bottle sample	femtomoles per kilogram (fmol/kg)
Cu_Cu_prime_D_CONC_BOTTLE_STDV	Free Cu concentration standard deviation from bottle sample	femtomoles per kilogram (fmol/kg)
Cu_Cu_prime_D_CONC_BOTTLE_95pctn_CI	Free Cu concentration 95% confidence interval from bottle sample	femtomoles per kilogram (fmol/kg)
Flag	Ocean Data View (ODV) quality flag. The standard Ocean Data View qualifying flags were used (reference all flags at <a href="https://www.bodc.ac.uk/data/codes_and_formats/odv_format/">https://www.bodc.ac.uk/data/codes_and_formats/odv_format/</a> or refer to metadata for code definitions).	unitless
Comments	Comments on data	unitless
CASTNO	Cast number; joined from BCO-DMO EPZT master events file	unitless
GEOTRC_EVENTNO	GEOTRACES event number; joined from BCO-DMO EPZT master events file	unitless
GEOTRC_INSTR	Sampling instrument; joined from BCO-DMO EPZT master events file	unitless
SAMPNO	Sequential sample number within the cast (usually corresponds to bottle number); joined from BCO-DMO EPZT master events file	unitless
GFISH_NO	GeoFish tow number; joined from BCO-DMO EPZT master events file	unitless
BTLNBR	Bottle number; typically 1-24; joined from BCO-DMO EPZT master events file	unitless
BTLNBR_FLAG_W	Bottle number quality flag; follows WOCE conventions. 2 = no problems noted; 3 = leaking; 4 = did not trip correctly; 9 = samples not drawn from this bottle. Joined from BCO-DMO EPZT master events file	unitless
ISO_DATETIME.UTC_START_EVENT	Date and time, formatted to the ISO 8601 standard, at the start of the sampling event, according to the event log. Format: YYYY-MM-DDTHH:MM:SS[.xx]Z. Joined from BCO-DMO EPZT master events file	unitless
EVENT_LAT	Latitude at the start of the event; north is positive; joined from BCO-DMO EPZT master events file	decimal degrees
EVENT_LON	Longitude at the start of the event; east is positive; joined from BCO-DMO EPZT master events file	decimal degrees
BTL_ISO_DATETIME.UTC	Date and time, formatted to the ISO 8601 standard, at the time of bottle firing. Format: YYYY-MM-DDTHH:MM:SS[.xx]Z. Joined from BCO-DMO EPZT master events file	unitless
BTL_LAT	Latitude of bottle firing; north is positive; joined from BCO-DMO EPZT master events file	decimal degrees

BTL_LON	Lonitude of bottle firing; east is positive; joined from BCO-DMO EPZT master events file	decimal degrees
ODF_CTDPRS	The ODF software acquisition measurement of pressure; joined from BCO-DMO EPZT master events file	decibars
SMDEPTH	Saunders-Mantyla depth (integrated; uses dynamic height); joined from BCO-DMO EPZT master events file	meters
FMDEPTH	Fofonoff-Millard depth (non-integrated; also used by SBE); joined from BCO-DMO EPZT master events file	meters
CTDPRS	CTD pressure; joined from BCO-DMO EPZT master events file	decibars
CTDDEPTH	CTD bottle firing depth; joined from BCO-DMO EPZT master events file	meters

[ [table of contents](#) | [back to top](#) ]

## Instruments

<b>Dataset-specific Instrument Name</b>	BASi Controlled Growth Mercury Electrode
<b>Generic Instrument Name</b>	BASi Controlled Growth Mercury Electrode
<b>Dataset-specific Description</b>	For CLE-AdCSV analyses
<b>Generic Instrument Description</b>	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. <a href="http://www.basinc.com/products/ec/cgme.php">http://www.basinc.com/products/ec/cgme.php</a>

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

<b>Dataset-specific Instrument Name</b>	GO-FLO Teflon Trace Metal
<b>Generic Instrument Name</b>	GO-FLO Teflon Trace Metal Bottle
<b>Generic Instrument Description</b>	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.

[ [table of contents](#) | [back to top](#) ]

## Deployments

<b>TN303</b>	
<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/499719">https://www.bco-dmo.org/deployment/499719</a>
<b>Platform</b>	R/V Thomas G. Thompson
<b>Report</b>	<a href="http://dmosev3.whoj.edu/data_docs/GEOTRACES/EPZT/GT13_EPZT_ODFReport_All.pdf">http://dmosev3.whoj.edu/data_docs/GEOTRACES/EPZT/GT13_EPZT_ODFReport_All.pdf</a>
<b>Start Date</b>	2013-10-25
<b>End Date</b>	2013-12-20
<b>Description</b>	A zonal transect in the eastern tropical South Pacific (ETSP) from Peru to Tahiti as the second cruise of the U.S.GEOTRACES Program. This Pacific section includes a large area characterized by high rates of primary production and particle export in the eastern boundary associated with the Peru Upwelling, a large oxygen minimum zone that is a major global sink for fixed nitrogen, and a large hydrothermal plume arising from the East Pacific Rise. This particular section was selected as a result of open planning workshops in 2007 and 2008, with a final recommendation made by the U.S.GEOTRACES Steering Committee in 2009. It is the first part of a two-stage plan that will include a meridional section of the Pacific from Tahiti to Alaska as a subsequent expedition. Figure 1. The 2013 GEOTRACES EPZT Cruise Track. [click on the image to view a larger version] Additional cruise information is available from the Rolling Deck to Repository (R2R): <a href="http://www.rvdata.us/catalog/TN303">http://www.rvdata.us/catalog/TN303</a>

[ [table of contents](#) | [back to top](#) ]

## Project Information

### U.S. GEOTRACES East Pacific Zonal Transect (GP16) (U.S. GEOTRACES EPZT)

**Website:** <http://www.geotraces.org/>

**Coverage:** Eastern Tropical Pacific - Transect from Peru to Tahiti (GP16)

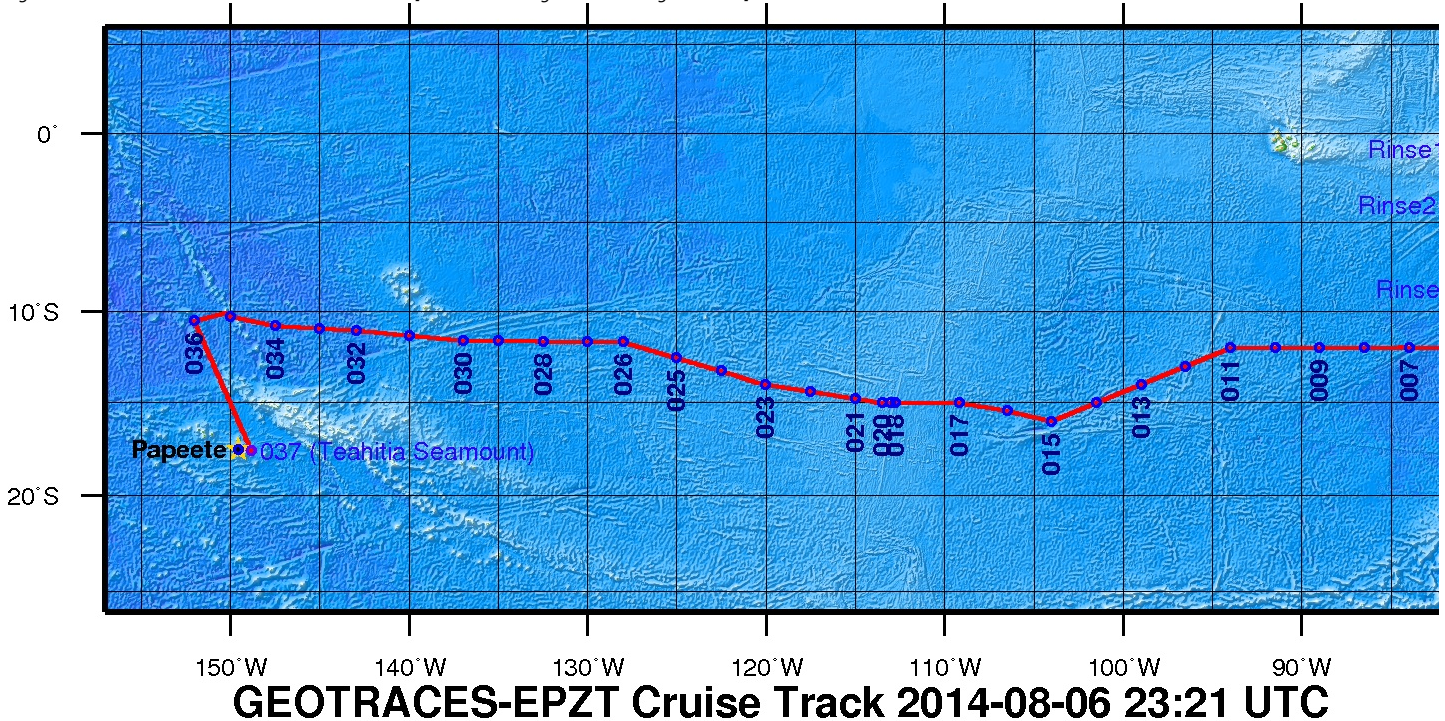
#### From the NSF Award Abstract

The mission of the International GEOTRACES Program (<https://www.geotraces.org/>), of which the U.S. chemical oceanography research community is a founding member, is "to identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions" (GEOTRACES Science Plan, 2006). In the United States, ocean chemists are currently in the process of organizing a zonal transect in the eastern tropical South Pacific (ETSP) from Peru to Tahiti as the second cruise of the U.S. GEOTRACES Program. This Pacific section includes a large area characterized by high rates of primary production and particle export in the eastern boundary associated with the Peru Upwelling, a large oxygen minimum zone that is a major global sink for fixed nitrogen, and a large hydrothermal plume arising from the East Pacific Rise. This particular section was selected as a result of open planning workshops in 2007 and 2008, with a final recommendation made by the U.S. GEOTRACES Steering Committee in 2009. It is the first part of a two-stage plan that will include a meridional section of the Pacific from Tahiti to Alaska as a subsequent expedition.

This award provides funding for management of the U.S. GEOTRACES Pacific campaign to a team of scientists from the University of Southern California, Old Dominion University, and the Woods Hole Oceanographic Institution. The three co-leaders will provide mission leadership, essential support services, and management structure for acquiring the trace elements and isotopes samples listed as core parameters in the International GEOTRACES Science Plan, plus hydrographic and nutrient data needed by participating investigators. With this support from NSF, the management team will (1) plan and coordinate the 52-day Pacific research cruise described above; (2) obtain representative samples for a wide variety of trace metals of interest using conventional CTD/rosette and GEOTRACES Sampling Systems; (3) acquire conventional JGOFS/WOCE-quality hydrographic data (CTD, transmissometer, fluorometer, oxygen sensor, etc) along with discrete samples for salinity, dissolved oxygen (to 1  $\mu\text{M}$  detection limits), plant pigments, redox tracers such as ammonium and nitrite, 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-type data to the GEOTRACES Data Center (and US data centers); and (6) coordinate cruise communications between all participating investigators, including preparation of a hydrographic report/publication.

**Broader Impacts:** The project is part of an international collaborative program that has forged strong partnerships in the intercalibration and implementation phases that are unprecedented in chemical oceanography. The science product of these collective missions will enhance our ability to understand how to interpret the chemical composition of the ocean, and interpret how climate change will affect ocean chemistry. Partnerships include contributions to the infrastructure of developing nations with overlapping interests in the study area, in this case Peru. There is a strong educational component to the program, with many Ph.D. students carrying out thesis research within the program.

Figure 1. The 2013 GEOTRACES EPZT Cruise Track. [click on the image to view a larger version]



#### US GEOTRACES Pacific Section: Measurement of the organic complexation of dissolved iron, copper and cobalt, and total dissolved cobalt (EPZT Fe Cu Co)

**Coverage:** East Pacific

##### Description from NSF award abstract:

Dissolved iron (Fe), copper (Cu), and cobalt (Co) are essential elements for phytoplankton growth which in turn influences the marine carbon cycle; however, despite this important role, the cycling, distribution, and bioavailability of these bioactive elements remains poorly understood. For example, strong organic ligands influence bioavailability and solubility, but it is unclear how interactions change throughout the water column under variable conditions. Recognizing a need for this data, researchers from the Bermuda Institute of Ocean Sciences, Woods Hole Oceanographic Institution, and Scripps Institution of Oceanography will measure the organic complexation of dissolved Fe, Cu, and Co as well as total dissolved Co concentrations during the 2013 GEOTRACES cruise which will transect the coastal upwelling zone off Peru, an intense oxygen minimum zone, the East Pacific Rise hydrothermal plume, and the oligotrophic waters near Tahiti. This study will result in a significant dataset on the speciation of these bioactive elements throughout the water column which will help assess the relationships between dissolved Fe, Cu, and Co distributions and ligand concentration gradients and will likely reveal large chemical gradients over this dynamic oceanographic region. As regards dissolved Co concentrations, these measurements should provide new insights on the marine biogeochemistry of the element, especially in relation to oxygen minimum zones and hydrothermal plumes.

[ [table of contents](#) | [back to top](#) ]

#### 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.

[ [table of contents](#) | [back to top](#) ]

**Funding**

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1233733</a>

[ [table of contents](#) | [back to top](#) ]