

# Dissolved (0.4 micron filtered) Fe, Zn and Cd isotope ratios and concentrations across GEOTRACES-EPZT, from cruise TN303, 2013

Website: <https://www.bco-dmo.org/dataset/643809>

Data Type: Cruise Results

Version: 3

Version Date: 2016-06-21

## Project

- » [U.S. GEOTRACES East Pacific Zonal Transect \(GP16\)](#) (U.S. GEOTRACES EPZT)
- » [GEOTRACES Pacific section: Dissolved Fe, Cd, and Zn isotopes](#) (EPZT Diss Fe Zn Cd)

## Program

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

Contributors	Affiliation	Role
<a href="#">John, Seth G.</a>	University of Southern California (USC)	Principal Investigator
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## Dataset Description

The FISH and BOTTLE data have been split into separate columns as per GEOTRACES Parameter Naming Conventions. The FISH data are to the far right.

\* To access the data with the FISH and BOTTLE data merged, see: [http://data.bco-dmo.org/jg/serv/BCO/GEOTRACES/EPZT/Fe\\_Zn\\_Cd\\_diss\\_joined....](http://data.bco-dmo.org/jg/serv/BCO/GEOTRACES/EPZT/Fe_Zn_Cd_diss_joined....)

### Related References:

Conway, T.M., Rosenberg, A.D., Adkins, J.F., and S.G. John. 2013. A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry. *Analytica Chimica Acta*, 793: 44-52.

John, S. 2012. Optimizing sample and spike concentrations for isotopic analysis by double-spike ICP-MS. *Journal of Analytical Atomic Spectrometry*, 27: 2123-2131.

## Methods & Sampling

Samples were provided from the GEOTRACES trace-metal clean sampling rosette and were sampled into acid-cleaned 1L or 4L LDPE bottles by the onboard GEOTRACES clean sampling team. Upon receipt of samples on shore, they were acidified to pH 2 using clean hydrochloric acid and left at this pH for at least 3 months before processing.

A preliminary analysis of Fe, Zn, and Cd concentration was performed by extraction of 10 mL seawater onto Nobias PA-1 resin at pH 5-7 and analysis on an Element ICPMS by isotope dilution. These data are generally not reported, except in rare cases where the concentration data based on 1L samples was not available. Data generated by this method are flagged (see below).

Every sample was simultaneously extracted and purified for the analysis of  $\delta^{56}\text{Fe}$ ,  $\delta^{66}\text{Zn}$ ,  $\delta^{114}\text{Cd}$ , [Fe], [Zn], and [Cd] using published methods (Conway *et al.*, 2013). Briefly, Fe, Zn, and Cd double-spikes were added to the acidified samples and allowed to equilibrate for > 1 hour. Metals were then extracted from seawater onto an ethylenediaminetriacetic acid resin (Nobias PA-1; Hitachi) for 2 hours at pH 2 and 2 hours at pH between 6-6.3. Metals were eluted off this resin using 3 N HNO<sub>3</sub>, and were then purified by anion exchange chromatography before being reconstituted in 0.1 N HNO<sub>3</sub> for analysis.

Concentrations and stable isotope ratios were determined simultaneously by analysis on a Neptune multi-collector ICP-MS. Fe and Zn were analyzed in high resolution mode, while Cd was analyzed in low resolution mode. Every sample was analyzed twice, and the mean isotope ratios are presented here, expressed relative to international isotope standards. Instrumental and procedural isotopic fractionation was corrected for using a double-spike data reduction scheme.

Concentrations were calculated using isotope-dilution to calculate ng of metal per sample, and then converted to nmol kg<sup>-1</sup> or pmol kg<sup>-1</sup> using the weight of each sample processed. Concentration numbers represent the mean of two ICP-MS analyses of each sample. The largest sources of error for concentration analyses are determining the weight of the sample and determining the volume of double-spike added to each sample. We approximate 2% error for each sample based on the combination of these two factors. Accuracy was checked by analysis of S, D1 and D2 SAFe reference standards (for which we determined values identical to the consensus values; see Conway *et al.*, 2013) and intercomparison with two other groups measuring trace metal concentrations on GP16 samples.

Analytical accuracy of stable isotope ratios is equal to the analytical precision (i.e. the analysis is free from systematic errors; John, 2012) and is calculated separately for each sample. Uncertainty for isotope ratios is expressed as the 2 sigma uncertainty on the average isotope ratio, calculated from a combination of the internal standard error of each of two measurements and the bracketing isotope standards used, as described in Conway *et al.*, (2013).

Data are flagged as follows:

1 (good): data appear to be of high quality

4 (no data): samples either were not analyzed, or there was a complete failure during analysis such as failure to recover the metals onto Nobias resin or failure of the instrument during analysis of this sample

7 (questionable): data based on "oceanographic consistency" these data do not appear to be correct, for example they fall very far off the trends apparent in other data above and below the point suggesting that they are "flyers"

8 (low-volume): concentration data from the 1L isotope sample was not available, so concentrations from the 10 mL samples have been used instead

## Data Processing Description

Version 3 - 2016-06-21: Revised error values for #10325, 10327, 10329 to 'nd'.

Version 2 - 2016-06-03: Changed element abbreviation to full name and removed 'EPZT' from dataset name.

Version 1 - 2016-04-29: Submitted by PI.

## BCO-DMO Processing:

- added conventional header with dataset name, PI name, version date
- renamed parameters to BCO-DMO and BODC standards
- #N/A replaced with nd
- sorted by station

**Additional 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, EXPCODE,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, CTDDDEPTH.

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.

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**Data Files**

File
<b>Fe_Zn_Cd_diss_joined_fish_btl.csv</b> (Comma Separated Values (.csv), 161.17 KB) <small>MD5:20997e018e7dc0b42181d16e928169f</small>
Primary data file for dataset ID 643809

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**Parameters**

Parameter	Description	Units
cruise_id	Official cruise identifier	text
STNNBR	GEOTRACES station number. PI-supplied values were identical to those in the intermediate US GEOTRACES master file.	unitless
lat_pi	station latitude provided by PI; north is positive	decimal degrees
lon_pi	station longitude provided by PI; east is positive	decimal degrees
depth_pi	Observation/sample depth in meters; Niskin sample depth calculated from CTD pressure. PI-supplied values.	meters
GEOTRC_SAMPNO	Unique identifying number for US GEOTRACES samples. PI-supplied values were identical to those in the intermediate US GEOTRACES master file	integer
GEOTRC_EVENTNO	Unique identifying number for US GEOTRACES sampling event. PI-supplied values were identical to those in the intermediate US GEOTRACES master file.	integer
CASTNO	Cast identifier numbered consecutively within a station. PI-supplied values were identical to those in the intermediate US GEOTRACES master file.	integer
ISO_DATETIME_UTC_START_EVENT	Event start date/time (UTC) formatted to ISO8601 standard. T indicates start of time string; Z indicates UTC. Calculated from original date and time fields. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	YYYY-mm-ddTHH:MM:SS.sSZ
SAMPNO	Sample number; Values were added from the intermediate US GEOTRACES master file (see Processing Description).	unitless
BTLNBR	Alphanumeric characters identifying bottle type (e.g. NIS representing Niskin and GF representing GOFLO) and position on a CTD rosette. PI-supplied values were identical to those in the intermediate US GEOTRACES master file.	text-integer
BTLNBR_FLAG_W	Quality flag: 2) ok; 3) questionable; 4) bad analysis; 5) sample lost	unitless
BTL_ISO_DATETIME_UTC	Bottle date/time (UTC) formatted to ISO8601 standard. T indicates start of time string; Z indicates UTC. Calculated from original date and time fields. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	YYYY-mm-ddTHH:MM:SS.sSZ
BTL_LAT	Latitude of bottle firing; north is positive. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	decimal degrees
BTL_LON	Longitude of bottle firing; east is positive. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	decimal degrees
Fe_D_CONC	Dissolved Fe concentration	nmo/kg
Fe_D_CONC_ERR	Dissolved Fe concentration standard deviation	nmo/kg
Fe_D_CONC_FLAG_W	Dissolved Fe concentration quality flag	unitless
ZN_D_CONC	Dissolved Zn concentration	nmo/kg
ZN_D_CONC_ERR	Dissolved Zn concentration standard deviation	nmo/kg
ZN_D_CONC_FLAG_W	Dissolved Zn concentration quality flag	unitless
Cd_D_CONC	Dissolved Cd concentration	pmo/kg
Cd_D_CONC_ERR	Dissolved Cd concentration standard deviation	pmo/kg
Cd_D_CONC_FLAG_W	Dissolved Cd concentration quality flag	unitless
Fe_56_D_DELTA	Fe stable isotope ratio; units of permil (o/oo)= ((54Fe/56Fe)sample/(54Fe/56Fe)IRMM-014-1)*1000	unitless
Fe_56_D_DELTA_ERR	Fe stable isotope ratio standard deviation	unitless
Fe_56_D_DELTA_FLAG_W	Fe stable isotope ratio quality flag	unitless
Zn66_D_DELTA	Zn stable isotope ratio; units of permil (o/oo) = ((66Zn/64Zn)sample/(66Zn/64Zn)Lyons JMC-1)*1000	unitless
Zn66_D_DELTA_ERR	Zn stable isotope ratio standard deviation	unitless
Zn66_D_DELTA_FLAG_W	Zn stable isotope ratio quality flag	unitless
Cd_114_D_DELTA	Cd stable isotope ratio; units of permil (o/oo) = ((114Cd/110Cd)sample/(114Cd/110Cd)NIST-3108 -1)*1000	unitless
Cd_114_D_DELTA_ERR	Cd stable isotope ratio standard deviation	unitless
Cd_114_D_DELTA_FLAG_W	Cd stable isotope ratio quality flag	unitless

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## Instruments

<b>Dataset-specific Instrument Name</b>	
<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>	
<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.

<b>Dataset-specific Instrument Name</b>	
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Mass Spectrometer
<b>Dataset-specific Description</b>	Neptune multi-collector ICP-MS
<b>Generic Instrument Description</b>	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

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## Deployments

### TN303

<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://dmoserv3.whoi.edu/data_docs/GEOTRACES/EPZT/GT13_EPZT_ODFReport_All.pdf">http://dmoserv3.whoi.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>

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## 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)

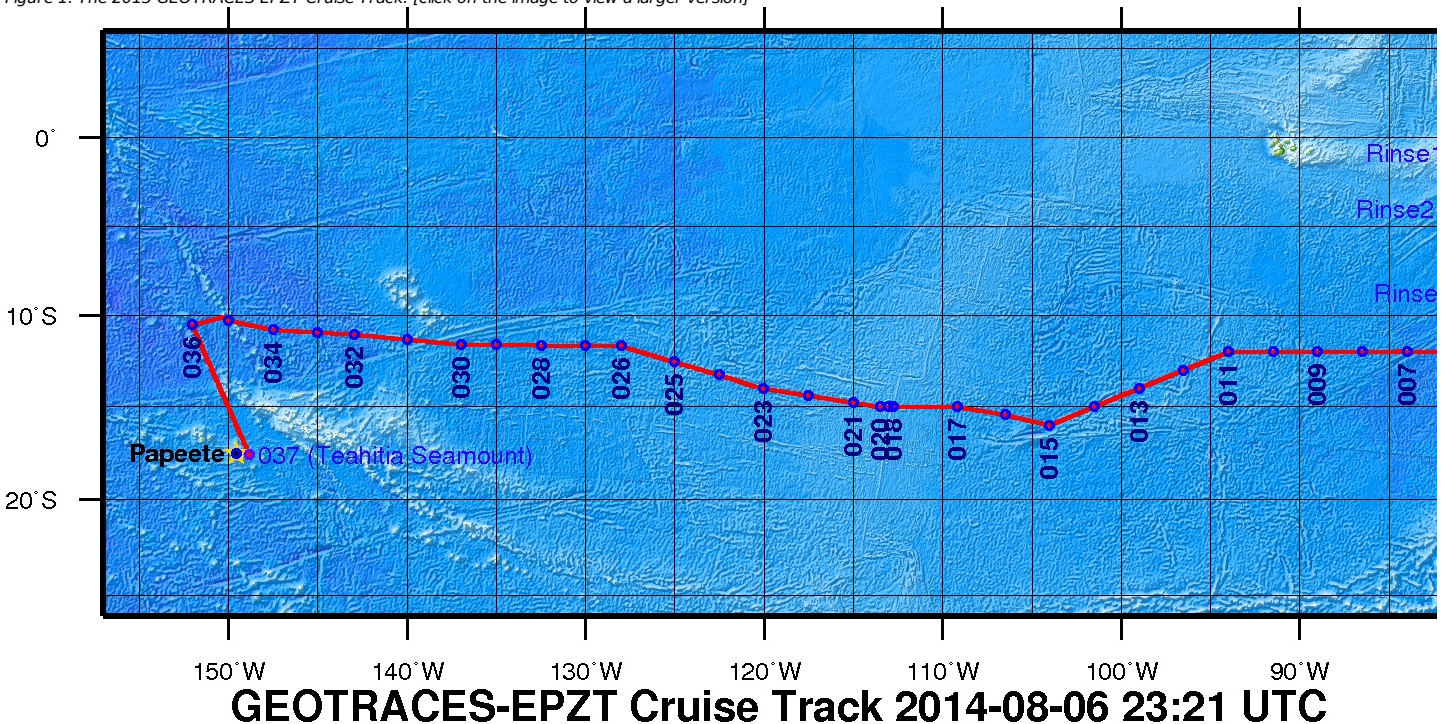
### From the NSF Award Abstract

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 uM 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]



## GEOTRACES Pacific section: Dissolved Fe, Cd, and Zn isotopes (EPZT Diss Fe Zn Cd)

**Coverage:** Eastern Tropical South Pacific

*Extracted from the NSF award abstract:*

Iron (Fe) and other trace metals have a profound impact on marine biogeochemistry. In about 20 to 50% of the world's oceans, primary productivity is limited because phytoplankton cannot obtain enough Fe to satisfy their physiological needs. Small changes in seawater Fe concentrations can therefore have an immense impact on the growth of phytoplankton, affecting the productivity of ecosystems and the sequestration of carbon in both the modern and ancient oceans. Other trace metals such as zinc (Zn), and cadmium (Cd) can be important nutrients for phytoplankton in their own right, and can be used as chemical tracers to explore processes such as nutrient supply and remineralization, ocean circulation, and earth's climate history.

In this project, a research team at the University of South Carolina at Columbia will measure dissolved Fe stable isotopes in samples collected on the US GEOTRACES Eastern Tropical South Pacific (ETSP) transect. GEOTRACES is an international effort to map the distribution of biogeochemically important metals in the oceans. Trace metal isotope ratios add a crucial dimension to the GEOTRACES mission because the information contained in isotope signals is often very different from what can be learned by concentration distributions alone. Along with Fe isotopes, they will simultaneously generate Cd and Zn isotope ratio data in some of the same samples. These data will be used to distinguish between competing hypotheses about trace-metal and nutrient distribution in the oceans, with a focus on two specific questions:

(1) What are the sources of bioavailable Fe to the oceans? Dust deposition, flux of reduced Fe from continental margin sediments, and hydrothermal vents have all been hypothesized as major contributors to the global dissolved Fe pool. The team will measure the stable Fe isotopic signatures of these fluxes at 'end-member' locations including surface waters (dust), the Peru oxygen minimum zone (reducing sediments), and the East Pacific Rise (hydrothermal vents). Basin-scale Fe isotopic distribution will then be studied in order to quantify how these various sources contribute to the global pool of biologically utilized Fe.

(2) What processes cycle Fe within the ocean? As Fe is cycled by various biological and inorganic processes, the team will track Fe isotopic composition in order to better understand how source-Fe isotopic signatures are modified through internal cycling, how iron is transferred between different pools such as dissolved and particulate phases, and the processes that allow dissolved and particulate Fe to become bioavailable.

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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
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1235150</a>

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