# Arsenate, iodide, and selenium concentrations collected from Go-FLO bottles during the R/V Thomas G. Thompson cruise TN303 from Peru to Tahiti in 2013 (U.S. GEOTRACES EPZT project)

Website: https://www.bco-dmo.org/dataset/647606

Version: 1

Version Date: 2017-01-03

#### Project

- » <u>U.S. GEOTRACES East Pacific Zonal Transect (GP16)</u> (U.S. GEOTRACES EPZT)
- » US GEOTRACES Pacific section: Characterizing the redox environment of the eastern tropical Pacific Ocean (EPZT\_Redox\_Elements)

#### **Program**

» U.S. GEOTRACES (U.S. GEOTRACES)

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#### Coverage

Spatial Extent: N:-10.2502 E:-77.3761 S:-16.0006 W:-152.0004

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

### **Dataset Description**

Data include dissolved species concentrations from EPZT GEOTRACES stations: Selenite (SeIV), Selenate (SeVI), Organic selenide (Org Se-II), Total Se, & elemental Se, arsenate (AsV), arsenite (AsIII), iodide and iodate.

## Access restrictions:

It is our understanding that access to the data will be restricted to the GEOTRACES Data Management Committee (DMC) and Standards and Intercalibration Committee (SIC) until the product is publicly released in the next Intermediate Data Product, currently August, 2017.

#### Methods & Sampling

Clean seawater samples were collected with a GEOTRACES CTD referred to as GT-C/12L GoFlo. For more information about the CTD on the GEOTRACES EPZT, see the <u>cruise report</u>. Selenium, Iodine and Arsenic species concentrations were processed with separate methodology as described below and in the "Processing Description" section. Bottle samples were collected at GEOTRACES EPZT stations (STNNBR in the dataset).

**Selenium:** For dissolved samples 0.45 um Supor membrane filtered seawater samples were placed into 1 L borosilicate glass bottles and acidified to pH < 2 by addition of 4 mL 6 M HCl. Samples were stored at room temperature in the dark.

lodide/lodate: Samples were pressurized with 6 psi nitrogen and seawater was passed through 0.2 um syringe filters into 60 mL all-polyethylene syringes fitted with 3-way polycarbonate valves to prevent contact with atmosphere before analysis.

Arsenic: 0.45 um filtered seawater samples were placed into 500 mL Teflon FEP bottles, refrigerated, and analyzed within 24 hours of collection.

#### **Data Processing Description**

Samples analyzed in triplicate and means computed. Standard additions of selenite were used for daily calibration on a representative sample and its slope applied to subsequent samples.

**lodide** concentrations were determined using cathodic square wave stripping analysis following Luther at al. (1988) and Tian and Nicolas (1995). A BASi model CGME electrode was used as follows: 10 mL sample and 100 mL 0.1% Triton, 5 min purge with oxygen free nitrogen, 0.2 mL addition of 1 M sodium sulfite to remove any remaining oxygen, followed by 1 min of purging. The voltammogram was recorded three times under the following conditions: drop size 11, deposition time 90 s, quiet time 5 s, scan increment 2 mV, scan range -120 mV to -700 mV, frequency 125 Hz and amplitude 25 mV. Precision was 1.9% RSD (n=10) and sensitivity 4.07 nA/nM. The method was calibrated using standard additions, with standards made from AnalR grade potassium iodide.

**lodate** was determined with the Wong and Brewer (1974) method using a spectrometer (Shimadzu 160 UV). In brief, a sample in a 10 cm quartz cuvette is acidified with sulfuric acid containing sulfanilamide to remove nitrite interference (Chapman and Liss 1977; Rue, Smith et al. 1997) and iodide added to form tri-iodide that is then determined at a wavelength of 535 nm. Standard addition of potassium iodate (Analar grade) was used for daily calibration on a representative sample and its slope applied to subsequent samples. Duplicate samples were run for every depth; triplicate samples were determined for the 0 addition seawater to allow an estimate of precision. Precision was better than 5% RSD at concentration above 100 nmol/L.

Dissolved selenite, selenite+ selenate, and total dissolved selenium concentrations were determined in triplicate using selective hydride generation/atomic absorption spectrometry following Cutter (1978), Cutter (1983), and Cutter and Bruland (1984). The standard addition method of calibration was used to assure accuracy (one sample on an analysis day was used and its slope applied to the other samples on that day). Selenate was calculated as the difference between selenite+selenate and selenite determinations, while organic selenide was the difference between total dissolved selenium and selenite+selenate determinations. Precision was always less than 10% RSD, but typically less than 5% RSD at the observed concentrations. Detection limits were 0.02 nmol/L for all selenium species.

Particulate elemental selenium concentrations were determined using a sulfite leach following Velinsky and Cutter (1990) and analyzed like selenite+selenate following Cutter (1978). Precision was ca. 10% RSD (n=3).

Arsenic speciation was determined using selective hydride generation, liquid nitrogen-cooled trapping, and then revolatilization and determination with gas chromatography/photoionization detection (Cutter et al., 1991; Cutter and Cutter, 2006). Calibration performed daily via the standard additions method, with a minimum of 4

additions of AsIII and AsV. The slope from the linear fit to these data was then applied to all samples for that day. Detection limits were 25 pmol/L for As(III) and As(V). Precision was better than 8% RSD.

#### DMO notes (for current data version 03 Jan 2017):

- \* new version of data based on re-submission
- \* renamed column cruise identifier to SECT\_ID (value EPZT)
- \* added column cruise id with values TN303 \* padded time column with leading 0 if hours was less than 2 digits (e.g. 836-> 0836)
- \* updated values for As V for stations 2 & 3

#### DMO notes (for data version 24 May 2016):

- changed "Cruise" (value EPZT throughout) to SECT\_ID
- \* added new column "cruise id" with value TN303
  \* added description for column CASTNO as this was not in the previous version
- \* DATE,TIME to PI\_DATE,PI\_TIME as this did not match the event times (~15-20 min difference)
- \* variable names changed to conform to GEOTRACES conventions

#### 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, 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\_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-supplied 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.

Chapman, P. and P. S. Liss (1977). "Effect of nitrite on spectrophotometric determination of iodate in seawater." Marine Chemistry 5(3): 243-249. http://dx.doi.org/10.1016/0304-

Cutter, G. A., and K. W. Bruland. "The marine biogeochemistry of selenium: A re-evaluation." Limnology and Oceanography 29.6 (1984): 1179-1192. http://dx.doi.org/10.4319/lo.1984.29.6.1179

Cutter, G.A. and L.S. Cutter, 2006. The biogeochemistry of arsenic and antimony in the North Pacific Ocean, Geochem, Geophys, Geosystems (G3), 7. Q05M08, http://dx.doi.org/10.1029/2005gc001159

Cutter, Gregory A. "Elimination of nitrite interference in the determination of selenium by hydride generation." Analytica Chimica Acta 149 (1983): 391-94. http://dx.doi.org/10.1016/s0003-2670(00)83200-6

Cutter, Gregory. "Species Determination of Selenium in Natural Waters." Analytica Chimica Acta 98 (1978): 59-66. http://dx.doi.org/10.1016/s0003-2670(01)83238-4

Cutter, L.S., G.A. Cutter, and M.L.C. San Diego McGlone. 1991. Simultaneous determination of inorganic arsenic and antimony species in natural waters using selective hydride generation with gas chromatography/photoionization detection. Anal. Chem. 63:1138 1142. http://dx.doi.org/10.1021/ac00011a015

Luther, G. W., C. B. Swartz, et al. (1988). "Direct determination of iodide in seawater by cathodic stripping square-wave voltammetry." Analytical Chemistry 60(17): 1721-

Rue, E. L., G. J. Smith, et al. (1997). "The response of trace element redox couples to suboxic conditions in the water column." Deep-Sea Research Part I-Oceanographic Research Papers 44(1): 113-134. http://dx.doi.org/10.1016/s0967-0637(96)00088-x

Tian, R. C. and E. Nicolas (1995). "Iodine speciation in the northwestern mediterranean-sea - method and vertical profile." Marine Chemistry 48(2): 151-156. http://dx.doi.org/10.1016/0304-4203(94)00048-j

Velinsky, D.I., and G.A. Cutter. "Determination of elemental selenium and pyrite-selenium in sediments." Analytica Chimica Acta 235 (1990): 419-425. http://dx.doi.org/10.1016/s0003-2670(00)82102-9

Wong, G. T. F. and P. G. Brewer (1974). "Determination and distribution of iodate in south-atlantic waters." Journal of Marine Research 32(1): 25-36.

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#### **Data Files**

As\_Se\_IO\_BOTTLE.csv(Comma Separated Values (.csv), 269.58 KB)

Primary data file for dataset ID 647606

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#### **Parameters**

Parameter	Description	Units
CASTNO	GEOTRACES cast number for that station.	unitless
STNNBR	Station number.	unitless
GEOTRC_EVENTNO	GEOTRACES event number.	unitless
GEOTRC_SAMPNO	GEOTRACES sample number.	unitless
EVENT_LON	Longitude according to the event log; West is negative	decimal degrees
EVENT_LAT	Latitude at the start of the event, according to the event log.	decimal degrees
ВТМДЕРТН	bottom Depth	meters
DEPTH	depth of sample	meters
SAMPNO	Bottle sample number	unitless
BTLNBR	Bottle number	unitless
PI_DATE	PI-supplied date in format YYYYMMDD	unitless
PI_TIME	PI-supplied time in format HHMM	unitless
As_III_D_CONC_BOTTLE	dissolved Arsenite concentration from a bottle sample	nanomoles per liter
As_V_D_CONC_BOTTLE	dissolved Arsenate concentration from a bottle sample	nanomoles per liter
Se_TD_CONC_BOTTLE	total dissolved Selenium concentration from a bottle sample	nanomoles per liter
Se_IV_D_CONC_BOTTLE	dissolved Selenite concentration from a bottle sample	nanomoles per liter
Se_VI_D_CONC_BOTTLE	dissolved Selenate concentration from a bottle sample	nanomoles per liter
Org_Se_II_CONC_BOTTLE	organic Selenide concentration from a bottle sample	nanomoles per liter
IODIDE_D_CONC_BOTTLE	dissolved iodide concentration from a bottle sample	nanomoles per liter
IO3_D_CONC_BOTTLE	dissolved iodate concentration from a bottle sample	nanomoles per liter
ISO_DATETIME_UTC_START_EVENT	Date and time (UTC) at start of the event according to the event log. Format is ISO 8601 standard YYYY-mm-ddTHH:MM:SS.xxZ. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	unitless
BTL_DATE	Date when the bottle was fired; according to the bottle file. Format yyyymmdd.	unitless
BTL_TIME	Time when the bottle was fired; according to the bottle file. Format HHMM.	unitless
BTL_LAT	Latitude of bottle firing; north is positive.	decimal degrees
BTL_LON	Longitude of bottle firing; east is positive.	decimal degrees
SECT_ID	Transect identifier for GEOTRACES Eastern Pacific Zonal Transect (EPZT)	unitless
cruise_id	Cruise identifier	untiless

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# Instruments

Dataset- specific Instrument Name	BASi model CGME electrode
Generic Instrument Name	BASi Controlled Growth Mercury Electrode
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. <a href="https://www.basinc.com/products/ec/cgme.php">https://www.basinc.com/products/ec/cgme.php</a>

Dataset- specific Instrument Name	GEOTRACES CTD
Generic Instrument Name	CTD Sea-Bird SBE 911plus
Instrument Description	The Sea-Bird SBE 911 plus is a type of CTD instrument package for continuous measurement of conductivity, temperature and pressure. The SBE 911 plus includes the SBE 9plus Underwater Unit and the SBE 11plus Deck Unit (for real-time readout using conductive wire) for deployment from a vessel. The combination of the SBE 9 plus and SBE 11 plus is called a SBE 911 plus. The SBE 9 plus uses Sea-Bird's standard modular temperature and conductivity sensors (SBE 3 plus and SBE 4). The SBE 9 plus CTD can be configured with up to eight auxiliary sensors to measure other parameters including dissolved oxygen, pH, turbidity, fluorescence, light (PAR), light transmission, etc.). more information from Sea-Bird Electronics

Dataset- specific Instrument Name	gas chromatography/photoionization detector
Generic Instrument Name	Gas Chromatograph
Dataset- specific Description	Processing description says it was used as described in the following reference. Cutter, L.S., G.A. Cutter, and M.L.C. San Diego-McGlone. 1991. Simultaneous determination of inorganic arsenic and antimony species in natural waters using selective hydride generation with gas chromatography/photoionization detection. Anal. Chem. 63:1138-1142. <a href="http://dx.doi.org/10.1021%2Fac00011a015">http://dx.doi.org/10.1021%2Fac00011a015</a>
Generic Instrument Description	Instrument separating gases, volatile substances, or substances dissolved in a volatile solvent by transporting an inert gas through a column packed with a sorbent to a detector for assay. (from SeaDataNet, BODC)

Dataset-specific Instrument Name	GO-FLO Bottle
Generic Instrument Name	GO-FLO Bottle
Generic Instrument Description	GO-FLO bottle cast used to collect water samples for pigment, nutrient, plankton, etc. The GO-FLO sampling bottle is specially designed 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	selective hydride generation/atomic absorption spectrometry
Generic Instrument Name	Spectrophotometer
	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

Dataset-specific Instrument Name	
Generic Instrument Name	UV Spectrophotometer-Shimadzu
	The Shimadzu UV Spectrophotometer is manufactured by Shimadzu Scientific Instruments (ssi.shimadzu.com). Shimadzu manufacturers several models of spectrophotometer; refer to dataset for make/model information.

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# Deployments

#### TN303

TN303	
Website	https://www.bco-dmo.org/deployment/499719
Platform	R/V Thomas G. Thompson
Report	http://dmoserv3.whoi.edu/data_docs/GEOTRACES/EPZT/GT13_EPZT_ODFReport_All.pdf
Start Date	2013-10-25
End Date	2013-12-20
Description	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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#### U.S. GEOTRACES East Pacific Zonal Transect (GP16) (U.S. GEOTRACES EPZT)

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

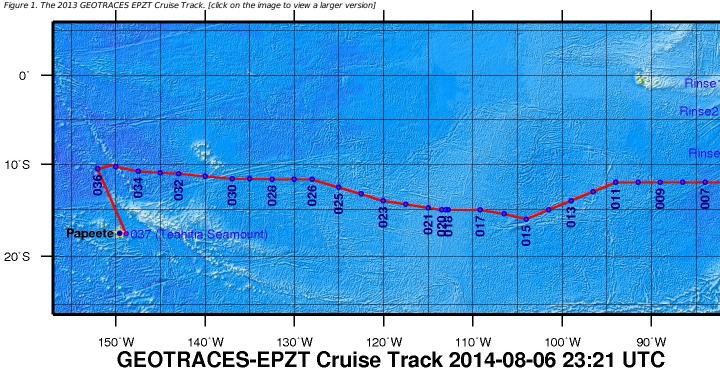
Coverage: Eastern Tropical Pacific - Transect from Peru to Tahiti (GP16)

#### 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.



US GEOTRACES Pacific section: Characterizing the redox environment of the eastern tropical Pacific Ocean (EPZT\_Redox\_Elements)

Coverage: Eastern Pacific

Extracted from the NSF award abstract:

The 2013 GEOTRACES Eastern Pacific Zonal Transect from Peru to Tahiti will cross an entensive oxygen deficient zone typically described as "suboxic"; however, measurements of sulfate reduction in this region suggest it may have some anoxic characteristics due to the presence of free sulfide. Redox conditions influence the solubility/stability of many trace elements which in turn affects their vertical and horizontal transport. A scientist from Old Dominion University plans to analyze water samples collected during the cruise for dissolved iodate/iodide, arsenic [As(III)/As(V)], selenium [Se(IV, VI), particulate Se(0), and nano- to picomolar hydrogen sulfide speciation (total, free/uncomplexed). These measurements, along with nitrate/nitrite, nitrous oxide, and iron species determined by other participants during the cruise, will be used to constrain the range of redox conditions within the oxygen deficient zone, assess the importance of in-situ reduction versus horizontal advection of the redox species, and the changing redox conditions within the hydrothermal plume of the East Pacific Rise. Availability of this data will also enable other researchers to determine the behavior of other redox sensitive trace elements in the 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-1235328

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