# Soluble iron (Fe) passed through 10 kDa cross-flow filter, from R/V Knorr cruise KN199-04 in the Subtropical northern Atlantic Ocean in 2010 (U.S. GEOTRACES NAT project)

Website: https://www.bco-dmo.org/dataset/3848

Version: 07 Jan 2013 Version Date: 2013-03-01

**Project** 

» U.S. GEOTRACES North Atlantic Transect (GA03) (U.S. GEOTRACES NAT)

#### **Program**

» U.S. GEOTRACES (U.S. GEOTRACES)

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## **Dataset Description**

Soluble iron (Fe), the Fe passing through a 10 kDa cross-flow filtration membrane, is reported in nmol Fe per kg of seawater. Samples were collected on the U.S. GEOTRACES North Atlantic Zonal Transect, Leg 1, in 2010.

In comparing this data to other published profiles of soluble Fe, it is valuable to know that soluble Fe is a highly operationally-defined parameter. The two most common methods of collecting soluble Fe samples are via 0.02 µm Anopore membrane filtration and by cross-flow filtration (this study). An intercalibration between the two methods used to collect soluble Fe samples on the U.S. Atlantic GEOTRACES cruises are described in this excerpt (PDF) from a Fitzsimmons manuscript (in preparation). The intercalibration determined that "soluble Fe produced by cross-flow filtration (10 kDa membrane) is only ~65-70% of the soluble Fe produced by Anopore filtration."

Please note that some US GEOTRACES data may not be final, pending intercalibration results and further analysis. If you are interested in following changes to US GEOTRACES NAT data, there is an RSS feed available via the BCO-DMO <u>US GEOTRACES project page</u> (scroll down and expand the "Datasets" section).

#### Methods & Sampling

Trace metal-clean seawater samples were collected using the U.S. GEOTRACES sampling system consisting of 24 Teflon-coated GO-FLO bottles that had been pre-rinsed with a 24+ hour treatment of filtered surface seawater at the beginning of the cruise (see Cutter & Bruland, 2012 for more information on the sampling system). At each station, the bottles were deployed open and tripped on ascent at 3 m/min. On deck, the bottles were kept in a trace metal clean sampling van over-pressurized with HEPA-filtered air, except immediately prior to and following deployments, in which cases they were covered on both ends with shower caps to avoid deck contamination.

During sampling in the clean van, the GO-FLO bottles were pressurized to  $\sim$ 0.4 atm with HEPA-filtered air, and their spigots were fitted with an acid-cleaned piece of Bev-a-Line tubing that fed into an Acropak-200 Supor capsule filter (0.2  $\mu$ m pore size made of polyethersulfone). Before use, this filter had been filled with filtered surface seawater that had been acidifed to pH 2 with 4x Vycor-distilled hydrochloric acid ('trace metal clean HCl') and left overnight to rinse. Before collecting any subsamples, at least 500 mL of seawater was passed through the filter (while eliminating air bubbles in the capsule reservoir). Subsamples were taken into acid-cleaned HDPE bottles after a single rinse. Acropak filters were used for at most 3 casts before a new filter was used, and they were stored empty in the refrigerator while not in use. GEOFish surface samples were taken using an all-plastic 'towed fish' pumping system as described in Bruland et al. 2005 at approximately 2 m depth and were subsampled identically.

Subsamples were immediately taken into a HEPA-filtered flow bench constructed in a 'plastic bubble' overpressurized with HEPA-filtered air. They were then further filtered through a cross-flow filtration system using a Pellicon XL filter (PLCGC) made of regenerated cellulose with a 10 kDa size cutoff. The cross-flow filtration system was otherwise constructed of acid-cleaned Teflon tubing. Total flow rate was calibrated as 12 mL/min, and the permeate and retentate solutions were each set to flow at an equal 6.0 mL/min (concentration factor of ~2); the retentate was not recycled. At the beginning of the cruise, the cross-flow filtration system was rinsed with 4L of 0.5M trace metal clean HCl. Between samples, 500 mL of pH 2 trace metal clean HCl was flushed through the system, and at least 300 mL of sample was flushed to waste before collecting the permeate subsamples in order to 'condition' the system with the sample seawater. Subsamples were taken into acid cleaned HDPE bottles after a single bottle rinse. All samples were filtered within 3-6 hours of being collected to avoid Fe loss to the bottle walls (Fitzsimmons & Boyle, 2012), and samples were acidified at sea to pH 2 with trace metal clean HCl.

Samples were analyzed at least a year after acidification over 11 analytical sessions by the isotope-dilution ICP-MS methods described in Lee et al. 2011, which includes pre-concentration on nitrilotriacetate (NTA) resin and analysis on a Micromass IsoProbe MC-ICP-MS. On each day of sample analyses, procedure blanks were determined using 12 replicates of 300  $\mu L$  of an in-house standard reference material seawater (SAFe surface underway), where the known amount of Fe in the 300  $\mu L$  was subtracted out. The procedure blank over the relevant sessions ranged from 0.006-0.129 nmol/kg, averaging 0.049 nmol/kg. Procedure blanks were very reproducible with an average standard deviation of 0.009 nmol/kg, resulting in a detection limit (3x this standard deviation) of 0.027 nmol/kg. Replicate analyses of the SAFe surface underway sample (not the official SAFe surface SRM but an in-house, large volume sample from the same cruise/site) averaged 0.083±0.035 nmol/kg (±1SD, n=39), which is within error of the consensus value of 0.090 nmol/kg. Replicate analyses of the SAFe D2 sample averaged 0.917±0.032 nmol/kg (±1SD, n=24, Bottle 446), which is within error of the consensus value of 0.90 nmol/kg.

#### References:

**Cutter**, G.A and Bruland, K.W. 2012. Rapid and noncontaminating sampling system for trace elements in global ocean surveys. Limnology & Oceanography: Methods 10: 425-436. doi: 10.4319/lom.2012.10.425 **Bruland**, K.W., Rue, E.L., Smith, G.J., and DiTullio, G.R. 2005. Iron, macronutrients and diatom blooms in the Peru upwelling regime: brown and blue waters of Peru. Marine Chemistry 93:81-103. doi: 10.1016/j.marchem.2004.06.011

**Fitzsimmons**, J.N. and Boyle, E.A. 2012. An intercalibration between the GEOTRACES GO-FLO and the MITESS/Vanes sampling systems for dissolved iron concentration analyses (and a closer look at adsorption effects). Limnology & Oceanography: Methods 10: 437-450.

**Lee**, J.-M., Boyle, E.A., Echegoyen-Sanz, Y., Fitzsimmons, J.N., Zhang, R., and Kayser, R.A. 2011. Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry. Analytica Chimica Acta 686: 93-101. doi: 10.1016/j.aca.2010.11.052

#### **Data Processing Description**

Samples were analyzed in triplicate, and average values shown in this dataset were only accepted if reproduced over at least two replicates; otherwise, the data was re-analyzed until a reproducible value was reached.

The standard Ocean Data View flags were used. A description of all flags is available on line at <a href="https://www.bodc.ac.uk/data/codes">https://www.bodc.ac.uk/data/codes</a> and formats/odv format/. Flags used in this dataset are as follows:

- 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.
- 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 only one replicate confirmed the reported value.)
- 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.
- 4 = Bad Value: An obviously erroneous data value.
- 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.
- 9 = Missing Value: The data value is missing. Any accompanying value will be a magic number representing absent data. (All samples collected were analyzed. Any missing data was not collected.)

#### BCO-DMO made the following changes:

- Parameter names were modified to conform with BCO-DMO naming conventions.
- Blank cells and values of '-999' were replaced with 'nd' to indicate 'no data'.
- Added ISO DateTime UTC from original date and time fields.
- Corrected event number, date, and time of sample #6000.

## Additional GEOTRACES Processing:

After the data were submitted to the International Data Management Office, BODC, the office noticed that important identifying information was missing in many datasets. With the agreement of BODC and the US GEOTRACES lead PIs, 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: station\_GEOTRC, cast\_GEOTRC (bottle and pump data only), event\_GEOTRC, sample\_GEOTRC, sample\_bottle\_GEOTRC (bottle data only), bottle\_GEOTRC (bottle data only), depth\_GEOTRC\_CTD (bottle data only), BTL\_ISO\_DateTime\_UTC (bottle data only), and GeoFish\_id (GeoFish data only). 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\_GT10, GT-C\_Bottle\_GT11, ODF\_Bottle\_GT10, and ODF\_Bottle\_GT11 datasets. Non-bottle parameters, including those from GeoFish tows, Aerosol sampling, and McLane Pumps, were taken from the Event\_Log\_GT10 and Event\_Log\_GT11 datasets. McLane pump cast numbers missing in event logs were taken from the Particulate Th-234 dataset submitted by Ken Buesseler.

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.

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## File

**SolubleFe\_GT10\_joined.csv**(Comma Separated Values (.csv), 87.09 KB) MD5:60ad74f1e63961ca6d82599c96228e66

Primary data file for dataset ID 3848

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# **Parameters**

Parameter Description		Units	
expo_code	_code Expedition code.		
cruise_name  GEOTRACES cruise identifier.		text	
station_GEOTRC	GEOTRACES station number; ranges from 1 through 12 for KN199-04 and 1 through 24 for KN204-01. Stations 7 and 9 were skipped on KN204-01. PI-supplied values were identical to those in the intermediate US GEOTRACES master file. Originally submitted as 'STNNBR', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions.	integer	
cast	integer		
event_GEOTRC  Unique identifying number for US GEOTRACES sampling events; ranges from 2001 to 2225 for KN199-04 events and from 3001 to 3282 for KN204-01 events. PI-supplied values were identical to those in the intermediate US GEOTRACES master file. Originally submitted as 'GEOTRC_EVENTNO', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions.		integer	
sample_GEOTRC	Unique identifying number for US GEOTRACES samples; ranges from 5033 to 6078 for KN199-04 and from 6112 to 8148 for KN204-01. PI-supplied values were identical to those in the intermediate US GEOTRACES master file. Originally submitted as 'GEOTRC_SAMPNO', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions.	integer	
sample_bottle_GEOTRC	Unique identification numbers given to samples taken from bottles; rangies from 1 to 24; often used synonymously with bottle number. PI-supplied values were identical to those in the intermediate US GEOTRACES master file. Originally submitted as 'SAMPNO', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions.	integer	

bottle_GEOTRC	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. Originally submitted as 'BTLNBR', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions.			
Bottle quality flag, following the WOCE protocol. See <u>exchange</u> <u>format description</u> .		unitless		
date	Date (UTC).	YYYYmmdd		
ime	Time (UTC). 24-hour clock.	ННММ		
lat	Latitude. South is negative.			
on	Longitude. West is negative.			
press	Pressure (from CTD).	decibars		
depth	Depth (from CTD); provided in original data submission.	meters		
Fe_sol	Soluble iron (Fe). The Fe passing through a 10 kDa cross-flow filtration membrane measured in nmol Fe per kilogram of seawater.			
Fe_sol_sd	d Standard deviation of replicates of Fe_sol.			
no_reps	Number of replicates.	integer		
Fe_sol_flag	Quality flag for Fe_sol. See 'Processing Description' for code definitions.	unitless		
date_bot	Date (UTC) when the bottle was fired.	YYYYmmdd		
ime_bot	Time (UTC) when the bottle was fired.	ННММ		
at_bot	Latitude when the bottle was fired. South is negative.	decimal degrees		
lon_bot	n_bot Longitude when the bottle was fired. West is negative.			

cruise_id	Official cruise identifier e.g. KN199-04 = R/V Knorr cruise number 199-04.	text
ISO_DateTime_UTC	Date/Time (UTC) formatted to ISO8601 standard. T indicates start of time string; Z indicates UTC. Calculated from date_bot and time_bot fields contributed by PI.	YYYY-mm- ddTHH:MM:SS.ssZ
cast_GEOTRC	Cast identifier, numbered consecutively within a station. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	integer
depth_GEOTRC_CTD	Observation/sample depth in meters, calculated from CTD pressure. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	meters
BTL_ISO_DateTime_UTC	Date and time (UTC) variable recorded at the bottle sampling time in ISO compliant format. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	YYYY-mm- ddTHH:MM:SS.ssZ
	This standard is based on ISO 8601:2004(E) and takes on the following form: 2009-08-30T14:05:00[.xx]Z (UTC time)	

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# Instruments

Dataset-specific Instrument Name	GeoFish
Generic Instrument Name	GeoFish Towed near-Surface Sampler
<b>Dataset-specific Description</b> GEOFish surface samples were taken using an all-plastic 'towed fish' pump system as described in Bruland et al. 2005.	
Generic Instrument Description	The GeoFish towed sampler is a custom designed near surface (

Dataset- specific Instrument Name	GO-FLO Bottle
Generic Instrument Name	GO-FLO Bottle
Dataset- specific Description	Trace metal-clean seawater samples were collected using the U.S. GEOTRACES sampling system consisting of 24 Teflon-coated GO-FLO bottles that had been pre-rinsed with a 24+ hour treatment of filtered surface seawater at the beginning of the cruise (see Cutter & Bruland, 2012).
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	Isotope-ratio Mass Spectrometer
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset- specific Description	Samples were analyzed by the isotope-dilution ICP-MS methods described in Lee et al. 2011, which includes pre-concentration on nitrilotriacetate (NTA) resin and analysis on a Micromass IsoProbe MC-ICP-MS
Generic Instrument Description	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

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# **Deployments**

KN199-04

Website	https://www.bco-dmo.org/deployment/58066
Platform	R/V Knorr
Report	http://bcodata.whoi.edu/US_GEOTRACES/AtlanticSection/Cruise_Report_for_Knorr_199_Final_v3.pdf
Start Date	2010-10-15
End Date	2010-11-04
Description	This cruise constitutes the first survey section as part of the U.S. participation in an international program named GEOTRACES. Funding: NSF OCE award 0926423 Science Objectives: To obtain state of the art trace metal and isotope measurements on a suite of samples taken on a midlatitude zonal transect of the North Atlantic. In particular, sampling targeted the oxygen minimum zone extending off the west African coast near Mauritania, the TAG hydrothermal field, and the western boundary current system along Line W. For additional information, please refer to the GEOTRACES program Web site (https://www.geotraces.org/) for overall program objectives and a summary of properties measured. Science Activities include seawater sampling via GoFLO and Niskin carousels, in situ pumping (and filtration), CTDO2 and transmissometer sensors, underway pumped sampling of surface waters, and collection of aerosols and rain. Hydrography, CTD and nutrient measurements were supported by the Ocean Data Facility (J. Swift) at Scripps Institution of Oceanography and funded through NSF Facilities. They provided an additional CTD rosette system along with nephelometer and LADCP. A trace metal clean Go-Flo Rosette and winch were provided by the group at Old Dominion University (G. Cutter) along with a towed underway pumping system. Additional cruise information is available from the Rolling Deck to Repository (R2R): <a href="https://www.rvdata.us/search/cruise/KN199-04">https://www.rvdata.us/search/cruise/KN199-04</a> Other Relevant Links: List of cruise participants: [ PDF ] Cruise track: JPEG image (from Woods Hole Oceanographic Institution, vessel operator) ADCP data are available from the Currents ADCP group at the University of Hawaii: KN199-04 ADCP

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## **Project Information**

#### U.S. GEOTRACES North Atlantic Transect (GA03) (U.S. GEOTRACES NAT)

Website: <a href="https://www.geotraces.org/">https://www.geotraces.org/</a>

**Coverage**: Subtropical western and eastern North Atlantic Ocean (GA03)

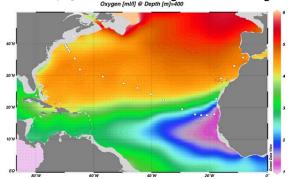
Much of this text appeared in an article published in OCB News, October 2008, by the OCB Project Office.

The first U.S. GEOTRACES Atlantic Section will be specifically centered around a sampling cruise to be carried out in the North Atlantic in 2010. Ed Boyle (MIT) and Bill Jenkins (WHOI) organized a three-day planning workshop that was held September 22-24, 2008 at the Woods Hole Oceanographic Institution. The main goal of the workshop, sponsored by the National Science Foundation and the U.S. GEOTRACES Scientific Steering Committee, was to design the implementation plan for the first U.S. GEOTRACES Atlantic Section. The primary cruise design motivation was to improve knowledge of the sources, sinks and internal cycling of Trace Elements and their Isotopes (TEIs) by studying their distributions along a section in the North Atlantic (Figure 1). The North Atlantic has the full suite of processes that affect TEIs, including strong meridional advection, boundary scavenging and source effects, aeolian deposition, and the salty Mediterranean Outflow. The North Atlantic is particularly important as it lies at the "origin" of the global Meridional Overturning Circulation.

It is well understood that many trace metals play important roles in biogeochemical processes and the carbon cycle, yet very little is known about their large-scale distributions and the regional scale processes that affect them. Recent advances in sampling and analytical techniques, along with advances in our understanding of their roles in enzymatic and catalytic processes in the open ocean provide a natural opportunity to make substantial advances in our understanding of these important elements. Moreover, we are motivated by the prospect of global change and the need to understand the present and future workings of the ocean's biogeochemistry. The GEOTRACES strategy is to measure a broad suite of TEIs to constrain the critical biogeochemical processes that influence their distributions. In addition to these "exotic" substances, more traditional properties, including

macronutrients (at micromolar and nanomolar levels), CTD, bio-optical parameters, and carbon system characteristics will be measured. The cruise starts at Line W, a repeat hydrographic section southeast of Cape Cod, extends to Bermuda and subsequently through the North Atlantic oligotrophic subtropical gyre, then transects into the African coast in the northern limb of the coastal upwelling region. From there, the cruise goes northward into the Mediterranean outflow. The station locations shown on the map are for the "fulldepth TEI" stations, and constitute approximately half of the stations to be ultimately occupied.

Figure 1. The proposed 2010 Atlantic GEOTRACES cruise track plotted on dissolved oxygen at 400 m depth. Data from the World Ocean Atlas (Levitus et al., 2005) were plotted using Ocean Data View (courtesy Reiner Schlitzer). [click on the image to view a larger version]

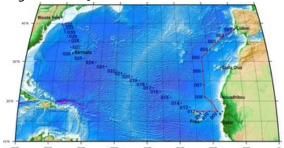


Hydrography, CTD and nutrient measurements will be supported by the Ocean Data Facility (J. Swift) at Scripps Institution of Oceanography and funded through NSF Facilities. They will be providing an additional CTD rosette system along with nephelometer and LADCP. A trace metal clean Go-Flo Rosette and winch will be provided by the group at Old Dominion University (G. Cutter) along with a towed underway pumping system.

The North Atlantic Transect cruise began in 2010 with KN199 leg 4 (station sampling) and leg 5 (underway sampling only) (Figure 2).

## KN199-04 Cruise Report (PDF)

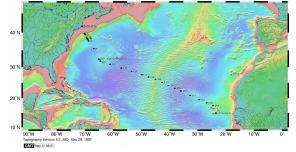
Figure 2. The red line shows the cruise track for the first leg of the US Geotraces North Atlantic Transect on the R/V Knorr in October 2010. The rest of the stations (beginning with 13) will be completed in October-December 2011 on the R/V Knorr (courtesy of Bill Jenkins, Chief Scientist, GNAT first leg). [click on the image to view a larger version]



The section completion effort resumed again in November 2011 with KN204-01A,B (Figure 3).

## KN204-01A, B Cruise Report (PDF)

Figure 3. Station locations occupied on the US Geotraces North Atlantic Transect on the R/V Knorr in November 2011. [click on the image to view a larger version]



Data from the North Atlantic Transect cruises are available under the Datasets heading below, and consensus values for the SAFe and North Atlantic GEOTRACES Reference Seawater Samples are available from the GEOTRACES Program Office: Standards and Reference Materials

**ADCP data** are available from the Currents ADCP group at the University of Hawaii at the links below:

KN199-04 (leg 1 of 2010 cruise; Lisbon to Cape Verde)

KN199-05 (leg 2 of 2010 cruise; Cape Verde to Charleston, NC)

KN204-01A (part 1 of 2011 cruise; Woods Hole, MA to Bermuda)

KN204-01B (part 2 of 2011 cruise; Bermuda to Cape Verde)

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## **Program Information**

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

Website: <a href="http://www.geotraces.org/">http://www.geotraces.org/</a>

Coverage: Global

**GEOTRACES** is a  $\underline{SCOR}$  sponsored program; and funding for program infrastructure development is provided by the  $\underline{U.S. National Science Foundation}$ .

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-0926197