

Total dissolved copper, estimates of free Cu²⁺, ligand concentrations, and conditional stability constants from R/V Knorr KN199-04, KN204-01, subtropical North Atlantic Ocean from 2010-2011 (U.S. GEOTRACES NAT project)

Website: <https://www.bco-dmo.org/dataset/3845>

Data Type: Cruise Results

Version: 1

Version Date: 2013-10-22

Project

» [U.S. GEOTRACES North Atlantic Transect](#) (U.S. GEOTRACES NAT)

Program

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

Contributors	Affiliation	Role
Moffett, James W.	University of Southern California (USC)	Principal Investigator
Jacquot, Jeremy	University of Southern California (USC)	Student
Copley, Nancy	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract

This dataset includes total dissolved copper, estimates of free Cu²⁺, ligand concentrations, and conditional stability constants from R/V Knorr cruises KN199-04 and KN204-01 in the subtropical North Atlantic Ocean from 2010-2011 (U.S. GEOTRACES NAT project)

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Dataset Description

Total dissolved copper and estimates of free Cu²⁺ and ligand concentrations and conditional stability constants.

Expanded/revised data was served on 5 Nov. 2013.

Please note that data may not be final, pending intercalibration results and further analysis. If you are interested in following changes to US GEOTRACES data, there is an RSS feed available from the [GEOTRACES-NAT](#) project page.

Acquisition Description

Samples for total dissolved Cu were acidified in accordance with the standard GEOTRACES protocol using Optima Grade hydrochloric acid.

Samples for speciation determination were processed on board, or were frozen in a -20 freezer for analysis

ashore.

Speciation measurements were performed on samples that were titrated with increasing amounts of Cu, and the change in Cu complexation was determined using competitive ligand exchange cathodic stripping voltammetry, as described in Moffett and Dupont (2007).

The raw data were fit to a speciation model using non-linear regression as described in Moffett and Dupont (2007).

Processing Description

All samples for total dissolved copper on this cruise were well above our detection limit of 100pM determined from the standard deviation of procedural blanks using our ICP-MS methods.

Data points below the detection limit of the cathodic stripping voltammetry technique (~ 0.15 nM) were not used in the titration. However, all titrations had a significant number of points to fit a non-linear regression curve. However, in instances where the fit did not converge, or converged at a non-realistic value (e.g. negative numbers) the data were flagged.

The standard error for $[\text{Cu}^{2+}]$ is asymmetric because it is not determined the same way - hence the different values in columns M and N.

The Cu^{2+} error propagation was derived from the standard deviations of K and [L] when used in equation 11 from Moffett and Dupont 2007 to calculate $[\text{Cu}^{2+}]$.

Moffett and Dupont, 2007. Cu complexation by organic ligands in the sub-arctic NW Pacific and Bering Sea. Deep-Sea Research I 54:586-595.

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), depth_GEOTRC_CTD_rounded (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.

Parameters

Parameter	Description	Units
cruise_id	Official cruise identifier e.g. KN199-04 = R/V Knorr cruise number 199-04.	text
date	UTC date	yyyymmdd
lat	latitude; North is positive	decimal degrees
lon	longitude; East is positive	decimal degrees
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 'GEOTRACES #', this parameter name has been changed to conform to BCO-DMO's GEOTRACES naming conventions.	integer
Cu	concentration of Cu	moles/liter
Cu_std_dev	1 standard deviation around mean Cu concentration	moles/liter
froz_fresh	whether the sample was fresh or had been frozen	text
Cu_plus2	concentration of free cupric ion Cu ²⁺	moles/liter
Cu2_plus_std_err	positive standard error of free Cu ²⁺ concentration	moles/liter
Cu2_minus_std_err	negative standard error of free Cu ²⁺ concentration	moles/liter
log_K	Log conditional stability constant of copper complexing ligand, L1	dimensionless
Li	concentration of the L1 ligand	nanomoles/liter
Li_std_dev	1 standard deviation around mean Li concentration	nanomoles/liter
flag	quality flag	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. Some GeoFish stations are denoted as X_to_Y indicating the tow occurred between stations X and Y. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
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
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. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
cast_GEOTRC	Cast identifier, numbered consecutively within a station. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
sample_bottle_GEOTRC	Unique identification numbers given to samples taken from bottles; ranges from 1 to 24; often used synonymously with bottle number. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless
bottle_GEOTRC	Alphanumeric characters identifying bottle type (e.g., NIS representing Niskin and GF representing GOFLO) and position on a CTD rosette. Values were added from the intermediate US GEOTRACES master file (see Processing Description).	dimensionless

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). This standard is based on ISO 8601:2004(E) and takes on the following form: 2009-08-30T14:05:00[.xx]Z (UTC time)	YYYY-mm-ddTHH:MM:SS.ssZ
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Instruments

Dataset-specific Instrument Name	GO-FLO Teflon Trace Metal
Generic Instrument Name	GO-FLO Teflon Trace Metal Bottle
Generic Instrument Description	GO-FLO Teflon-lined Trace Metal free sampling bottles are used for collecting water samples for trace metal, nutrient and pigment analysis. The GO-FLO sampling bottle is designed specifically to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

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

Dataset-specific Instrument Name	Mass Spectrometer
Generic Instrument Name	Mass Spectrometer
Dataset-specific Description	The Element 2 ICP-MS manufactured by Thermo Scientific was used to measure [D-Cu]. http://www.thermoscientific.com/ecom/servlet/productsdetail_11152__119...
Generic Instrument Description	General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components.

Dataset-specific Instrument Name	BASi Controlled Growth Mercury Electrode
Generic Instrument Name	BASi Controlled Growth Mercury Electrode
Dataset-specific Description	The Controlled Growth Mercury Electrode (CGME) manufactured by Bioanalytical Systems (BASi) to measure [Cu ²⁺], [L] and K.
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. http://www.basinc.com/products/ec/cgme.php

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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	<p>KN199-04 is the US GEOTRACES Zonal North Atlantic Survey Section cruise planned for late Fall 2010 from Lisboa, Portugal to Woods Hole, MA, USA. 4 November 2010 update: Due to engine failure, the scheduled science activities were canceled on 2 November 2010. On 4 November the R/V KNORR put in at Porto Grande, Cape Verde and is scheduled to depart November 8, under the direction of Acting Chief Scientist Oliver Wurl of Old Dominion University. The objective of this leg is to carry the vessel in transit to Charleston, SC while conducting science activities modified from the original plan. Planned scientific activities and operations area during this transit will be as follows: the ship's track will cross from the highly productive region off West Africa into the oligotrophic central subtropical gyre waters, then across the western boundary current (Gulf Stream), and into the productive coastal waters of North America. During this transit, underway surface sampling will be done using the towed fish for trace metals, nanomolar nutrients, and arsenic speciation. In addition, a port-side high volume pumping system will be used to acquire samples for radium isotopes. Finally, routine aerosol and rain sampling will be done for trace elements. This section will provide important information regarding atmospheric deposition, surface transport, and transformations of many trace elements. The vessel is scheduled to arrive at the port of Charleston, SC, on 26 November 2010. The original cruise was intended to be 55 days duration with arrival in Norfolk, VA on 5 December 2010. funding: NSF OCE award 0926423 Science Objectives are to obtain state of the art trace metal and isotope measurements on a suite of samples taken on a mid-latitude zonal transect of the North Atlantic. In particular sampling will target 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. In addition, the major biogeochemical provinces of the subtropical North Atlantic will be characterized. For additional information, please refer to the GEOTRACES program Web site (GEOTRACES.org) for overall program objectives and a summary of properties to be 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 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. List of cruise participants: [PDF] Cruise track: JPEG image (from Woods Hole Oceanographic Institution, vessel operator) Additional information may still be available from the vessel operator: WHOI cruise planning synopsis Cruise information and original data are available from the NSF R2R data catalog. ADCP data are available from the Currents ADCP group at the University of Hawaii: KN199-04 ADCP</p>

KN204-01

Website	https://www.bco-dmo.org/deployment/58786
Platform	R/V Knorr
Report	http://bcodata.whoi.edu/US_GEOTRACES/AtlanticSection/STS_Prelim_GT11_Doc.pdf
Start Date	2011-11-06
End Date	2011-12-11
Description	<p>The US GEOTRACES North Atlantic cruise aboard the R/V Knorr completed the section between Lisbon and Woods Hole that began in October 2010 but was rescheduled for November-December 2011. The R/V Knorr made a brief stop in Bermuda to exchange samples and personnel before continuing across the basin. Scientists disembarked in Praia, Cape Verde, on 11 December. The cruise was identified as KN204-01A (first part before Bermuda) and KN204-01B (after the Bermuda stop). However, the official deployment name for this cruise is KN204-01 and includes both part A and B. Science activities included: ODF 30 liter rosette CTD casts, ODU Trace metal rosette CTD casts, McLane particulate pump casts, underway sampling with towed fish and sampling from the shipboard "uncontaminated" flow-through system. Full depth stations are shown in the accompanying figure (see below). Additional stations to sample for selected trace metals to a depth of 1000 m are not shown. Standard stations are shown in red (as are the ports) and "super" stations, with extra casts to provide large-volume samples for selected parameters, are shown in green. Station spacing is concentrated along the western margin to evaluate the transport of trace elements and isotopes by western boundary currents. Stations across the gyre will allow scientists to examine trace element supply by Saharan dust, while also contrasting trace element and isotope distributions in the oligotrophic gyre with conditions near biologically productive ocean margins, both in the west, to be sampled now, and within the eastern boundary upwelling system off Mauritania, sampled last year. The cruise was funded by NSF OCE awards 0926204, 0926433 and 0926659. Additional information may be available from the vessel operator site, URL: http://www.whoi.edu/cruiseplanning/synopsis.do?id=1662. Cruise information and original data are available from the NSF R2R data catalog. ADCP data are available from the Currents ADCP group at the University of Hawaii at the links below: KN204-01A (part 1 of 2011 cruise; Woods Hole, MA to Bermuda) KN204-01B (part 2 of 2011 cruise; Bermuda to Cape Verde)</p>

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Project Information

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

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

Coverage: Subtropical western and eastern North Atlantic Ocean

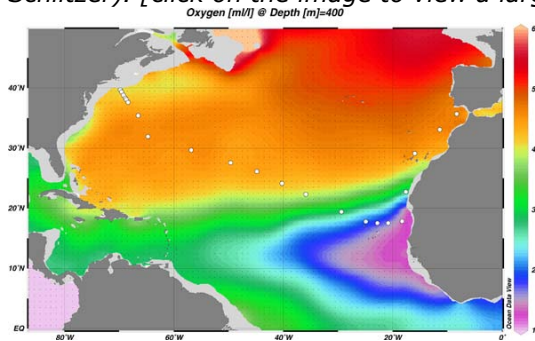
Much of this text appeared in an article published in OCB News, October 2008, by the OCB Project Office.

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]

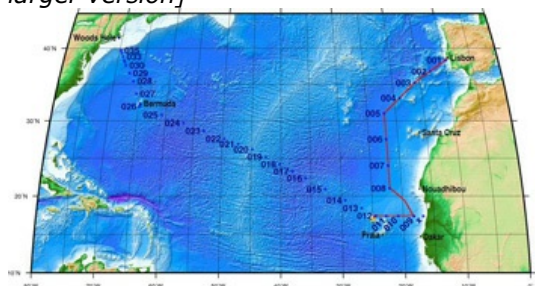


Hydrography, CTD and nutrient measurements will be supported by the Ocean Data Facility (J. Swift) at Scripps Institution of Oceanography and funded through NSF Facilities. They will be providing an additional CTD rosette system along with nephelometer and LADCP. A trace metal clean Go-Flo Rosette and 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 \(PDF\)](#)

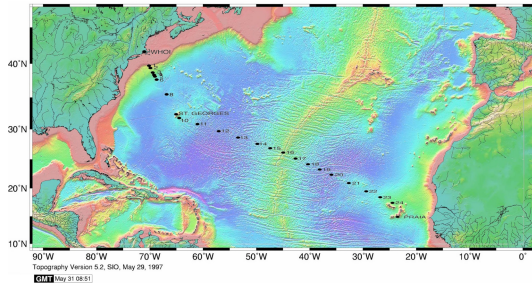
Figure 2. The red line shows the cruise track for the first leg of the US Geotraces North Atlantic Transect on the R/V Knorr in October 2010. The rest of the stations (beginning with 13) will be completed in October-December 2011 on the R/V Knorr (courtesy of Bill Jenkins, Chief Scientist, GNAT first 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: <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-0927387

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