Dissolved Ba, Cd, Cu, Ga, Mn, Ni, and V concentration data from the US GEOTRACES Arctic Expedition (GN01, HLY1502) from August to October 2015

Website: https://www.bco-dmo.org/dataset/772645
Data Type: Cruise Results
Version: 1
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Project
» U.S. Arctic GEOTRACES Study (U.S. GEOTRACES Arctic)
» GEOTRACES Arctic Section: Methane, vanadium, barium, and gallium as process indicators in the Arctic Ocean (GEOTRACES Arctic Methane V Ba Ga)

Program
» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
Shiller, Alan M.	University of Southern Mississippi	Principal Investigator
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract
Dissolved Ba, Cd, Cu, Ga, Mn, Ni, and V concentration data from the US GEOTRACES Arctic Expedition (GN01, HLY1502) from August to October 2015. Clean seawater samples were collected using a GEOTRACES CTD referred to as GT-C/12L GoFlo. Additional near surface samples were collected using either a small boat or through the ice using Teflon coated Tygon tubing and a trace metal clean pump (IWAKI, model WMD-30LFY-115).

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Coverage

Spatial Extent: **N**:89.995 **E**:179.5926 **S**:60.165 **W**:-179.8082
Temporal Extent: 2015-08-12 - 2015-10-08

Acquisition Description

Clean seawater samples were collected using a GEOTRACES CTD referred to as GT-C/12L GoFlo. For more information, see the cruise report. Additional near surface samples were collected using either a small boat or through the ice using Teflon coated Tygon tubing and a trace metal clean pump (IWAKI, model WMD-30LFY-115).

Water samples were filtered through pre-cleaned, 0.2 µm Pall Acropak Supor filter capsules as described elsewhere (e.g., Cutter et al., 2012; Hatta et al., 2015). Filtered water was collected in 125 mL HDPE bottles (Nalgene) that had been precleaned by soaking in hot 1.2 M HCl (reagent grade) for at least 8 h with subsequent thorough rinsing with ultrapure distilled deionized water (Barnstead E-pure). Small boat and under-ice samples were first collected into large acid-washed carboys and subsampled into 125 mL bottles.

Dissolved Ga was determined by isotope dilution ICP-MS using a ThermoFisher Element 2 operated in low resolution. Samples were concentrated using $Mg(OH)_2$ co-precipitation (e.g., Shiller & Bairamadgi, 2006; Zurbrick et al., 2012). Briefly, in this technique, a small addition (~70 µL) of clean aqueous ammonia is added to the acidified seawater sample (~7.5 mL) which precipitates a fraction of the dissolved magnesium as the hydroxide, which in turn, scavenges the gallium from solution. An enriched isotope spike of known concentration was prepared using purified enriched ^{71}Ga (99.8%), obtained from Oak Ridge National Laboratories.

Because there is a significant interference of doubly charged ^{138}Ba with ^{69}Ga, the precipitate was washed three times with a solution of high purity 0.1% NH_4OH to minimize residual Ba. The precipitate was then dissolved in 550 mL ultrapure 3% HNO3 (Seastar Chemicals, Baseline) and analyzed in low resolution using a ThermoFinnigan Element 2 High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS). Isotopes monitored on the ICP-MS were ^{69}Ga, ^{71}Ga, and ^{138}Ba. A slight correction for residual Ba was made based on the ratio of responses at masses 69 and 138 to a Ba standard solution. Because the residual salt content varied from sample to sample, it was not possible to matrix-match the Ba correction

standard. However, typically, this correction affected the final result by < 2.5 pmol/kg; where higher Ba corrections were noted, the sample was reprecipitated and re-analyzed because of concerns about the accuracy of applying the Ba standard correction to samples of high salt content.

The reagent blank contribution to the dissolved Ga analysis is typically 0.6 pmol/kg and the detection limit (based on 3 times the standard deviation of the blank) is 0.3 pmol/kg. Repeated runs of US GEOTRACES intercalibration samples (GS and GD), in-house reference solutions, and cast overlap samples suggest a precision of ± 4%; the limit of detection for Ga was 1.5 pmol/kg. Recovery of the method, as determined by repeated analysis of a spiked and unspiked seawater sample was 100 ± 7%.

Dissolved Ba was measured using a ThermoFisher Element 2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and the isotope dilution method as described by Jacquet et al. (2005). Aliquots (50 µL) of each sample were spiked with 25 µL of a ^{135}Ba-enriched solution (~170 nM) and then diluted 30-fold with 0.2 µm ultrapure filtered water. A sample of ~93% enriched ^{135}Ba was obtained from Oak Ridge National Laboratories for use as the enriched isotope spike. The ICP-MS was operated in low resolution and both ^{135}Ba and ^{138}Ba were determined. The samples were bracketed every 10 samples with a blank and the spike ^{135}Ba solution. The volumes of the spikes, samples and dilution water were accurately assessed by calibrating each pipette by weight. The reproducibility error of this method was estimated by comparing samples collected at the same depths on different casts at the same station. For 12 pairs of these replicate samples, the average absolute deviation of 0.7 nmol/kg or typically 1.5%. Repeated runs of runs of US GEOTRACES intercalibration samples and in-house reference solutions suggest a similar precision; the limit of detection for barium was 0.7 nmol/kg. Our precision is similar to that reported by other labs for Ba (e.g., Jacquet et al., 2005).

Dissolved V, Ni, Cu, Cd and Mn were determined using 14 mL of sample that was spiked with a mixture of isotopically-enriched Ni-62, Cu-65, Cd-111, and V-50 (Oak Ridge Nat'l. Labs). Each spike was >90% enriched in the listed isotopes, except for V-50 (0.25% natural abundance) which was 44.3% enriched. The sample/spike ratio was chosen so as to have the analytical isotope ratios approximately the geometric mean of the natural and enriched spike isotope ratios. Samples were then extracted/pre-concentrated using a SeaFAST system (Elemental Scientific, Inc.) operated in offline mode. A 10-mL sample loop was employed and the elution volume was 750 µL. A similar online SeaFAST extraction procedure is described by Hathorne et al. (2012) for rare earth elements. The extracted samples were subsequently analyzed using a Thermo-Fisher high resolution ICP-MS with an Apex-FAST high efficiency sample introduction system with Spiro desolvator (Elemental Scientific, Inc.). All elements were determined in medium resolution, except Cd which was determined in low resolution. For Mn-55 the V, Ni, and Cu spikes served as internal standards. Calibration was checked by analysis of a large-volume composite North Atlantic surface seawater sample. Spiked (with a natural

isotopic abundance elemental spike) and unspiked aliquots of this sample were analyzed twice in each analytical run. Ti-47 and Cr-52 were monitored to correct for any Ti-50 or Cr-50 isobaric interference on V-50; the correction was generally <1%. Likewise, Mo-98 was monitored to correct for MoO^+ interference on Cd isotopes.

The reproducibility error of this method was estimated by comparing samples collected at the same depths on different casts at the same station as well as by repeated measurement of GEOTRACES reference waters and an in-house standard. Recovery of the method was determined by repeated analysis of a spiked and unspiked seawater. The recoveries, precisions, and comparisons to reference waters are shown in Table 1 (see Supplemental Files).

Processing Description

Quality control:
Data are flagged using the WOCE Hydrographic Program (WHP) bottle parameter data quality codes, as follows:
1 = Sample for this measurement was drawn from water bottle but analysis not received. Note that if water is drawn for any measurement from a water bottle, the quality flag for that parameter must be set equal to 1 initially to ensure that all water samples are accounted for.
2 =Acceptable measurement.
3 = Questionable measurement.
4 = Bad measurement.
5 = Not reported.
6 = Mean of replicate measurements (Number of replicates should be specified in the -.DOC file and replicate data tabulated).
7 = Manual chromatographic peak measurement.
8 = Irregular digital chromatographic peak integration.
9 = Sample not drawn for this measurement from this bottle.

BCO-DMO Processing:
- modified parameter names (replaced ":" with underscore);
- replaced blank cells in CTDPRS column with "nd" (no data).

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Parameters

Parameter	Description	Units

CRUISE	Cruise identifier: HLY 1502	unitless
SECT_ID	GEOTRACES cruise identifier: GA01	unitless
GEOTRC_EVENT	GEOTRACES Event number	unitless
GEOTRC_SAMPNO	GEOTRACES Sample number	unitless
STNNBR	Station number	unitless
CASTNO	Cast number	unitless
LATITUDE	Latitude North	decimal degrees
LONGITUDE	Longitude East	decimal degrees
CTDPRS	Pressure, from CTD sensor	decibars
CTDDEPTH	Depth, derived from CTD sensor	meters
Ga_D_CONC_BOTTLE	Dissolved gallium	picomoles per kilogram (pmol/kg)
QV_WOCEBOTTLE_Ga_D_CONC_BOTTLE	WHP bottle parameter data quality codes	unitless
Ba_D_CONC_BOTTLE	Dissolved barium	nanomoles per kilogram (nmol/kg)
QV_WOCEBOTTLE_Ba_D_CONC_BOTTLE	WHP bottle parameter data quality codes	unitless
Cd_D_CONC_BOTTLE	Dissolved cadmium	nanomoles per kilogram (nmol/kg)
QV_WOCEBOTTLE_Cd_D_CONC_BOTTLE	WHP bottle parameter data quality codes	unitless

V_D_CONC_BOTTLE	Dissolved vanadium	nanomoles per kilogram (nmol/kg)
QV_WOCEBOTTLE_V_D_CONC_BOTTLE	WHP bottle parameter data quality codes	unitless
Ni_D_CONC_BOTTLE	Dissolved nickel	nanomoles per kilogram (nmol/kg)
QV_WOCEBOTTLE_Ni_D_CONC_BOTTLE	WHP bottle parameter data quality codes	unitless
Cu_D_CONC_BOTTLE	Dissolved copper	nanomoles per kilogram (nmol/kg)
QV_WOCEBOTTLE_Cu_D_CONC_BOTTLE	WHP bottle parameter data quality codes	unitless
Mn_D_CONC_BOTTLE	Dissolved manganese	nanomoles per kilogram (nmol/kg)
QV_WOCEBOTTLE_Mn_D_CONC_BOTTLE	WHP bottle parameter data quality codes	unitless
SOURCE	TM = samples from GoFLO bottles on GEOTRACES carousel; s-boat = samples from clean pump ussed aboard small boat; i-hole = samples colelcted under the ice using a clean pump	unitless

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Instruments

Dataset-specific Instrument Name	ThermoFisher Element 2 ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Generic Instrument Description	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.

Dataset-specific Instrument Name	ThermoFinnigan Element 2 High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS)
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Generic Instrument Description	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.

Dataset-specific Instrument Name	GT-C/12L GoFlo
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	Teflon coated Tygon tubing and a trace metal clean pump (IWAKI, model WMD-30LFY-115)
Generic Instrument Name	Pump
Generic Instrument Description	A pump is a device that moves fluids (liquids or gases), or sometimes slurries, by mechanical action. Pumps can be classified into three major groups according to the method they use to move the fluid: direct lift, displacement, and gravity pumps

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Deployments

HLY1502

Website	https://www.bco-dmo.org/deployment/638807
Platform	USCGC Healy
Report	http://dmoserv3.whoi.edu/data_docs/GEOTRACES/Arctic/ARC01-report.pdf
Start Date	2015-08-09
End Date	2015-10-12
Description	US GEOTRACES Arctic cruise: The cruise began in Dutch Harbor, Alaska on 08 October 2015. After a station in the Bering Sea, Healy cruised to the North Pole on a westerly track before returning to the Canadian margin on an easterly track, returning to Dutch Harbor on 10 October 2015.

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Project Information

U.S. Arctic GEOTRACES Study (U.S. GEOTRACES Arctic)

Coverage: Arctic Ocean; Sailing from Dutch Harbor to Dutch Harbor

Description from NSF award abstract: In pursuit of its goal "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", in 2015 the International GEOTRACES Program will embark on several years of research in the Arctic Ocean. In a region where climate warming and general environmental change are occurring at amazing speed, research such as this is important for understanding the current state of Arctic Ocean geochemistry and for developing predictive capability as the regional ecosystem continues to warm and influence global oceanic and climatic conditions. The three investigators funded on this award, will manage a large team of U.S.scientists who will compete through the regular NSF proposal process to contribute their own unique expertise in marine trace metal, isotopic, and carbon cycle geochemistry to the U.S. effort. The three managers will be responsible for arranging and overseeing at-sea technical services such as hydrographic measurements, nutrient analyses, and around-the-clock management of on-deck sampling activites upon which all participants depend, and for organizing all pre- and post-cruise technical support and scientific meetings. The management team will also lead educational outreach activities for the general public in Nome and Barrow, Alaska, to explain the significance of the study to these communities and to learn from residents' insights on observed changes in the marine system. The project itself will provide for the support and training of a number of pre-doctoral students and post-doctoral researchers. Inasmuch as the Arctic Ocean is an epicenter of global climate change, findings of this study are expected to advance present capability to forecast changes in regional and globlal ecosystem and climate system functioning. As the United States' contribution to the International GEOTRACES Arctic Ocean initiative, this project will be part of an ongoing multi-national effort to further scientific knowledge about trace elements and isotopes in the world ocean. This U.S. expedition will focus on the western Arctic Ocean in the boreal summer of 2015. The scientific team will consist of the management team funded through this award plus a team of scientists from U.S. academic institutions who will have successfully competed for and received NSF funds for specific science projects in time to participate in the final stages of cruise planning. The cruise track segments will include the Bering Strait, Chukchi shelf, and the deep Canada Basin. Several stations will be designated as so-called super stations for intense study of atmospheric aerosols, sea ice, and sediment chemistry as well as water-column processes. In total, the set of coordinated international expeditions will involve the deployment of ice-capable research ships from 6 nations (US, Canada, Germany, Sweden, UK, and Russia) across different parts of the Arctic Ocean, and application of state-of-the-art methods to unravel the complex dynamics of trace metals and isotopes that are important as oceanographic and biogeochemical tracers in the sea.

GEOTRACES Arctic Section: Methane, vanadium, barium, and gallium as process

indicators in the Arctic Ocean (GEOTRACES Arctic Methane V Ba Ga)

Coverage: Arctic Circle

NSF Award Abstract: In this project, an investigator participating in the 2015 U.S. GEOTRACES Arctic expedition will make measurements of methane, a dissolved trace gas, as well as the dissolved trace elements of gallium, barium, and vanadium in the Arctic Ocean. In common with other multinational initiatives in the International GEOTRACES Program, the goals of the U.S. Arctic expedition are 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. Some trace elements are essential to life, others are known biological toxins, and still others are important because they can be used as tracers of a variety of physical, chemical, and biological processes in the sea. The trace elements and gas measured as part of this project will be used as tracers for a variety of processes such as river and atmospheric inputs to the Arctic Ocean, as well as circulation in the region. The knowledge and experience gained from this project will be incorporated into courses in oceanography and marine chemistry, as well as be shared through public outreach activities. The project will support the scientific training of a graduate student. The tracers to be measured as part of this study, methane, gallium, barium, and vanadium, will provide important information about oceanic circulation and water inputs to the Arctic. Gallium is likely to prove a sensitive tracer for Atlantic versus Pacific water components in the western Arctic Ocean, an issue of interest in circulation studies and also relevant to projections of the stability of methane hydrates on the Arctic shelves. Barium is of interest because it has been shown to be an indicator of fluvial inputs and contributions to the halocline. This is pertinent to understanding upper ocean circulation in the Arctic as well as to freshwater contributions to the Atlantic Meridional Overturning Circulation. For vanadium, the large proportion of shelf area in the Arctic makes this an ideal region to examine whether shelf sediment uptake determines surface ocean vanadium depletion. For methane, Arctic waters are a significant source of this Greenhouse Gas to the atmosphere and global change is likely exacerbating its release. Determination of the methane distribution will therefore be of interest in and of itself, although it is also a potentially valuable indicator of interactions with the shelf as well as of river inputs. Overall, results from this study will lead to an increased understanding of key ocean biogeochemical and physical processes including cross margin exchange of materials, sources of water in the Arctic Ocean, and fluxes of methane to the atmosphere.

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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-1436312

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