Dissolved gallium (Ga) from the US GEOTRACES GP17-OCE cruise on R/V Roger Revelle (RR2214) in the South Pacific and Southern Oceans from December 2022 to January 2023

Website: https://www.bco-dmo.org/dataset/939225 Data Type: Cruise Results Version: 1 Version Date: 2024-10-02

Project

» <u>US GEOTRACES GP17 Section: South Pacific and Southern Ocean (GP17-OCE)</u> (GP17-OCE)

Program

» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role
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Abstract

Dissolved gallium (Ga) was determined in association with a US GEOTRACES cruise (GP17-OCE/RR2214) in the South Pacific and Southern Ocean. The cruise sampled formation regions for globally distributed water masses, the return flow of Pacific Deep Water into the Southern Ocean, hydrothermally influenced waters, margin waters, and a gradient of low to high productivity with varying limiting nutrients. The cruise track investigates circulation through the Antarctic Circumpolar Current (ACC) and formation of intermediate waters important for upper ocean nutrient supply. The overall circulation/productivity/export/recycling trap of this region also affects how oceanic element-element relationships develop. For Ga, its distribution can provide insight into dust delivery, which recent work has suggested may be higher than previously thought in the study area. Ga's limited reactivity also allows its distribution to be used for water mass deconvolution, which could be usefully applied to the ACC and intermediate water formation regions. Data include dissolved Ga concentrations from bottle and towed fish samples.

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Coverage

Location: South Pacific and Southern Oceans Spatial Extent: N:-19.99986 E:-75.09712 S:-67.00022 W:-152.00026 Temporal Extent: 2022-12-03 - 2023-01-24 Clean seawater samples were collected using a GEOTRACES CTD referred to as GT-C/12L GoFlo, and also from the Super-GeoFISH towed surface vehicle. For more information, see the GP17-OCE cruise report.

Water samples were filtered through pre-cleaned, 0.2-micrometer (μ m) Pall Acropak Supor filter capsules as described elsewhere (e.g., Cutter et al., 2014; Hatta et al., 2015). Filtered water was collected in 125-milliliter (mL) HDPE bottles (Nalgene) that had been precleaned by soaking in hot 1.2 M HCl (reagent grade) for at least 8 hours with subsequent thorough rinsing with ultrapure distilled deionized water (Barnstead E-pure).

Dissolved gallium (Ga) was determined by isotope dilution ICP-MS using a ThermoFisher Element XR operated in low resolution (Gilbert et al., 2023). Samples (20-30 mL) were concentrated using a SeaFAST system; a dilute HF rinse was used for column cleaning between samples. An enriched isotope spike of known concentration was prepared using purified enriched 71Ga (99.8%), obtained from Oak Ridge National Laboratories. The substantial sample pre-concentration of this method allows for ICP-MS analysis using medium resolution which eliminates isobaric interferences including doubly charged 138Ba with 69Ga.

The reagent blank contribution to the dissolved Ga analysis is typically 0.6 picomoles per kilogram (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 \pm 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 \pm 7%.

See attached Intercalibration Report for additional information.

Data Processing Description

The raw ICP-MS count rate data were converted to concentrations using Excel.

Quality Flags: Quality flags were applied following the GEOTRACES policy (<u>https://www.geotraces.org/geotraces-quality-flag-policy/</u>), which recommends the SeaDataNet Scheme:

- 0 = no quality control;
- 1 = good value;
- 2 = probably good value;
- 3 =probably bad value;
- 4 = bad value;
- 5 = changed value;
- 6 = value below detection; (see attached Supplemental File for detection limits for Be-7 samples)
- 7 =value in excess;
- 8 = interpolated value;
- 9 = missing value;
- A = value phenomenon uncertain.

BCO-DMO Processing Description

- Imported original file "RR2214 dataTemplate.xlsx" into the BCO-DMO system.

- Renamed fields to comply with BCO-DMO naming conventions.
- Created the Start_ISO_DateTime_UTC field in ISO 8601 format.

- Corrected the latitude and longitude values for event 20230111.0203.001, Sample ID 18120. (Values were reversed in the original file.)

- Removed the following empty fields: Gear ID, End Date UTC, End Time UTC, End Latitude, End Longitude

- Saved final file as "939225_v1_gp17-oce_dissolved_ga.csv".

Problem Description

No problems noted. SeaDataNet quality flags were used.

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Related Publications

Cutter, G.A., Andersson, P., Codispoti, L., Croot, P., Francois, R., Lohan, M., Obata, H., van der Loeff, M. R. (2014) Sampling and Sample-Handing Protocols for GEOTRACES Cruises (cookbook) Version 2.0; December 2014. <u>http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook_v2.pdf</u> *Methods*

Gilbert, M., Ho, P., Whitmore, L., & Shiller, A. (2023). Automated determination of gallium in seawater using seaFAST pre-concentration and high-resolution inductively-coupled plasma mass spectrometry. Analytica Chimica Acta, 1241, 340799. https://doi.org/<u>10.1016/j.aca.2023.340799</u> *Methods*

Hatta, M., Measures, C. I., Wu, J., Roshan, S., Fitzsimmons, J. N., Sedwick, P., & Morton, P. (2015). An overview of dissolved Fe and Mn distributions during the 2010–2011 U.S. GEOTRACES north Atlantic cruises: GEOTRACES GA03. Deep Sea Research Part II: Topical Studies in Oceanography, 116, 117–129. doi:10.1016/j.dsr2.2014.07.005 Methods

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Parameters

Parameter	Description	Units
Station_ID	Station ID number	unitless
Event_ID	Event ID number	unitless
Start_ISO_DateTime_UTC	Date and time (UTC) when event started in ISO 8601 format	unitless
Start_Date_UTC	Date when event started	unitless
Start_Time_UTC	Time (UTC) when event started	unitless
Start_Latitude	Latitude when event started, S is negative	decimal degrees
Start_Longitude	Longitude when event ended, W is negative	decimal degrees
Rosette_Position	Position of bottle on rosette from which sample was drawn	unitless
Sample_ID	GEOTRACES Sample ID	unitless
Sample_Depth	Depth of sample in water column	meters (m)
Ga_D_CONC_BOTTLE_hxhmr3	Concentration of dissolved Ga from bottle samples	picomoles per kilogram (pmol/kg)
SD1_Ga_D_CONC_BOTTLE_hxhmr3	Standard deviation of Ga_D_CONC_BOTTLE_hxhmr3	picomoles per kilogram (pmol/kg)
Flag_Ga_D_CONC_BOTTLE_hxhmr3	SeaDataNet quality flag for Ga_D_CONC_BOTTLE_hxhmr3	unitless
Ga_D_CONC_FISH_dhewdf	Concentration of dissolved Ga from Super- GeoFISH samples	picomoles per kilogram (pmol/kg)
SD1_Ga_D_CONC_FISH_dhewdf	Standard deviation of Ga_D_CONC_FISH_dhewdf	picomoles per kilogram (pmol/kg)
Flag_Ga_D_CONC_FISH_dhewdf	SeaDataNet quality flag for Ga_D_CONC_FISH_dhewdf	unitless

Instruments

Dataset-specific Instrument Name	Super-GeoFISH towed surface vehicle
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	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	ThermoFisher Element XR
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset- specific Description	High resolution inductively coupled plasma mass spectrometer, Element XR, ThermoFisher
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	SeaFAST system
Generic Instrument Name	SeaFAST Automated Preconcentration System
Dataset-specific Description	Automated Preconcentration System for Undiluted Seawater, seaFAST, Elemental Scientific.
Generic Instrument Description	The seaFAST is an automated sample introduction system for analysis of seawater and other high matrix samples for analyses by ICPMS (Inductively Coupled Plasma Mass Spectrometry).

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Deployments

RR2214

Website	https://www.bco-dmo.org/deployment/905754
Platform	R/V Roger Revelle
Report	https://www.bodc.ac.uk/resources/inventories/cruise_inventory/reports/rogerrevelle_rr2214.pdf
Start Date	2022-12-01
End Date	2023-01-25
Description	The U.S. GEOTRACES GP17-OCE expedition departed Papeete, Tahiti (French Polynesia) on December 1st, 2022 and arrived in Punta Arenas, Chile on January 25th, 2023. The cruise took place in the South Pacific and Southern Oceans aboard the R/V Roger Revelle with a team of 34 scientists led by Ben Twining (Chief Scientist), Jessica Fitzsimmons, and Greg Cutter (Co-Chief Scientists). GP17 was planned as a two-leg expedition, with its first leg (GP17-OCE) as a southward extension of the 2018 GP15 Alaska-Tahiti expedition and a second leg (GP17-ANT; December 2023-January 2024) into coastal and shelf waters of Antarctica's Amundsen Sea. The GP17-OCE section encompassed three major transects: (1) a southbound pseudo-meridional section (~152-135 degrees West) from 20 degrees South to 67 degrees South; (2) an eastbound zonal transect from 135 degrees West to 100 degrees West; (3) and a northbound section returning to Chile (100-75 degrees West). Additional cruise information is available from the following sources: R2R: https://www.rvdata.us/search/cruise/RR2214 CCHDO: https://cchdo.ucsd.edu/cruise/33RR20221201 More information can also be found at: https://usgeotraces.ldeo.columbia.edu/content/gp17-oce

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Project Information

US GEOTRACES GP17 Section: South Pacific and Southern Ocean (GP17-OCE) (GP17-OCE)

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

Coverage: Papeete, Tahiti to Punta Arenas, Chile

The U.S. GEOTRACES GP17-OCE expedition departed Papeete, Tahiti (French Polynesia) on December 1st, 2022 and arrived in Punta Arenas, Chile on January 25th, 2023. The cruise took place in the South Pacific and Southern Oceans aboard the R/V Roger Revelle (cruise ID RR2214) with a team of 34 scientists lead by Ben Twining (Chief Scientist), Jessica Fitzsimmons and Greg Cutter (Co-Chief Scientist). GP17 was planned as a two-leg expedition, with its first leg (GP17-OCE) as a southward extension of the 2018 GP15 Alaska-Tahiti expedition and a second leg (GP17-ANT; December 2023-January 2024) into coastal and shelf waters of Antarctica's Amundsen Sea.

The South Pacific and Southern Oceans sampled by GP17-OCE play critical roles in global water mass circulation and associated global transfer of heat, carbon, and nutrients. Specific oceanographic regions of interest for GP17-OCE included: the most oligotrophic gyre in the global ocean, the Antarctic Circumpolar Current (ACC) frontal region, the previously unexplored Pacific- Antarctic Ridge, the Pacific Deep Water (PDW) flow along the continental slope of South America, and the continental margin inputs potentially emanating from South America.

Further information is available on the <u>US GEOTRACES website</u> and in the <u>cruise report</u> (PDF).

NSF Project Title: Collaborative Research: Management and Implementation of US GEOTRACES GP17 Section: South Pacific and Southern Ocean (GP17-OCE)

NSF Award Abstract:

This award will support the management and implementation of a research expedition from Tahiti to Chile that will enable sampling for a broad suite of trace elements and isotopes (TEI) across oceanographic regions of importance to global nutrient and carbon cycling as part of the U.S. GEOTRACES program. GEOTRACES is a global effort in the field of Chemical Oceanography, the goal of which is to understand the distributions of trace elements and their isotopes in the ocean. Determining the distributions of these elements and isotopes will

increase understanding of processes that shape their distributions, such as ocean currents and material fluxes, and also the processes that depend on these elements, such as the growth of phytoplankton and the support of ocean ecosystems. The proposed cruise will cross the South Pacific Gyre, the Antarctic Circumpolar Current, iron-limited Antarctic waters, and the Chilean margin. In combination with a proposed companion GEOTRACES expedition on a research icebreaker (GP17-ANT) that will be joined by two overlapping stations, the team of investigators will create an ocean section from the ocean's most nutrient-poor waters to its highly-productive Antarctic polar region - a region that plays an outsized role in modulating the global carbon cycle. The expedition will support and provide management infrastructure for additional participating science projects focused on measuring specific external fluxes and internal cycling of TEIs along this section.

The South Pacific Gyre and Pacific sector of the Southern Ocean play critical roles in global water mass circulation and associated global transfer of heat, carbon, and nutrients, but they are chronically understudied for TEIs due to their remote locale. These are regions of strong, dynamic fronts where sub-surface water masses upwell and subduct, and biological and chemical processes in these zones determine nutrient stoichiometries and tracer concentrations in waters exported to lower latitudes. The Pacific sector represents an end member of extremely low external TEI surface fluxes and thus an important region to constrain inputs from the rapidly-changing Antarctic continent. Compared to other ocean basins, TEI cycling in these regions is thought to be dominated by internal cycling processes such as biological uptake, regeneration, and scavenging, and these are poorly represented in global ocean models. The cruise will enable funded investigators to address research questions such as: 1) what are relative rates of external TEI fluxes to this region, including dust, sediment, hydrothermal, and cryospheric fluxes? 2) What are the (micro) nutrient regimes that support productivity, and what impacts do biomass accumulation, export, and regeneration have on TEI cycling and stoichiometries of exported material? 3) What are TEI and nutrient stoichiometries of subducting water masses, and how do scavenging and regeneration impact these during transport northward? This management project has several objectives: 1) plan and coordinate a 55-day research cruise in 2021-2022; 2) use both conventional and trace-metal 'clean' sampling systems to obtain TEI samples, as well as facilitate sampling for atmospheric aerosols and large volume particles and radionuclides; 3) acquire hydrographic data and samples for salinity, dissolved oxygen, algal pigments, and macro-nutrients; and deliver these data to relevant repositories; 4) ensure that proper QA/QC protocols, as well as GEOTRACES intercalibration protocols, are followed and reported; 5) prepare the final cruise report to be posted with data; 6) coordinate between all funded cruise investigators, as well as with leaders of proposed GP17-ANT cruise; and 7) conduct broader impact efforts that will engage the public in oceanographic research using immersive technology. The motivations for and at-sea challenges of this work will be communicated to the general public through creation of immersive 360/Virtual Reality experiences, via a collaboration with the Texas A&M University Visualization LIVE Lab. Through Virtual Reality, users will experience firsthand what life and TEI data collection at sea entail. Virtual reality/digital games and 360° experiences will be distributed through GEOTRACES outreach websites, through PI engagement with local schools, libraries, STEM summer camps, and adult service organizations, and through a collaboration with the National Academy of Sciences.

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Program Information

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

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

Coverage: Global

GEOTRACES is a <u>SCOR</u> sponsored program; and funding for program infrastructure development is provided by the <u>U.S. National Science Foundation</u>.

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)	<u>OCE-1925503</u>

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