Solid phase extracted (SPE) metal distributions collected on 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/993613
Data Type: Cruise Results
Version: 1
Version Date: 2026-02-03

Project
» US GEOTRACES GP17 Section: South Pacific and Southern Ocean (GP17-OCE) (GP17-OCE)
» Collaborative Research: US GEOTRACES GP-17-OCE: Molecular speciation of trace element-ligand complexes in the South Pacific Ocean (GP17-OCE Trace element-ligand complexes)

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

Contributors	Affiliation	Role
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Abstract

Molecular speciation affects the solubility, bioavailability, toxicity, scavenging and regeneration rates, and water column residence times of trace elements in the ocean. The molecular speciation of trace elements is what microbes "sense" and respond to. Here, we report the molecular speciation of iron and iodine in water samples collected as part of the US GEOTRACES GP17 expedition from Tahiti to Punta Areanas, Chile. Dissolved organic matter in filtered seawater was recovered by solid phase extraction onto hydrophobic resins, and recovered with organic solvent. Trace element organic complexes were characterized and quantified by liquid chromatography coupled to inductively coupled mass spectrometry.

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Coverage

Location: Southeastern Pacific Subtropical Gyre to Southeastern Pacific sector of Southern Ocean
Spatial Extent: **N**:-19.894775 **E**:-75.097173 **S**:-67.000262 **W**:-152.000291
Temporal Extent: 2022-12-25 - 2023-01-24

Methods & Sampling

Sample collection and preparation:
Each water sample was filtered directly from the trace metal clean GTC rosette/Go-Flo bottle sampler through a 0.2-micrometer (µm) Pall Acropak-200 Supor cartridge into a trace metal grade acid-cleaned 4-liter (L) polycarbonate bottle for siderophore analysis or an acid-cleaned 2- or 4-L Nalgene LDPE bottle for dissolved iron (Fe) analysis. Samples for siderophores were pumped at 20 milliliters per minute (mL/min) through Bond-Elut ENV solid phase extraction (SPE) columns (1 gram (g), 6 milliliters (mL), P/N 12255012, Agilent Technologies) that had been previously activated by passing 6 mL each of distilled methanol (MeOH, Optima LCMS grade, Fisher Scientific) and ultrapure water (qH$_2$O, 18.2 megaohm (MΩ)) through the column. SPE columns were frozen (-20 degrees Celsius (°C)) immediately after sample collection and returned to the laboratory for processing. Filtered water samples for dissolved Fe concentration analysis were acidified to pH ~2 with the addition of the equivalent of 1 mL of 12 N teflon-distilled HCl back on shore and left for at least six months before processing.

Siderophore Processing:
SPE columns were thawed and washed with 6 mL qH$_2$O (to reduce salts) and the qH$_2$O wash was discarded. Ligands were then eluted with 6 mL distilled MeOH into acid-cleaned 10 mL polypropylene tubes. Process blanks were prepared in parallel by eluting activated SPE columns with 6 mL qH$_2$O followed by 6 mL MeOH. The methanol fraction was collected as the process blank. For consistency among samples, the qH$_2$O wash and MeOH extraction were performed by a trace metal clean liquid handler (model GX271, Gilson).

A 10-microliter (µL) stock solution of 2.2 micromolar (µM) Ga-Desferrioxamine-E (Ga-DFOE) was added to each sample as an internal standard. The sample was concentrated to ~500 µL by vacuum centrifugation (SpeedVac, Thermo Scientific; 35 °C, 5 hours). A 100 µL aliquot of the sample was taken, mixed with 100 µL of qH2O, and immediately analyzed by LC-MS.

To prepare the Ga-DOFE internal standard, 0.5 milligrams (mg) desferrioxamine-E (DFOE; Biophore Research) was dissolved with sonication in 1 mL distilled MeOH. Then, 10 µL of 200 mM gallium nitrate in qH2O adjusted to pH 1 with nitric acid (Optima grade, Fisher Scientific) was added to complex DFOE. The solution was diluted with 4 mL qH2O to make 5 mL of standard. To remove excess Ga, 500 µL of the solution was applied to a SPE column (C18; 100 mg, 1 mL, Agilent Technologies), which had been previously activated with 2 mL each of distilled MeOH and qH2O. The column was washed with 2 mL qH2O to remove excess Ga, and the Ga-DFOE eluted with 2 mL MeOH. The MeOH eluant was collected and then diluted with qH2O to a final volume of 20 mL.

Quantitative analyses of siderophores:
Chromatographic analyses were performed on a bioinert Dionex Ultimate 3000 liquid chromatograph (LC) system fitted with a loading pump, a nano pump, and a 10-port switching valve. During the loading phase, 200 µL of sample were withdrawn into the sample loop, then applied to a C18 trap column (3.5 µm, 0.5 millimeter (mm) x 35 mm, P/N 5064-8260, Agilent Technologies) by the loading pump at 25 microliters per minute (µL/min) for 10 minutes. The loading solvent is a mixture of 95% solvent A (5 millimolar (mM) aqueous ammonium formate, Optima, Fisher Scientific) and 5% solvent B (5 mM methanolic ammonium formate). During the elution phase, the solvent was delivered by a nano pump at 10 µL/min, and the trap column outflow directed onto two C18 columns (3.5 µm, 0.5 mm x 150 mm, P/N 5064-8262, Agilent Technologies) connected in series. Samples were separated with an 80 minute linear gradient from 95% solvent A and 5% solvent B to 95% solvent B, followed by isocratic elution at 95% solvent B for 10 minutes. Meanwhile, the loading pump solvent was switched to 100% qH$_2$O, the flow rate increased to 35 µL/min and directed as a post column make-up flow, which was infused with the column eluant into an inductively coupled mass spectrometer. The high aqueous content of the combined flow serves to minimize the effect of changes in solvent composition (in this case increasing methanol content during the analysis) on the detector response to Fe, Ga, and Al. For Station 39, the HPLC eluant at 10 µL/min was directed into the ICPMS without post column infusion of qH$_2$O.

The combined flow from the LC (45 µL/min) was analyzed using a Thermo Scientific iCAP Q ICPMS fitted with a perfluoroalkoxy micronebulizer (PFA-ST, Elemental Scientific), and a cyclonic spray chamber cooled to 4 °C. Measurements were made in kinetic energy discrimination (KED) mode, with a helium collision gas flow of 4-4.5 mL/min to minimize isobaric 40Ar16O+ interferences on 56Fe. Oxygen was introduced into the sample carrier gas at 25 mL/min to prevent the formation of reduced organic deposits onto the ICPMS skimmer and sampling cones. Isotopes monitored were 56Fe (integration time 0.05 seconds), 54Fe (0.02 seconds), 57Fe (0.02 seconds), 69Ga (0.05 seconds), 71Ga (0.02 seconds), and 27Al (0.02 seconds).

The Fe detector response was calibrated using the siderophore ferrichrome, which elutes at ~40 minutes in our chromatographic analysis. Stock solutions of 250 µM ferrichrome were diluted to prepare standards with 2 nanomolar (nM), 5 nM, 10 nM, 20 nM, and 40 nM of the siderophore. Then, 5 µL of 2.2 µM Ga-DFOE was added to 995 µL of each standard, a 100 µL aliquot was taken, mixed with 100 µL of qH$_2$O, and analyzed by LC-ICPMS. A plot of the ratio 56Fe(ferrichrome):69Ga (Ga-DFOE) peak areas against ferrichrome/Ga-DFOE concentration yields a linear relationship (r^2 ~0.999) for the response of the ICPMS detector to Fe between

0.2-4 pmoles of ferrichrome. Calibrations and process blanks were made for every 10-20 samples analyzed, with only small changes (RSD ~30%) were observed in the slope of the calibration relationship over the course of the two years of sample analysis. Concentrations of Fe ligands in each sample were measured by plotting the FeL/Ga-DFOE peak area on the appropriate calibration curve.

Data Processing Description

Raw intensity ICPMS data over time were exported in '.csv' format. We used a custom Python script (v3.10.9) to integrate peak areas and calculate concentrations based on an external calibration curve (link: https://github.com/tanil07/LC-ICPMS-integration-and-combining-with-metadata).

BCO-DMO Processing Description

- Imported original file "GP17_OCE_DSPEE_concentration.xlsx" into the BCO-DMO system.
- Renamed fields to comply with BCO-DMO naming conventions.
- Added Event_Date (YYYY-MM-DD) column based on the Event column.
- Saved the final file as "993613_v1_gp17-oce_iron_organic_ligands.csv".

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Parameters

Parameter	**Description**	**Units**
Station	Cruise station identifier	unitless
GEOTRACES_ID	Unique GEOTRACES identifier for each water-column sample	unitless
Cast	Cast number	unitless
Event	Event number	unitless
Event_Date	Date when sampling event was recorded	unitless
Seafloor	Bottom depth of the sampling location	meter (m)
Latitude	Latitude of sapling event; negative = south	decimal degrees
Longitude	Longitude of sampling event; negative = west	decimal degrees
Depth	Sample collection depth	meter (m)
TotalFeLigands_56_DSPEENV_CONC_BOTTLE	Total SPE dissolved iron concentration in nM [integrated retention time interval 13-58 min]	nanomole per litre (nM)
HydrophilicFeLigands_56_DSPEENV_CONC_BOTTLE	Hydrophilic SPE dissolved iron concentration in nM [integrated retention time interval 13-30 min]	nanomole per litre (nM)
IntermediateFeLigands_56_DSPEENV_CONC_BOTTLE	Intermediate SPE dissolved iron concentration in nM [integrated retention time interval 30-41 min]	nanomole per litre (nM)
HydrophobicFeLigands_56_DSPEENV_CONC_BOTTLE	Hydrophobic SPE dissolved iron concentration in nM [integrated retention time interval 41-58 min]	nanomole per litre (nM)
TotalIodine_127_DSPEENV_CONC_BOTTLE	Total SPE dissolved iodine concentration in nM [integrated retention time interval 13-58 min]	nanomole per litre (nM)

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Instruments

Dataset-specific Instrument Name	vacuum centrifugation (SpeedVac, Thermo Scientific)
Generic Instrument Name	Concentrator Device
Generic Instrument Description	A concentrator is a device designed to increase the weight per unit volume of a substance. This category includes vacuum centrifuge concentrator, which include a vacuum chamber within which a centrifuge rotor is mounted for spinning a plurality of vials containing a solution at high speed while subjecting the solution to a vacuum condition for concentration and evaporation. Alternative names: sample concentrator; speed vacuum; speed vac.

Dataset-specific Instrument Name	trace metal clean GTC rosette/Go-Flo bottle sampler
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	Dionex Ultimate 3000 liquid chromatograph
Generic Instrument Name	High-Performance Liquid Chromatograph
Generic Instrument Description	A High-performance liquid chromatograph (HPLC) is a type of liquid chromatography used to separate compounds that are dissolved in solution. HPLC instruments consist of a reservoir of the mobile phase, a pump, an injector, a separation column, and a detector. Compounds are separated by high pressure pumping of the sample mixture onto a column packed with microspheres coated with the stationary phase. The different components in the mixture pass through the column at different rates due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase.

Dataset-specific Instrument Name	Thermo Scientific iCAP Q ICPMS
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	Model GX271 Gilson Liquid Handler
Generic Instrument Name	Liquid handler
Generic Instrument Description	A device that is used for automated liquid transfer and handling.

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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 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 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 US GEOTRACES website and in the cruise report (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.

Collaborative Research: US GEOTRACES GP-17-OCE: Molecular speciation of trace element-ligand complexes in the South Pacific Ocean (GP17-OCE Trace element-ligand complexes)

Coverage: South Pacific Ocean

NSF Award Abstract:
All microscopic life in the ocean requires iron to grow and to thrive. This iron is supplied by dust that is carried from land out across the ocean by strong winds, or by volcanic activity deep within the ocean. However, large areas of the ocean are very remote from both land and deep-sea volcanic activity, and the amount of iron that reaches these areas is quite small. In these regions microscopic life is often limited by the very low concentrations of iron that characterize this environment. To use iron, microbes must first extract it from seawater. To do this, some microbes have the ability to manufacture unique organic compounds called

siderophores that are specifically designed to capture iron from seawater and transport it into the cell. The presence of siderophores in seawater acts as a signal to know where in the ocean iron may be limiting microbial productivity.

US GEOTRACES program is a cooperative, multi-investigator effort to make high quality, high-resolution measurements of metal concentrations across representative sections of major ocean basins. GEOTRACES data will serve as a benchmark against which future measurements, made as the ocean responds to climate change, can be referenced. Most biologically important metals in the ocean are bound to organic compounds such as siderophores, and the goals of our project are to identity and measure these metal-organic complexes at the molecular level on a section across the South Pacific and Southern Oceans between Tahiti and Antarctica. The section will consist of ~ 30 evenly spaced sites where samples of seawater will be collected from the surface to the bottom of the ocean. Trace-metal organic complexes will be extracted from these samples and analyzed in the laboratory for iron, copper, cobalt, nickel, zinc, manganese, and iodine containing complexes. The molecular identities, concentrations and water column distributions of these complexes will be determined and used to assess how microbes acquire and use trace metals and other nutrients. In parallel, select samples will also be collected and analyzed for microbial genomes to provide information on which classes of microbes manufacture and use siderophores to acquire iron. Data will be archived in national and international databases. The project activities will help train the next generation of marine scientists and inform the public about how science can inform us about the ocean.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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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-2422713
NSF Division of Ocean Sciences (NSF OCE)	OCE-2045223

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