Dissolved total (dCo) and labile Co (ICo) measurements 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/932707 Data Type: Cruise Results Version: 1 Version Date: 2024-07-15

Project

 » US GEOTRACES GP17 Section: South Pacific and Southern Ocean (GP17-OCE) (GP17-OCE)
» US GEOTRACES GP17-OCE and GP17-ANT: Cobalt Biogeochemical Cycling and Phytoplankton Protein Biomarkers in the Pacific and Southern Oceans (GP17-OCE and GP17-ANT Cobalt and Protein Biomarkers)

Program

» U.S. GEOTRACES (U.S. GEOTRACES)

Contributors	Affiliation	Role	
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Abstract

Despite the scarcity of cobalt in the global ocean, it plays important roles in some cellular functions, both in its role as a central factor in vitamin B12, and as an inorganic protein cofactor. Consequently, its distribution and speciation in marine environments is an important factor in understanding the activity of marine biota. Dissolved cobalt often displays a 'hybrid' profile type, with biological uptake dominating in the surface waters and removal by scavenging onto particles in the mesopelagic and below. These scavenging processes limit the accumulation of dissolved Co in the deep ocean. The relative contributions of scavenging and surface biological uptake are variable regionally due to both chemical and biological factors: recent research shows that dCo inventories may be intimately tied to the manganese redox cycle and formation of Mn oxides, and thus is heavily influenced by oxygen availability and local microbial community structure. Variability in Co usage - and by extension, its stoichiometry with respect to macronutrients - could be the result of differing uses of and needs for Co-utilizing metalloenzymes between taxa, and the plasticity of individual organisms with regards to metal availability. This dataset includes dissolved total (dCo) and labile Co (ICo) measurements from the GP17-OCE expedition, which occurred from 1 December 2022 to 25 January 2023, and traversed the South Pacific and a portion of the Southern Ocean. dCo samples are UV-irradiated before measurement, and so include both ligand bound and free Co. ICo samples are not UV-irradiated, thus represent the free Co inventory and that which is very weakly bound. ICo can be considered as the more bioavailable fraction. These samples were analyzed using competitive ligand exchange cathodic stripping voltammetry with a hanging mercury drop electrode. The dissolved Co distribution is understudied in much of the ocean, including the Southern Ocean. Given the contribution of the Southern Ocean to global deep water formation, the influences on the dCo inventory in this region likely impact Co supply in all ocean basins.

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Coverage

Location: South Pacific, Pacific sector of Southern Ocean Spatial Extent: N:-19.894775 E:-75.097173 S:-67.004865 W:-152.000291 Temporal Extent: 2022-12-03 - 2023-01-24

Methods & Sampling

Our sampling methodology was in alignment with the GEOTRACES cookbook. Seawater samples were collected by onboard supertechs with the GEOTRACES Trace Element Carousel sampling system (GTC). In short, this includes a trace metal clean rosette bearing 24 12-liter (L) Go-Flo bottles (General Oceanics), a Vectran cable, winch and A-frame system, and a clean sampling van (as in Cutter and Bruland 2012). Surface samples were collected using a trace metal clean towfish upon station arrival. Cobalt (Co) samples were filtered in the clean van using a 0.2 micromolar (μ M) Acropak-500 capsule (Pall) into 60 milliliters (mL) LDPE bottles (Nalgene) that had been prepared with the following process: 1 week soak in Citranox detergent, Milli-Q water (Millipore) rinse, 2 week soak in 10% HCl (JT Baker, Reagent grade, in Milli-Q), <0.1% HCl rinse. Sample bottles were filled completely, leaving no headspace. Samples to be analyzed for labile cobalt (ICo) were stored in doubled plastic bags at 4 degrees Celsius (°C) until analysis. Total cobalt (dCo) samples were packed in groups of up to six bottles. Each group of bottles was put in an open plastic bag, which was then placed and sealed inside a heat-sealable bag containing one oxygen-absorbing satchel (Mitsubishi Gas Chemical RP-3K) for each bottle, then stored at 4°C.

Dissolved cobalt analysis was performed in a trace metal clean lab at Woods Hole Oceanographic Institution within 10 months of cruise completion using competitive ligand exchange cathodic stripping voltammetry (CLE-CSV) with a hanging mercury drop electrode (HMDE). This method was developed by Saito and Moffett (2001): also see Saito et al., 2010 and Hawco et al., 2016, for method modifications. For dCo measurements only, samples were irradiated in acid-rinsed guartz tubes for 1 hour using a Metrohm 705 UV Digestor to degrade organic Co ligands prior to analysis. For both dCo and ICo measurements, 11 mL of sample was aliguoted into acid-washed 15 mL polypropylene vials. 38.8 microliters (µL) of 0.1 M dimethylglyoxime (DMG, Sigma Aldrich) in Optima-grade methanol (Fisher Scientific) was added. To eliminate dCo contamination from DMG, DMG was first dissolved in 10^-3 M EDTA, then recrystallized over ice and dried before being redissolved in methanol. For ICo samples, DMG was allowed to equilibrate with the sample seawater for at least 8 hours before proceeding. DMG binds free or weakly bound Co as Co(DMG)2, which was the actual measured species in this method. Following DMG addition, 130 µL of 0.5 M N-(2-hydroxyethyl)piperazine-N-(3-propanesulfonic acid) (EPPS, Sigma Aldrich) was added. EPPS was passed through a Chelex 100 resin column prepared through repeated rinses with Optima HCI and NH4 as described by Price et al. (1989). 8.5 mL of sample solution was then transferred using an autosampler (Metrohm 858 Sample Processor) to the Teflon analysis cup of a Metrohm 663 VA Stand fitted with an HMDE. The VA stand interacted with a Metrohm µAutolabIII through an IME663 interface. All instruments were managed using the Nova 2.1.6 software (Metrohm). 1.5 mL of 1.5 M NaNO2 (Merck) solution, also prepared with rinsed Chelex 100 resin (Price et al., 1989), was also added using the autosampler, then this mixture was purged with HEPA-filtered Ultra-high Purity N₂ (Airgas) for 180 seconds. Each sample underwent multiple scans sequences, described as follows. The sample mixture was purged with N2 for 20 seconds. A new Hg drop surface was produced by the working electrode. The sample mixture was then stirred while a voltage of -0.6 volts (V) was applied through the Hg drop for 90 seconds to promote deposition of the Co(DMG)2 complex. Following a 15 second equilibration period, a fast linear sweep from -0.6 to -1.4 V at 5 votils per second (V s-1) reduced Co(II) in the Co(DMG)2 complex to Co(0), which resulted in a reduction peak centered on -1.15 V. Triplicate scans were performed for each sample to determine method precision. 4 subsequent additions of 25 picomolar (pM) CoCl2 (Fisher Scientific) were then added to the sample by the autosampler and each followed by a scan in order to create a standard curve that was specific to each sample.

Analytical blanks were prepared by UV-irradiating filtered seawater for 1 hour, then passing irradiated seawater through a column of cleanly prepared Chelex 100 resin (Biorad) (Price et al., 1989). Seawater was then irradiated again to eliminate any organic material that may have been introduced by the chelexing process. Blanks were then run in the same manner as dCo samples. Multiple blanks were run for each unique combination of reagent batches (DMG, EPPS and NaNO2).

All metadata was copied from the finalized cruise event log.

Other Information:

Limit of detection of Cobalt: 2.7 pM

Intercalibration: Several GEOTRACES community intercalibration standards (SAFe S, D1 and D2) were run intermittently throughout the sample processing period. As intercalibration standards are acidified for storage, samples were adjusted to pH 7.5-8.5 with dropwise additions of a negligible volume of ammonia hydroxide (NH4OH) and UV-irradiated immediately before analysis. They were then measured as dCo samples. All measured standards were within one standard deviation of the consensus values.

SAFe D1 - measured = $42.3 \pm 1.4 \text{ pM}$ (n=3); consensus = $44.3 \pm 4.6 \text{ pM}$ (converted from pmol/kg)

SAFe D2 - measured = $45.3 \pm 1.2 \text{ pM}$ (n=2); consensus = $44.6 \pm 2.8 \text{ pM}$ (converted from pmol/kg)

SAFe S1 - measured = 4.7 ± 2.8 pM (n=4); consensus = 4.7 ± 1.2 pM (converted from pmol/kg)

Occupation of GEOTRACES crossover station: GP17-OCE Station 1, located at 19° S, 152°W, was a crossover station with the 2018 GP15 expedition. Analysis for both cruises was performed in the Saito lab using the method described for this dataset. The total dCo depth profiles from both occupations are wellmatched. A mean offset of 4 pM is present deeper in the water column (\geq 2200 meters (m)), which is notable but not statistically significant (two tailed t-test, t =2.23, P = 0.051). The average deep water (\geq 2200 m) dCo value is 26.7 \pm 3.4 pM (n = 7) for the GP17-OCE measurements and 22.7 \pm 2.5 pM (n = 5) for GP15. In both profiles, dCo is undetectable at the surface. In the GP15 profile, the dCo maximum is located at 500 m, while the GP17-OCE measurements reach their maximum at 625 m. dCo remains elevated from the depth of the dCo maximum to around 1100 m in both profiles. The dCo values measured in this mesopelagic maximum are higher for the GP17-OCE expedition than the GP15 expedition. Variability in the upper water column is expected due to interannual and seasonal changes in mixing and production, the former of which is evident from the deviations present in the salinity profile in the upper 400 m between the two cruises. Changes in production and remineralization efficiency could also contribute to the comparatively increased mid-depth dCo maximum we observe in the GP17-OCE data. Regardless, the major vertical features observed on GP15 are robustly replicated from the GP17-OCE re-occupation, and dCo concentrations are comparable throughout the water column. The results of this crossover station comparison provide good confidence for the inter-cruise consistency of our method.

Data consistency: Samples were analyzed with technical triplicates performed through repeated 'no-addition' scans by the electrode system. Consistency of the instrument was monitored by regular measurement of house standards made from 2 batches of UV-irradiated Equatorial Pacific seawater collected on the KN195-05 expedition (dCo = $18.02 \pm 3.9 \text{ pM}$, n = 18 and dCo = $12.46 \pm 2.0 \text{ pM}$, n = 23).

Data Processing Description

All instruments were controlled by the NOVA 2.1.6 program (Metrohm). This program also generated the data files used for downstream processing. The linear relationship between the peak height corresponding to the reduction of Co(II) in the Co(DMG)2 complex to Co(0) and the concentration of Co was leveraged to allow the calculation of sample Co concentration using simple linear regression. As DMG was added in excess, all available Co was assumed to be bound as Co(DMG)2. Peak height was measured using a custom peak-finding program written in Python (https://github.com/annaliesemeyer/dCoVoltammetry; DOI: 10.5281/ZENODO.11204512). Briefly, a polynomial baseline was fit to each scan, then subtracted to allow for the sensitive detection of the Co reduction peak maximum and peak edges. The identified edge and maximum locations were transferred back onto the original scan such that the peak height could be calculated as the vertical distance between the peak maximum and a line connecting the peak edges. Polynomial fit parameters could also be adjusted to promote ideal identification of the peak features as needed. The program then determined Co concentration via linear regression using the peak heights for all scans associated with a sample and its standard curve. The value derived from the x-intercept of the linear regression line is presented here to better characterize samples with low concentrations where the peaks associated with the triplicate scans were too small to be precisely measured. The quality of the measurement was manually assured by inspecting the R² values of the regression and standard deviation of triplicate scans. However, as these triplicate scans are not true technical replicate measurements, standard deviation of sample measurements is used here only to assess within-sample scan quality and consistency and thus are not reported with this dataset. In cases where an individual scan within a sample scan set failed, the failed scan was removed and concentration of the sample was determined with the remaining values. Final concentrations were calculated by subtracting the average blank value of the appropriate reagent batch from the measured sample concentration in order to identify any Co contamination introduced by the reagents.

BCO-DMO Processing Description

- Imported original file "RR2214_Saito_dCo.xlsx" into the BCO-DMO system.
- Flagged "-999" as a missing data value (missing data are empty/blank in the final CSV file)
- Renamed fields to comply with BCO-DMO naming conventions.
- Created date-time fields in ISO 8601 format.
- Saved the final file as "932707_v1_gp17-oce_dissolved_total_and_labile_cobalt.csv"

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Data Files

File

932707_v1_gp17-oce_dissolved_total_and_labile_cobalt.csv(Comma Separated Values (.csv), 120.73 KB) MD5:c6d7d9c827e62e66b5d3204957c70dda

Primary data file for dataset ID 932707, version 1

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Related Publications

Annaliese Meyer. (2024). *annaliesemeyer/dCoVoltammetry: v1.0.1* (Version v1.0.1) [Computer software]. Zenodo. https://doi.org/<u>10.5281/ZENODO.11204512</u> *Software*

Cutter, G. A., & Bruland, K. W. (2012). Rapid and noncontaminating sampling system for trace elements in global ocean surveys. Limnology and Oceanography: Methods, 10(6), 425–436. doi:<u>10.4319/lom.2012.10.425</u> *Methods*

Hawco, N. J., Ohnemus, D. C., Resing, J. A., Twining, B. S., & Saito, M. A. (2016). A dissolved cobalt plume in the oxygen minimum zone of the eastern tropical South Pacific. Biogeosciences, 13(20), 5697–5717. doi:<u>10.5194/bg-13-5697-2016</u> *Methods*

Price, N.M, Harrison, G.I., Hering, J.G., Hudson, R.J., Nirel, P.M.V., Palenik, B., & Morel, F.M.M. (1989) Preparation and Chemistry of the Artificial Algal Culture Medium Aquil, Biological Oceanography, 6:5-6, 443-461, DOI: <u>10.1080/01965581.1988.10749544</u> *Methods*

Saito, M. A., & Moffett, J. W. (2001). Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean work. Marine Chemistry, 75(1-2), 49–68. doi:<u>10.1016/s0304-4203(01)00025-1</u> *Methods*

Saito, M. A., Goepfert, T. J., Noble, A. E., Bertrand, E. M., Sedwick, P. N., & DiTullio, G. R. (2010). A seasonal study of dissolved cobalt in the Ross Sea, Antarctica: micronutrient behavior, absence of scavenging, and relationships with Zn, Cd, and P. Biogeosciences, 7(12), 4059–4082. doi:<u>10.5194/bg-7-4059-2010</u> *Methods*

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Parameters

Parameter	Description	Units
Station_ID	Station ID number	unitless
Event_ID	Cruise event ID number	unitless
Gear_ID	Gear used to collect samples, GTC = GEOTRACES Trace Element Carousel Sampling System, Fish = trace metal clean surface towfish	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
End_ISO_DateTime_UTC	Date and time (UTC) when event ended in ISO 8601 format	unitless
End_Date_UTC	Date when event ended	unitless
End_Time_UTC	Time (UTC) when event ended	unitless
Start_Latitude	Latitude when event started, S is negative	decimal degrees
Start_Longitude	Longitude when event started, W is negative	decimal degrees
End_Latitude	Latitude when event ended, S is negative	decimal degrees
End_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)
Co_D_CONC_BOTTLE_lg4vkh	Total dissolved cobalt concentration from GTC casts	picomolar (pM)
SD1_Co_D_CONC_BOTTLE_lg4vkh	Standard deviation of Co_D_CONC_BOTTLE_lg4vkh	picomolar (pM)

Flag_Co_D_CONC_BOTTLE_lg4vkh	Quality control flag associated with total dissolved cobalt measurement from GTC	unitless
Co_DL_CONC_BOTTLE_odwv1j	Labile dissolved cobalt concentration from GTC casts	picomolar (pM)
SD1_Co_DL_CONC_BOTTLE_odwv1j	Standard deviation of Co_DL_CONC_BOTTLE_odwv1j	picomolar (pM)
Flag_Co_DL_CONC_BOTTLE_odwv1j	Quality control flag associated with labile dissolved cobalt measurement from GTC	unitless
Co_DL_CONC_FISH_mmzk4i	Labile dissolved cobalt concentration from towfish	picomolar (pM)
SD1_Co_DL_CONC_FISH_mmzk4i	Standard deviation of Co_DL_CONC_FISH_mmzk4i	picomolar (pM)
Flag_Co_DL_CONC_FISH_mmzk4i	Quality control flag associated with labile dissolved cobalt measurement from towfish	unitless
Co_D_CONC_FISH_6ltauy	Total dissolved cobalt concentration from towfish	picomolar (pM)
SD1_Co_D_CONC_FISH_6ltauy	Standard deviation of Co_D_CONC_FISH_6ltauy	picomolar (pM)
Flag_Co_D_CONC_FISH_6ltauy	Quality control flag associated with total dissolved cobalt measurement from towfish	unitless

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Instruments

Dataset- specific Instrument Name	Seabird 9/11+ carousel/CTD
Generic Instrument Name	CTD Sea-Bird SBE 911plus
Generic Instrument Description	The Sea-Bird SBE 911 plus is a type of CTD instrument package for continuous measurement of conductivity, temperature and pressure. The SBE 911 plus includes the SBE 9plus Underwater Unit and the SBE 11plus Deck Unit (for real-time readout using conductive wire) for deployment from a vessel. The combination of the SBE 9 plus and SBE 11 plus is called a SBE 911 plus. The SBE 9 plus uses Sea-Bird's standard modular temperature and conductivity sensors (SBE 3 plus and SBE 4). The SBE 9 plus CTD can be configured with up to eight auxiliary sensors to measure other parameters including dissolved oxygen, pH, turbidity, fluorescence, light (PAR), light transmission, etc.). more information from Sea-Bird Electronics

Dataset- specific Instrument Name	24 12-liter Go-Flo bottles (General Oceanics)
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	Metrohm 858 Sample Processor (2.858.0010)	
Generic Instrument Name	Laboratory Autosampler	
Generic Instrument Description	Laboratory apparatus that automatically introduces one or more samples with a predetermined volume or mass into an analytical instrument.	

Dataset- specific Instrument Name	Metrohm 663 VA Stand (2.663.0020) fitted with an MME pro (6.1256.020); and Metrohm Interface for 663 VA Stand (IME663.S)
Generic Instrument Name	Metrohm 663 VA Stand mercury electrode
Generic Instrument Description	The Metrohm 663 VA stand forms the wet chemical part of a polarographic and voltammetric analytical system. It features a mercury electrode, an Ag/AgCl reference electrode and a glassy carbon counter electrode. The size of the mercury drop and the stirrer speed are set manually on the VA Stand. The VA Stand can be operated in Dropping Mercury Electrode (DME), Hanging Mercury Drop Electrode (HMDE) and Static Mercury Drop Electrode (SMDE) modes. The VA Stand can be controlled by a potentiostat in conjunction with the Metrohm IME663 interface.

Dataset- specific Instrument Name	Metrohm µAutolab III
Generic Instrument Name	Metrohm microAutolab
Generic Instrument Description	A computer-controlled compact potentiostat/galvanostat for electrochemical research and electroanalysis. It has a potentiostat bandwidth of 500 kHz, an input impedance of >100 GOhm and features an analog integrator. The instrument can supply a maximum current of 80 mA with an accuracy of 0.2% and a resolution of 0.0003%. Potential accuracy is 0.2% and potential resolution is 3 uV. The instrument can perform almost all electrochemical techniques including voltammetry, fuel cell, battery, biosensors, electroplating, coatings and corrosion. The NOVA software controls the microAutolab II version, which has an external USB interface, and the microAutolab III version, which features an integrated USB interface inside the instrument. microAutolab I is not supported in NOVA.

Dataset-specific Instrument Name	t Metrohm 705 UV Digestor (2.705.0016) and Metrohm UV Mercury Vapor Lamp (6.2804.030)	
Generic Instrument Name	UV Digester	
Generic Instrument Description	Digestion instrument for UV photolysis of water samples	

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 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.

US GEOTRACES GP17-OCE and GP17-ANT: Cobalt Biogeochemical Cycling and Phytoplankton Protein Biomarkers in the Pacific and Southern Oceans (GP17-OCE and GP17-ANT Cobalt and Protein Biomarkers)

NSF Award Abstract:

Dissolved metals have an important role as micronutrients that influence marine photosynthesis and the overall carbon cycle. Of these metals, cobalt is one of the scarcest elements. Cobalt has an unusual behavior in the environment in that it is strongly influenced by both nutrient uptake processes in the upper water column and scavenging removal processes in the mid-water and deep ocean. There is also growing evidence of cobalt's importance within marine biological processes where different chemical forms of cobalt have been observed to influence primary productivity. In addition, protein biomolecules bind most metals within organisms, and the study of proteins within marine microbes can provide useful information about how microbes respond to environmental influences. In this proposal, the investigator will study the biogeochemistry of cobalt and selected proteins across the South Pacific and Southern Oceans as part of the GEOTRACES GP17-OCE and

GP17-ANT expeditions. GEOTRACES is a global program that studies the distribution of trace elements and isotopes. The project will support a graduate student and a postdoctoral researcher.

The distributions of dissolved and labile cobalt will be determined across the South Pacific and the Southern Ocean on these two expeditions. Moreover, microbial proteins representative of nutrient and micronutrient stresses will be measured across surface transects to compare to the distributions of metals. The Southern Ocean and Antarctica coastal regions are of interest for cobalt research because vitamin B12, which contains a cobalt atom, has been observed to influence phytoplankton growth in Antarctic polynyas due strong seasonal demand and increased glacial iron inputs. Recent data suggests that this increased B12 use by the biota may be shifting the Co biogeochemical cycle in multiple ways, and this project will explore these dynamics and compare it with historical data. Cobalt will be measured using cathodic stripping voltammetry after ultraviolet radiation to remove metal-binding ligands. Proteins will be measured by metaproteomic methods that use nanospray liquid chromatography high resolution mass spectrometry and metatranscriptomic databases. Metaproteomic results will be incorporated into the Ocean Protein Portal for broader use in research and education.

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 <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.

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-2048774</u>

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