Depth profiles of seawater dissolved 232Th, 230Th, and 231Pa from R/V Sonne cruise SO245 (UltraPac, GPpr09) during Dec 2015 to Jan 2016

Website: https://www.bco-dmo.org/dataset/813133 Data Type: Cruise Results Version: 1 Version Date: 2020-06-03

Project

» Supply and removal of trace elements in the subtropical South Pacific (GPpr09) (UltraPac Trace Elements)

Program

» U.S. GEOTRACES (U.S. GEOTRACES)

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Abstract

This dataset contains depth profiles of seawater dissolved 232Th, 230Th, and 231Pa from R/V Sonne cruise SO245 (UltraPac, GPpr09).

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Coverage

Spatial Extent: N:-23.490667 **E**:-84.930117 **S**:-39.310683 **W**:-169.971433 **Temporal Extent**: 2015-12-27 - 2016-01-24

Dataset Description

This dataset contains depth profiles of seawater dissolved 232Th, 230Th, and 231Pa from R/V Sonne cruise SO245 (UltraPac, GPpr09).

Dataset Notes:

Radionuclide concentrations are given as micro-Becquerel (10-6 Bq, μBq or micro-Bq) per kg seawater for 230Th and 231Pa, and pmol (10-12 mol) per kg seawater for 232Th. A Becquerel is the SI unit for radioactivity and is defined as 1 disintegration per second. These units are recommended by the GEOTRACES community.

"Dissolved" (D) here refers to that which passed through a 0.45 μ m AcropakTM 500 filter capsule sampled

from conventional Niskin bottles.

For dissolved, seawater was weighed directly in the laboratory to determine sample size, taking into account acid added at sea. Concentrations below detection are listed as "bdl". The abbreviation "nd" refers to no data available.

Parameter names are adopted based on a recommendation from the GEOTRACES community (<u>http://www.egeotraces.org/Parameter_Naming_Conventions.html</u>).

This is data measured at Lamont-Doherty Earth Observatory of Columbia University (LDEO).

Methods & Sampling

Dissolved data:

Water samples were collected with a Sea-Bird Electronics CTD carousel fitted with 24 12-liter PVC Niskin bottles. The carousel was lowered from the ship with steel wire. Niskin bottles were equipped with nylon-coated closure springs and Viton O-rings. After collection seawater was drained with Teflon-lined TygonTM tubing and filtered through Pall AcropakTM 500 filters on deck (gravity filtration, 0.8/0.45 μ m pore size) into Fisher I-Chem series 300 LDPE cubitainers. Approximately 10L was collected per desired depth. Prior to the cruise, the tubing, filters, and cubitainers were cleaned by immersion in 1.2 M HCl (Fisher Scientific Trace Metal Grade) for 4-5 days. Once filtered, samples were adjusted to a pH ~2 with ultra-clean 6 M HCl (Fisher Scientific OPTIMA grade), double-bagged, stored in pallet boxes on-deck until the end of the cruise and then at room temperature once shipped to the participating laboratories analysis.

Analytical methods for dissolved radionuclides:

In the on-shore laboratory, ~5L of seawater was transferred into a new acid-cleaned cubitainer, weighed to determine sample size, taking into account the weight of the cubitainer and of the acid added at sea. Then weighed aliguots of the artificial isotope yield monitors 229Th (20 pg) and 233Pa (0.5 pg) and 15 mg dissolved Fe were added to each sample. After allowing 1 day for spike equilibration, the pH of each sample was raised to 8.3-8.7 by adding ~12 mL of concentrated NH4OH (Fisher Scientific OPTIMA grade) which caused iron (oxy)hydroxide precipitates to form. Each sample cubitainer was fitted with a nozzle cap, inverted, and the Fe precipitate was allowed to settle for 2 days. After 2 days, the nozzle caps were opened and the pH~8.3-8.7 water was slowly drained, leaving only the iron oxyhydroxide precipitate and 250-500mL of water. The Fe precipitate was transferred to centrifuge tubes for centrifugation and rinsing with Milli-Q H2O (>18 M Ω) to remove the major seawater ions. The precipitate was then dissolved in 16 M HNO3 (Fisher Scientific OPTIMA grade) and transferred to a Teflon beaker for a high-temperature (180-200°C) digestion with HCIO4 and HF (Fisher Scientific OPTIMA grade) on a hotplate in a HEPA-filtered laminar flow hood. After total dissolution of the sample, another precipitation of iron (oxy)hydroxide followed and the precipitate was washed with Mill-O H2O. centrifuged, and dissolved in 12 M HCl for a series of anion-exchange chromatography using 6 mL polypropylene columns each containing a 1 mL bed of Bio-rad resin (AG1-X8, 100-200 mesh size) and a 45 µm porous polyethylene frit (Anderson et al. 2012). The final column elutions were dried down at 180°C in the presence of 2 drops of HCIO4 and taken up in approximately 1 mL of 0.16 M HNO3/0.026 M HF for mass spectrometric analysis.

Concentrations of 232Th, 230Th, and 231Pa were calculated by isotope dilution, relative to the calibrated tracers 229Th and 233Pa added at the beginning of sample processing. Analyses were carried out on a Thermo-Finnegan ELEMENT XR Single Collector Magnetic Sector ICP-MS, equipped with a high-performance Interface pump (let Pump), and specially-designed sample (X) and skimmer (let) cones to ensure the highest possible sensitivity. All measurements were made in low-resolution mode (Δm/M≈300), peak jumping in Escan mode across the central 5% of the flat-topped peaks. Measurements were made on a MasCom[™] SEM; 229Th, 230Th,231Pa, and 233Pa were measured in Counting mode, while the 232Th signals were large enough that they were measured in Analog mode. Two solutions of SRM129, a natural U standard, were run multiple times throughout each run. One solution was in a concentration range where 238U and 235U were both measured in counting mode, allowing us to determine the mass bias/amu (typical values varied from -0.01/amu to 0.03/amu). In the other, more concentrated solution, 238U was measured in Analog mode and 235U was measured in Counting mode, yielding a measurement of the Analog/Counting Correction Factor. These corrections assume that the mass bias and Analog Correction Factor measured on U isotopes can be applied to Th and Pa isotope measurements. Each sample measurement was bracketed by measurement of an aliquot of the run solution, used to correct for the instrumental background count rates. To correct for tailing of 232Th into the minor Th and Pa isotopes, a series of 232Th standards were run at concentrations bracketing the expected 232Th concentrations in the samples. The analysis routine for these standards was identical to

the analysis routine for samples, so we could see the changing beam intensities at the minor masses as we increased the concentration of the 232Th standards. The 232Th count rates in our Pa fractions are quite small, reflecting mainly reagent blanks, compared to the 232Th signal intensity in the Th fraction. The regressions of 230Th, 231Pa, and 233Pa signals as a function of the 232Th signal in the standards was used to correct for tailing of 232Th in samples.

Water samples were analyzed in batches of 15. Procedural blanks were determined by processing two 4-5 L of Milli-Q water in an acid-cleaned cubitainer acidified to pH ~2 with 6 M HCl as a sample in each batch. An aliquot of two intercalibrated working standard solutions of 232Th, 230Th and 231Pa, SW STD 2010-1 referred to by Anderson et al. (2012) and SW STD 2015-1 which has lower 232Th activity (more similar to Pacific seawater conditions), were also processed like a sample in each batch. Samples were corrected using the pooled average of all procedural blanks run during processing of SO245 samples. The average procedural blanks for 232Th, 230Th, and 231Pa were about 7 pg, 0.5 fg, and 0.03 fg respectively.

Derived parameters:

Th_230_D_XS_CONC_BOTTLE - The dissolved excess Th-230 concentration refers to the measured dissolved Th-230 corrected for a contribution of Th-230 due to the partial dissolution of uranium-bearing minerals, or lithogenics. Thereby the dissolved excess represents solely the fraction of Th-230 produced in the water by decay of dissolved uranium-234. We estimate the lithogenic Th-230 using measuring dissolved Th-232 and a lithogenic Th-230/Th-232 ratio of 4.0e-6 (atom ratio) as determined by Roy-Barman et al. (2002) and a conversion factor to convert picomoles to micro-Becquerels.

Th_230_D_XS_CONC_BOTTLE = Th_230_D_CONC_BOTTLE - 4.0e-6 *1.7473e5 * Th_232_D_CONC_BOTTLE

Pa_231_D_XS_CONC_BOTTLE - The dissolved excess Pa-231 concentration refers to the measured dissolved Pa-231 corrected for a contribution of Pa-231 due to the partial dissolution of uranium-bearing minerals, or lithogenics. Thereby the dissolved excess represents solely the fraction of Pa-231 produced in the water by decay of dissolved uranium-235. We estimate the lithogenic Pa-231 using measuring dissolved Th-232 and a lithogenic Pa-231/Th-232 ratio of 8.8e-8 (atom ratio) which is derived from assuming an average upper continental crustal U/Th ratio (Taylor and McClennan, 1995) and secular equilibrium between Pa-231 and U-235 in the lithogenic material. An additional conversion factor is needed to convert picomoles to micro-Becquerels.

Pa_231_D_XS_CONC_BOTTLE = Pa_231_D_CONC_BOTTLE - 8.8e-8 * 4.0370e5 * Th_232_D_CONC_BOTTLE

The correction for dissolved 231Pa and 230Th derived from dissolution of lithogenic particles, when calculating xs230Th and xs231Pa is small. Therefore, even for a sample where the 232Th, used to make the correction, is flagged as bad, the error contributed in calculating xs230Th and xs231Pa is small, so they are flagged as questionable (2). See the Processing Description for complete quality flag definitions.

Data Processing Description

Data Processing:

The reported errors for radionuclide concentrations represent the propagation of one sigma errors based on the standard isotope ratios collected by ICP-MS, estimated error in the 229Th or 233Pa spike concentration, and the blank correction of the individual isotopes.

Analysis of all samples was completed over the course of multiple years. A correction was made to account for the ingrowth of 230Th and 231Pa due to the decay of the natural 234U and 235U preserved in the acidified samples during the period of time between sample collection and U-Th/Pa separation during anion exchange chromatography. Thus, the reported 230Th and 231Pa concentrations have been corrected to represent their concentrations at the time of sampling. U concentrations in the samples were estimated using the salinity (S) measured from the CTD and the U-Salinity relationship in seawater (Owens et al. 2011), [U] = (0.100*S - 0.326) ng U (g seawater)-1. We used seawater U-isotopic compositions of 234U/238 U = 1.1468 activity ratio (Andersen et al., 2010), and 238U/235U = 137.824 mole ratio (Weyer et al., 2008), to calculate [234U] and [235U] respectively based on [U].

Individual uncertainties for thorium were calculated to include contributions from (a) blank correction using the variance of the blanks measured over the course of the analyses, (b) standard error of the ratios of the analysis (typically close to counting statistics) and (c) spike calibration. For Pa we also included assessment of the uncertainty from the yield correction, mass bias and machine background. In order to assess the reproducibility of the procedure, repeat analyses were performed on the GEOTRACES 2010-1 and 2015-1

standards. For standards run alongside SO245 samples, the reproducibility for each isotope was 0.71% for 230Th, 1.09% for 232Th and 1.94% for 231Pa on SW STD 2010-1, and was 0.47% for 230Th, 2.26% for 232Th and 2.04% for 231Pa on SW STD 2015-1.

Data quality flags:

SeaDataNet data quality flags have been assigned to all reported parameters except for the derived parameters Th_230_D_XS_CONC_BOTTLE and Pa_231_D_XS_CONC_BOTTLE. More information on SeaDataNet flags is available from GEOTRACES at http://www.geotraces.org/library-88/geotraces-policies/1577-geotraces-guality-flag-policy and from SeaDataNet at https://www.seadatanet.org/Standards/Data-Quality-Control. In summary:

- 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 (BDL);
- 7 =value in excess;
- 8 = interpolated value;
- 9 = missing value.

Flag definitions for Th_230_D_XS_CONC_BOTTLE:

- 1 = Both 230Th and $\overline{232Th}$ data good;
- 2 = 232Th data bad but 230Th data good;
- 3 = 230Th data bad.

Flag definitions for Pa_231_D_XS_CONC_BOTTLE:

- 1 = Both 231Pa and 232Th data good;
- 2 = 232Th data bad but 231Pa data good;
- 3 = 231Pa data bad.

BCO-DMO Processing:

- renamed fields;
- rounded values to precision request by data submitter;
- added ISO8601 date/time columns.

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Data Files

File
dissolved_Th_Pa.csv(Comma Separated Values (.csv), 31.15 KB) MD5:e31836448772c83b1d41dc2d73d67521
Primary data file for dataset ID 813133

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Related Publications

Andersen, M. B., Stirling, C. H., Zimmermann, B., & Halliday, A. N. (2010). Precise determination of the open ocean 234U/238U composition. Geochemistry, Geophysics, Geosystems, 11(12), n/a-n/a. doi:<u>10.1029/2010gc003318</u> *Methods*

Anderson, R. F., Fleisher, M. Q., Robinson, L. F., Edwards, R. L., Hoff, J. A., Moran, S. B., ... Francois, R. (2012). GEOTRACES intercalibration of 230Th, 232Th, 231Pa, and prospects for 10Be. Limnology and Oceanography: Methods, 10(4), 179–213. doi:<u>10.4319/lom.2012.10.179</u> *Methods*

Auro, M. E., Robinson, L. F., Burke, A., Bradtmiller, L. I., Fleisher, M. Q., & Anderson, R. F. (2012).

Improvements to 232-thorium, 230-thorium, and 231-protactinium analysis in seawater arising from GEOTRACES intercalibration. Limnology and Oceanography: Methods, 10(7), 464–474. doi:<u>10.4319/lom.2012.10.464</u> *General*

Cheng, H., Edwards, R. L., Hoff, J., Gallup, C. D., Richards, D. A., & Asmerom, Y. (2000). The half-lives of uranium-234 and thorium-230. Chemical Geology, 169(1-2), 17–33. doi:<u>10.1016/s0009-2541(99)00157-6</u> *General*

Owens, S. A., Buesseler, K. O., & Sims, K. W. W. (2011). Re-evaluating the 238U-salinity relationship in seawater: Implications for the 238U-234Th disequilibrium method. Marine Chemistry, 127(1-4), 31–39. doi:<u>10.1016/j.marchem.2011.07.005</u> *Methods*

Roy-Barman, M., Coppola, L., & Souhaut, M. (2002). Thorium isotopes in the western Mediterranean Sea: an insight into the marine particle dynamics. Earth and Planetary Science Letters, 196(3-4), 161–174. doi:<u>10.1016/s0012-821x(01)00606-9</u> Methods

Taylor, S. R., & McLennan, S. M. (1995). The geochemical evolution of the continental crust. Reviews of Geophysics, 33(2), 241. doi:<u>10.1029/95rg00262</u> *Methods*

Weyer, S., Anbar, A. D., Gerdes, A., Gordon, G. W., Algeo, T. J., & Boyle, E. A. (2008). Natural fractionation of 238U/235U. Geochimica et Cosmochimica Acta, 72(2), 345–359. doi:<u>10.1016/j.gca.2007.11.012</u> *Methods*

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Parameters

Parameter	Description	Units
Station_ID	Station number	unitless
Start_Date_UTC	Start date (UTC); format: DD/MM/YYYY	unitless
Start_Time_UTC	Start time (UTC); format: hh:mm	unitless
Start_ISO_DateTime_UTC	Start date and time (UTC) formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	unitless
End_Date_UTC	End date (UTC); format: DD/MM/YYYY	unitless
End_Time_UTC	End time (UTC); format: hh:mm	unitless
End_ISO_DateTime_UTC	End date and time (UTC) formatted to ISO8601 standard: YYYY-MM-DDThh:mmZ	unitless
Start_Latitude	Start latitude	degrees North
Start_Longitude	Start longitude	degrees East
End_Latitude	End latitude	degrees North
End_Longitude	End longitude	degrees East
Event_ID	Event number	unitless
Sample_ID	Sample number	unitless
Sample_Depth	Sample depth	meters (m)
Th_230_D_CONC_BOTTLE_tf6m7p	Dissolved Th-230 concentration	uBq/kg
SD1_Th_230_D_CONC_BOTTLE_tf6m7p	One standard deviation of Th_230_D_CONC_BOTTLE_tf6m7p	uBq/kg
Flag_Th_230_D_CONC_BOTTLE_tf6m7p	Quality flag for Th_230_D_CONC_BOTTLE_tf6m7p	unitless
Th_232_D_CONC_BOTTLE_lffbvx	Dissolved Th-232 concentration	pmol/kg
SD1_Th_232_D_CONC_BOTTLE_lffbvx	One standard deviation of Th_232_D_CONC_BOTTLE_lffbvx	pmol/kg
Flag_Th_232_D_CONC_BOTTLE_lffbvx	Quality flag for Th_232_D_CONC_BOTTLE_lffbvx	unitless
Pa_231_D_CONC_BOTTLE_rrjlxc	Dissolved Pa-231 concentration	uBq/kg
SD1_Pa_231_D_CONC_BOTTLE_rrjlxc	One standard deviation of Pa_231_D_CONC_BOTTLE_rrjlxc	uBq/kg
Flag_Pa_231_D_CONC_BOTTLE_rrjlxc	Quality flag for Pa_231_D_CONC_BOTTLE_rrjlxc	unitless
Th_230_D_XS_CONC_BOTTLE	Dissolved Th-230 concentration corrected for the dissolution of lithogenic minerals, thereby isolating the dissolved Th-230 produced by decay of dissolved uranium (see metadata for full explanation)	uBq/kg
SD1_Th_230_D_XS_CONC_BOTTLE	One standard deviation of Th_230_D_XS_CONC_BOTTLE	uBq/kg
Flag_Th_230_D_XS_CONC_BOTTLE	Quality flag for Th_230_D_XS_CONC_BOTTLE	unitless
Pa_231_D_XS_CONC_BOTTLE	Dissolved Pa-231 concentration corrected for the dissolution of lithogenic minerals (see metadata for full explanation)	uBq/kg
SD1_Pa_231_D_XS_CONC_BOTTLE	One standard deviation of Pa_231_D_XS_CONC_BOTTLE	uBq/kg
Flag_Pa_231_D_XS_CONC_BOTTLE	Quality flag for Pa_231_D_XS_CONC_BOTTLE	unitless

Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	Centrifuge
Generic Instrument Description	A machine with a rapidly rotating container that applies centrifugal force to its contents, typically to separate fluids of different densities (e.g., cream from milk) or liquids from solids.

Dataset- specific Instrument Name	Sea-Bird Electronics CTD
Generic Instrument Name	CTD Sea-Bird
Generic Instrument Description	Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics, no specific unit identified. This instrument designation is used when specific make and model are not known. See also other SeaBird instruments listed under CTD. More information from Sea-Bird Electronics.

Dataset- specific Instrument Name	Thermo-Finnegan ELEMENT XR Single Collector Magnetic Sector 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	12-liter PVC Niskin bottles
Generic Instrument Name	Niskin bottle
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

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Deployments

SO245

Website	https://www.bco-dmo.org/deployment/813132
Platform	R/V Sonne
Report	https://datadocs.bco- dmo.org/docs/302/UltraPac_Trace_Elements/data_docs/awi_doi_10.2312_cr_so245.pdf
Start Date	2015-12-17
End Date	2016-01-28

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Project Information

Supply and removal of trace elements in the subtropical South Pacific (GPpr09) (UltraPac Trace Elements)

Coverage: South Pacific Gyre between Peru and Tahiti

NSF Award Abstract:

With funding from this RAPID award, an American research team at the Lamont-Doherty Earth Observatory of Columbia University will study the supply and removal of trace elements in the South Pacific Subtropical Gyre (SPSG). This will be done in the context of an international program (UltraPac) under the direction of Dr. Tim Ferdelman of the Max Planck Institute in Breman, Germany, who has invited the Lamont-Doherty team to join the German scientists aboard their expedition on the Research Vessel Sonne (December 2015 - January 2016) between Antofagasta, Chile and Wellington, New Zealand. UltraPac is a coordinated interdisciplinary study of the SPSG, including research on microbiology, molecular biology, zooplankton, aerosols, trace metals, nitrogen fixation, carbon and nutrient biogeochemistry, among other topics. The American team will measure dissolved and particulate concentrations of long-lived, naturally-occurring radioisotopes in the uranium and thorium decay series that can be used to provide constraints on the rates of supply and removal of trace elements within this regime. The project will also provide education, training and professional development for two PhD students that would otherwise be unavailable through other aspects of their PhD research. It will also provide an opportunity for the students to network with foreign collaborators, which will be very beneficial to their long-term career development.

This project will enable the Lamont-Doherty scientists to quantify the rates of supply and removal of trace elements in the severely undersampled SPSG, the ocean's largest biogeographic province, characterized by a hyper-oligotrophic (low biological productivity) ecosystem and ultra-low dust fluxes. Evaluating the supply of trace elements from dust provides critical information about sources of essential micronutrients that influence the ecology and biogeochemistry of the SPSG. The award will cover the travel expenses for two people to participate in the cruise, shipping to and from the cruise, and instrument fees to analyze samples collected on the cruise. Comparing scavenging results from the SPSG with results from recent studies of other biogeographic providences, including the North Pacific Subtropical Gyre, the Subarctic North Pacific, the North Atlantic Subtropical Gyre and the Eastern Tropical South Pacific, will build toward the team's long-range goal of characterizing the intensity of trace element removal from the ocean in terms of environmental, ecological and biogeochemical characteristics of ocean biogeographic provinces. The deep water column of the SPSG is influenced by the hydrothermal plume emanating from the East Pacific Rise. Comparing SPSG results with those from regions lacking significant influence by hydrothermal plumes will also enable them to constrain the role of these plumes in defining the global distribution of trace elements in the deep ocean. This effort should provide rates of supply and removal of biologically essential micronutrients, and of other trace elements, in an end-member ocean regime that is not scheduled for sampling by a GEOTRACES ocean section, thus filling a gap in the global database for trace elements and isotopes under development by GEOTRACES. Results will be obtained using GEOTRACES-compliant methods, and made available through the GEOTRACES database for use by investigators in other fields.

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-1555726</u>

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