Particulate Acid-Volatile Sulfide (pAVS) and Chromium Reducible Sulfide (pCRS) from Leg 1 (Seattle, WA to Hilo, HI) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1814) on R/V Roger Revelle from September to October 2018

Website: https://www.bco-dmo.org/dataset/873765
Data Type: Cruise Results
Version: 1
Version Date: 2022-05-04

Project
» US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)
» US GEOTRACES PMT: hydrogen sulfide as a strong ligand affecting trace metal cycling (PMT Hydrogen Sulfide)

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

Contributors	Affiliation	Role
Cutter, Gregory A.	Old Dominion University (ODU)	Principal Investigator, Contact
Buckley, Nicole R.	Old Dominion University (ODU)	Co-Principal Investigator
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract
This dataset includes water column particulate Acid-Volatile Sulfide (pAVS) and Chromium Reducible Sulfide (pCRS) data from a McLane pump from Leg 1 (Seattle, WA to Hilo, HI) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1814) conducted on R/V Roger Revelle from September to October 2018.

Table of Contents

- Coverage
- Dataset Description
  - Methods & Sampling
  - Data Processing Description
- Data Files
- Related Publications
- Related Datasets
- Parameters
- Instruments
- Deployments
- Project Information
- Program Information
- Funding

Coverage

Spatial Extent: **N**:56.1 **E**:-152 **S**:19.7 **W**:-157
Temporal Extent: 2018-09-24 - 2018-10-21

Methods & Sampling

Methodology:
Particulate acid volatile sulfide (pAVS) was determined at sea using the Radford-Knoery and Cutter (1993) method. This method entails placing the frozen Supor filter into a gas stripping vessel with DDI water and purging with helium, acidification to 1 M hydrochloric acid, and then gas stripping and cryogenically trapping the hydrogen sulfide and subsequent quantification using a gas chromatograph coupled with a flame photometric detector. The particulate chromium reducible sulfide (pCRS) was determined back at the ODU laboratory using the Radford-Knoery and Cutter (1993) method like pAVS but acidifying the QMA filter to 4 M hydrochloric acid with the addition of 1 M chromium (II) chloride.

Sampling and analytical procedures:

Particulate sulfide samples were collected using modified McLane in-situ pumps with two mini-MULVFS filter holders (Bishop et al., 2012). One of the holders contained a 51 µm polyester mesh prefilter and particles were collected on a 0.8 µm polyethersulfone Supor membrane filter (0.8 – 51 µm size fraction). The Supor filters had between 100 and 1,100 L filtered through them with an average of 400 L. The other filter holder contained the same prefilter but collected particles on a Whatman QMA quartz fiber filter (1 – 51 µm size fraction) and filtered between 300 and 1,540 L with an average of 1,100 L filtration volume. Excess seawater was removed using a vacuum pump within an hour of pump recovery. Both the Supor and QMA filters were then subsampled in the trace metal clean lab by P. Lam's (UCSD) pump team and placed in cryovials that were subsequently stored frozen at -80°C until analysis. A subfraction of the Supor and QMA filters for particulate sulfide analysis were analyzed, yielding 12.5% and 2.3% of each filter with average filter volumes of 49.5 L and 23.4 L, respectively.

The pAVS samples were analyzed at sea when time allowed. Upon analysis, the frozen Supor filter was placed in a 50 mL gas stripping vessel with 10 mL of DDI water and purged with helium (100 mL/min) for 2 minutes. After 2 minutes has passed, the cryogenic trap was immersed in liquid nitrogen and 1 M hydrochloric acid was injected through the Teflon septum and stripped/trapped the gases for 15 minutes before quantifying pAVS using a gas chromatograph coupled with a flame photometric detector.

The pCRS samples were analyzed back at the ODU laboratory by the end of November 2019. Upon analysis, the frozen QMA filter was placed in the 50 mL gas stripping vessel with 10 mL of DDI water and purged with helium (100 mL/min) for 2 minutes. After 2 minutes has passed, the cryogenic trap was immersed in liquid nitrogen and 4 M hydrochloric acid and 1 M chromium (II) chloride were injected through the Teflon septum and stripped/trapped for 20 minutes before quantifying pCRS using a gas chromatography coupled with a flame photometric detector. Each day prior to analysis, chromium (II) chloride blanks were recorded and later applied as corrections to the pCRS concentration due to the addition of the chromium (II) chloride as a reducing agent.

This method has particle detection limits of 0.2 pmol S for acid volatile sulfide and 2 pmol S for chromium reducible sulfide (Radford-Knoery & Cutter, 1993) which corresponds to relative detection limits of 0.004 pmol L-1 pAVS and 0.085 pmol L-1 pCRS with average filtered volumes of 49.5 L and 23.4 L, respectively. Both pAVS and pCRS samples were analyzed mostly in single analyses, however, previous studies report pAVS and pCRS precision near 10% RSD (Cutter & Kluckhohn, 1999; Cutter & Radford-Knoery, 1991). To ensure accuracy, the H2S and OCS gases are calibrated using permeation tubes whose permeation rates have been gravimetrically measured for 2-4 years. By trapping and measuring known amounts of permeated H2S and OCS over a range of times, linear calibration curves for each gas were assembled daily and applied to the unknown samples.

Instruments:
These samples were processed following the analytical apparatus first stated by Radford-Knoery and Cutter (1993). All details can be found in that publication.

A Hewlett Packard (HP) 5890 Series II gas chromatograph coupled with a HP flame photometric detector (model 19256A) was used in the quantification of pAVS and pCRS. The output signal from the detector was processed using a PeakSimple Chromatography Data System (model 333). Hydrogen (130 mL/min) and air (130 mL/min) are used for the flame photometric detector's flame while ultra-high purity helium is used as the carrier gas (30 mL/min) and the stripping gas (100 mL/min). While cylinders were used as the source of air and ultra-high purity helium, a VWR hydrogen generator (model H2PEM-165) was used for the hydrogen source. A VWR circulating water bath (model 1130S) was used to maintain 40°C for H2S and OCS permeation devices (Metronics) which were used to calibrate the instrument for H2S and OCS.

Known Problems/Issues:
Occasionally, there were technological errors where the connection between the detector and the PeakSimple data system became loose and resulted in peaks that were cut off and thus could no longer be quantified. These data have been flagged 9 according to the SeaDataNet scheme.

Quality Flags:
The SeaDataNet scheme was used to assign data quality flags to samples. More information can be found at https://www.seadatanet.org/Standards/Data-Quality-Control.

The reported codes for flagged data are:
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
7 = value in excess
8 = interpolated value
9 = missing value

Data Processing Description

Data Processing:
The output signal from the flame photometric detector was processed using a PeakSimple Chromatography Data System (model 333). The sulfide peaks were manually integrated in the PeakSimple software and converted to a value in pmol S/L using the slope calculated from the system's calibration immediately before or after processing the samples and the filtration volume of each subfraction of the main filter.

BCO-DMO Processing:
- corrected dates and times for those that were incrementing in Excel;
- re-named fields to comply with BCO-DMO naming conventions;
- added date/time columns in ISO8601 format.

[table of contents | back to top]

Data Files

File
pAVS_pCRS_Leg1.csv (Comma Separated Values (.csv), 13.95 KB) MD5:bca7c0903848542b7da10e58ab88ead7
Primary data file for dataset ID 873765

[table of contents | back to top]

Related Publications

Bishop, J. K. B., Lam, P. J., & Wood, T. J. (2012). Getting good particles: Accurate sampling of particles by large volume in-situ filtration. Limnology and Oceanography: Methods, 10(9), 681–710. doi:10.4319/lom.2012.10.681
Methods

Cutter, G. A., & Kluckhohn, R. S. (1999). The cycling of particulate carbon, nitrogen, sulfur, and sulfur species (iron monosulfide, greigite, pyrite, and organic sulfur) in the water columns of Framvaren Fjord and the Black Sea. Marine Chemistry, 67(3–4), 149–160. https://doi.org/10.1016/s0304-4203(99)00056-0
Methods

Cutter, G. A., & Radford-Knoery, J. (2013). Determination of Carbon, Nitrogen, Sulfur, and Inorganic Sulfur Species in Marine Particles. Geophysical Monograph Series, 57–63. https://doi.org/10.1029/gm063p0057
Methods

Radford-Knoery, J., & Cutter, G. A. (1993). Determination of carbonyl sulfide and hydrogen sulfide species in natural waters using specialized collection procedures and gas chromatography with flame photometric detection. Analytical Chemistry, 65(8), 976–982. doi:10.1021/ac00056a005
Methods

[table of contents | back to top]

Related Datasets

IsContinuedBy

Cutter, G. A., Buckley, N. R. (2022) **Particulate Acid-Volatile Sulfide (pAVS) and Chromium Reducible Sulfide (pCRS) from Leg 2 (Hilo, HI to Papeete, French Polynesia) of the US GEOTRACES Pacific Meridional Transect (PMT) cruise (GP15, RR1815) on R/V Roger Revelle from Oct to Nov 2018.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2022-05-05 doi:10.26008/1912/bco-dmo.873792.1 [view at BCO-DMO]
Relationship Description: GP15 was made up of two cruise legs, RR1814 (Leg 1) and RR1815 (Leg 2).

[table of contents | back to top]

Parameters

Parameter	Description	Units
Station_ID	Station number	unitless
Start_Date_UTC	Date (UTC) at start of sample collection; format: DD/MM/YYYY	unitless
Start_Time_UTC	Time (UTC) at start of sample collection; format: hh:mm	unitless
Start_ISO_DateTime_UTC	Date and time (UTC) at start of sample collection in ISO8601 format: YYYY-MM-DDThh:mmZ	unitless
End_Date_UTC	Date (UTC) at end of sample collection; format: DD/MM/YYYY	unitless
End_Time_UTC	Time (UTC) at end of sample collection; format: hh:mm	unitless
End_ISO_DateTime_UTC	Date and time (UTC) at end of sample collection in ISO8601 format: YYYY-MM-DDThh:mmZ	unitless
Start_Latitude	Latitude at start of sample collection	decimal degrees North
Start_Longitude	Longitude at start of sample collection	decimal degrees East
End_Latitude	Latitude at end of sample collection (not recorded)	decimal degrees North
End_Longitude	Longitude at end of sample collection (not recorded)	decimal degrees East
Event_ID	Event number	unitless
Sample_ID	GEOTRACES sample number	unitless
Sample_Depth	Sample depth	meters (m)
CRS_SPT_CONC_PUMP_gdxntc	Particulate chromium reducible sulfide (pCRS) determined in situ (pump) for small particles	picomoles per liter (pmol/L)
SD1_CRS_SPT_CONC_PUMP_gdxntc	One standard deviation of CRS_SPT_CONC_PUMP_gdxntc	picomoles per liter (pmol/L)
Flag_CRS_SPT_CONC_PUMP_gdxntc	Quality flag for CRS_SPT_CONC_PUMP_gdxntc	unitless
AVS_SPT_CONC_PUMP_zix9yr	Particulate acid volatile sulfide (pAVS) determined in situ (pump) for small particles	picomoles per liter (pmol/L)
SD1_AVS_SPT_CONC_PUMP_zix9yr	Standard deviation of AVS_SPT_CONC_PUMP_zix9yr	picomoles per liter (pmol/L)

Flag_AVS_SPT_CONC_PUMP_zix9yr	Quality flag for AVS_SPT_CONC_PUMP_zix9yr	unitless

[table of contents | back to top]

Instruments

Dataset-specific Instrument Name	VWR circulating water bath (model 1130S)
Generic Instrument Name	circulating water bath
Generic Instrument Description	A device designed to regulate the temperature of a vessel by bathing it in water held at the desired temperature. [Definition Source: NCI]

Dataset-specific Instrument Name	HP flame photometric detector (model 19256A)
Generic Instrument Name	flame photometric detector
Generic Instrument Description	The determination of sulfur or phosphorus containing compounds is the job of the flame photometric detector (FPD). This device uses the chemiluminescent reactions of these compounds in a hydrogen/air flame as a source of analytical information that is relatively specific for substances containing these two kinds of atoms. The emitting species for sulfur compounds is excited S2. The lambda max for emission of excited S2 is approximately 394 nm. The emitter for phosphorus compounds in the flame is excited HPO (lambda max = doublet 510-526 nm). In order to selectively detect one or the other family of compounds as it elutes from the GC column, an interference filter is used between the flame and the photomultiplier tube (PMT) to isolate the appropriate emission band. The drawback here being that the filter must be exchanged between chromatographic runs if the other family of compounds is to be detected.

Dataset-specific Instrument Name	Hewlett Packard (HP) 5890 Series II gas chromatograph
Generic Instrument Name	Hewlett Packard 5890 Series II gas chromatograph
Generic Instrument Description	A gas chromatograph that separates and analyses compounds that do not degrade or decompose in the gas phase. The sample is dissolved in a solvent and vaporised in the instrument. A chemically inert gas, (e.g. helium or nitrogen) carries the vaporised analyte through a stationary phase which is coated inside the capillary column that is maintained at an elevated temperature. The analyte mixture separates on the stationary phase leading to chromatographic separation of the molecules. The HP 5890 Series II is completely customisable depending on the application, with choices of inlets, columns, detectors, sampling systems, flow and pressure control components. Optional detectors include Flame Ionization Detector (FID), Nitrogen-Phosphorus Detector (NPD), Electron Capture Detector (ECD), Thermal Conductivity Detector (TCD), Photoionisation Detector (PID), Flame Photometric Detector (FPD) and mass spectrometer. The instrument was originally manufactured by Hewlett Packard (HP), but part of this business was sold to Agilent Technologies in 1999. This model is no longer in production.

Dataset-specific Instrument Name	VWR hydrogen generator (model H2PEM-165)
Generic Instrument Name	hydrogen generator
Generic Instrument Description	A gas generator that generates hydrogen gas.

Dataset-specific Instrument Name	modified McLane in-situ pumps
Generic Instrument Name	McLane Pump
Generic Instrument Description	McLane pumps sample large volumes of seawater at depth. They are attached to a wire and lowered to different depths in the ocean. As the water is pumped through the filter, particles suspended in the ocean are collected on the filters. The pumps are then retrieved and the contents of the filters are analyzed in a lab.

Dataset-specific Instrument Name	mini-MULVFS
Generic Instrument Name	Multiple Unit Large Volume Filtration System
Generic Instrument Description	The Multiple Unit Large Volume Filtration System (MULVFS) was first described in Bishop et al., 1985 (doi: 10.1021/ba-1985-0209.ch009). The MULVFS consists of multiple (commonly 12) specialized particulate matter pumps, mounted in a frame and tethered to the ship by a cable (Bishop et al., 1985; Bishop and Wood, 2008). The MULVFS filters particulates from large volumes of seawater, although the exact protocols followed will vary for each project.

[table of contents | back to top]

Deployments

RR1814

Website	https://www.bco-dmo.org/deployment/776913
Platform	R/V Roger Revelle
Report	https://datadocs.bco-dmo.org/docs/geotraces/GEOTRACES_PMT/casciotti/data_docs/GP15_Cruise_Report_with_ODF_Report.pdf
Start Date	2018-09-18
End Date	2018-10-21
Description	Additional cruise information is available from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/RR1814

[table of contents | back to top]

Project Information

US GEOTRACES Pacific Meridional Transect (GP15) (U.S. GEOTRACES PMT)

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

Coverage: Pacific Meridional Transect along 152W (GP15)

A 60-day research cruise took place in 2018 along a transect form Alaska to Tahiti at 152° W. A description of the project titled "*Collaborative Research: Management and implementation of the US GEOTRACES Pacific Meridional Transect*", funded by NSF, is below. Further project information is available on the US GEOTRACES website and on the cruise blog. A detailed cruise report is also available as a PDF.

Description from NSF award abstract:

GEOTRACES is a global effort in the field of Chemical Oceanography in which the United States plays a major role. The goal of the GEOTRACES program is to understand the distributions of many elements and their isotopes in the ocean. Until quite recently, these elements could not be measured at a global scale. Understanding the distributions of these elements and isotopes will increase the understanding of processes that shape their distributions and also the processes that depend on these elements. For example, many "trace elements" (elements that are present in very low amounts) are also important for life, and their presence or absence can play a vital role in the population of marine ecosystems. This project will launch the next major U.S. GEOTRACES expedition in the Pacific Ocean between Alaska and Tahiti. The award made here would support all of the major infrastructure for this expedition, including the research vessel, the sampling equipment, and some of the core oceanographic measurements. This project will also support the personnel needed to lead the expedition and collect the samples.

This project would support the essential sampling operations and infrastructure for the U.S. GEOTRACES Pacific Meridional Transect along 152° W to support a large variety of individual science projects on trace element and isotope (TEI) biogeochemistry that will follow. Thus, the major objectives of this management proposal are: (1) plan and coordinate a 60 day research cruise in 2018; (2) obtain representative samples for a wide variety of TEIs using a conventional CTD/rosette, GEOTRACES Trace Element Sampling Systems, and in situ pumps; (3) acquire conventional CTD hydrographic data along with discrete samples for salinity, dissolved oxygen, algal pigments, and dissolved nutrients at micro- and nanomolar levels; (4) ensure that proper QA/QC protocols are followed and reported, as well as fulfilling all GEOTRACES intercalibration protocols; (5) prepare and deliver all hydrographic data to the GEOTRACES Data Assembly Centre (via the US BCO-DMO data center); and (6) coordinate all cruise communications between investigators, including preparation of a hydrographic report/publication. This project would also provide baseline measurements of TEIs in the Clarion-Clipperton fracture zone (~7.5°N-17°N, ~155°W-115°W) where large-scale deep sea mining is planned. Environmental impact assessments are underway in partnership with the mining industry, but the effect of mining activities on TEIs in the water column is one that could be uniquely assessed by the GEOTRACES community. In support of efforts to communicate the science to a wide audience the investigators will recruit an early career freelance science journalist with interests in marine science and oceanography to participate on the cruise and do public outreach, photography and/or videography, and social media from the ship, as well as to submit articles about the research to national media. The project would also support several graduate students.

US GEOTRACES PMT: hydrogen sulfide as a strong ligand affecting trace metal cycling (PMT Hydrogen Sulfide)

NSF Award Abstract:
Trace metals like iron and zinc are essential for the growth of the microscopic plants (phytoplankton) that dominate photosynthesis in the sunlit surface ocean. Other trace metals like copper or mercury are highly toxic to these same organisms. Even at concentrations of as low as one gram in a trillion grams of seawater, trace elements can alter the community consumption of carbon dioxide and the production of oxygen by ocean ecosystems. The resulting beneficial and/or toxic response depends on the chemical form of each trace metal. Dissolved in seawater, these metals can exist either as individual, free ions or attached to other dissolved chemical compounds, generically called ligands. Complexation is the process by which trace metals become chemically attached to ligands. This project will study the complexation of six biologically important trace metals with a ligand known as hydrogen sulfide. Data from work done during an expedition in the Pacific Ocean from Alaska to Tahiti will provide new scientific insight on hydrogen sulfide's importance in controlling essential and toxic metal bioavailability in various marine waters and thus have scientific impact on ocean carbon and ecosystem models. A graduate student will play a leading role in the project. Educational opportunities will be greatly enhanced by working alongside other world-class scientists as a participant in a large collaborative program. Additional graduate learning and outreach will include communicating experiences and research findings with the public with a blog and by interactions with undergraduate students as a teaching assistant.

In the oxygenated ocean, hydrogen sulfide is biologically produced in sunlit surface waters and emitted from hydrothermal vents on ocean ridges. It can then complex dissolved trace metals or react with them to form insoluble metal sulfides. In both cases, the abundance and cycling of essential trace elements would be affected and the importance of these reactions are currently not known. These sulfide - trace metal studies will be conducted as part of the 2018 US GEOTRACES Pacific Meridional Transect (PMT), a cruise track that allows sampling of productive coastal waters, low nutrient surface waters, and plumes of metal- and sulfide-rich hydrothermal waters near the bottom. The dissolved ions of hydrogen sulfide will be measured at sea soon after collection. Metal sulfides contained in and on particles will also be filtered and analyzed. This project will address several specific scientific questions. To what degrees does sulfide complexation vary as a function of the various biological and chemical regimes encountered? Are essential metals removed by precipitating with hydrogen sulfide in the upper water column? Does the reaction of metals with hydrogen sulfide in hydrothermal waters stabilize these dissolved complexes and allow long range transport? Related study will develop from close collaborations with other GEOTRACES scientists studying trace metals and their complexation with ligands other that sulfide, providing overall context and novel capacity to fully understand trace element cycles in the ocean.

[table of contents | back to top]

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.

[table of contents | back to top]

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1737342

[table of contents | back to top]