Trace metal and organic iron ligand data collected during the PLUME RAIDERS cruise (RR2106) on the R/V Roger Revelle from 18 September - 6 November 2021 along the 16-18°S section of the Southern East Pacific Rise.

Website: https://www.bco-dmo.org/dataset/944890 Data Type: Cruise Results Version: 1 Version Date: 2024-12-03

Project

» Collaborative Research: Are Low-Temperature Hydrothermal Vents an Important but Overlooked Source of Stabilized Dissolved Iron to the Ocean? (PLUME RAIDERS)

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Abstract

This dataset includes the concentrations of total dissolvable iron and manganese, dissolved iron and manganese, and dissolved organic iron-binding ligands collected on the PLUME RAIDERS expedition. Samples were collected during the PLUME RAIDERS cruise (RR2106) on the R/V Roger Revelle from 18 September – 6 November 2021. The main study area was located along the 16-18°S section of the Southern East Pacific Rise, and the sampling was focused near the ride crest at depths below 1,500 m. Both the total dissolvable and dissolved iron and manganese concentrations were determined shipboard using flow injection analysis. The total organic iron-binding ligand data was generated both shipboard and in the lab using competitive ligand exchange adsorptive cathodic stripping voltammetry. The siderophore concentrations were measured following a solid phase extraction step, and then eluents were measured using inductively coupled plasma mass spectrometry. The dissolvable and dissolved metal data was generated by Dr. Joe Resing and Nathan Buck at NOAA-PMEL and the ligand and siderophore data was generated by Dr. Laura Moore and Dr. Randelle Bundy at the University of Washington.

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Coverage

Location: Sub-tropical South Pacific between 16-18 deg South, primarily below 1500 m.

Methods & Sampling

Seawater collection

Seawater was collected using 10 L Teflon-coated GO-Flo bottles (General Oceanics) with the U.S. GEOTRACES trace metal rosette sampling system (Cutter and Bruland, 2012). The rosette was additionally outfitted with a miniature autonomous plume recorder (MAPR; (Baker, 1997) which included an oxidation reduction potential (ORP) and light scattering sensors, and an ultra-short baseline (USBL) transponder to ensure precise site locations on repeat casts. Two bottles were tripped at every depth to ensure adequate volumes of seawater were obtained for sample analysis. Samples were taken for dissolved gases, total dissolvable Fe (dtFe) and total dissolvable Mn (tdMn), dissolved Fe (dFe) and dissolved Mn (dMn), and total suspended particle analysis, all of which were sampled from even numbered bottles. All cleaning and sampling procedures were done according to GEOTRACES cookbook protocols (Cutter et al., 2017; Cutter and Bruland, 2012).

Dissolved and total dissolvable iron and manganese analyses

All samples for tdFe, dFe, tdMn, and dMn were measured shipboard using flow injection analysis (FIA) and analyzed within 6-8 hours of sample collection. The dFe, tdFe, dMn, and tdMn samples were measured using direct injection FIA with spectrophotometric detection modified from (Measures et al., 1995) and detailed in (Sedwick et al., 2008) for Fe and from (Resing and Mottl, 1992) for Mn. Detection limits for Mn and Fe were 1 nM and 1.5 nM, respectively.

Organic iron-binding ligand analyses

Samples for dFe-binding organic ligands were measured using competitive ligand exchange adsorptive cathodic stripping voltammetry (CLE-ACSV) (Abualhaija and van den Berg, 2014; Rue and Bruland, 1995). All titrations were performed on a controlled growth mercury electrode (CGME, Bioanalytical Systems Incorporated) equipped with an Ag/AgCl reference electrode and platinum auxiliary electrode, with a mercury drop size of 14 and acid-cleaned Teflon analytical cell (Bioanalytical Systems Incorporated). Samples for which dFe concentrations were less than 10 nM were first analyzed using the forward titration method using a 5 µM salicyladoxime analytical window (Abualhaija and van den Berg, 2014). Briefly, samples were thawed, and 10 mL were aliquoted into each of 15 acid-cleaned and conditioned Teflon vials (Savillex Corporation). Then 10 µL of 1.5 M boric acid buffer (boric acid, Alfa Aesar 99.99% metals basis, in 0.4 N Optima NH4OH, Fisher Scientific) was added to each vial for a final concentration of 5 μ M to achieve a pH of 8.2. Next 12.5 μ L of 4M salicylaldoxime (Fluka > 98% assay in Optima MeOH, Fisher Scientific) was then added to each vial for a final concentration of 5µM. The dFe standards (Diluted from SpexCertiPrep in pH 2 HCl) were then added to each vial, ranging 0-10 nM for final concentrations. Aliguots were then equilibrated overnight prior to electrochemical analysis using differential pulse stripping voltammetry (0 to -800 mV), with a 120-180s deposition period with stirring at 0 mV. After the final aliquot was analyzed, 5 nM of dFe standard was added and the aliquot was remeasured to ensure complete titration of the ligands. Peak heights were obtained using ECD-Soft and ligand concentrations and binding strengths were calculated using ProMCC (Omanović et al., 2015) with an inorganic side reaction coefficient of $\log \alpha_{Fe'} = 10$ (Abualhaija and van den Berg, 2014).

For samples where forward titrations showed no curvature, indicating excess ligands were present, or in the case where dFe in the sample was > 10 nM, reverse titrations were completed, employing 1-nitroso-2-naphthol (NN) as the competing ligand. The procedure and theory are described in detail elsewhere (Hawkes et al., 2013). Briefly, samples were thawed and 10 mL were aliquoted into 10 acid-cleaned and conditioned Teflon vials (Savillex Corporation). Then 10 μ L of boric acid buffer was added to each vial for a final concentration of 5 μ M and pH of 8.2. The NN standard (Sigma Aldrich) was prepared in methanol (Optima, Fisher Scientific) and was then added to each vial to achieve final concentrations ranging 0-40 μ M, and aliquots were left to equilibrate overnight. After equilibration, samples were analyzed electrochemically using linear sweep voltammetry (-150 to -650 mV) after a 5-minute nitrogen purge (ultra high purity, Airgas) and a 120 s deposition time at -50 mV. Three standard additions of dFe standard were added to the final aliquot and analyzed to calculate the amount of dFe that was exchangeable with NN under the analytical conditions. The estimates of exchangeable dFe often exceeded the ambient dFe concentrations in the samples. In these cases, all ambient dFe was assumed to be exchangeable. Peak heights were obtained using ECD-Soft, and ligand concentrations and binding strengths were calculated using publicly available R code (Hawkes et al., 2013) with the unsaturated Fe fit with log $\alpha_{Fe'}$ = 9.8 as the inorganic side reaction coefficient.

Siderophore analyses

At sea, four liters of 0.2 µm filtered seawater (Acropak 200, Pall Corporation) were collected for siderophore analyses. Prior to solid phase extraction, columns were activated with 2 column volumes of ultrapure methanol (Fisher, Optima grade) and rinsed with 2 column volumes of ultrapure Milli-Q water. Filtered seawater samples were then pumped continuously (~15-18 mL min-1) onto a Bond Elut solid phase extraction column (1g ENV, 6 mL, Agilent Technologies). After solid phase extraction, columns were again rinsed with at least 2 column volumes of Milli-Q water to flush remaining sea salts then stored frozen at -20°C prior to analysis. In the laboratory, columns were thawed in the dark at room temperature and then rinsed with 2 column volumes of Milli-Q water to remove any additional salts. Columns were then eluted with 12 mL ultrapure methanol into 15 mL acid-washed and methanol-rinsed falcon tubes. Eluent was then concentrated to ~0.5 mL on a vacuum concentrator with a refrigerated vapor trap (SpeedVac, Thermo Scientific) and transferred to clean 2 mL low density polyethylene vials. Extracts were weighed to determine exact volumes then frozen at -20°C until analysis.

Samples were analyzed using liquid chromatography (LC) coupled to an inductively coupled plasma mass spectrometer (ICP-MS) and an electrospray ionization mass spectrometer (ESI-MS). For each analysis, 100 μ L of sample was combined with a spike of 15 μ L of 5 μ M cyanocobalamin internal standard then injected and separated using a Dionex 3000 LC system equipped with a ZORBAX-SB C18 trap column (0.5x35 mm, 3.5 μ m, Agilent technologies) and a ZORBBAX-SB C18 working column (0.5x150 mm, 5 μ m, Agilent technologies) after the method of (Li et al., 2021). For each sample, a 62.5 μ L injection was loaded onto the trap column at 25 μ L/min with a 5-minute isocratic elution of solvent C (5% Optima methanol in 95% Milli-Q water, with 5 mM ammonium formate). Samples were then separated on working column using a flow rate of 40 μ L/min at 30°C beginning with a 5-minute isocratic elution of 95% solvent A (Milli-Q water with 5 mM ammonium formate) and 5% solvent B (Optima methanol with 5 mM ammonium formate buffer) followed by a 20 minute gradient from 95% solvent B to 95% solvent B, then a 10-minute isocratic elution at 95% solvent B, followed by a 5 minute gradient from 90% solvent B to 95% solvent B, then a 5-minute isocratic elution at 95% solvent B and a 13 minute conditioning step at 5% solvent B prior to the next injection. The same chromatography structure was used for both LC-ICP-MS and LC-ESI-MS (Boiteau et al., 2016; Bundy et al., 2018; Park et al., 2023).

Samples were introduced from the LC to the ICP-MS (iCAP-RQ; Thermo Scientific) via a PFA-ST nebulizer (Elemental Scientific) and spray chamber cooled to 2.7°C. The ICP-MS was equipped with platinum sample and skimmer cones and a 10% oxygen flow was added to the sample chamber to prevent organic matter precipitation on the cones. Analyses were made in kinetic energy discrimination (KED) mode with a helium collision flow rate of 4.0-4.2 mL/min. ⁵⁶Fe peaks were identified using an in-house R code with a peak threshold of 700 counts above the large background of non-chromatographically resolved dFe-binding organic matter. All identified 56Fe peaks were considered putative siderophores. Putative siderophore concentrations were calculated using a standard curve of ferrioxamine E (25-200 nM) (Boiteau et al., 2016; Bundy et al., 2018; Park et al., 2023). A 50 nM ferrioxamine E standard followed by a MilliQ blank were analyzed every six samples to adjust for instrument drift and ensure minimal carryover between samples.

Data Processing Description

Organic iron-binding ligands

Peak heights were obtained using ECD-Soft, and ligand concentrations and binding strengths were calculated using publicly available R code (Hawkes et al., 2013) with the unsaturated Fe fit with $\log \alpha_{Fe'} = 9.8$ as the inorganic side reaction coefficient.

BCO-DMO Processing Description

* adjusted parameter names to comply with database requirements

* added ISO_DateTime_UTC to dataset

* Added flags (under detection limit) as separate column to preserve numeric column formats. Changed flag BDL (1 occurrence) to ND for consistency (in column dMn_nM_flag).

Related Publications

Abualhaija, M. M., & van den Berg, C. M. G. (2014). Chemical speciation of iron in seawater using catalytic cathodic stripping voltammetry with ligand competition against salicylaldoxime. Marine Chemistry, 164, 60–74. doi:<u>10.1016/j.marchem.2014.06.005</u> *Methods*

Boiteau, R. M., & Repeta, D. J. (2015). An extended siderophore suite from Synechococcus sp. PCC 7002 revealed by LC-ICPMS-ESIMS. Metallomics, 7(5), 877–884. https://doi.org/<u>10.1039/c5mt00005j</u> *Methods*

Bundy, R. M., Boiteau, R. M., McLean, C., Turk-Kubo, K. A., McIlvin, M. R., Saito, M. A., Van Mooy, B. A. S., & Repeta, D. J. (2018). Distinct Siderophores Contribute to Iron Cycling in the Mesopelagic at Station ALOHA. Frontiers in Marine Science, 5. https://doi.org/<u>10.3389/fmars.2018.00061</u> *Methods*

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*

Cutter, Gregory, Casciotti, Karen, Croot, Peter, Geibert, Walter, Heimbürger, Lars-Eric, Lohan, Maeve, Planquette, Hélène, van de Flierdt, Tina (2017) Sampling and Sample-handling Protocols for GEOTRACES Cruises. Version 3, August 2017. Toulouse, France, GEOTRACES International Project Office, 139pp. & Appendices. DOI: http://dx.doi.org/<u>10.25607/OBP-2</u> *Methods*

Hawkes, J. A., Gledhill, M., Connelly, D. P., & Achterberg, E. P. (2013). Characterisation of iron binding ligands in seawater by reverse titration. Analytica Chimica Acta, 766, 53–60. https://doi.org/<u>10.1016/j.aca.2012.12.048</u> *Methods*

Measures, C. I., Yuan, J., & Resing, J. A. (1995). Determination of iron in seawater by flow injection analysis using in-line preconcentration and spectrophotometric detection. Marine Chemistry, 50(1-4), 3–12. doi:<u>10.1016/0304-4203(95)00022-j</u> *Methods*

Omanović, D., Garnier, C., & Pižeta, I. (2015). ProMCC: An all-in-one tool for trace metal complexation studies. Marine Chemistry, 173, 25–39. doi:<u>10.1016/j.marchem.2014.10.011</u> *Methods*

Park, J., Durham, B. P., Key, R. S., Groussman, R. D., Bartolek, Z., Pinedo-Gonzalez, P., Hawco, N. J., John, S. G., Carlson, M. C. G., Lindell, D., Juranek, L. W., Ferrón, S., Ribalet, F., Armbrust, E. V., Ingalls, A. E., & Bundy, R. M. (2023). Siderophore production and utilization by marine bacteria in the North Pacific Ocean. Limnology and Oceanography, 68(7), 1636–1653. Portico. https://doi.org/<u>10.1002/lno.12373</u> *Methods*

Resing, J. A., & Mottl, M. J. (1992). Determination of manganese in seawater using flow injection analysis with on-line preconcentration and spectrophotometric detection. Analytical Chemistry, 64(22), 2682–2687. doi:<u>10.1021/ac00046a006</u> *Methods*

Rue, E. L., & Bruland, K. W. (1995). Complexation of iron(III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. Marine Chemistry, 50(1-4), 117–138. doi:<u>10.1016/0304-4203(95)00031-1</u> *Methods*

Sedwick, P. N., Bowie, A. R., & Trull, T. W. (2008). Dissolved iron in the Australian sector of the Southern Ocean (CLIVAR SR3 section): Meridional and seasonal trends. Deep Sea Research Part I: Oceanographic Research Papers, 55(8), 911–925. https://doi.org/<u>10.1016/j.dsr.2008.03.011</u> *Methods*

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Parameters

Parameter	Description	Units
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GT_number	geotraces number for each sample	unitless
Cruise	cruise name	unitless
Station	station name	unitless
Cast_number	cast number	unitless
Rosette	rosette type, either trace metal or hydrothermal (regular CTD)	unitless
Site_Name	name of each process study site	unitless
Station_ID	extended number assocaited with each station (needed for NOAA)	unitless
Bottle_Position	bottle position on rosette	unitless
Nisken_number	Niskin bottle number	unitless
Date	date	unitless
Time_GMT	time	unitless
ISO_DateTime_UTC	Date Time in ISO format (UTC timzone)	unitless
Pressure_dbar	pressure	dbars
Depth_m	depth	meters
Temp_degC	temperature	degrees celsius
Salinity_PSU	salinty	psu
Sigma_Theta_kg_m3	density	kg/m3
ORP_mv	oxidation reduction potential	millivolts
Longitude	longitude, west is negative	decimal degrees

Latitude	latitude, south is negative	decimal degrees
tFe_nM	total dissolvable iron	nanomolar
dFe_nM	dissolved iron	nanomolar
dFe_nM_flag	flag for dissolved iron: ND = below detection limit	unitless
tMn_nM	total dissolvable manganese	nanomolar
tMn_nM_flag	flag for otal dissolvable manganese: ND = below detection limit	unitless
dMn_nM	dissolved manganese	nanomolar
dMn_nM_flag	flag for dissolved manganese: ND = below detection limit	unitless
Siderophores_pM	siderophore concentration	picomolar
Siderophores_pM_flag	flag for siderophore concentration: ND = below detection limit	unitless
Free_Fe_pM	inorganic dissolved Fe	picomolar
error_Free_Fe_pM	95% confidence interval of inorganic Fe	picomolar
L_nM	organic iron-binding ligand concentration, ND is below detection limit	nanomolar
error_L_nM	95% confidence interval of orgnaic Fe binding ligands	nanomolar
logK	conditional stability constant of Fe-binding ligands, ND is below detection limit	unitless
error_logK	95% confidence interval of orgnaic Fe binding ligand condtional stability constant	unitless

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Instruments

Dataset- specific Instrument Name	CTD profiler (Seabird Scientific)
Generic Instrument Name	CTD - profiler
Generic Instrument Description	The Conductivity, Temperature, Depth (CTD) unit is an integrated instrument package designed to measure the conductivity, temperature, and pressure (depth) of the water column. The instrument is lowered via cable through the water column. It permits scientists to observe the physical properties in real-time via a conducting cable, which is typically connected to a CTD to a deck unit and computer on a ship. The CTD is often configured with additional optional sensors including fluorometers, transmissometers and/or radiometers. It is often combined with a Rosette of water sampling bottles (e.g. Niskin, GO-FLO) for collecting discrete water samples during the cast. This term applies to profiling CTDs. For fixed CTDs, see https://www.bco-dmo.org/instrument/869934 .

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Deployments

RR2106	

Website	https://www.bco-dmo.org/deployment/944918
Platform	R/V Roger Revelle
Start Date	2021-09-18
End Date	2021-11-06

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Project Information

Collaborative Research: Are Low-Temperature Hydrothermal Vents an Important but Overlooked Source of Stabilized Dissolved Iron to the Ocean? (PLUME RAIDERS)

Coverage: Southern East Pacific Rise

NSF Award Abstract:

Hydrothermal vents are hot springs on the seafloor. They are often thousands of meters below the surface of the ocean along the large volcanic mountain ranges called the mid-ocean ridges. Relatively little is known about these hydrothermal vents because they exist so far from the ocean surface. Instead of lava, these vents emit warm to hot fluids (from several ^oC up to 350 ^oC) into the ocean, and contain high concentrations of a wide range of dissolved chemicals. One of these chemicals, iron, has been studied extensively by ocean scientists because of its importance as an essential nutrient for the microscopic photosynthetic algae called phytoplankton that grow in surface ocean waters. Scientists once thought that most of the dissolved iron coming out of hydrothermal vent fluids would quickly precipitate (form a solid and sink) near the vents, as a result of chemical reactions between the hot vent fluid and cold seawater, and therefore only small amounts of dissolved iron could be transported from the deep sea mid-ocean ridges to surface waters where phytoplankton grow. However, on a recent scientific expedition over one of the most active mid-ocean ridges called the southern East Pacific Rise (SEPR), scientists discovered that much of the dissolved iron discharged from the SEPR hydrothermal vents was in fact transported thousands of kilometers across the deep ocean. In addition, computer simulations suggest that a substantial amount of this 'hydrothermal iron' is transported as far as the surface waters of the Southern Ocean around Antarctica, where it could support the growth of phytoplankton.

Scientists from the University of Washington, Woods Hole Oceanographic Institution and Old Dominion University will return to the SEPR aboard a research ship and make additional measurements to better understand how hydrothermal vents add dissolved iron to the deep ocean. They will use specialized sampling equipment, including unmanned miniature submarines called autonomous underwater vehicles (AUVs), to map the distribution of hydrothermal vents in this region, and collect water samples from both high temperature (250-350 °C) and low temperature (< 150 °C) vents. These samples will be analyzed for chemicals that are enriched in the hydrothermal vent fluids, such as iron, manganese and helium-3, which will provide information on the chemical changes that occur as the hydrothermal vent fluids mix with surrounding seawater and are carried away from the SEPR. The scientists will use their observations and chemical analyses to address the following major questions: 1) are there more hydrothermal vents along mid ocean ridges than previously thought? and (2) are low temperature hydrothermal vents especially favorable for stabilizing dissolved iron, and ultimately transporting it to the surface ocean where it supports phytoplankton growth?

The project will contribute to the education and training of a graduate student and two senior undergraduate students, and outcomes will be incorporated into high school STEM curricula. The research activities will be communicated via public lectures and media releases, and project results will be disseminated to the scientific community by conference presentations, publications in peer-reviewed scientific journals, and freely available on-line archived data.

Along thousands of kilometers of the seafloor volcanic chains known as the mid-ocean ridges, hydrothermal vents discharge hot, acidic, metal-rich fluids into the deep ocean. These submarine hot springs are a major gateway for the exchange of heat and chemicals between the solid earth and the deep ocean, and have received intensive scientific study during the last 40 years. This research has overwhelmingly focused on high temperature (~200-350°C) hydrothermal vents. Lower temperature (<150°C) hydrothermal venting has received relatively little attention, although results from recent observational and modeling studies point to the greater abundance of low temperature discharge along the mid-ocean ridges, and its potential importance for the input of elements and chemical compounds into the deep ocean. Among the elements that are enriched in hydrothermal vent fluids, iron has received attention because of its role as an essential nutrient for primary production in the surface ocean. It has long been thought that most of the dissolved iron discharged by hydrothermal vents is lost from solution close to mid-ocean ridge sources, and thus of limited importance for ocean chemistry. But this view has been challenged by recent studies which suggest that chemical stabilization of hydrothermal dissolved iron may facilitate its long-range transport in the deep ocean. In particular, results from the US GEOTRACES program have revealed the lateral transport of a plume of hydrothermal dissolved iron over several thousand kilometers westward from its source region on the southern East Pacific Rise (SEPR).

In this project, investigators from the University of Washington, Woods Hole Oceanographic Institution and Old Dominion University will carry out a field research program on the SEPR to test the overarching hypothesis that diffuse low-temperature hydrothermal venting is a major a source of chemically-stabilized dissolved iron to the deep ocean, and hence plays an important but previously overlooked role in the ocean iron cycle. The shipbased field program will use an autonomous underwater vehicle equipped with in-situ optical and chemical sensors to identify plumes of both diffuse (low-temperature) and discrete (high-temperature) hydrothermal discharge along the SEPR. Emissions from multiple sites of both low and high temperature hydrothermal venting will be sampled for shipboard and post-cruise analyses of iron and other trace metals, and the inert hydrothermal "tracer" helium-3. The resulting data will be used to test two specific hypotheses: (1) the population of active hydrothermal venting is conducive to the chemical stabilization of dissolved iron, thus facilitating its export to the ocean interior and ultimately to surface ocean where it supports primary production by phytoplankton. The information obtained in this research will facilitate inclusion of iron and other trace elements in numerical models of ocean biology and biogeochemistry, which will improve the ability to predict how the ocean will respond to and modulate future climatic and environmental changes.

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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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	<u>OCE-1756402</u>

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