Dissolved organic Fe-binding ligand data from the FRidge (GA13) expedition on RRS James Cook (cruise JC156) from December 2017 to February 2018

Website: https://www.bco-dmo.org/dataset/923065
Data Type: Cruise Results
Version: 1
Version Date: 2024-03-21

Project
» Are strong ligands and dissolved iron tightly coupled in hydrothermal systems? (organic iron ligands in hydrothermal systems)

Contributors	Affiliation	Role
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Abstract
Samples were collected as part of the 2017-2018 U.K. GEOTRACES GA13 section cruise along the Mid-Atlantic Ridge (Cruise JC156 on RRS James Cook). Water samples from 11 venting and near venting locations were collected using a Seabird 911 conductivity, temperature, and depth (CTD) titanium rosette using conducting Kevlar wire with an oxidation-reduction potential (ORP) sensor to detect plumes. Teflon coated OTE (Ocean Test Equipment) bottles were pressurized to approximately 7 psi with 0.2 µm filtered air using an oil-free compressor. A Sartobran 300 (Sartorius) filter capsule (0.2 µm) was used to collect filtered seawater samples into clean 250 mL LDPE sample bottles. Bottles and caps were rinsed 3 times with the filtered sample before being filled. Samples were stored frozen at -20°C for organic iron-binding ligand characterization by voltammetry using competitive ligand exchange adsorptive cathodic stripping voltammetry. All dissolved organic iron-binding ligand samples were measured with a BASi controlled growth mercury electrode with an Ag/AgCl¬- reference electrode and platinum auxiliary electrode (Bioanalytical Systems Incorporated) using previously established methods for forward titrations (Buck et al., 2015, 2018; Bundy et al., 2018; Abualhaija and van den Berg, 2014; Hawkes et al., 2013 (Planet. Sci. Lett.)). Reverse titrations (Hawkes et al., 2013 (Anal. Chim. Acta)) were completed on 10 samples from Broken Spur, and TAG hydrothermal vent fields with dissolved iron concentrations between 19.01-90.25 nM.

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Coverage

Location: North Atlantic Mid-Atlantic Ridge (~ 29N, -40E)
Spatial Extent: **N**:37.29 **E**:-32.28 **S**:26.03 **W**:-45.12

Methods & Sampling

Sampling and cruise transect

Samples were collected as part of the 2017-2018 U.K. GEOTRACES GA13 section cruise along the Mid-Atlantic Ridge. Water samples from 11 venting and near venting locations were collected using a Seabird 911 conductivity, temperature, and depth (CTD) titanium rosette using conducting Kevlar wire with an oxidation-reduction potential (ORP) sensor to detect plumes. Teflon coated OTE (Ocean Test Equipment) bottles were pressurized to approximately 7 psi with 0.2 micrometers (µm) filtered air using an oil-free compressor. A Sartobran 300 (Sartorius) filter capsule (0.2 µm) was used to collect filtered seawater samples into clean 250 milliliter (mL) LDPE sample bottles. Bottles and caps were rinsed 3 times with the filtered sample before being filled. Samples were stored frozen at -20 degrees Celsius (°C) for organic iron-binding ligand characterization by voltammetry and mass spectrometry.

Iron-binding ligand concentration and binding strengths measured with competitive ligand exchange-adsorptive cathodic stripping voltammetry

Iron-binding ligand concentrations and binding strengths were determined by competitive ligand exchange-adsorptive cathodic stripping voltammetry (CLE-ACSV) with a BASi controlled growth mercury electrode (CGME) with an Ag/AgCl- reference electrode and platinum auxiliary electrode (Bioanalytical Systems Incorporated). Using previously established methods (Buck et al., 2015, 2018; Bundy et al., 2018; Abualhaija and van den Berg, 2014; Hawkes et al., 2013 (Planet. Sci. Lett.)). 40 frozen filtrate (<0.2 µm) samples with dissolved iron concentrations between 0.41-11.67 nanomolar (nM) (Table S1-S2 of Hoffman et al., 2023) were thawed in a 4°C fridge prior to analysis. A 15-point titration curve was analyzed for each sample. Briefly, within each titration, every point sequentially received 10 mL of sample, 7.5 micromolar (µM) of borate-ammonium buffer, 10 µM salicylaldoxime (SA) as the added ligand, and a dissolved Fe addition. Data was collected using the Epsilon Eclipse Electrochemical Analyzer (v.213) with a deposition time of 120 seconds and analyzed using ElectroChemical Data Software (v2001-2014) and ProMCC (v2008-2018) to determine peak areas and iron-binding ligand parameters, respectively.

Reverse Titration-CLE-ACSV

Reverse titration-CLE-ACSV (RT-CLE-ACSV) (Hawkes et al., 2013 (Anal. Chim. Acta)) was completed on 10 samples from Broken Spur, and TAG hydrothermal vent fields with dissolved Fe concentrations between 19.01-90.25 nM (Table S1-S2 of Hoffman et al., 2023). Briefly, a 10-point titration curve was analyzed for each sample with each titration point consisting of 10 mL of sample buffered with 7.5 µM boric acid and the competitive ligand 1-nitroso-2-napthol (NN). All samples were analyzed on a BASi Controlled Growth Mercury Electrode (CGME) with the Epsilon Eclipse Electrochemical Analyzer (v.213) and deposition time of 120 seconds. For each sample, the competitive ligand NN was added in concentrations of 0.5, 1, 2, 3, 4, 6, 9, 15, 20, and 40 µM. Samples were equilibrated overnight and purged with N_2 (99.99% UHP) for 5 minutes before analysis. At the end of each titration, three dissolved iron additions (3-15 nM) were added to the final titration point to get the total concentration of iron in equilibrium with the natural ligands. Data was analyzed using ElectroChemical Data Software (v2001-2014) to acquire peak areas and a package in R using the model parameters of $\beta_{FeNN3} = 5.12 \times 10^{16}$, Xmin = 0.8, Xmax = 0.9, and *c1high* = 0.75 to determine the iron-binding ligand parameters (Hawkes et al., 2013 (Anal. Chim. Acta)). These parameters were chosen based on the recommendations for undersaturated samples and titrations curves where ipmax was not reached (Hawkes et al., 2013 (Anal. Chim. Acta)). All other parameters within the model we kept at the default values.

Data Processing Description

Forward titrations were analyzed using ElectroChemical Data Software (v2001-2014) and ProMCC (v2008-2018) to determine peak areas and Fe-binding ligand parameters, respectively.

Reverse titration data was analyzed using ElectroChemical Data Software (v2001-2014) to acquire peak areas and a package in R using the model parameters of $\beta_{FeNN3} = 5.12 \times 10^{16}$, Xmin = 0.8, Xmax = 0.9, and *c1high* = 0.75 to determine the Fe-binding ligand parameters (Hawkes et al., 2013 (Anal. Chim. Acta)).

Additional data for siderophore analyses have been deposited on Massive under the DOI 10.25345/C5V97ZW7N.

Microbial 16S rRNA data have been deposited on GenBank under the accession number BioProject #PRJNA865382.

BCO-DMO Processing Description

- Imported original file "FRidge_GA13_CSV_data_final_bcodmo.xlsx" into the BCO-DMO system.
- Flagged "NaN" as a missing data identifier. Missing data are empty/blank in the final CSV file.
- Renamed fields to comply with BCO-DMO naming conventions.
- Saved the final file as "923065_v1_ga13_diss_org_fe-binding_ligands.csv".

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Data Files

File	
923065_v1_ga13_diss_org_fe-binding_ligands.csv	(Comma Separated Values (.csv), 4.15 KB) MD5:da194bf71e6b69636cd9adff12eac119
Primary data file for dataset ID 923065, version 1	

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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:10.1016/j.marchem.2014.06.005
Methods

Buck, K. N., Sedwick, P. N., Sohst, B., & Carlson, C. A. (2018). Organic complexation of iron in the eastern tropical South Pacific: Results from US GEOTRACES Eastern Pacific Zonal Transect (GEOTRACES cruise GP16). Marine Chemistry, 201, 229–241. https://doi.org/10.1016/j.marchem.2017.11.007
Methods

Buck, K. N., Sohst, B., & Sedwick, P. N. (2015). The organic complexation of dissolved iron along the U.S. GEOTRACES (GA03) North Atlantic Section. Deep Sea Research Part II: Topical Studies in Oceanography, 116, 152–165. doi:10.1016/j.dsr2.2014.11.016
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/10.3389/fmars.2018.00061
Methods

Hawkes, J. A., Connelly, D. P., Gledhill, M., & Achterberg, E. P. (2013). The stabilisation and transportation of dissolved iron from high temperature hydrothermal vent systems. Earth and Planetary Science Letters, 375, 280–290. https://doi.org/10.1016/j.epsl.2013.05.047
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/10.1016/j.aca.2012.12.048
Methods

Hoffman, C. L., Monreal, P. J., Albers, J. B., Lough, A. J. M., Santoro, A. E., Mellett, T., Buck, K. N., Tagliabue, A., Lohan, M. C., Resing, J. A., & Bundy, R. M. (2023). Microbial strong organic ligand production is tightly coupled to iron in hydrothermal plumes. https://doi.org/10.1101/2023.01.05.522639
Results

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Related Datasets

IsRelatedTo

Randelle M. Bundy. (2022). MassIVE MSV000090721 - Hydrothermal Siderophore Analysis on UK GEOTRACES GA13 (FRidge) [Data set]. MassIVE. https://doi.org/10.25345/C5V97ZW7N

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Parameters

Parameter	Description	Units
Cruise	cruise number for the expedition	unitless
Latitude_deg_N	Latitude in degrees north	decimal degrees
Longitude_deg_E	Longitude in degrees east (negative values = West)	decimal degrees
Station	Station number	unitless
Geotraces_ID	Geotraces number for the corresponding sample	unitless
Depth_m	sample depth	meters (m)
dFe_nM	dissolved iron concentration	nanomoles per liter (nmol L-1)
L1_nM	dissolved organic iron-binding ligand concentration of L1 ligands	nanomoles per liter (nmol L-1)
L1_err_nM	95% confidence interval of dissolved organic iron-binding ligand L1 concentration	nanomoles per liter (nmol L-1)
L2_nM	dissolved organic iron-binding ligand concentration of L2 ligands	nanomoles per liter (nmol L-1)
L2_err_nM	95% confidence interval of dissolved organic iron-binding ligand L2 concentration	nanomoles per liter (nmol L-1)
L3_nM	dissolved organic iron-binding ligand concentration of L3 ligands	nanomoles per liter (nmol L-1)
L3_err_nM	95% confidence interval of dissolved organic iron-binding ligand L3 concentration	nanomoles per liter (nmol L-1)
LT_nM	dissolved organic iron-binding ligand concentration of total ligands	nanomoles per liter (nmol L-1)
LT_err_nM	95% confidence interval of dissolved organic iron-binding ligand total concentration	nanomoles per liter (nmol L-1)

logK1	dissolved organic iron-binding ligand strength of L1 ligands	unitless
logK1_err	95% confidence interval of dissolved organic iron-binding ligand L1 strength	unitless
logK2	dissolved organic iron-binding ligand strength of L2 ligands	unitless
logK2_err	95% confidence interval of dissolved organic iron-binding ligand L2 strength	unitless
logK3	dissolved organic iron-binding ligand strength of L3 ligands	unitless
log_K3_err	95% confidence interval of dissolved organic iron-binding ligand L3 strength	unitless

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Instruments

Dataset-specific Instrument Name	BASi Controlled Growth Mercury Electrode
Generic Instrument Name	BASi Controlled Growth Mercury Electrode
Dataset-specific Description	All samples were analyzed on a BASi Controlled Growth Mercury Electrode (CGME) with the Epsilon Eclipse Electrochemical Analyzer (v.213).
Generic Instrument Description	Bioanalytical Systems (BASi) Mercury drop electrodes are generated by the BASi Controlled Growth Mercury Electrode (CGME) in three modes: DME (Dropping Mercury Electrode) - mercury is allowed to flow freely from the reservoir down the capillary and so the growth of the mercury drop and its lifetime is controlled by gravity. (The optional 100 um capillary is recommended for this mode.) SMDE (Static Mercury Drop Electrode) - the drop size is determined by the length of time for which the fast-response capillary valve is opened, and the drop is dislodged by a drop knocker. The dispense/knock timing is microprocessor-controlled and is typically coordinated with the potential pulse or square-wave waveform. This mode can also used to generate the Hanging Mercury Drop Electrode required for stripping experiments. CGME (Controlled Growth Mercury Electrode) - the mercury drop is grown by a series of pulses that open the capillary valve. The number of pulses, their duration, and their frequency can be varied by PC control, providing great flexibility in both the drop size and its rate of growth. This CGME mode can be used for both polarographic and stripping experiments. http://www.basinc.com/products/ec/cgme.php

Dataset-specific Instrument Name	Epsilon Eclipse Electrochemical Analyzer
Generic Instrument Name	BASi EC-epsilon 2 Autoanalyzer
Dataset-specific Description	All samples were analyzed on a BASi Controlled Growth Mercury Electrode (CGME) with the Epsilon Eclipse Electrochemical Analyzer (v.213).
Generic Instrument Description	The Bioanalytical Systems EC epsilon is a family of potentiostat/galvanostats for electrochemistry. The most basic epsilon instrument can be used for standard techniques, as well as chronopotentiometry for materials characterization (e.g., characterization of transition metal complexes by cyclic voltammetry and controlled potential electrolysis, or of biosensors by cyclic voltammetry and constant potential amperometry). Pulse, square wave, and stripping techniques can be added by a software upgrade, and a second channel can be added by a hardware upgrade. http://www.basinc.com/products/ec/epsilon/

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

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Deployments

JC156

Website	https://www.bco-dmo.org/deployment/923071
Platform	RRS James Cook
Report	https://www.bodc.ac.uk/resources/inventories/cruise_inventory/reports/jc156.pdf
Start Date	2017-12-20
End Date	2018-02-01
Description	See more about this cruise at: https://www.bodc.ac.uk/resources/inventories/cruise_inventory/report/16349/

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Project Information

Are strong ligands and dissolved iron tightly coupled in hydrothermal systems? (organic iron ligands in hydrothermal systems)

Coverage: Mid-Atlantic Ridge and Escanaba Trough

NSF Award Abstract:
This award is funded in whole or in part under the American Rescue Plan Act of 2021 (Public Law 117-2).

Iron is one of the most abundant elements in the Earth’s crust, but it is extremely diluted in the ocean. Iron-poor surface waters limit the growth of microscopic marine life, called phytoplankton, and their ability to remove carbon from the atmosphere and surface ocean. However, over the last few decades, our understanding of how iron enters the ocean has evolved. Recent data has shown that deep-sea hot springs, also known as hydrothermal vents, impact global iron budgets and are important for surface iron supply. Hydrothermal vents are found globally along volcanic spreading centers where new seafloor is created through tectonic activity. The new porous seafloor allows seawater to circulate through the hot, chemically reactive rocks to create hydrothermal fluids. These fluids are less dense (hotter, 300-400°C) than deep ocean waters (2°C), so the water exiting the vents rises while mixing with ambient seawater, eventually forming hydrothermal plumes. These nutrient-rich plumes can extend for 10-1000s of kilometers into the ocean interior. To account for the long-range transport of hydrothermal iron into the ocean interior, models have shown that stabilizing agents (i.e. organic ligands) are needed to prevent iron from precipitating and settling to the seafloor. However, we still do not know the sources and identities of these organic ligands, as well as how common they are in various hydrothermal systems across the global ocean. Investigating these mechanism(s) for hydrothermal iron stabilization across different vent systems will provide insight into both local and long-range iron utilization by deep-sea marine microorganisms and phytoplankton in the surface ocean.

In this project, the sources, concentration, and identities of iron-binding organic ligands in hydrothermal plumes from four different volcanic spreading centers will be examined to understand their impact on iron stabilization and transport into the ocean interior. The major aim of this research is to test whether (1) the concentrations of strong organic ligands tightly control the distal transport of hydrothermally derived dissolved iron in neutrally buoyant plumes across a variety of hydrothermal vent systems and (2) investigate if microbes from hydrothermal systems are responsible for production of these strong organic ligands (i.e. siderophores). This work will use a combination of existing samples and samples of opportunity that will be collected during an upcoming field expedition, each from distinct spreading centers. These findings would significantly enhance our understanding of hydrothermal iron transport and aid in future modeling efforts on the fate of hydrothermal iron in the global iron cycle. This project will support the training of two early career scientists, an undergraduate intern, and STEM workshop kits for middle school programs about deep-sea environments, which will be developed in collaboration and made freely available through the NOAA Pacific Marine Environmental Education and Outreach webpage.

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)	OCE-2122928

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