# Spectral data from high pressure liquid chromatography coupled to mass spectrometry from R/V Thomas G. Thompson cruise TN303 in the Eastern Tropical Pacific from October to December 2013

**Website**: https://www.bco-dmo.org/dataset/739337
**Data Type**: Cruise Results
**Version**: 1
**Version Date**: 2018-06-27

**Project**
» The Biogeochemistry of Dissolved Iron-ligands in Marine Cyanobacteria and Seawater (Trace metal ligands)

| Contributors | Affiliation | Role |
|---|---|---|
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## Dataset Description

The mass spectral datafiles have been deposited at the Center for Computational Mass Spectrometry.

### Methods & Sampling

**Sample collection and processing:** Trace-metal clean filtered seawater was pumped by a tow-fish from 3m depth along the cruise track of the US GEOTRACES EPZT (GP16) cruise from October-December 2013 (Boiteau et al. 2016, Table S1). Each sample represents an integrated average signal across a wide region. Between 400-600L of seawater was filtered continuously at a flow rate of 250mL/min and extracted through custom-made solid phase extraction (SPE) columns packed with 20g ENV resin (Bondesil, Agilent). Prior to sample collection, SPE columns were activated with distilled methanol, flushed with ultra-high purity water (qH2O), acidified to pH 2 with dilute hydrochloric acid, and finally rinsed with qH2O. Samples were stored at -20 degrees C and returned to the laboratory for further analyses. Thawed SPE columns were rinsed with 500mL of qH2O, to remove salts and organic ligands were eluted with 250mL of methanol (MeOH). Extracts were concentrated by rotary evaporation and the final volume was adjusted to 6mL with qH2O. Samples were stored at -20 degrees C in polytetrafluoroethylene (PTFE) vials. Aliquots (1mL) of each concentrated sample were removed and spiked with 20uL of 50uM cyanocobalamin (Sigma Aldrich) as an internal standard. A sample blank was also collected by pumping only 200mL of filtered seawater through an SPE column, which was frozen, processed, and analyzed with the six seawater samples.

**Liquid chromatography:** Organic extracts were separated on an Agilent 1260 series bioinert high pressure liquid chromatography (HPLC) system fitted with a C8 column (Hamilton, 2.1x100mm, 3um particle size) and polyetheretherketone (PEEK) tubing and connectors. Ligands were eluted with (A) 5mM aqueous ammonium formate and (B) 5mM ammonium formate in distilled MeOH using a 50 minute gradient from 10-90% B, followed by isocratic elution at 90% B for 10 minutes at a flow rate of 0.2mL/min. A post column PEEK flow

splitter directed 50uL/min into the ICPMS or ESIMS.

**Inductively coupled plasma mass spectrometry (ICPMS):** The method for LC-ICPMS analysis was modified from Boiteau et al. (Analytical Chemistry, 2013). The flow of the LC column was coupled directly to a quadrupole ICPMS (iCAP Q, Thermo Scientific) using a perfluoroalkoxy micronebulizer (PFA-ST, Elemental Scientific) and a cyclonic spray chamber cooled to 0 degrees C. Oxygen gas was introduced to the plasma at 25 mL/min to prevent the deposition of reduced organics on the cones. The ICPMS was equipped with platinum sampler and skimmer cones. 56Fe, 57Fe, and 59Co were monitored with an integration time of 0.05 seconds each. Measurements were made in kinetic energy discrimination mode with a He collision gas introduced at a rate of 4.2 mL/min to remove ArO+ interferences on 56Fe. Peak areas were integrated and used to calculate concentrations with a six-point calibration curve of a ferrioxamine E standard solution (retention time = 19.8 min). Since only the iron-bound form is quantified by LC-ICPMS, samples were titrated with excess iron citrate and re-analyzed to quantify total siderophore concentrations. A 1:10 addition of the iron citrate stock solution was sufficient to saturate the unbound iron complexes.

**Electrospray ionization mass spectrometry (ESIMS) analysis:** For determination of the siderophore mass, the flow from the LC was coupled to an Orbitrap Fusion mass spectrometer (Thermo Scientific) equipped with a heated electrospray ionization source. ESI source parameters were set to a capillary voltage of 3500 V, sheath, auxiliary and sweep gas flow rates of 12, 6, and 2 (arbitrary units), and ion transfer tube and vaporizer temperatures of 300 degrees C and 75 degrees C. MS1 scans were collected in high resolution (450 K) positive mode. High energy collision induced dissociation (HCD) MS2 spectra were collected on the ion trap mass analyzer. Ions were trapped using a quadrupole isolation window of 1 m/z and were then fragmented using an HCD collision energy of 35%. Details of data analysis (41) are provided in the Supporting information.

#### Data Processing Description

The in-house algorithms used to process the data are deposited here: https://github.com/rboiteau/LC-ICPMS-ESIMS-feature-detection

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## Related Publications

Boiteau, R. M., Mende, D. R., Hawco, N. J., McIlvin, M. R., Fitzsimmons, J. N., Saito, M. A., … Repeta, D. J. (2016). Siderophore-based microbial adaptations to iron scarcity across the eastern Pacific Ocean. Proceedings of the National Academy of Sciences, 113(50), 14237–14242. doi:10.1073/pnas.1608594113
*Methods*

,
*Results*

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## Parameters

*Parameters for this dataset have not yet been identified*

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## Instruments

| | |
|---|---|
| **Dataset-specific Instrument Name** | Thermo-scientific iCap-Q mass spectrometer |
| **Generic Instrument Name** | Mass Spectrometer |
| **Generic Instrument Description** | General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components. |

| | |
|---|---|
| **Dataset-specific Instrument Name** | Thermo-scientific Orbitrap Fusion masss spectrometer |
| **Generic Instrument Name** | Mass Spectrometer |
| **Generic Instrument Description** | General term for instruments used to measure the mass-to-charge ratio of ions; generally used to find the composition of a sample by generating a mass spectrum representing the masses of sample components. |

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## Deployments

**TN303**

| | |
|---|---|
| **Website** | https://www.bco-dmo.org/deployment/499719 |
| **Platform** | R/V Thomas G. Thompson |
| **Report** | http://dmoserv3.whoi.edu/data_docs/GEOTRACES/EPZT/GT13_EPZT_ODFReport_All.pdf |
| **Start Date** | 2013-10-25 |
| **End Date** | 2013-12-20 |
| **Description** | A zonal transect in the eastern tropical South Pacific (ETSP) from Peru to Tahiti as the second cruise of the U.S.GEOTRACES Program. This Pacific section includes a large area characterized by high rates of primary production and particle export in the eastern boundary associated with the Peru Upwelling, a large oxygen minimum zone that is a major global sink for fixed nitrogen, and a large hydrothermal plume arising from the East Pacific Rise. This particular section was selected as a result of open planning workshops in 2007 and 2008, with a final recommendation made by the U.S.GEOTRACES Steering Committee in 2009. It is the first part of a two-stage plan that will include a meridional section of the Pacific from Tahiti to Alaska as a subsequent expedition. Figure 1. The 2013 GEOTRACES EPZT Cruise Track. [click on the image to view a larger version] Additional cruise information is available from the Rolling Deck to Repository (R2R): http://www.rvdata.us/catalog/TN303 |

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## Project Information

**The Biogeochemistry of Dissolved Iron-ligands in Marine Cyanobacteria and Seawater (Trace metal ligands)**

**Website**: http://www.whoi.edu/page.do?pid=130796

**Coverage**: Equatorial Pacific, Coastal California

NSF Award Abstract:

Micronutrient trace metals, such as iron and cobalt, are critical to all life on earth, and their availability in the environment can regulate the primary productivity in a region. In the ocean, up to 99.9% of dissolved iron, and to a lesser extent cobalt, are bound by strong organic binding molecules, known as ligands which control what fraction of these metals is available to organisms. To understand carbon and nutrient cycling in many remote areas of the ocean where trace metals limit primary production, it is important to understand the distribution and cycling of ligands. In this study, a researcher at the Woods Hole Oceanographic Institute will use novel techniques to assess the diversity and composition of natural iron and cobalt binding ligands in laboratory cultures of the globally abundant marine cyanobacteria Prochlorococcus and in seawater samples from the South Pacific Subtropical Gyre. This study will add significantly to the interpretation of iron and cobalt availability, and help to link measurements of elemental metal distributions, ligand concentrations and binding strengths, and assessments of the microbial community.

Broader Impacts: Results from the project would be incorporated into graduate level organic geochemistry classes taught by the proponent and be made publically available through the Massachusetts Institute of Technology and Woods Hole Oceanographic Institution websites. One graduate student would be supported and trained as part of this project. It is anticipated that undergraduate students would also have the opportunity to participate in the study during the summer months and learn about organic geochemistry, microbial biogeochemistry, and modeling.

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## Funding


| Funding Source | Award |
|---|---|
| NSF Division of Ocean Sciences (NSF OCE) | OCE-1356747 |


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