Dissolved Fe(II) from the southbound leg of the US GEOTRACES Arctic cruise (HLY1502) on USCGC Healy from August to October 2015

Website: https://www.bco-dmo.org/dataset/811614
Data Type: Cruise Results
Version: 2
Version Date: 2020-09-23

Project
» U.S. Arctic GEOTRACES Study (GN01) (U.S. GEOTRACES Arctic)

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

Contributors	Affiliation	Role
Lam, Phoebe J.	University of California-Santa Cruz (UCSC)	Principal Investigator
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Abstract

Dissolved Fe(II) concentrations were determined using an automated flow injection analysis system (FeLume II Waterville Analytical) employing a luminol chemiluminescence based detection system as described in King et al. (1995) and Heller et al. (2017). From published and ongoing work in the Peru and Chile oxygen minimum zones an optimized methodology for Fe(II) detection by luminol has been described in Croot et al. (2019). This work details some of the challenges and limitations of using luminol for dFe(II) detection. It should be noted that as Fe(II) is a transient redox species with a short half life in oxygenated seawater that is dependent on dissolved oxygen and pH, it is not possible to archive (preserve) samples for later analysis. Intercalibrations for Fe(II) have yet to be conducted in the context of GEOTRACES studies and should be pursued where logistically possible.

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Coverage

Spatial Extent: **N**:87.824 **E**:-147.8504 **S**:71.999 **W**:-162.5408
Temporal Extent: 2015-09-10 - 2015-10-08

Dataset Description

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(1995) and Heller et al. (2017).

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Methods & Sampling

Samples for in-situ dissolved Fe(II) (dFe(II)) detection (see Supplemental Files: Table 1 and Figure 1):
157 samples were as soon as possible analysed from the Geotraces carousel from Stn 38-66;
5 ice samples from Stn43 /46 (operated by Ana Aguilar, Rob Rember);
3 small boat surface samples from Stan60,61,66 (operated by Ana Aguilar, Rob Rember);
1 Multicorer niskin sample from Stn66 (operated by Greg Cutter).

Shipboard measurements were performed by Dr. Maija I. Heller for Fe(II) following a method by King et al. The photomultiplier (PMT) for analysis was borrowed from the FS Polarstern (Germany) at the North Pole from scientist Micha Rijkenberg, NIOZ, (Netherlands) since the PMT owned by UCSC (USA) was damaged at the beginning of the cruise, likely due to a bad power supply.

Dissolved Fe(II) concentrations were determined using an automated flow injection analysis system (FeLume II Waterville Analytical) employing a luminol chemiluminescence based detection system (King et al, 1995). Luminol, prepared in 18.2 MO Milli-Q water and buffered to pH 10.3 with ultra pure ammonia (here used quartz distilled at UCSC), reacts with an Fe(II)- containing solution, resulting in luminol oxidation with concurrent chemiluminescent emission (Rose & Waite, 2001; Croot & Laan, 2002). The FeLume was fitted with a standard quartz flow cell and a Hamamatsu HC135 photon counter configured with the following settings: flow rate: 2.5 mL per minute; photon counter integration time: 200 ms; load time: 20–40 s. The mixing and reaction occur in a spiral flow cell positioned in front of a photomultiplier tube. The sample and luminol reagent were directly continually mixed in the flow cell by omitting the injection valve (Rose & Waite, 2001; Hopkinson & Barbeau, 2007; Roy et al, 2008). Once the signal was in steady-state, the mean of the last 50 data points was used to determine the signal. Fe(II) was quantified by 6-8 standard additions of Fe(II) (typically 0.025, 0.05, 0.1, 0.2, 0.4 and 0.8 nM) to samples of seawater which were stored in the dark for several days and showed low initial signals for Fe(II). A 0.01 M Fe(II) stock solution was prepared with ferrous sulfate (Sigma) in 0.2 M HCl. A working Fe(II) standard solution (100 nM) was prepared daily. Detection limits were determined for dark corrected aged seawater samples where ferrous Fe was negligible based on a standard 3r evaluation of the baseline signal (Moffett, et al. 2007; Kondo & Moffett, 2013; Heller et al., 2017).

Instrumentation:
The chemiluminescence was detected with a Hamamatsu HC135 Photon counter build into a flow injection system (FeLume, Waterville Analytical, US) borrowed from NIOZ (Netherlands) as described above (Rijkenberg et al., 2014).

Problem Report:
The required PMT for analysis was borrowed from the FS Polarstern (Germany) at the North Pole from NIOZ scientist Micha Rijkenberg, (Netherlands), since the PMT owned by UCSC (USA) was damaged at the very beginning of the cruise, most likely by a faulty power supply.

Data Processing Description

Quality Control:
See Supplemental File "Figure 2" for examples for standard additions of Fe(II) and blank calculation of the above described method.

Quality Flags:
All data have been assigned quality flags using the GTSPP convention and interpretation. Values below the detection limit were flagged as QF=6 in the GTSPP convention (also adopted by SeaDataNet and recommended by the GEOTRACES programme):

1 = good—passed lab QC and oceanographically consistent;

2 = possibly good—oceanographically consistent, but have minor sampling/instrumental issues;

3 = possibly bad—not oceanographically consistent, or have major sampling/instrumental issues;

4 = bad—failed lab QC or known issue with samples;

6 = below detection limit;

9 = data missing (including all "nd").

BCO-DMO Processing:

Version history:

2020-05-15 - original data version;

2020-09-23 - made corrections to the following duplicate, erroneous sample and event numbers:

-- when {Event_ID} == '6303', replaced {Sample_ID} 11891 with 11591;

-- when {Start_Time_UTC} == '2015-09-10T10:19:00.00Z', replaced {Event_ID} 6249 with 6253.

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Data Files

File
dissolved_Fe_II.csv(Comma Separated Values (.csv), 26.40 KB) <div align=center>MD5:60e275ccef518c418f7c0dd874bc88b7</div> Primary data file for dataset ID 811614

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Supplemental Files

File
Figure 1 filename: Figure1.JPG   (JPEG Image (.jpg), 93.44 KB) MD5:c0371ba668889d89fe39a21f696e873b Figure 1: Station map for dissolved Fe(II) detection. Note that dFe(II) was only be sampled/detected in southbound basins of the GN01 cruise because of a damage to equipment owned by UCSC at the beginning of the expedition. Associated with GN01 Dissolved Fe dataset contributed by Phoebe Lam.
Figure 2 filename: Figure2.JPG   (JPEG Image (.jpg), 126.54 KB) MD5:d29eca9f55f8d573de9171b4e734950f Figure 2: Examples for standard additions of Fe(II) and blank calculation of the above described method. Associated with GN01 Dissolved Fe dataset contributed by Phoebe Lam.
Table 1 filename: Table1.JPG   (JPEG Image (.jpg), 150.83 KB) MD5:a7faa866271c4b68de8db4d6d1f1d672 Table 1: List of samples for in-situ dissolved Fe(II) (dFe(II)) detection; associated with GN01 Dissolved Fe dataset contributed by Phoebe Lam.

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Related Publications

Croot, P. L., & Laan, P. (2002). Continuous shipboard determination of Fe(II) in polar waters using flow injection analysis with chemiluminescence detection. Analytica Chimica Acta, 466(2), 261–273. doi:10.1016/s0003-2670(02)00596-2 <u>https://doi.org/10.1016/S0003-2670(02)00596-2</u>
Methods

Croot, P. L., Heller, M. I., & Wuttig, K. (2019). Redox Processes Impacting the Flux of Iron(II) from Shelf Sediments to the OMZ along the Peruvian Shelf. ACS Earth and Space Chemistry, 3(4), 537–549. doi:<u>10.1021/acsearthspacechem.8b00203</u>
Methods

Heller, M. I., Lam, P. J., Moffett, J. W., Till, C. P., Lee, J.-M., Toner, B. M., & Marcus, M. A. (2017). Accumulation of Fe oxyhydroxides in the Peruvian oxygen deficient zone implies non-oxygen dependent Fe oxidation. Geochimica et Cosmochimica Acta, 211, 174–193. doi:10.1016/j.gca.2017.05.019
Methods

Hopkinson, B. M., & Barbeau, K. A. (2007). Organic and redox speciation of iron in the eastern tropical North Pacific suboxic zone. Marine Chemistry, 106(1-2), 2–17. doi:10.1016/j.marchem.2006.02.008
Methods

King, D. W., Lounsbury, H. A., & Millero, F. J. (1995). Rates and Mechanism of Fe(II) Oxidation at Nanomolar Total Iron Concentrations. Environmental Science & Technology, 29(3), 818–824. doi:10.1021/es00003a033
Methods

Kondo, Y., & Moffett, J. W. (2013). Dissolved Fe(II) in the Arabian Sea oxygen minimum zone and western tropical Indian Ocean during the inter-monsoon period. Deep Sea Research Part I: Oceanographic Research Papers, 73, 73–83. doi:10.1016/j.dsr.2012.11.014
Methods

Moffett, J. W., Goepfert, T. J., & Naqvi, S. W. A. (2007). Reduced iron associated with secondary nitrite maxima in the Arabian Sea. Deep Sea Research Part I: Oceanographic Research Papers, 54(8), 1341–1349. doi:10.1016/j.dsr.2007.04.004
Methods

Rijkenberg, M. J. A., Middag, R., Laan, P., Gerringa, L. J. A., van Aken, H. M., Schoemann, V., … de Baar, H. J. W. (2014). The Distribution of Dissolved Iron in the West Atlantic Ocean. PLoS ONE, 9(6), e101323. doi:10.1371/journal.pone.0101323
Methods

Rose, A. L., & Waite, T. D. (2001). Chemiluminescence of Luminol in the Presence of Iron(II) and Oxygen: Oxidation Mechanism and Implications for Its Analytical Use. Analytical Chemistry, 73(24), 5909–5920. doi:10.1021/ac015547q
Methods

Roy, E. G., Jiang, C., Wells, M. L., & Tripp, C. (2008). Determining Subnanomolar Iron Concentrations in Oceanic Seawater Using a Siderophore-Modified Film Analyzed by Infrared Spectroscopy. Analytical Chemistry, 80(12), 4689–4695. doi:10.1021/ac800356p
Methods

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Parameters

Parameter	Description	Units
Station_ID	Station number	unitless
Start_Date_UTC	Date at start of sampling; format: YYYYMMDD	unitless
Start_Time_UTC	Date and time (UTC) at start of sampling; format: YYYY-MM-DDThh:mm:ss.ssZ	unitless
End_Date_UTC	Date at end of sampling; format: YYYYMMDD	unitless
End_Time_UTC	Date and time (UTC) at end of sampling; format: YYYY-MM-DDThh:mm:ss.ssZ	unitless
Start_Latitude	Latitude at start of sampling	degrees North

Start_Longitude	Longitude at start of sampling	degrees East
End_Latitude	Latitude at end of sampling	degrees North
End_Longitude	Longitude at end of sampling	degrees East
Event_ID	Event number	unitless
Sample_ID	GEOTRACES sample number	unitless
Sample_Depth	Sample depth	meters (m)
Fe_II_D_CONC_BOTTLE_07ordp	Concentration of dissolved Fe(II) from bottle samples	nanomoles per kilogram (nmol/kg)
SD1_Fe_II_D_CONC_BOTTLE_07ordp	One standard deviation of Fe_II_D_CONC_BOTTLE_07ordp	nanomoles per kilogram (nmol/kg)
Flag_Fe_II_D_CONC_BOTTLE_07ordp	Quality flag for Fe_II_D_CONC_BOTTLE_07ordp	unitless
Fe_II_D_CONC_ICE	Concentration of dissolved Fe(II) from ice samples	nanomoles per kilogram (nmol/kg)
SD1_Fe_II_D_CONC_ICE	One standard deviation of Fe_II_D_CONC_ICE	nanomoles per kilogram (nmol/kg)
Flag_Fe_II_D_CONC_ICE	Quality flag for Fe_II_D_CONC_ICE	unitless
Fe_II_D_CONC_BOAT_PUMP_wfzk5t	Concentration of dissolved Fe(II) from boat pump samples	nanomoles per kilogram (nmol/kg)
SD1_Fe_II_D_CONC_BOAT_PUMP_wfzk5t	One standard deviation of Fe_II_D_CONC_BOAT_PUMP_wfzk5t	nanomoles per kilogram (nmol/kg)
Flag_Fe_II_D_CONC_BOAT_PUMP_wfzk5t	Quality flag for Fe_II_D_CONC_BOAT_PUMP_wfzk5t	unitless
Sample_Type	Sample type	unitless
Notes	Notes/comments	unitless

Instruments

Dataset-specific Instrument Name	FeLume II Waterville Analytical
Generic Instrument Name	Flow Injection Analyzer
Generic Instrument Description	An instrument that performs flow injection analysis. Flow injection analysis (FIA) is an approach to chemical analysis that is accomplished by injecting a plug of sample into a flowing carrier stream. FIA is an automated method in which a sample is injected into a continuous flow of a carrier solution that mixes with other continuously flowing solutions before reaching a detector. Precision is dramatically increased when FIA is used instead of manual injections and as a result very specific FIA systems have been developed for a wide array of analytical techniques.

Dataset-specific Instrument Name	
Generic Instrument Name	GO-FLO Teflon Trace Metal Bottle
Generic Instrument Description	GO-FLO Teflon-lined Trace Metal free sampling bottles are used for collecting water samples for trace metal, nutrient and pigment analysis. The GO-FLO sampling bottle is designed specifically to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

Dataset-specific Instrument Name	photomultiplier
Generic Instrument Name	Photomultiplier
Generic Instrument Description	An instrument containing a photoelectric cell and a series of electrodes, used to detect and amplify the light from very faint sources.

Dataset-specific Instrument Name	Hamamatsu HC135
Generic Instrument Name	Photon Counter
Generic Instrument Description	Photon counting is a technique in which individual photons are counted using some single-photon detector (SPD).

Deployments

HLY1502

Website	https://www.bco-dmo.org/deployment/638807
Platform	USCGC Healy
Report	https://datadocs.bco-dmo.org/docs/302/geotraces/GEOTRACES_ARCTIC/data_docs/cruise_reports/healy1502.pdf
Start Date	2015-08-09
End Date	2015-10-12
Description	Arctic transect encompassing Bering and Chukchi Shelves and the Canadian, Makarov and Amundsen sub-basins of the Arctic Ocean. The transect started in the Bering Sea (60°N) and traveled northward across the Bering Shelf, through the Bering Strait and across the Chukchi shelf, then traversing along 170-180°W across the Alpha-Mendeleev and Lomonosov Ridges to the North Pole (Amundsen basin, 90°N), and then back southward along ~150°W to terminate on the Chukchi Shelf (72°N). Additional cruise information is available in the GO-SHIP Cruise Report (PDF) and from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/HLY1502

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Project Information

U.S. Arctic GEOTRACES Study (GN01) (U.S. GEOTRACES Arctic)

Website: https://www.geotraces.org/

Coverage: Arctic Ocean; Sailing from Dutch Harbor to Dutch Harbor (GN01)

Description from NSF award abstract:
In pursuit of its goal "to identify processes and quantify fluxes that control the distributions of key trace elements and isotopes in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions", in 2015 the International GEOTRACES Program will embark on several years of research in the Arctic Ocean. In a region where climate warming and general environmental change are occurring at amazing speed, research such as this is important for understanding the current state of Arctic Ocean geochemistry and for developing predictive capability as the regional ecosystem continues to warm and influence global oceanic and climatic conditions. The three investigators funded on this award, will manage a large team of U.S.scientists who will compete through the regular NSF proposal process to contribute their own unique expertise in marine trace metal, isotopic, and carbon cycle geochemistry to the U.S. effort. The three managers will be responsible for arranging and overseeing at-sea technical services such as hydrographic measurements, nutrient analyses, and around-the-clock management of on-deck sampling activites upon which all participants depend, and for organizing all pre- and post-cruise technical support and scientific meetings. The management team will also lead educational outreach activities for the general public in Nome and Barrow, Alaska, to explain the significance of the study to these communities and to learn from residents' insights on observed changes in the marine system. The project itself will provide for the support and training of a number of pre-doctoral students and post-doctoral researchers. Inasmuch as the Arctic Ocean is an epicenter of global climate change, findings of this study are expected to advance present capability to forecast changes in regional and globlal ecosystem and climate system functioning.

As the United States' contribution to the International GEOTRACES Arctic Ocean initiative, this project will be part of an ongoing multi-national effort to further scientific knowledge about trace elements and isotopes in the world ocean. This U.S. expedition will focus on the western Arctic Ocean in the boreal summer of 2015. The scientific team will consist of the management team funded through this award plus a team of scientists from U.S. academic institutions who will have successfully competed for and received NSF funds for specific science projects in time to participate in the final stages of cruise planning. The cruise track segments will include the Bering Strait, Chukchi shelf, and the deep Canada Basin. Several stations will be designated as so-called super stations for intense study of atmospheric aerosols, sea ice, and sediment chemistry as well as water-column processes. In total, the set of coordinated international expeditions will involve the deployment of ice-capable research ships from 6 nations (US, Canada, Germany, Sweden, UK, and Russia) across different parts of the

Arctic Ocean, and application of state-of-the-art methods to unravel the complex dynamics of trace metals and isotopes that are important as oceanographic and biogeochemical tracers in the sea.

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.

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1535854
NSF Division of Ocean Sciences (NSF OCE)	OCE-1438977