# Fe(II) measured shipboard on the GP17-ANT RVIB Palmer cruise NBP24-01 in the Amundsen Sea from November 2023 to January 2024

Website: https://www.bco-dmo.org/dataset/982741

**Data Type**: Cruise Results

Version: 1

Version Date: 2025-08-19

#### **Project**

» <u>Collaborative Research: US GEOTRACES GP17-ANT: Iron redox cycling in the Amundsen Sea in the water column</u> and shelf sediments (GP17-ANT Iron Redox)

Contributors	Affiliation	Role
Moffett, James W.	University of Southern California (USC)	Principal Investigator
Floback, Alexis	University of Southern California (USC)	Scientist
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

#### Abstract

Fe(II) was measured shipboard on the GEOTRACES GP17 (NBP2401) cruise within an hour of collection. Samples were collected from cores obtained by multicoring and from the water column using a trace metal clean rosette. Samples were analyzed by chemiluminescence, utilizing the oxidation of luminol, which is catalyzed by Fe(II). Most samples were collected within the Amundsen Sea Polynya, near the sediment water interface and in surface waters containing a large Phaeocystis bloom. Significant elevated Fe(II) was found near the sediment water interface in areas beneath zones of high primary production, where we might reasonably anticipate high concentrations of sinking organic matter. Phaeocystis blooms also had very high concentrations. Surprisingly, there was an elevated signal in the lower water column associated with circumpolar deep water, and we are unsure of where the Fe(II) came from. In general, higher bottom water concentrations of Fe(II) were associated with strong gradients in Fe(II) in porewaters close to the interface.

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#### Coverage

Location: Amundsen Sea

**Spatial Extent**: N:-60.001 E:-90.991 S:-74.382 W:-132.906

Temporal Extent: 2023-12-09 - 2024-01-13

#### Methods & Sampling

All reagents were prepared in acid-washed opaque low-density polyethylene (LDPE) bottles, to prevent trace metal contamination or degradation of the reagents by light. The luminol reagent was initially prepared as a concentrate, by mixing 0.796 grams (g) sodium luminol (Sigma), 250 milliliters (mL) Optima grade ammonium hydroxide solution (Fisher), high-purity water (18.2 megohms per centimeter ( $M\Omega$  cm<sup>-1</sup>)), and approximately 45 mL Optima grade hydrochloric acid (Fisher) to reach a final volume of 1 liter (L) and a pH of 10.25. To produce the working reagent,

the concentrated mixture was diluted in high-purity water by a factor of four and heated at 50 degrees Celsius (°C) for 9 to 12 hours in either an oven or a hot water bath. DTPA was prepared in high-purity water with final concentrations of 50 millimolar (mM) DTPA (Sigma-Aldrich) and 200 mM NaOH (Aldrich, trace metals basis). EDTA was prepared in high-purity water with a final concentration of 50 mM EDTA (Aldrich, trace metals basis) and 100 mM NaOH (Aldrich, trace metals basis). The MOPS (3-(N-Morpholino)propanesulfonic acid) buffer was prepared with a final concentration of 100 mM MOPS (Sigma) and 50 mM NaOH (Aldrich, trace metals basis) in high-purity water, so that the final pH was 7.2. All reagents were used within 1 month of preparation.

Because iron(II) oxidizes rapidly in seawater, standards were prepared individually and analyzed immediately. A primary stock of  $10^{-2}$  M Fe(II) was prepared by dissolving ammonium iron(II) sulfate in high-purity water acidified to pH 2 using Optima grade hydrochloric acid (Fisher). The low pH slows oxidation to negligible levels, but the standard was replaced monthly. A working stock was prepared by diluting the primary stock by a factor of  $10^4$  in high purity, creating a  $10^{-6}$  M solution at pH 6. This solution would oxidize to a significant extent within several hours, so it was always prepared fresh immediately before a calibration curve or an experiment using standards. This working stock was then added to iron(II) free seawater, acquired by filtering seawater through a 0.2 micrometer (µm) filter and storing in an opaque bottle at room temperature for at least 24 hours.

Dissolved iron(II) concentrations were measured using a luminol chemiluminescence-based FeLume flow-injection system (Waterville Analytical), with data collection and integration controlled by Waterville Analytical software. The hardware was similar to that used in a number of previous open-ocean studies. A standard quartz flow cell was used in conjunction with a Hamamatsu HC135 photon counter. The flow rate through the peristaltic pump was 2 milliliters per minute (mL min<sup>-1</sup>). The photon counter integration time was 200 milliseconds (ms), with two measurements per second for up to 360 seconds. All samples were introduced in acid-washed Teflon bottles.

#### **Data Processing Description**

Fe(II) was determined from raw photon counting data using linear regression, as described in the methods section above.

We estimated the difference between time of sampling and analysis. By combining our data with independent estimates of oxidation rates as a function of the very cold temperatures in the region, we can estimate the Fe(II) concentration at the point of sampling. The estimated Fe(II) concentrations at the time of collection are reported in the dataset.

#### **BCO-DMO Processing Description**

- Converted original file, "NBP2401 Moffett Fe(II)R2.xlsx" to CSV format, "NBP2401 Moffett Fe(II)R2.csv".
- Imported "NBP2401 Moffett Fe(II)R2.csv" into the BCO-DMO data processing system.
- Renamed fields to comply with BCO-DMO naming conventions.
- Removed the following empty columns: End\_Date\_UTC, End\_Time\_UTC, End\_Latitude, End\_Longitude, Rosette\_Position.
- Created date-time column in ISO 8601 format.
- Saved the final file as "982741 v1 amundsen sea nbp2401 fe2.csv".

#### **Problem Description**

We encountered isolated problems. Contamination at Station 3 ruined those samples, but the issues were resolved. A revised dataset will be generated when we receive the total dissolved iron data.

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#### **Related Publications**

Bolster, K. M., Heller, M. I., & Moffett, J. W. (2018). Determination of iron(II) by chemiluminescence using masking ligands to distinguish interferences. Limnology and Oceanography: Methods, 16(11), 750–759. doi:10.1002/lom3.10279

Methods

# **Parameters**

Parameter	Description	Units
Station_ID	Station ID number	unitless
Event_ID	Event ID number	unitless
Gear_ID	Sampling instrument	unitless
Start_ISO_DateTime_UTC	Date and time (UTC) at start of sampling event in ISO 8601 format	unitless
Start_Date_UTC	Date at start of sampling event	unitless
Start_Time_UTC	Time (UTC) at start of sampling event	unitless
Start_Latitude	Latitude at start of sampling event	decimal degrees North
Start_Longitude	Longitude at start of sampling event	decimal degrees East
Sample_ID	GEOTRACES sample ID number	unitless
Sample_Depth	Sample depth	meters (m)
Fe_II_D_CONC_BOTTLE_tgwzl1_1	Concentration of dissolved Fe(II)	
Fe_II_D_CONC_BOTTLE_tgwzl1_2	Time-corrected concentration of dissolved Fe(II); estimated dissolved Fe(II) at time of collection, using published estimates of oxidation rates and calculating the time between sampling (bottle closure) and analysis.	
SD1_Fe_II_D_CONC_BOTTLE_tgwzl1	Standard deviation	picomoles per liter (pmol/L)
Delta_time	Delta between sampling and analysis time, in minutes	minutes
Flag_Fe_II_D_CONC_BOTTLE_tgwzl1	SeaDataNet quality flag as described at https://www.geotraces.org/geotraces-quality-flag-policy/	unitless
Notes	Notes/comments	unitless

# Instruments

Dataset- specific Instrument Name	FeLume flow-injection system (Waterville Analytical)
Generic Instrument Name	Flow Injection Analyzer
Dataset- specific Description	FeLume Chemiluminescence System (Waterville Analytical, Inc.)
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.

<b>Dataset-specific Instrument Name</b>	
Generic Instrument Name	GeoFish Towed near-Surface Sampler
Generic Instrument Description	The GeoFish towed sampler is a custom designed near surface (

Dataset- specific Instrument Name	GEOTRACES Rosette (GTC Rosette)
Generic Instrument Name	GO-FLO Bottle
Dataset- specific Description	The GTC rosette, including the Dynacon winch with 7300 m of sheathed conducting cable with Vectran strength member, block, clean laboratory van, SeaBird custom-built carousel (newly purchased) and SBE-9/11plus CTD/deck unit, and 24 x 12 L Go-Flo bottles (plus spares), were provided by the Cutter group (ODU) and the UNOLS East Coast Van and Winch Pools.
Generic Instrument Description	GO-FLO bottle cast used to collect water samples for pigment, nutrient, plankton, etc. The GO-FLO sampling bottle is specially designed to avoid sample contamination at the surface, internal spring contamination, loss of sample on deck (internal seals), and exchange of water from different depths.

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# **Deployments**

NBP2401

Website	https://www.bco-dmo.org/deployment/969543	
Platform	RVIB Nathaniel B. Palmer	
Report	https://www.bodc.ac.uk/resources/inventories/cruise_inventory/reports/nathanielbpalmer_nbp2401.pdf	
Start Date	2023-11-28	
End Date	2024-01-28	
Description	See more information at: R2R <a href="https://www.rvdata.us/search/cruise/NBP2401">https://www.bodc.ac.uk/resources/inventories/cruise_inventory/report/18091/</a> US GEOTRACES <a href="https://usgeotraces.ldeo.columbia.edu/content/gp17-ant">https://usgeotraces.ldeo.columbia.edu/content/gp17-ant</a> Description: The U.S. GEOTRACES GP17-ANT expedition departed Punta Arenas, Chile on November 29th, 2023 and arrived in Lyttelton, New Zealand on January 28th, 2024. The cruise took place in the Amundsen Sea aboard the R/V Nathaniel B. Palmer with a team of 35 scientists led by Peter Sedwick (Old Dominion University), Phoebe Lam (University of California, Santa Cruz), and Robert Sherrell (Rutgers University). GP17 was planned as a two-leg expedition, with its first leg (GP17-OCE) as a southward extension of the 2018 GP15 Alaska-Tahiti expedition and this second leg (GP17-ANT) into coastal and shelf waters of Antarctica's Amundsen Sea.	

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### **Project Information**

Collaborative Research: US GEOTRACES GP17-ANT: Iron redox cycling in the Amundsen Sea in the water column and shelf sediments (GP17-ANT Iron Redox)

Coverage: Amundsen Sea

#### NSF Award Abstract:

The Amundsen Sea is one of the most rapidly changing areas along the Antarctic coast, with some of the fastest rates of glacial melting on the continent. There is great interest in the role of iron in controlling primary production and carbon and nutrient cycling within the Amundsen Sea, and it is probably an important source of iron to offshore waters of the Southern Ocean, which are rich in nutrients but iron limited. The work is part of the US GEOTRACES GP17-ANT cruise to the Amundsen Sea, a multi-investigator study of trace elements and isotope cycling. This work will study how iron is mobilized from sediments at the seafloor of the Amundsen basin. Such mobilization is influenced by two factors directly linked to climate change. Glacial melting increases ice-free areas known as polynyas, which experience large blooms of phytoplankton. Organic matter from these blooms eventually reaches the seafloor, creating low-oxygen conditions that accelerate iron transport into the overlying waters. Moreover, accelerated melting of glaciers will increase the transport of this iron to the surface via the buoyant "meltwater pump" along the glacier/ocean interface. These processes create feedbacks between climate and biological productivity that must be understood to develop models with a useful predictive capability. The broader impacts include partnering with University of Southern California Joint Educational Project and a PolarTREC teacher to create curriculum based on GEOTRACES Antarctic Expedition, which will be disseminated to 15 elementary school in Los Angeles area and develop online data exploration modules to encourage data-based learning in oceanography classes.

This collaborative project will investigate iron redox cycling between sediments and water column of the Amundsen Sea and exchange with the Southern Ocean by determining iron (II) concentrations and redox kinetics in the water column as well as fluxes of iron and other elements from the seafloor to the water column from porewater measurements. A major objective of the US GEOTRACES GP17-ANT cruise is to study the exchange of iron between the Amundsen Sea and the Southern Ocean. The proposed work is essential to identifying the sources of iron and controls on source fluxes as well as internal transformations that will determine its fate. The data product from the project will be integrated with the results of other investigators in a synthesis effort after the cruise, including dissolved and particulate iron and related metals like manganese, as well as important tracers of sediment sources like radium isotopes. Iron(II) oxidizes very slowly in these cold waters, and kinetics will be combined with iron(II) bottom water concentrations and benthic fluxes to evaluate the importance of the slow oxidation kinetics on iron transport away from the benthic boundary layer. Benthic-derived iodine (denoted as "excess iodine"), will be utilized as an important semi-conservative tracer of iron inputs. Iodine is a useful comparative element because both iron and iodine accumulate in sediments under oxidizing conditions and are released under reducing conditions. Iodine is of interest in its own right because Antarctic Shelf waters are a massive source of reactive iodine species to the atmosphere.

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-2124188

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