Iron speciation in hydrothermal plume particles determined by synchrotron X-ray absorption spectroscopy of samples collected on R/V Atlantis cruise AT50-15 at the Juan de Fuca Ridge in 2023

Website: https://www.bco-dmo.org/dataset/986833
Data Type: Cruise Results
Version: 1
Version Date: 2025-12-03

Project
» Collaborative Research: Hydrothermal Estuaries: What Sets the Hydrothermal Flux of Fe and Mn to the Oceans? (Hydrothermal Estuaries)

Contributors	Affiliation	Role
Toner, Brandy Marie	University of Minnesota Twin Cities (UMTC)	Principal Investigator
Matzen, Sarick	University of Minnesota Twin Cities (UMTC)	Scientist
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract
The goal of this project was to determine the rates and key processes by which hydrothermally sourced iron and manganese are exported to the oceans. The field research was conducted at the Endeavour Segment of the Juan de Fuca Ridge using in situ filtration (AUV Sentry with SUPR sampler) and shipboard filtration (trace metal CTD rosette) for the particulate size class (solids caught by a filter with 0.2 micron pore size). The field work was conducted on R/V Atlantis AT50-15 from August 28th to September 15th, 2023. Iron speciation in filter-bound particles was analyzed by synchrotron fluorescence microprobe and iron 1s X-ray absorption near edge structure (XANES) spectroscopy. These data will be useful for comparison with other datasets concerning trace metals from the Hydrothermal Estuaries project. Sarick Matzen collected the samples in collaboration with John Breier (AUV Sentry and SUPR sampler) and Jessica Fitzsimmons (trace metal CTD rosette) as part of the Hydrothermal Estuaries study led by Chris German. Sarick Matzen and Brandy Toner were responsible for access to the National Synchrotron Light Source (NSLS II) beamline 4-BM (X-ray Fluorescence Microprobe XFM), data collection, and data curation.

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Coverage

Location: Juan de Fuca Ridge
Spatial Extent: **N**:47.96659 **E**:-129.0903 **S**:47.92974 **W**:-129.1921
Temporal Extent: 2023-08-28 - 2023-09-15

Methods & Sampling

Synchrotron microprobe X-ray absorption imaging and spectroscopy allows for the investigation of iron speciation at specific points on a filter-bound sample. Microprobe iron 1s X-ray absorption near edge structure (µXANES) spectra were collected on filter-bound hydrothermal plume particles at the hard X-ray microprobe beamline XFM (4-BM), National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory. Data collection and analysis methods were similar to prior studies of particulate iron from deep-sea hydrothermal systems (Toner et al. 2009; Hoffman et al. 2020; Stewart et al. 2021). The monochromator energy was calibrated with a standard iron foil with the inflection point set to 7110.75 eV. Particles were located using X-ray fluorescence mapping followed by XANES spectra collection in fluorescence mode at a series of points for each filter-bound sample.

Data Processing Description

Fluorescence mode XANES spectra were energy calibrated, averaged, pre-edge subtracted, and post-edge normalized in the freeware Athena (Ravel and Newville 2005). An Athena project file (.prj) is provided for each sample. Each individual spectrum has been provided with normalization parameters applied (.nor) and without normalization parameters applied (.xmu). Both types of files can be opened using a text reader (e.g. Notepad) or spreadsheet (e.g. Excel, Google sheets).

Athena is a freeware for organizing, processing, and analyzing X-ray absorption spectroscopy data. It is commonly used at synchrotron facilities and by scientists globally. Athena has an easy to learn graphical user interface and excellent documentation (Ravel and Newville 2005; Ravel 2016).

Each Athena project file (extension .prj) contains a list of ready-to-use XANES spectra from the sample indicated in the file name and description. Data users are encouraged to view the spectra using the provided input 'energy shift' and 'normalization and background removal parameters' included in the project file. Modifications to the parameters can be made to this dataset join it with the user's own database. Individual spectra can be exported as individual files (that can be opened as .txt). The commonly used formats with normalization parameters applied (.nor) or without normalization parameters applied (.xmu) using the "File" -> "Save each marked group as..." menu.

BCO-DMO Processing Description

- Created a CSV containing the sample metadata (station, lat, lon, etc.) provided in the submission tool. Added columns containing the file names and cruise ID.
- Saved the final file as "986833_v1_fexanes_at50-15.csv".
- Created a .zip file named "FeXANES_spectra_CSV.zip" containing all of the CSV files.
- Created a .zip file named "Fe_XANES_spectra_PRJ.zip" containing all of the PRJ files.

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Related Publications

Breier, J. A., Jakuba, M. V., Saito, M. A., Dick, G. J., Grim, S. L., Chan, E. W., McIlvin, M. R., Moran, D. M., Alanis, B. A., Allen, A. E., Dupont, C. L., & Johnson, R. (2020). Revealing ocean-scale biochemical structure with a deep-diving vertical profiling autonomous vehicle. Science Robotics, 5(48). https://doi.org/10.1126/scirobotics.abc7104
Methods

Breier, J. A., Sheik, C. S., Gomez-Ibanez, D., Sayre-McCord, R. T., Sanger, R., Rauch, C., Coleman, M., Bennett, S. A., Cron, B. R., Li, M., German, C. R., Toner, B. M., & Dick, G. J. (2014). A large volume particulate and water multi-sampler with in situ preservation for microbial and biogeochemical studies. Deep Sea Research Part I: Oceanographic Research Papers, 94, 195–206. https://doi.org/10.1016/j.dsr.2014.08.008
Methods

Hoffman, C. L., Schladweiler, C. S., Seaton, N. C. A., Nicholas, S. L., Fitzsimmons, J. N., Sherrell, R. M., German, C. R., Lam, P. J., & Toner, B. M. (2020). Diagnostic Morphology and Solid-State Chemical Speciation of Hydrothermally Derived Particulate Fe in a Long-Range Dispersing Plume. ACS Earth and Space Chemistry, 4(10), 1831–1842. https://doi.org/10.1021/acsearthspacechem.0c00067

Methods

Ravel, B. (2016). ATHENA: XAS Data Processing.
https://bruceravel.github.io/demeter/documents/Athena/index.html
Software

Ravel, B., & Newville, M. (2005). ATHENA,ARTEMIS,HEPHAESTUS: data analysis for X-ray absorption spectroscopy usingIFEFFIT. Journal of Synchrotron Radiation, 12(4), 537–541. doi:10.1107/s0909049505012719 https://doi.org/10.1107/S0909049505012719
Methods

Stewart, B. D., Sorensen, J. V., Wendt, K., Sylvan, J. B., German, C. R., Anantharaman, K., Dick, G. J., Breier, J. A., & Toner, B. M. (2021). A multi-modal approach to measuring particulate iron speciation in buoyant hydrothermal plumes. Chemical Geology, 560, 120018. https://doi.org/10.1016/j.chemgeo.2020.120018
Methods

Toner, B. M., Fakra, S. C., Manganini, S. J., Santelli, C. M., Marcus, M. A., Moffett, J. W., … Edwards, K. J. (2009). Preservation of iron(II) by carbon-rich matrices in a hydrothermal plume. Nature Geoscience, 2(3), 197–201. doi:10.1038/ngeo433
Methods

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Parameters

Parameter	Description	Units
cruise_id	Cruise ID	unitless
Sample_code_number	Sample ID	unitless
Station_number	Station number	unitless
Latitude	Latitude of sample collection	unitless
Longitude	Longitude of sample collection	unitless
Water_depth_m	Depth of sample collection	meters
Collection_mode	Sample collection method	unitless
CSV_file	Name of the CSV file for this sample. One .csv file per sample is provided that contains XANES data for each spot within a sample. Data have been screened for quality and energy calibrated. When available, multiple scans were averaged. Spectra were exported without pre-edge subtraction or post-edge normalization. No smoothing or other modifications (e.g. monochromator glitches remain) were made to spectra. All parameters are defined in the file header.	unitless
PRJ_file	Name of the PRJ file for this sample. An Athena project file with extension .prj containing synchrotron iron 1s (or K-edge) X-ray absorption near edge structure (XANES) spectra is provided for each sample. To access the Athena freeware, download Demeter (https://bruceravel.github.io/demeter/). Data have been screened for quality. When available, multiple scans were averaged and the resulting spectra were pre-edge subtracted, post-edge normalized, and energy calibrated. No smoothing or other modifications (e.g. monochromator glitches remain) were made to spectra.	unitless

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Instruments

Dataset-specific Instrument Name	AUV Sentry
Generic Instrument Name	AUV Sentry
Dataset-specific Description	Samples collected with AUV Sentry/SUPR sampler were filtered in situ through 0.2 SUPR PES filters. SUPR sampling system deployed on AUV Sentry (Breier et al. 2014; Breier et al. 2020).
Generic Instrument Description	The autonomous underwater vehicle (AUV) Sentry is a fully autonomous underwater vehicle capable of exploring the ocean down to 6,000 meters (19,685 feet) depth. Sentry builds on the success of its predecessor the ABE, with improved speed, range, and maneuverability. Sentry's hydrodynamic shape also allows faster ascents and descents. Sentry carries a superior science sensor suite and an increased science payload enabling it to be used for both mid-water and near-seabed oceanographic investigations. Sentry produces bathymetric, sidescan, subbottom, and magnetic maps of the seafloor and is capable of taking digital bottom photographs in a variety of deep-sea terrains such as mid-ocean ridges, deep-sea vents, and cold seeps at ocean margins. Sentry is uniquely able to operate in extreme terrain, including volcano caldera and scarps. Sentry's navigation system uses a doppler velocity log and inertial navigation system, aided by acoustic navigation systems (USBL or LBL). The USBL system also provides acoustic communications, which can be used to obtain the vehicle state and sensor status as well as to retask the vehicle while on the bottom. In addition its standard sensors, Sentry has carried a variety of science-supplied sensors, including the Nakamura redox potential probe, ACFR 3-D imaging system, and the Tethys in-situ mass spectrometer. Sentry can be used to locate and quantify hydrothermal fluxes. Sentry is also capable of a much wider range of oceanographic applications due to its superior sensing suite, increased speed and endurance, improved navigation, and acoustic communications. Sentry can be used as a stand alone vehicle or in tandem with Alvin or an ROV to increase the efficiency of deep-submergence investigations. More information is available from the operator site at URL: http://www.whoi.edu/main/sentry

Dataset-specific Instrument Name	SUPR Sampler
Generic Instrument Name	SUPR Sampler
Dataset-specific Description	Samples collected with AUV Sentry/SUPR sampler were filtered in situ through 0.2 SUPR PES filters. SUPR sampling system deployed on AUV Sentry (Breier et al. 2014; Breier et al. 2020).
Generic Instrument Description	The Suspended Particulate Rosette Sampler (SuPR or SUPR) is a high-volume time-series sampler that autonomously collects 14 water samples onto 142 mm membrane filters. It can be deployed on moorings and CTD water rosettes, but it was designed with a custom high-throughput valve for high-speed sampling of rising hydrothermal plumes by remotely operated vehicles. The original SUPR sampler was designed specifically for particulate sampling and compatibility with in situ optical analysis techniques. The SUPR sampler was redesigned in 2011 to enable a wider range of sample types. Based on the success of the SUPR V2 system, the design was optimized to achieve a smaller size and allow for AUV deployments - achieving the SUPR V3 version. Originally developed at Woods Hole Oceanographic Institution, the SUPR is now manufactured by McLane. References: https://www.breierlab.info/SUPR.html https://mclanelabs.com/supr-landing/ Breier et al., 2009. https://doi.org/10.1016/j.dsr.2009.04.005 Breier et al., 2014 https://doi.org/10.1016/j.dsr.2014.08.008

Dataset-specific Instrument Name	trace metal CTD rosette
Generic Instrument Name	Trace Metal Bottle
Dataset-specific Description	The field research was conducted at the Endeavour Segment of the Juan de Fuca Ridge using in situ filtration (AUV Sentry with SUPR sampler) and shipboard filtration (trace metal CTD rosette) for the particulate size class.
Generic Instrument Description	Trace metal (TM) clean rosette bottle used for collecting trace metal clean seawater samples.

Dataset-specific Instrument Name	X-ray Fluorescence Microprobe (XFM) beamline 4-BM
Generic Instrument Name	X-ray fluorescence analyzer
Dataset-specific Description	X-ray Fluorescence Microprobe (XFM) beamline 4-BM, National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory, USA. See https://www.bnl.gov/nsls2/programs/imaging.php
Generic Instrument Description	Instruments that identify and quantify the elemental constituents of a sample from the spectrum of electromagnetic radiation emitted by the atoms in the sample when excited by X-ray radiation.

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Deployments

AT50-15

Website	https://www.bco-dmo.org/deployment/989978
Platform	R/V Atlantis
Start Date	2023-08-25
End Date	2023-09-14
Description	See more information from R2R: https://www.rvdata.us/search/cruise/AT50-15

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Project Information

Collaborative Research: Hydrothermal Estuaries: What Sets the Hydrothermal Flux of Fe and Mn to the Oceans? (Hydrothermal Estuaries)

Coverage: Juan de Fuca Ridge

NSF Award Abstract:
Like volcanoes on land, the mid-ocean ridges that cross the ocean floor are not continuously erupting; however, the magmatic heat present just beneath the surface can continue to drive hot springs, just like the

ones found within the crater of the "super volcano" at Yellowstone. In our recent work, we have shown that the chemicals released into the oceans from seafloor hot-springs can be dispersed all across the oceans. Now our interest has focused in on one element in particular, iron. This is one of the most abundant elements in every planetary body in the Universe yet it is vanishingly rare in Earth's oceans today. Set against that, it is essential to just about every form of life on Earth from the simplest and most ancient strains of microbes to the most complex animals including humans. In Earth's oceans, the lack of this "essential micro-nutrient" has been found to limit how much life can flourish near both the south and north poles in the Pacific Ocean in the sunlit surface ocean even though the supply of sunlight and other major nutrients (phosphorous, nitrogen) should be more than adequate. Our newest research suggests that iron released from hydrothermal plumes (where the concentrations coming from vents are more than 1 million times higher than normal ocean water) could play a major role. Despite undergoing massive dilution as hydrothermal solutions leave the vents and traverse thousands of kilometers through the oceans, we believe that at least some of the iron released from deep sea hot springs can survive this journey and make a significant impact on how much live exists in Earth's polar oceans and how much CO2 it draws down from the atmosphere. To investigate that idea, this project will study the fate of iron released from a hydrothermal vent over a length scale that hasn't been studied before - from the first 1km through the ocean out to 100km away from the vent-site. This will fill a gap in our knowledge between what happens right at a vent-site (as studied by research submarines) and what happens to ocean chemistry all across Earth's entire ocean basins (as studied by a huge international research project called GEOTRACES). Our work will use a 3D computational model to predict where the plume of material from a vent in the Northeast Pacific Ocean should escape to after it is erupted from some vents at a volcanic system called the Juan de Fuca Ridge. We will then use an advanced autonomous free-swimming robot to search out in the predicted plume area, first to test the accuracy of our predicted model and, second, to collect samples from the hydrothermal plume from where it first forms to as far out as we can follow it. The samples we collect will include both filtered seawater and the particulate material (whether mineralogical or microbiological) that we can extract from the filters. Together, this will allow us to track the fate of the iron and other key physical and geochemical tracers down-plume away from the vents, to work out where it ends up (in the water and in the sediments) and also how fast those processes happen. The work we do will also help plan how to conduct similar robotics-based exploration on future space missions beyond Earth where it has been hypothesized that seafloor events also exist (e.g. Saturn's moon Enceladus) and where, if we are really lucky, we may find that life is hosted based on the energy from seafloor volcanoes, just as happens here on Earth. We have a resident artist embedded in our program who has already begun experimenting with the use of air-flow and sound in her sculptures to help communicate the complex nature of these plumes. She will join our cruise, and work with our team post-cruise to design and hopefully build a sculpture that that could potentially result in a large and long-term outdoor installation.

The international GEOTRACES program has revealed that iron (Fe) is released ubiquitously from submarine ridges to the deep ocean. Results from US GEOTRACES section GP16 showed that both dissolved and particulate (colloidal) Fe may persist so far as to be able to influence primary productivity in High-Nutrient/Low-Chlorophyll (HNLC) regions of the Southern Ocean. As a complement to these sectional studies, we propose a detailed process study to elucidate the mechanisms by which hydrothermally sourced Fe can persist across the oceans at the scale that GEOTRACES has revealed. Specifically, while the "persistent" Fe in a hydrothermal plume appears to behave quasi-conservatively from 100km to 4000km across the SE Pacific Ocean, it is also known that the majority of the Fe present at the Southern EPR on that US GEOTRACES GP16 cruise did not persist over the 100km separation between that station and the next deep ocean station beyond the ridge crest. To fill that gap, this project will conduct a coupled modelling and field study to investigate the fate of hydrothermally sourced Fe at ranges of 0-1, 1-10 and 10-100km down-plume away from a well established vent-source. To begin, we will use the detailed micro-bathymetry and the long-term current meter data available from the Main Endeavour Segment of the Juan de Fuca Ridge to implement a recently developed 3D theoretical plume dispersion model that can predict both the detailed 3D dispersion trajectory and the rate of flow within the hydrothermal plume away from two long-studied and well characterized Main Endeavour Field (MEF) vents. At sea, we will use that predictive model to guide Sentry autonomous underwater vehicle (AUV) surveys that will follow the plume "down-wind" and "across-plume" to compile a 3D survey using in-situ sensors [optical, redox, conductivity, temperature, depth (CTD)] that will allow us to (1) confirm (and better constrain) the predictive model, and to (2) map out the shape and trajectory of the plume to provide context for discrete water column samples that we will collect - both from the AUV and from a trace metal clean CTD-rosette. Sampling from the AUV will use the latest generation of SUPR samplers designed for the CLIO trace-metal-clean water sampler. This will suffice for samples of dissolved, colloidal and particulate trace metals and collection of filtered material for grain-by-grain mineralogical and biogeochemical analyses. That sampling program will be backed up by larger volume sampling down-plume using a CTD-rosette to augment our AUV-based program with helium isotope analyses (to track extents of physical plume dilution at increasing distances downwind and across plume) and for complementary ligand and organic compound analyses to investigate the role that organic complexation might play in protecting reduced species of Fe [and manganese (Mn), too] against oxidative precipitation and removal from the oceanic water column. Post cruise, our combination of biogeochemical measurements and improved 3D physical modelling will not only be able to provide new insights into the processes that control the fluxes of Fe and Mn to the oceans from hydrothermal venting but also the length scales over which those processes take effect. Finally, because our 3D theoretical model includes velocities, we also anticipate being able to deduce the rates at which these processes occur.

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-1851106

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