Stable isotopic composition of total, deionized-water-soluble, and dilute-acetic-acid-soluble aerosol iron from analysis of composite aerosol samples collected at Tudor Hill, Bermuda between Nov 2018 and March 2020

Website: https://www.bco-dmo.org/dataset/937008
Data Type: Cruise Results
Version: 1
Version Date: 2024-09-11

Project
» NSFGEO-NERC: Collaborative Research: Using Time-series Field Observations to Constrain an Ocean Iron Model (BAIT)
» Collaborative Research: Determining the isotopic signature of iron released via ligand-mediated dissolution of atmospheric dust in the surface ocean (Dust Ligand Interactions)

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

Contributors	Affiliation	Role
Conway, Timothy M.	University of South Florida (USF)	Principal Investigator
Boiteau, Rene Maurice	Oregon State University (OSU)	Co-Principal Investigator
Sedwick, Peter N.	Old Dominion University (ODU)	Co-Principal Investigator
Toth, Eniko	University of South Florida (USF)	Scientist
Sohst, Bettina	Old Dominion University (ODU)	Technician
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract

These data include the stable isotopic composition (δ56Fe relative to the IRMM-014 standard) of total, deionized-water-soluble, and dilute-acetic-acid-soluble aerosol Fe, from analysis of composite aerosol samples collected during ~weekly intervals on the sampling tower at Tudor Hill, Bermuda, between November 2018 and March 2020. These provide estimates of the δ56Fe signature of Fe deposited to the region during the BAIT project. Dust samples were collected by staff of the Bermuda Institute of Ocean Sciences, and the Tudor Hill tower facility is managed by Dr. Andrew Peters, with funding from NSF. Aerosol sample processing was done in the laboratory of Dr. Peter Sedwick at Old Dominion University, and analysis for δ56Fe was carried out in the laboratory of Dr. Tim Conway at the University of South Florida.

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Coverage

Location: Tudor Hill Tower, Bermuda
Spatial Extent: **Lat**:32.265 **Lon**:-64.879
Temporal Extent: 2018-11-26 - 2020-03-16

Methods & Sampling

Weekly sampling was conducted at Tudor Hill, Bermuda from November 2018 to March 2020. The sampling tower platform is approximately 30 meters above sea level with coordinates of 32.265°N, 64.879°W.

The following collection and chemical processing methods are reproduced from related dataset https://www.bco-dmo.org/dataset/906770 (doi: 10.26008/1912/bco-dmo.906770.1) and Sedwick et al. (2023).

Composite samples of bulk aerosol were collected atop the 23-meter height sampling tower at Tudor Hill, Bermuda, on an approximately weekly basis from November 2018 through March 2020, bracketing the four BAIT project cruises. A high-volume (~700 liters per minute) air sampler was used to collect aerosols on acid-cleaned Whatman-41 cellulose filters (8"x10", 20-micrometer nominal pore size), which collect particles as small as 1 micrometer (µm) with >90% efficiency (Stafford and Ettinger, 1972). The coastal Tudor Hill site faces into the prevailing southwesterly winds, so aerosols were only collected during winds >1 meter per second (m s-1) from the 210°-315° sector in order to avoid local sources. Sample filters were stored in zip-lock polyethylene bags in a vacuum desiccator at room temperature. For analysis of total aerosol iron, 1/16th portions of the aerosol sample filters were digested with a mixture of ultrapure concentrated nitric and hydrofluoric acids and hydrogen peroxide (Fisher Optima) in Teflon vessels (Morton et al., 2013), using a microwave heating system (CEM MARS 6), then evaporated on a hot plate and diluted to volume with 2% (v/v) ultrapure nitric acid. Replicate 1/16 portions of the aerosol filters were also subjected to a flow-through leaching procedure modified from Buck et al. (2006). Briefly, the aerosol filter portions were placed atop an acid-washed 0.2 µm pore polycarbonate membrane filter loaded into a perfluoroalkoxy (PFA) resin filtration tower (Savillex), leached with 250 milliliters (mL) of high-purity deionized water (DIW, Barnstead Nanopure, >18.2 MΩ-cm resistivity), and the leachate acidified to 0.4% (v/v) with 6 M ultrapure hydrochloric acid (Fisher Optima) for analysis of "DIW-soluble aerosol iron". The same filter portions were then subjected to a batch leaching procedure modified from Kadko et al. (2019) using 25% acetic acid (HOAc, Fisher Optima) and 0.02 M hydroxylamine hydrochloride (Sigma) at 90 degrees Celsius (°C), and the supernatant leachate was evaporated and then diluted in 2% ultrapure nitric acid (Fisher Optima) for analysis of "HOAc-soluble aerosol iron". Field blanks for the aerosols (an acid-cleaned filter) were deployed on the Tudor Hill tower and processed in the same manner as samples, but without operating the aerosol sampler pump.

Iron (Fe) isotope Analysis:
Subsamples of the total digested, DIW-leached, and HOAc leached aerosol samples were taken for Fe isotope analysis at the University of South Florida. Samples were then processed for dissolved Fe isotope and concentration analysis at the University of South Florida following Sieber et al. (2019), modified from Conway et al. (2013) and Conway et al. (2019). For all samples a 57Fe-58Fe double spike was added prior to chemical processing, in an approximate 1:2 sample:spike ratio based on expected concentrations from other analysis. Total digest aliquots were then evaporated to dryness, while leached samples were put through a batch extraction using Nobias PA-1 chelating resin. All samples were refluxed with a HNO3-H2O2 solution to digest organics, followed by purification by anion-exchange chromatography using AG-MP1 resin. Isotope analyses were then performed on a Thermo Neptune Plus MC-ICPMS in the Tampa Bay Plasma Facility at the University of South Florida using the double spike technique via a ~100 microliters per minute (uL min-1) PFA nebulizer and Apex Ω introduction introduction system, Pt Jet Sampler cone and an Al X skimmer cone.

Fe stable isotope ratios are expressed in delta notation (δ56Fe) relative to the IRMM-014 standard. A secondary Fe standard, NIST-3126, was analyzed over 44 sessions to provide an estimate of long-term instrumental precision. We obtain a value of +0.36 ± 0.05‰ (2SD, n = 524; runs = 37), in agreement with consensus values (Hunt et al. 2022; Conway et al., 2013). Therefore, we consider a 2SD uncertainty of 0.05‰ as an estimate of analytical precision, and have applied it to all samples, except for low concentration samples where the larger internal error is considered a more conservative estimate of uncertainty. The isotope method described above yields a total procedural blank of ~0.4 nanograms (ng) Fe (n = 5) per sample, which corresponds to less than 0.5% of sample measured here. Aerosol compositions have not been corrected for blank contribution.

Data Processing Description

Data were processed in Microsoft Excel using an-in house double spike reduction scheme from Sieber et al. (2021), based on Siebert et al. (2001).

BCO-DMO Processing Description

- Imported original file "Conway_BAIT_Aerosols_V1.0.xlsx" into the BCO-DMO system.
- Renamed fields to comply with BCO-DMO naming conventions.
- Saved final file as "937008_v1_bait_aerosol_fe_isotopes.csv".

Problem Description

No aerosol samples were collected during the period of 16 September to October 14, 2019, owing to the passage of Hurricane Humberto and subsequent loss of electrical power at the Tudor Hill sampling site.

We use the SeaDataNet scheme to flag data, as recommended by GEOTRACES, where data we believe is accurate is flagged as 2, and missing is 9.

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Data Files

File
937008_v1_bait_aerosol_fe_isotopes.csv(Comma Separated Values (.csv), 6.52 KB) MD5:64268b9ae212219d3dba7fcd58994dcb Primary data file for dataset ID 937008, version 1

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Related Publications

Buck, C. S., Landing, W. M., Resing, J. A., & Lebon, G. T. (2006). Aerosol iron and aluminum solubility in the northwest Pacific Ocean: Results from the 2002 IOC cruise. Geochemistry, Geophysics, Geosystems, 7(4), n/a–n/a. doi:10.1029/2005gc000977
Methods

Conway, T. M., Hamilton, D. S., Shelley, R. U., Aguilar-Islas, A. M., Landing, W. M., Mahowald, N. M., & John, S. G. (2019). Tracing and constraining anthropogenic aerosol iron fluxes to the North Atlantic Ocean using iron isotopes. Nature Communications, 10(1). https://doi.org/10.1038/s41467-019-10457-w
Methods

Conway, T. M., Rosenberg, A. D., Adkins, J. F., & John, S. G. (2013). A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry. Analytica Chimica Acta, 793, 44–52. doi:10.1016/j.aca.2013.07.025
Methods

Hunt, H. R., Summers, B. A., Sieber, M., Krisch, S., Al-Hashem, A., Hopwood, M., Achterberg, E. P., & Conway, T. M. (2022). Distinguishing the influence of sediments, the Congo River, and water-mass mixing on the distribution of iron and its isotopes in the Southeast Atlantic Ocean. Marine Chemistry, 247, 104181. https://doi.org/10.1016/j.marchem.2022.104181
Methods

Kadko, D., Aguilar-Islas, A., Bolt, C., Buck, C. S., Fitzsimmons, J. N., Jensen, L. T., Landing, W. M., Marsay, C. M., Rember, R., Shiller, A. M., Whitmore, L. M., & Anderson, R. F. (2019). The residence times of trace elements determined in the surface Arctic Ocean during the 2015 US Arctic GEOTRACES expedition. Marine Chemistry, 208, 56–69. https://doi.org/10.1016/j.marchem.2018.10.011

Methods

Morton, P. L., Landing, W. M., Hsu, S.-C., Milne, A., Aguilar-Islas, A. M., Baker, A. R., … Zamora, L. M. (2013). Methods for the sampling and analysis of marine aerosols: results from the 2008 GEOTRACES aerosol intercalibration experiment. Limnology and Oceanography: Methods, 11(2), 62–78. doi:10.4319/lom.2013.11.62
Methods

Sedwick, P. N., Sohst, B. M., Buck, K. N., Caprara, S., Johnson, R. J., Ohnemus, D. C., Sofen, L. E., Tagliabue, A., Twining, B. S., & Williams, T. E. (2023). Atmospheric Input and Seasonal Inventory of Dissolved Iron in the Sargasso Sea: Implications for Iron Dynamics in Surface Waters of the Subtropical Ocean. Geophysical Research Letters, 50(6). Portico. https://doi.org/10.1029/2022GL102594
Methods

Sieber, M., Conway, T. M., de Souza, G. F., Hassler, C. S., Ellwood, M. J., & Vance, D. (2021). Isotopic fingerprinting of biogeochemical processes and iron sources in the iron-limited surface Southern Ocean. Earth and Planetary Science Letters, 567, 116967. https://doi.org/10.1016/j.epsl.2021.116967
Methods

Sieber, M., Conway, T. M., de Souza, G. F., Obata, H., Takano, S., Sohrin, Y., & Vance, D. (2019). Physical and biogeochemical controls on the distribution of dissolved cadmium and its isotopes in the Southwest Pacific Ocean. Chemical Geology, 511, 494–509. doi:10.1016/j.chemgeo.2018.07.021
Methods

Siebert, C., Nägler, T. F., & Kramers, J. D. (2001). Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry. Geochemistry, Geophysics, Geosystems, 2(7), n/a–n/a. doi:10.1029/2000gc000124
Methods

Stafford, R. G., & Ettinger, H. J. (1972). Filter efficiency as a function of particle size and velocity. Atmospheric Environment (1967), 6(5), 353–362. https://doi.org/10.1016/0004-6981(72)90201-6
Methods

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Related Datasets

IsRelatedTo

Sedwick, P. N., Sohst, B., Williams, T. E. (2023) **Atmospheric concentrations of aerosol iron from samples collected at Tudor Hill Bermuda between November 2018 and March 2020.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-08-26 doi:10.26008/1912/bco-dmo.906770.1 [view at BCO-DMO]
Relationship Description: This dataset provides Fe concentrations for these aerosol samples.

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Parameters

Parameter	Description	Units
Latitude	Latitude of sampling tower at Tudor Hill, Bermuda	decimal degrees North
Longitude	Longitude of sampling tower at Tudor Hill, Bermuda	decimal degrees East
Aerosol_sample_ID	Unique identifier for each aerosol sample	unitless

Start_datetime_UTC	Start date and time (UTC) of aerosol sampling in ISO 8601 format	unitless
End_datetime_UTC	End date and time (UTC) of aerosol sampling in ISO 8601 format	unitless
Fe_56_54_D_DELTA_DIW_soluble_aerosol	Fe isotopic composition of DIW soluble aerosols, expressed as δ56Fe (‰) = {[(56Fe/54Fe)sample / (56Fe/54Fe)IRMM-014] – 1} × 1000 compared to the IRMM-014 Fe standard.	per mil (‰)
SD2_Fe_56_54_D_DELTA_DIW_soluble_aerosol	Standard error for Fe_56_54_D_DELTA_DIW_soluble_aerosol. 2SD denotes the 2SE internal error of analysis. This should be taken to represent precision except when it is <0.05 permil - in this case, 0.05 should be assumed to represent 2SD precision based on long term analysis of a secondary Fe standard.	per mil (‰)
Flag_Fe_56_54_D_DELTA_DIW_soluble_aerosol	Quality flag for Fe_56_54_D_DELTA_DIW_soluble_aerosol	unitless
Fe_56_54_D_DELTA_Total_aerosol	Fe isotopic composition of total soluble aerosols, expressed as δ56Fe (‰) = {[(56Fe/54Fe)sample / (56Fe/54Fe)IRMM-014] – 1} × 1000 compared to the IRMM-014 Fe standard.	per mil (‰)
SD2_Fe_56_54_D_DELTA_Total_aerosol	Standard error for Fe_56_54_D_DELTA_Total_aerosol. 2SD denotes the 2SE internal error of analysis. This should be taken to represent precision except when it is <0.05 permil - in this case, 0.05 should be assumed to represent 2SD precision based on long term analysis of a secondary Fe standard.	per mil (‰)
Flag_Fe_56_54_D_DELTA_Total_aerosol	Quality flag for Fe_56_54_D_DELTA_Total_aerosol	unitless
Fe_56_54_D_DELTA_HOAc_soluble_aerosol	Fe isotopic composition of HOAc soluble aerosols, expressed as δ56Fe (‰) = {[(56Fe/54Fe)sample / (56Fe/54Fe)IRMM-014] – 1} × 1000 compared to the IRMM-014 Fe standard.	per mil (‰)
SD2_Fe_56_54_D_DELTA_HOAc_soluble_aerosol	Standard error for Fe_56_54_D_DELTA_HOAc_soluble_aerosol. 2SD denotes the 2SE internal error of analysis. This should be taken to represent precision except when it is <0.05 permil - in this case, 0.05 should be assumed to represent 2SD precision based on long term analysis of a secondary Fe standard.	per mil (‰)

Flag_Fe_56_54_D_DELTA_HOAc_soluble_aerosol	Quality flag for e_56_54_D_DELTA_HOAc_soluble_aerosol	unitless

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Instruments

Dataset-specific Instrument Name	high-volume air sampler
Generic Instrument Name	Aerosol Sampler
Generic Instrument Description	A device that collects a sample of aerosol (dry particles or liquid droplets) from the atmosphere.

Dataset-specific Instrument Name	Thermo Neptune Plus MC-ICPMS
Generic Instrument Name	Multi Collector Inductively Coupled Plasma Mass Spectrometer
Generic Instrument Description	A Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) is a type of mass spectrometry where the sample is ionized in a plasma (a partially ionized gas, such as Argon, containing free electrons) that has been generated by electromagnetic induction. A series of collectors is used to detect several ion beams simultaneously. A MC-ICPMS is a hybrid mass spectrometer that combines the advantages of an inductively coupled plasma source and the precise measurements of a magnetic sector multicollector mass spectrometer. The primary advantage of the MC-ICPMS is its ability to analyze a broader range of elements, including those with high ionization potential that are difficult to analyze by Thermal Ionization Mass Spectrometry (TIMS). The ICP source also allows flexibility in how samples are introduced to the mass spectrometer and allows the analysis of samples introduced either as an aspirated solution or as an aerosol produced by laser ablation.

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Project Information

NSFGEO-NERC: Collaborative Research: Using Time-series Field Observations to Constrain an Ocean Iron Model (BAIT)

Coverage: Bermuda Atlantic Time-Series Study region, waters of the western Subtropical North Atlantic Gyre (ca. 30°N-33°N, 62°W-65°W)

NSF and NERC Award Abstract:
Iron is an essential nutrient for the growth of phytoplankton in the oceans. As such, iron plays key roles in regulating marine primary production and the cycling of carbon. It is thus important that models of ocean biology and chemistry consider iron, in order to explore past, present and future variations in marine productivity and the role of the ocean in the global carbon cycle. In this joint project involving researchers in the U.S. and the U.K., supported by both NSF and the Natural Environment Research Council (U.K.), field data from the Bermuda Atlantic Time-series Study (BATS) region will be combined with an established, state-of-the-art ocean biogeochemical model. By leveraging the known seasonal-scale physical, chemical and biological changes in the BATS region, the oceanographic context provided by the BATS core data, and an existing model of the regional physical circulation, the proposed study will yield process-related information that is of general applicability to the open ocean. In particular, the proposed research will focus on understanding the

atmospheric input, biological uptake, regeneration and scavenging removal of dissolved iron in the oceanic water column, which have emerged as major uncertainties in the ocean iron cycle. The project will include significant educational and training contributions at the K-12, undergraduate, graduate and postdoctoral levels, as well as public outreach efforts that aim to explain the research and its importance.

The ability of ocean models to simulate iron remains crude, owing to an insufficient understanding of the mechanisms that drive variability in dissolved iron, particularly the involvement of iron-binding ligands, colloids and particles in the surface input, biological uptake, regeneration and scavenging of dissolved iron in the upper ocean. Basin-scale data produced by the GEOTRACES program provide an important resource for testing and improving models and, by extension, our mechanistic understanding of the ocean iron cycle. However such data provide only quasi-synoptic 'snapshots', which limits their utility in isolating and identifying the processes that control dissolved iron in the upper ocean. The proposed research aims to provide mechanistic insight into these governing processes by combining time-series data from the BATS region with numerical modeling experiments. Specifically, seasonally resolved data on the vertical (upper 2,000 meters) and lateral (tens of kilometers) distributions of particulate, dissolved, colloidal, soluble and ligand-bound iron species will be obtained from the chemical analysis of water column samples collected during five cruises, spanning a full annual cycle, shared with the monthly BATS program cruises. These data, along with ancillary data from the BATS program, will be used to test and inform numerical modeling experiments, and thus derive an improved understanding of the mechanisms that control the distribution and dynamics of dissolved iron in the oceanic water column.

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.

This is a project jointly funded by the National Science Foundation’s Directorate for Geosciences (NSF/GEO) and the National Environment Research Council (NERC) of the United Kingdom (UK).

Collaborative Research: Determining the isotopic signature of iron released via ligand-mediated dissolution of atmospheric dust in the surface ocean (Dust Ligand Interactions)

Coverage: North Atlantic Subtropical Gyre

NSF Award Abstract:
Iron (Fe) is a crucial nutrient for microbial growth in the oceans, impacting the carbon cycle and the climate system, but Fe does not dissolve readily in seawater and so its availability limits phytoplankton growth over much of the surface oceans. One of the most significant ways by which Fe reaches the surface oceans is through deposition of wind-blown dust; however, for this Fe to be available for biological growth, it must dissolve and be kept in solution bound to organic molecules. Despite this known importance, the mechanisms of dust dissolution and the identity of the organic molecules keeping Fe in solution remain poorly understood. This study will focus on using laboratory and field experiments to better understand how natural organic molecules present in seawater enhance the release of Fe from Saharan desert dust, the organic molecules produced by microbes in response to dust, the isotopic fractionation of Fe associated with dust dissolution, and ultimately the role of ligand-mediation dissolution in determining the role of dust in the marine Fe cycle. For outreach activities, the proposers would tutor refugee high school students from Africa/Asia in math and science to help them get integrated into the U.S. school system and discuss science with the public by participation in the St. Petersburg Science Festival. Three graduate students and undergraduate interns would be supported and trained as part of this project.

Scientists from the University of South Florida and Oregon State University will collect natural North Atlantic dust at the Tudor Hill Tower on Bermuda over a yearly cycle and characterize the weekly bulk and water-soluble Fe isotopic and elemental composition of the dust. Appropriate subsamples of this dust, representing both the Saharan and non-Saharan (anthropogenically-influenced) seasons will then be dissolved in seawater, with dissolution mediated by ligands with a range of Fe binding stability constants (natural ligands as well as defined marine siderophores). Incubations of dust will also be carried out with natural biological communities collected from the Gulf of Mexico and at the Bermuda Atlantic Time Series site in the North Atlantic. The investigators will characterize the amount and isotopic signature of the Fe released in each experiment, the microbial community response to dust in the incubations (DNA, cell counting and identification), and the ligands present in the natural organic matter used for experiments and produced in the incubations. Comparison of the abiotic and biological experiments will allow investigation of the magnitude of the biological effects on dust dissolution. The experiments will allow the investigators to provide a mechanistic understanding of factors that affect dust dissolution rates, especially the role of different specific organic ligands in enhancing and stabilizing the release of iron in the surface ocean, and the net signature of iron released. From this, the investigators will provide new constraints for the marine iron isotope cycle in the ocean, specifically testing the hypothesis that the net release of Fe from dust is isotopically heavy due to complexation with organic ligands, but that the size of this fractionation depends on the binding strength and presence of different ligands. The outcomes of this process study will provide a framework for models and interpretation of large scale field studies such as GEOTRACES, as well as enhancing the research community's ability to interpret aerosol and oceanic iron isotope data.

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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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.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1829833
NSF Division of Ocean Sciences (NSF OCE)	OCE-1829643
NSF Division of Ocean Sciences (NSF OCE)	OCE-1829686

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