Iodine speciation and isotope data from iodine tracer experiments on the R/V Falkor in June 2018

Website: https://www.bco-dmo.org/dataset/865703
Data Type: Cruise Results
Version: 1
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Project
» Collaborative Research: Experimental constraints on the rates and mechanisms of iodine redox transformations in seawater (Iodine Redox)

Contributors	Affiliation	Role
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Abstract
This dataset includes results from iodine tracer experiments conducted on the R/V Falkor (cruise number FK180624) in June and July 2018. Samples were collected at the Eastern Tropical North Pacific oxygen deficient zone (ETNP ODZ) from five targeted depths (95, 105, 145, 168, and 475 meters) at 14N, 110W and one depth (151 meters) at 14N, 115W.

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Coverage

Spatial Extent: **N**:14 **E**:-110 **S**:14 **W**:-115
Temporal Extent: 2018-06 - 2018-07

Methods & Sampling

See Hardisty et al., 2021 for a detailed description. A brief description is provided below.

Samples were collected onboard the R/V Falkor at the ETNP ODZ in June and July of 2018 (cruise number FK180624). For the present study, we targeted five depths (95, 105, 145, 168, and 475 meters) at 14N, 110W and one depth (151 meters) at 14N, 115W. Briefly, seawater from the Niskin bottles was collected within <0.5 hours of retrieval into ground-glass reagent bottles and prioritized prior to that necessary for other chemical analyses. The bottles were first rinsed 3x with the sample seawater which was discarded. The bottle was allowed to overflow its volume 3x while seawater was continuously added. A glass stopper was added so that it displaced seawater at the neck of the bottle. This entire process lasted <5 minutes for each sample collected. The samples were then immediately stored in a refrigerator at 4 degrees C prior to setting up the experiments, which were within 3 hours of sample collection. Unfiltered seawater was used for the experimental incubations

at all depths. For one depth, 151 meters, we performed an additional experiment with 0.2 um filtered seawater. All tracer addition and seawater aliquoting for the experimental setup was performed in a glove bag flushed with N2 at 3x its volume and then episodically flushed throughout the experimental setup. For each bottle collected, a pipette was used to remove water from the top at a volume similar to that of the tracer to be added in the subsequent step. A 127IO−3 spike and additional I− radiotracer with a known 129I/127I ratio.

The amended seawater was then aliquoted in triplicate into individual 30-60 mL glass serum bottles representing each time point. To remove potential O2 contamination relicts from the sampling process, the seawater was immediately bubbled for 20-30 minutes with helium through a needle with vented headspace. The samples were incubated in the dark at 11 degrees C for up to 60 hours. Triplicate sample bottles were independently incubated for each time point, which varied between incubations but were generally at 0, 12, 24, 48, and 60 hours. Upon harvesting, samples were immediately filtered through a 0.2 um filter and stored in the dark at 4 degrees C.

The concentrations of I− from the incubations were determined shipboard <2 weeks after sample collection via the methods outlined in Moriyasu et al. (2020) via a hanging mercury drop (Hg) electrode and a calomel reference electrode.

Iodine isotope ratios were determined via the methods outlined in Hardisty et al., (2020) and Hardisty et al., (2021) using chromatographic separation and subsequent analysis via multi-collector ICPMS.

Data Processing Description

Data Processing:
Matlab was used for processing iodine isotope data.

BCO-DMO Processing:
- Adjusted field/parameter names to comply with BCO-DMO naming conventions;
- Missing data identifier 'NA' replaced with 'nd' (BCO-DMO's default missing data identifier);
- Added a conventional header with dataset name, PI names, version date.

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Data Files

File	
ETNP_Iodate_Reduction_Expts.csv	(Comma Separated Values (.csv), 2.00 KB) MD5:94e04cf428b69e07530d56ad3e511f3f
Primary data file for dataset ID 865703	

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Related Publications

Hardisty, D. S., Horner, T. J., Evans, N., Moriyasu, R., Babbin, A. R., Wankel, S. D., … Nielsen, S. G. (2021). Limited iodate reduction in shipboard seawater incubations from the Eastern Tropical North Pacific oxygen deficient zone. Earth and Planetary Science Letters, 554, 116676. doi:10.1016/j.epsl.2020.116676
Results

Hardisty, D. S., Horner, T. J., Wankel, S. D., Blusztajn, J., & Nielsen, S. G. (2020). Experimental observations of marine iodide oxidation using a novel sparge-interface MC-ICP-MS technique. Chemical Geology, 532, 119360. doi:10.1016/j.chemgeo.2019.119360
General

Moriyasu, R., Evans, Z. C., Bolster, K. M., Hardisty, D. S., & Moffett, J. W. (2020). The Distribution and Redox Speciation of Iodine in the Eastern Tropical North Pacific Ocean. Global Biogeochemical Cycles, 34(2). doi:10.1029/2019gb006302 https://doi.org/10.1029/2019GB006302
Methods

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Parameters

Parameter	Description	Units
Depth	Depth of sample taken	meters
Filtered	Sample filtered (yes/no)	unitless
Time_hours	Time point in hours	hours
Total_Iodide	Total concentration of Iodide	nanomolar (nM)
Iodide_129I_127I	Ratio of Iodine 129/127	unitless
Iodide_129I_127I_SD	One standard deviation of Iodide_129I_127I	unitless

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Instruments

Dataset-specific Instrument Name	BASi Controlled Growth Mercury Electrode
Generic Instrument Name	BASi Controlled Growth Mercury Electrode
Dataset-specific Description	All iodide concentrations were determined via a hanging mercury drop (Hg) electrode and a calomel reference electrode. These instruments obtain information about an analyte by applying a potential and measuring the current produced in the analyte.
Generic Instrument Description	Bioanalytical Systems (BASi) Mercury drop electrodes are generated by the BASi Controlled Growth Mercury Electrode (CGME) in three modes: DME (Dropping Mercury Electrode) - mercury is allowed to flow freely from the reservoir down the capillary and so the growth of the mercury drop and its lifetime is controlled by gravity. (The optional 100 um capillary is recommended for this mode.) SMDE (Static Mercury Drop Electrode) - the drop size is determined by the length of time for which the fast-response capillary valve is opened, and the drop is dislodged by a drop knocker. The dispense/knock timing is microprocessor-controlled and is typically coordinated with the potential pulse or square-wave waveform. This mode can also used to generate the Hanging Mercury Drop Electrode required for stripping experiments. CGME (Controlled Growth Mercury Electrode) - the mercury drop is grown by a series of pulses that open the capillary valve. The number of pulses, their duration, and their frequency can be varied by PC control, providing great flexibility in both the drop size and its rate of growth. This CGME mode can be used for both polarographic and stripping experiments. http://www.basinc.com/products/ec/cgme.php

Dataset-specific Instrument Name	ThermoFinnigan Neptune MC-ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	All iodine isotope ratios were measured on a ThermoFinnigan Neptune MC-ICP-MS at the WHOI Plasma Facility. An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

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Deployments

FK180624

Website	https://www.bco-dmo.org/deployment/776768
Platform	R/V Falkor
Start Date	2018-06-24
End Date	2018-07-15

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Project Information

Collaborative Research: Experimental constraints on the rates and mechanisms of iodine redox transformations in seawater (Iodine Redox)

Coverage: Martha's Vineyard Sound and the Eastern Tropical North Pacific oxygen deficient zone

NSF Award Abstract:
The goal of this study is to constrain the chemical and biological reactions controlling the iodine cycle in the marine environment. Seawater iodine plays a key role in the cycling of carbon, dissolved oxygen, and ozone, and has been hypothesized to also influence the elemental cycles of manganese and nitrogen. The composition of iodine in sedimentary rocks has also been proposed as an archive of ancient seawater oxygen availability. Unfortunately, few constraints currently exist on iodine reaction rates and mechanisms in seawater, limiting quantitative applications. To remedy this, scientists from Michigan State University (MSU) and Woods Hole Institute of Oceanography (WHOI) will use a rare iodine isotope, iodine-129, as a tracer of iodine chemical reactions in controlled seawater incubations designed to determine specific reaction rates and mechanisms from two end-member environments: well-oxygenated mid-Atlantic seawater as part of the United Kingdom-based Atlantic Meridional Transect (AMT) annual time series and low oxygen zones in the Pacific Ocean. The project will contribute to building the future United States STEM (Science Technology, Engineering and Mathematics)-trained workforce via the training of one graduate student and at least one undergraduate student from the campus of MSU. This includes hands-on field training and experience through two research cruises, extensive analytical training at WHOI, as well as experience in Earth system modeling simulations of iodine-oxygen interactions at the modern and ancient sea surface. The experimental constraints are designed to inform broader modeling of iodine-related chemical cycles for scientific communities including atmospheric and marine chemists, environmental regulators, and geologists.

The redox potential of iodate-iodide is uniquely poised for probable applications as both a redox tracer of Oxygen Minimum Zone (OMZ)-like conditions in modern and past oceans as well as a critical component of air-sea exchange reactions regulating tropospheric ozone levels. However, a currently limited understanding of the first-order rates and mechanisms of iodine redox transformations in seawater limits applications, which our research seeks to address. Specifically: (1) Marine iodate production, the oxidized and most abundant species, has yet to be observed experimentally despite the fact that most marine inputs from estuarine and other sources consist of the reduced species, iodide. Mass balance demands that in situ marine oxidation is widespread. The oxidant is unknown, but it is unlikely oxygen (O2) due to thermodynamic barriers. (2) Unconstrained in situ processes drive significant accumulation of reduced iodide in photic waters globally, particularly at low latitudes, which ultimately act as a major tropospheric ozone sink. (3) Constraints on rates and reaction mechanisms in OMZs are limited despite iodine being amongst the first redox-sensitive species to reduce under declining O2. We will employ an isotope tracer—iodine-129 as both iodide and iodate—in shipboard seawater incubation experiments to determine the rates and mechanisms of iodine redox transformations governing these widespread trends. This method will be deployed across the largest known gradients in marine iodine speciation—the Eastern Tropical North Pacific oxygen minimum zone and a latitudinal transect of photic and sub-photic waters as part of the Atlantic Meridional Transect. Incubation experiments from these cruises will be used to place first order constraints on the rates of iodine redox transformations at high- and low-[O2], the loci of most intense iodine redox cycling (both vertically and spatially), as well as the mechanisms driving redox transformations. Controls will test oxidants, biotic versus abiotic processes, as well as interactions and comparisons with similar redox cycles such as manganese and nitrogen.

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-1829406

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