Iodine incubation data collected from RRS Discovery cruise AMT-30 during February 23 - March 27th, 2023

Website: https://www.bco-dmo.org/dataset/970249
Data Type: Other Field Results
Version: 1
Version Date: 2025-07-30

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 the incubation data described in the following study abstract (see "Related Datasets" for more data from this study): The oxidized iodine species, iodate, is abundant in well-oxygenated marine waters and can be tracked in sediments to reconstruct ancient oxygen availability. Despite known modern marine spatial variations in both iodate and reduced iodide, the rates, pathways, and locations of iodate formation remain poorly understood for temporal gradients across Earth history. To quantify rates and pathways of iodate formation across an ocean basin, we performed ship-board tracer experiments in euphotic waters with known gradients in iodine speciation on an Atlantic Meridional Transect (45°S and 37°N). We performed incubations at depths corresponding to 7% and 1% of ambient surface light levels, thus tracking the boundaries of the deep chlorophyl maximum (DCM), from 11 stations along the transect. All incubations were spiked with a 129I (t1/2 ~15.7 My) tracer and mimicked ambient conditions. We observed iodate production via multiple pathways. The most common observation was a lack of significant iodate production, with iodate production limited to 7 of the 22 locations and nearly exclusively observed at the DCM and outside the nitrogen and iron limited South Atlantic Gyre. Iodate formation from direct iodide oxidation is inferred in only two locations based on increases in iodate 129I/127I ratios. At the other locations, decreases in iodate 129I/127I ratios imply that rapid reactions with and overturning of alternative natural iodine pools, likely iodine intermediates, are an important factor for iodate production. Our work emphasizes that the rates and pathways of iodate production are spatially heterogenous in the Atlantic Ocean. Future work is needed to determine the drivers, temporal variations, and trends within global ocean basins.

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Coverage

Location: Atlantic Meridional Transect Falkland Islands to United Kingdom
Spatial Extent: **N**:37.783555 **E**:-18.766899 **S**:-18.01677 **W**:-47.816875
Temporal Extent: 2023-02-23 - 2023-03-27

Methods & Sampling

Sampling:

Seawater samples were collected via a CTD rosette deployed to a maximum depth of 500 m during the AMT-30 transect cruise. Depth profile samples from the solar noon CTD Niskin bottles were taken every three days at 11 of the 54 total stations, with 12 samples per cast (250 mL each) ranging from 5 m to 500 m depth for a total of 132 samples for iodide analysis along the transect. Sample containers were rinsed 3 times with sample seawater prior to filling. Samples were filtered to remove bacteria and other particles through 0.8 µm pre-filters followed by 0.2 µm filters (AcropakTM 1500 Supor Capsule, Pall Corporation) using a Masterflex pump and then placed into opaque 60 mL bottles and frozen at -20°C (Campos et al., 1996).

Additionally, larger volume, unfiltered samples (1-3 L) were collected from depths corresponding to light levels of 7% and 1% (the extent of the DCM) for use in the incubation experiments. The iodine isotope (mostly $^{129}I^-$) spike was added to the larger volume first to homogenize the iodine speciation and respective isotope ratio before aliquoting into replicates. The larger volumes were spiked to a target concentration of 70 nM $^{129}I^-$ solution (Eckert and Ziegler Isotope Products©) (Schnur et al., 2024, Hardisty et al., 2020, Ştreangă et al., 2024, Hardisty et al., 2021). Notably, the isotope spike included a NaI carrier, which also contained $^{127}I^-$, and was added at a volume so total iodide added was approximately 140 nM ($^{129}I/^{127}I$ of I^- ~1).

We highlight that, while the spike is mostly iodide, it has trace amounts of iodate resulting in detectable $^{129}I/^{127}I$ for the iodate pool in each experiment. This effect is similar to previous studies and is maintained in order to prime the iodate pool with ^{129}I so that increases and decreases in the $^{129}I/^{127}I$ isotope ratio are detectable via MC-ICP-MS, which cannot resolve natural background $^{129}I/^{127}I$ ratios, which are on the order of 10^{-12} (Qi et al., 2024, Qi et al., 2023, Nagai et al., 2015, Wefing et al., 2019, Casacuberta et al., 2018, Zhang et al., 2023, He et al., 2013).

Each spiked carboy was split into triplicate 250 mL incubations (Schnur et al., 2024). Incubations occurred within on-deck flow-through incubators with screens replicating the light levels and chillers maintaining temperatures of the sample depths. Samples for t_0 were immediately subsampled after adding the spike. All subsamples were filtered at 0.2 µm to end interaction with biology/particles, put into amber high-density polyethylene (HDPE) Nalgene bottles, and frozen at -20°C. All subsamples (t_0, t_1, t_2) were ~60 mL. Incubation conditions were monitored for phytoplankton and microbial analysis onboard (see next section). Incubations at the beginning southernmost leg of the cruise were run for ~6 days and this was shortened based on taxonomic analysis indicating cell losses on longer timescales. All samples were stored frozen (at -20°C) until analysis at Michigan State University.

Analytical Methods:

Methods are adapted from Hardisty et al., (2020) and Schnur et al., (2024) and are summarized below.

Iodide concentration was measured in depth profiles and iodide and iodate concentration were measured in incubation time points using an established ion-exchange chromatography protocol from Hardisty et al., (2020) and Schnur et al., (2024) and summarized below.

The iodine speciation was conducted using glass columns packed with PYREX glass wool and 1 mL of AG1-X8 resin, which were pre-cleaned to eliminate residual iodine before sample processing. Iodide was eluted from the seawater matrix after iodate and a dissolved organic iodine (DOI) were released from the resin. Iodate and DOI fractions were collected independently, but DOI was not measured. The iodate fraction was then reduced to iodide using concentrated hydrochloric acid (HCl) and 0.3M sodium bisulfite ($NaHSO_3$). This fraction underwent a second round of chromatography on cleaned resin as performed previously for iodide.

For quality control, a 200ppb iodide solution (diluted from a 1000 ± 4 µg mL^{-1} iodide standard in 1% tetraethylammonium (TEA)) or dissolved solid KIO_3 in 18.2 MΩ·cm water was processed through the columns alongside the samples to assess elution efficiency and yield of iodide and iodate, respectively. 18.2 MΩ·cm water blanks were included for each column set to check for contamination, and at least one replicate sample was processed in each column set to evaluate reproducibility. Iodide concentrations [$^{127}I^-$] were measured in diluted samples at Michigan State University using a Thermo Scientific iCap triple-quad inductively coupled plasma mass spectrometer (ICP-MS-TQ), in both single-quad (SQ) and triple-quad (TQ) modes with O_2 reaction cell gas. Data correction was performed using internal standards (In, Rh, and Cs) from Inorganic Ventures©. Multi-point calibration curves and column standards were serially diluted from 1000 ± 4 µg mL^{-1} iodide standard in 1% TEA. Iodate recovery yields from the processed KIO_3 standard solutions were 90-95%, while iodide yields were near-complete (~100%).

Iodine isotope ratios ($^{129}I/^{127}I$) were analyzed at the Woods Hole Oceanographic Institution (WHOI) using a Thermo Finnegan Neptune MC-ICP-MS, following previous methods , which are summarized below. These measurements were performed on aliquots of the eluted iodine species (I^- and IO_3^-) recovered during the ion exchange chromatography used for ICP-MS concentration analysis. Each day before sample analyses were performed, the instrument was tuned to maximize beam intensity for accuracy of the instrument. Seven Faraday cups L3, L2, L1, C, H1, H2 and H3 were used to monitor the ^{126}Te, ^{127}I, ^{128}Te, ^{129}I, ^{130}Te, ^{131}Xe and ^{132}Xe isotopes, respectively. Mass bias corrections were applied using a 500 ppb Te solution (Inorganic Ventures©), and potential isobaric interferences on both Te and I were tracked by monitoring ^{131}Xe over the course of sample analysis. Iodine samples were introduced into the instrument using a gas-based "sparge" method in which an inert Ar carrier gas containing Te originating from Aridus II desolvation system is bubbled through the sample where volatilized iodine is carried with the Ar and Te into the MC-ICP-MS plasma. The collected data were corrected for interferences and instrumental mass bias to yield a final $^{129}I/^{127}I$ ratio and paired standard deviation.

Data Processing Description

Matlab (R2024a 24.1.0) was used for processing iodine isotope data.

BCO-DMO Processing Description

* Adjusted parameter names for consistency and database requirements
* Added ISO_DateTime_AST & ISO_DateTime_UTC for reuse purposes
* Converted - to blank values

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Data Files

File
970249_v1_incubation.csv(Comma Separated Values (.csv), 23.50 KB) MD5:e98e0cfdd0b7b3fee14d33a351fd34fc Primary data file for dataset ID 970249, version 1

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Related Publications

Fentzke, K. P., Rees, A. P., Tarran, G. A., Breimann, S. A., Blusztajn, J., Nielsen, S. G., & Hardisty, D. S. (2025). Euphotic iodate production along an Atlantic Meridional Transect. Chemical Geology, 693, 122988. https://doi.org/10.1016/j.chemgeo.2025.122988
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
Methods

Schnur, A. A., Sutherland, K. M., Hansel, C. M., & Hardisty, D. S. (2024). Rates and pathways of iodine speciation transformations at the Bermuda Atlantic Time Series. Frontiers in Marine Science, 10.

https://doi.org/10.3389/fmars.2023.1272870
Methods

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Related Datasets

IsRelatedTo

Hardisty, D. (2025) **Iodine depth profile data collected from RRS Discovery cruise AMT-30 from February 23 - March 27th, 2023.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2025-07-30 doi:10.26008/1912/bco-dmo.970242.1 [view at BCO-DMO]
Relationship Description: Iodine depth profile data collected from RRS Discovery AMT-30 during Feb. 23-March 27 2023 Related dataset submission from the same study and same cruise

IsDerivedFrom

Breimann, S., & Woodward, E. M. S. (2024). *Atlantic Meridional Transect cruise AMT30 (DY157) micro-molar nutrient measurements from CTD bottle samples collected in 2023.* (Version 1) [Data set]. NERC EDS British Oceanographic Data Centre NOC. https://doi.org/10.5285/177B9993-7509-BDAA-E063-7086ABC0540F

Tarran, Glen A. (2025). *Abundance of microbial bacteria and phytoplankton through the water column during the AMT30 (DY157) cruise in February-March 2023* (Version 1) [Data set]. NERC EDS British Oceanographic Data Centre NOC. https://doi.org/10.5285/3399C06E-FE93-62AB-E063-7086ABC0C2E1

Wright, Roseanna L. (2023). *AMT30 (DY157) CTD profiles (pressure, temperature, salinity, potential temperature, density, fluorescence, attenuation, transmittance, downwelling and upwelling PAR, dissolved oxygen concentration) calibrated and binned to 1 dbar, from the Atlantic Meridional Transect between February-March 2023.* (Version 1) [Data set]. NERC EDS British Oceanographic Data Centre NOC. https://doi.org/10.5285/FE044ED6-9B79-6023-E053-6C86ABC09D9E

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Parameters

Parameter	Description	Units
sample_ID	unique identification number for every sample taken for analysis, including from CTD niskin bottles for depth profiles and for incubation samples	unitless
station_number	station number associated with each location sampled during AMT-30	unitless
latitude	latitude a given sample was initially extracteed from the niskin rosette	decimal degrees
longitude	longitude a given sample was initially extracteed from the niskin rosette	decimal degrees
light_percent	the estimated ligjht percent at the depth of sample relative to the surface	percent (%)

incubation_time	the time relative to start at which a subsample was taken from a given incubation time series	unitless
Date_Collected_AST	the date within the Atlantic Standard time zone a given sample was collected and fixed for later analysis	unitless
Time_Collected_AST	the time within the Atlantic Standard time zone a given sample was collected and fixed for later analysis	unitless
ISO_DateTime_Collected_AST	the datetime in ISO format within the Atlantic Standard time zone a given sample was collected and fixed for later analysis	unitless
depth_m	the depth from which a given sample was collected from the niskin rosette	meters (m)
iodate_concentration	the concentration of iodate measured via ICPMS	nanomolar (nM)
iodide_concentration	the concentration of iodide measured via ICPMS	nanomolar (nM)
R_iodate	the isotope ratio of iodate measured via MCICPMS	unitless
R_iodate_sd	the analytical uncertainty of iodate isotope ratio	unitless
R_iodide	the isotope ratio of iodide measured via MCICPMS	unitless
R_iodide_sd	the analytical uncertainty of iodate isotope ratio	unitless
Date_Collected_UTC	the date within the coordinated universal time zone a given sample was collected and fixed for later analysis	unitless
Time_Collected_UTC	the time within the coordinated universal time zone a given sample was collected and fixed for later analysis	unitless
ISO_DateTime_Collected_UTC	the datetime in ISO format within the coordinated universal time zone a given sample was collected and fixed for later analysis	unitless

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Instruments

Dataset-specific Instrument Name	Triple Quadrupole Inductively-Coupled Plasma Mass Spectrometry (ICP-MS-TQ)
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	All iodide and iodate concentrations were measured via a Triple Quadrupole Inductively-Coupled Plasma Mass Spectrometry (ICP-MS-TQ) after ion exchange chromatography with AG1-X8 resin (Hardisty 2020) was used to separate species from whole seawater samples.
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.

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 Woods Hole Oceanographic Institute (WHOI) Plasma Facility (Hardisty et al., 2020).
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

AMT30

Website	https://www.bco-dmo.org/deployment/970243
Platform	RRS Discovery
Report	https://doi.org/10.17031/d2vs-eg36
Start Date	2023-02-21
End Date	2022-03-27

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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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