Nitrate+nitrite and nitrate-only d15N from R/V S.A. Agulhas II cruises VOY016 and VOY019 in the Southern Ocean south of Africa during 2015-2016

Website: https://www.bco-dmo.org/dataset/805546
Data Type: Cruise Results
Version: 1
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Project
» High-resolution, Assemblage-specific Records of Diatom-bound N Isotopes from the Indian Sector of the Antarctic Ocean (Diatom-bound_N_Isotopes)
» Understanding the nitrogen isotopes of planktonic foraminifera: A modern Sargasso Sea study (N Isotopes Foraminifera)
» MRI: Acquisition of Stable Isotope Instrumentation for the Biogeosciences at Princeton University (stable isotope instrumentation)

Contributors	Affiliation	Role
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Abstract
Nitrate+nitrite and nitrate-only d15N from the Southern Ocean south of Africa. The dataset includes hydrocast (depth-profile) and underway (surface; intake at 7 m depth) data. The former is accompanied by hydrographic data obtained during the CTD cast.

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Coverage

Spatial Extent: **N**:-39.4109 **E**:38.4987 **S**:-54.0003 **W**:0.0002
Temporal Extent: 2015-07-26 - 2016-05-09

Dataset Description

Nitrate+nitrite and nitrate-only δ15N from the Southern Ocean south of Africa. The dataset includes hydrocast (depth-profile) and underway (surface; intake at 7 m depth) data. The former is accompanied by hydrographic data obtained during the CTD cast.

Methods & Sampling

Seawater samples were collected aboard the R/V S.A. Agulhas II (from CTD Niskin bottles and the underway intake) and immediately frozen at −20°C until analysis. Hydrographic data for each profile station were acquired from a conductivity-temperature depth (CTD) sensor mounted on the Niskin bottle rosette.

An aliquot of each seawater sample was treated with sulfamic acid to remove nitrite (Granger & Sigman, 2009). Both nitrate+nitrite and nitrate-only samples were measured for concentration by chemiluminescence (Braman & Hendrix, 1989) and isotope composition using the denitrifier method (Sigman et al., 2001). Briefly, sample nitrate or nitrate+nitrite is converted to N_2O gas by denitrifying bacteria and measured for N isotope composition by GC-IRMS with an on-line N_2O extraction and purification system (Sigman et al., 2001; Casciotti et al., 2002; Weigand et al., 2016). The pooled standard deviations (1σ) of replicate denitrifier measurements was 0.09‰ for nitrate+nitrite $\delta^{15}N$ and 0.06‰ for nitrate-only $\delta^{15}N$.

Hydrographic profiles were acquired by a Sea-Bird conductivity-temperature depth sensor during each cast. The isotopic composition of N_2O was measured at Princeton University by GC-IRMS using a Thermo MAT 253 mass spectrometer with a purpose-built on-line N_2O extraction and purification system.

See methods section of Smart et al. (2020) for more detail.

Data Processing Description

Isotope ratio measurements were referenced against automated injections from an N_2O from a gas cylinder, and then calibrated to N_2 in air using two international reference materials IAEA-N3 and USGS-34 that were included in every run. An in-house N_2O standard was also measured along with each batch of samples to monitor mass spectrometry.

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Data Files

File
seawater_isotopes.csv (Comma Separated Values (.csv), 38.58 KB) MD5:c0d3c8c1efbd0cb285a089dbfa927132 Primary data file for dataset ID 805546

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Related Publications

Braman, R. S., & Hendrix, S. A. (1989). Nanogram nitrite and nitrate determination in environmental and biological materials by vanadium(III) reduction with chemiluminescence detection. Analytical Chemistry, 61(24), 2715–2718. doi:10.1021/ac00199a007
Methods

Casciotti, K. L., Sigman, D. M., Hastings, M. G., Böhlke, J. K., & Hilkert, A. (2002). Measurement of the Oxygen Isotopic Composition of Nitrate in Seawater and Freshwater Using the Denitrifier Method. Analytical Chemistry, 74(19), 4905–4912. doi:10.1021/ac020113w
Methods

De Boyer Montégut, C. (2004). Mixed layer depth over the global ocean: An examination of profile data and a profile-based climatology. Journal of Geophysical Research, 109(C12). doi:10.1029/2004JC002378
Methods

Granger, J., & Sigman, D. M. (2009). Removal of nitrite with sulfamic acid for nitrate N and O isotope analysis with the denitrifier method. Rapid Communications in Mass Spectrometry, 23(23), 3753–3762. doi:10.1002/rcm.4307
Methods

Sigman, D. M., Casciotti, K. L., Andreani, M., Barford, C., Galanter, M., & Böhlke, J. K. (2001). A Bacterial Method for the Nitrogen Isotopic Analysis of Nitrate in Seawater and Freshwater. Analytical Chemistry, 73(17), 4145–

4153. doi:10.1021/ac010088e
Methods

Smart, S. M., Fawcett, S. E., Ren, H., Schiebel, R., Tompkins, E. M., Martínez-García, A., … Sigman, D. M. (2020). The Nitrogen Isotopic Composition of Tissue and Shell-Bound Organic Matter of Planktic Foraminifera in Southern Ocean Surface Waters. Geochemistry, Geophysics, Geosystems, 21(2). doi:10.1029/2019gc008440 https://doi.org/10.1029/2019GC008440
Results

Smart, S. M., Ren, H., Fawcett, S. E., Schiebel, R., Conte, M., Rafter, P. A., … Sigman, D. M. (2018). Ground-truthing the planktic foraminifer-bound nitrogen isotope paleo-proxy in the Sargasso Sea. Geochimica et Cosmochimica Acta, 235, 463–482. doi:10.1016/j.gca.2018.05.023
Results

Weigand, M. A., Foriel, J., Barnett, B., Oleynik, S., & Sigman, D. M. (2016). Updates to instrumentation and protocols for isotopic analysis of nitrate by the denitrifier method. Rapid Communications in Mass Spectrometry, 30(12), 1365–1383. doi:10.1002/rcm.7570
Methods

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Parameters

Parameter	Description	Units
cruise	Cruise identifier	unitless
ship	Ship name	unitless
ISO_DateTime_UTC	Date and time formatted to ISO8601 standard. Format: yyyy-mm-ddTHH:MM:SSZ	unitless
date	Date; format: yyyy-mm-dd	unitless
time	Time; format: HH:MM	unitless
latitude	Latitude; positive values = North	decimal degrees
longitude	Longitude; positive values = East	decimal degrees
depth_sample	The depth at which the niskin bottle was closed (from which seawater was collected for analysis)	meters (m)
depth_ctd	Depth of the nearest CTD sensor measurements, extracted from the continuous CTD files (where bottle files were not available)	meters (m)
pressure_ctd	Pressure	decibars (db)
temperature_ctd	Temperature measured by CTD	degrees Celsius

salinity_ctd	Salinity measured by CTD	psu
oxygen_ctd	Oxygen measured by CTD	milliliters per liter (ml/l)
fluorescence_ctd	Fluorescence measured by CTD	milligrams per cubic meter (mg/m3)
potdens_calc	Potential density, calculated from temperature and salinity	kilograms per cubic meter (kg/m3)
MLD_calc	Calculated mixed layer depth at each profile station, defined as the closest depth to the surface at which potential density is greater by greater than or equal to 0.03 kg/m3 than the value at a reference depth of 11 m (the shallowest depth common to every CTD station), based on the criterion of de Boyer Montégut et al. (2004).	meters (m)
d15N_avg_nitrate_nitrite	Average d15N. d15N is the nitrogen isotopic composition of a sample (nitrate+nitrite) expressed in delta notation (d15N in units of per mil, ‰) relative to atmospheric N2, where d15N = {[(15N/14N)sample/(15N/14N)atmN2] – 1} × 1000	per mil vs AIR
d15N_stdev_nitrate_nitrite	Standard deviation of d15N (nitrate+nitrite)	per mil vs AIR
d15N_n_nitrate_nitrite	Number of replicate measurements of d15N (nitrate+nitrite)	unitless
conc_avg_nitrate_nitrite	Concentration of nitrate+nitrite in a seawater sample	micromolar (uM)
conc_stdev_nitrate_nitrite	Standard deviation of nitrate+nitrite concentration	micromolar (uM)
conc_n_nitrate_nitrite	Number of replicate measurements of nitrate+nitrite concentration	unitless
d15N_avg_nitrate	Average d15N. d15N is the nitrogen isotopic composition of a sample (nitrate only) expressed in delta notation (d15N in units of per mil, ‰) relative to atmospheric N2, where d15N = {[(15N/14N)sample/(15N/14N)atmN2] – 1} × 1000	per mil vs AIR
d15N_stdev_nitrate	Standard deviation of d15N (nitrate only)	per mil vs AIR
d15N_n_nitrate	Number of replicate measurements of d15N (nitrate only)	unitless
conc_avg_nitrate	Concentration of nitrate in a seawater sample	micromolar (uM)

conc_stdev_nitrate	Standard deviation of nitrate concentration	micromolar (uM)
conc_n_nitrate	Number of replicate measurements of nitrate concentration	unitless

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Instruments

Dataset-specific Instrument Name	Sea-Bird conductivity-temperature depth sensor
Generic Instrument Name	CTD Sea-Bird
Generic Instrument Description	A Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics. This instrument designation is used when specific make and model are not known or when a more specific term is not available in the BCO-DMO vocabulary. Refer to the dataset-specific metadata for more information about the specific CTD used. More information from: http://www.seabird.com/

Dataset-specific Instrument Name	Thermo MAT 253
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Generic Instrument Description	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

Dataset-specific Instrument Name	CTD Niskin bottles
Generic Instrument Name	Niskin bottle
Generic Instrument Description	A Niskin bottle (a next generation water sampler based on the Nansen bottle) is a cylindrical, non-metallic water collection device with stoppers at both ends. The bottles can be attached individually on a hydrowire or deployed in 12, 24, or 36 bottle Rosette systems mounted on a frame and combined with a CTD. Niskin bottles are used to collect discrete water samples for a range of measurements including pigments, nutrients, plankton, etc.

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Deployments

VOY016

Website	https://www.bco-dmo.org/deployment/805402
Platform	R/V S.A. Agulhas II
Start Date	2015-07-22
End Date	2015-08-15
Description	VOY016: Winter Cruise 2015, Good Hope Line. Subantarctic Atlantic, between South Africa and Antarctic winter sea-ice edge (at 56.4°S, 0.3°E).

VOY019

Website	https://www.bco-dmo.org/deployment/805403
Platform	R/V S.A. Agulhas II
Start Date	2016-04-07
Description	VOY019: Marion Cruise 2016. Subantarctic Indian, between South Africa and Marion/Prince Edward Islands (at 46.9°S, 37.7°E).

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Project Information

High-resolution, Assemblage-specific Records of Diatom-bound N Isotopes from the Indian Sector of the Antarctic Ocean (Diatom-bound_N_Isotopes)

Coverage: Kerguelen Plateau

Description from NSF award abstract:
The high concentration of the major nutrients nitrate and phosphate is a fundamental characteristic of the Antarctic Zone in the Southern Ocean and is central to its role in global ocean fertility and the global carbon cycle. The isotopic composition of diatom-bound organic nitrogen is one of the best hopes for reconstructing the nutrient status of polar surface waters over glacial cycles, which in turn may hold the explanation for the decline in atmospheric carbon dioxide during ice ages. The PIs propose to generate detailed diatom-bound nitrogen isotope (δ15Ndb) records from high sedimentation rate cores from the Kerguelen Plateau. Because the cores were collected at relatively shallow seafloor depths, they have adequate planktonic and benthic foraminifera to develop accurate age models. The resulting data could be compared with climate records from Antarctic ice cores and other archives to investigate climate-related changes, including the major steps into and out of ice ages and the millennial-scale events that occur during ice ages and at their ends. The records generated in this project will provide a critical test of hypotheses for the cause of lower ice age CO2.

This study will contribute to the goal of understanding ice ages and past CO2 changes, which both have broad implications for future climate. Undergraduates will undertake summer internships, with the possibility of extending their work into junior year projects and senior theses. In addition, the PI will lead modules for two Princeton programs for middle school teachers and will host a teacher for a six-week summer research project.

Understanding the nitrogen isotopes of planktonic foraminifera: A modern Sargasso Sea study (N Isotopes Foraminifera)

Coverage: Sargasso Sea

NSF Award Abstract:

Nitrogen (N) and phosphorus are the two nutrients required in large quantity by phytoplankton in the ocean, and together they limit productivity throughout most of the tropical, subtropical, and temperate ocean. Both the cycling of N and its input/output budget have been argued to control the fertility of the ocean and the ocean's role in setting atmospheric CO2. The CaCO3 tests of foraminifera can represent a substantial fraction of marine sediments and have been used extensively in paleoceanography; they are an obvious target for isotopic analysis of microfossil-bound organic matter.

In recent years, researchers at Princeton have developed a protocol for the isotopic analysis of foraminiferal shell-bound N. The current protocol is at least 100 times more sensitive than typical on-line combustion, allowing for rapid progress with a N isotope archive that was previously not feasible to measure. Measurements on surface sediments and a downcore record from the Caribbean show the promise of foraminifera-bound del15N (fb-del15N) to provide both a robust N isotope archive for paleoceanography, and one with a unique potential of richness, given the existence of multiple foraminiferal species with different depth habitats and behaviors. Moreover, the finding from the Caribbean Sea record -- reduced N fixation in ice age Atlantic -- has changed the scientific conversation about the nature of the input/output budget of oceanic fixed N and its potential to change ocean fertility and atmospheric CO2. However, the controls on fb-del15N have not yet been adequately studied.

In this project, as a first major step in developing a foundation for the paleoceanographic application of fb-del15N, the same Princeton University team will study its genesis in the water column, transport to the seafloor, and early diagenesis. They will undertake this study in the Sargasso Sea south of Bermuda. This is one of the best studied regions of the ocean, in general and with respect to foraminifera, and a region that has been has been a focus of the N isotope research of the PI for the last decade and others previously. Moreover, its significant seasonality -- in physical oceanography, biogeochemistry, and foraminiferal species abundance -- will facilitate the effort to understand the controls on fb-del15N at a mechanistic level. The research team will participate in six Bermuda Atlantic Time-series Study (BATS) cruises over two years, collecting foraminifera and other N forms likely to provide insight into the controls on fb-del15N. From the nearby Oceanic Flux Program (OFP) moored sediment traps and from shallow sediments collected in the region, they will pick foraminifera shells and again make relevant ancillary measurements. This work will establish the relationship of foraminiferal biomass to shell-bound del15N for different species, and comparison of the foraminiferal isotope data with the upper ocean N pools will yield empirical isotopic relationships and work toward a mechanistic insight of fb-del15N (e.g., the importance of different N pools to the diets of different foraminifera; the role of algal symbionts). The sediment trap and surface sediment data will support the plankton tow data by integrating over longer time scales and will also address questions regarding late stage (e.g., gametogenic) calcification and the early diagenesis of fb-del15N and fb-N content.

Broader Impacts: This study will yield an improved understanding of the nutrient dynamics of foraminifera, a class of organisms whose shells are a central tool in micropaleontology and paleoclimatology. The project will also build on the principal investigator's involvement in the Bermuda Institute of Ocean Sciences as an asset for integrating ocean-related education and research at both the undergraduate and graduate levels.

MRI: Acquisition of Stable Isotope Instrumentation for the Biogeosciences at Princeton University (stable isotope instrumentation)

NSF Award Abstract:

Intellectual Merit:
The PIs are requesting funds to acquire a suite of instruments for stable isotope (N) research, including a denitrifier-based, natural abundance isotope system, a tracer isotope system, and general purpose natural abundance peripherals for an existing mass spectrometer. Specific instruments requested include a Thermo Electron MAT 253 stable isotope mass spectrometer, a Thermo DeltaVAdvantage stable isotope mass spectrometer with peripherals, an EA peripheral for combustion-based isotope analysis, and a GasBench II carbon dioxide preparation and purification system. The proposed instrumentation would enable research efforts examining natural stable isotope abundances that include ocean biogeochemistry and paleoceanography, terrestrial biogeochemistry, carbon isotopes in Precambrian Earth history. Stable isotope tracer research would include nitrification, nitrogen fixation, and carbon partitioning during biostimulation.

Broader Impacts:
The PIs state that the proposed instrumentation would expand the research capabilities of the institution and specifically the Departments of Geosciences and Ecology and Evolutionary Biology. The improvements to the

denitrifier method will also serve to expand the capabilities of the ocean research community at large. Additionally, the proposed instrumentation will enable method development and provide training for undergraduate students at the institution and those participating in a collaborative effort with the University of Cape Town.

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Funding

Funding Source	Award
NSF Division of Polar Programs (NSF PLR)	PLR-1401489
NSF Division of Ocean Sciences (NSF OCE)	OCE-1060947
NSF Division of Ocean Sciences (NSF OCE)	OCE-0922345

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