

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

Version Date: 2020-03-06

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)

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|-----------------------------------|---|------------------------|
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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 $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ and 0.06‰ for nitrate-only $\delta^{15}\text{N}$.

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](https://doi.org/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](https://doi.org/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](https://doi.org/10.1029/2004JC002378)
<https://doi.org/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](https://doi.org/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](https://doi.org/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](https://doi.org/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](https://doi.org/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 $d15N = \{[(15N/14N)_{sample}/(15N/14N)_{atmN2}] - 1\} \times 1000$ | 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 $d15N = \{[(15N/14N)_{sample}/(15N/14N)_{atmN2}] - 1\} \times 1000$ | 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 | Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics, no specific unit identified. This instrument designation is used when specific make and model are not known. See also other SeaBird instruments listed under CTD. More information from Sea-Bird Electronics. |

| | |
|---|--|
| 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 ($\delta^{15}\text{N}_{\text{db}}$) 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 CO_2 .

This study will contribute to the goal of understanding ice ages and past CO_2 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 $\delta^{15}\text{N}$ (fb- $\delta^{15}\text{N}$) 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- $\delta^{15}\text{N}$ have not yet been adequately studied.

In this project, as a first major step in developing a foundation for the paleoceanographic application of fb- $\delta^{15}\text{N}$, 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 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- $\delta^{15}\text{N}$ 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- $\delta^{15}\text{N}$. 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 $\delta^{15}\text{N}$ 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- $\delta^{15}\text{N}$ (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- $\delta^{15}\text{N}$ 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 DeltaV Advantage 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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