Planktic foraminifer tissue and shell d15N from net tows on 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/805653 Data Type: Cruise Results Version: 1 Version Date: 2020-03-10

Project

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

» <u>Understanding the nitrogen isotopes of planktonic foraminifera: A modern Sargasso Sea study</u> (N Isotopes Foraminifera)

» <u>MRI: Acquisition of Stable Isotope Instrumentation for the Biogeosciences at Princeton University</u> (stable isotope instrumentation)

Contributors	Affiliation	Role
<u>Sigman, Daniel M.</u>	Princeton University	Principal Investigator
<u>Smart, Sandi M.</u>	Stellenbosch University	Contact
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract

This dataset synthesizes net-tow data (foraminifera and zooplankton measurements) with tow-depth seawater measurements (physical and chemical properties) and surface measurements of bulk suspended particulate organic nitrogen (PON) collected from the underway intake (7 m depth).

Table of Contents

- <u>Coverage</u>
- Dataset Description
 - Methods & Sampling
 - Data Processing Description
- Data Files
- <u>Related Publications</u>
- Parameters
- Instruments
- Deployments
- <u>Project Information</u>
- Funding

Coverage

Spatial Extent: N:-40.9588 **E**:38.4761 **S**:-53.9942 **W**:0.0483 **Temporal Extent**: 2015-07-27 - 2016-05-09

Dataset Description

This dataset synthesizes net-tow data (foraminifera and zooplankton measurements) with tow-depth seawater measurements (physical and chemical properties) and surface measurements of bulk suspended particulate organic nitrogen (PON) collected from the underway intake (7 m depth).

Planktic foraminifera were collected by towing a 200-µm-mesh plankton net for 90 min at a target depth within the upper mixed layer. Approximately 90% of the tow material was preserved in a 5-10% pH-buffered formalin solution and stored at 4°C until sorting for foraminifera (Ren et al., 2012). The remaining 10% was size fractionated and frozen at -20°C for element and isotope analysis of zooplankton. During each tow, bulk (>0.3 µm) suspended PON and nitrate samples were collected from the underway intake (at 7 m depth) and frozen at -80°C and -20°C, respectively, until isotope analysis. *In situ* (i.e., tow-depth) nitrate samples and auxiliary hydrographic data come from CTD casts performed on station before the start of each net tow.

Foraminifera were separated by species, rinsed briefly with Milli-Q and crushed open to expose (non-shellbound) tissue. Tissue N was converted to nitrate using the persulfate oxidation method (Nydahl, 1978; Knapp et al., 2005). Remnant shell material (having been oxidatively cleaned) was transferred, rinsed six times with Milli-Q and oven dried at 50°C. Shell samples were then dissolved with hydrochloric acid to release shell-bound organics for persulfate oxidation (Nydahl, 1978; Knapp et al., 2005). For both tissue- and shell-derived nitrate (from persulfate oxidation) as well as seawater nitrate, samples were measured for concentration by chemiluminescence (Braman & Hendrix, 1989) and N isotope composition using the denitrifier method and gas chromatography—isotope ratio mass spectrometry (GC-IRMS) (Sigman et al., 2001; Casciotti et al., 2002; Weigand et al., 2016). The N isotope composition of bulk PON and size-fractionated zooplankton were measured by elemental analyser-IRMS.

The isotopic composition of N₂O was measured either at Princeton University (USA) or the Max Planck Institute for Chemistry (MPIC; Germany) by GC-IRMS using a Thermo MAT 253 mass spectrometer with a purpose-built on-line N₂O extraction and purification system. Bulk PON and size-fractionated zooplankton samples were measured at the University of Cape Town using a Thermo Scientific FLASH 2000 elemental analyzer coupled to a Thermo Scientific Delta V Plus mass spectrometer. Hydrographic data were acquired by a Sea-Bird conductivity-temperature depth sensor during each cast.

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

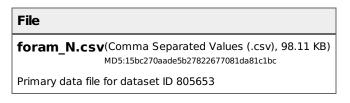
Data Processing Description

At Princeton and MPIC, N isotope measurements were referenced against automated injections of N₂O from a gas cylinder, and then calibrated to N₂ in air using international reference materials: IAEA-N3 and USGS-34 nitrate standards in the case of seawater samples, or USGS-40 and USGS-41 amino acid standards in the case of foraminifer (oxidized) samples. Oxidized samples were additionally corrected for the contribution of the N blank associated with the persulfate oxidizing reagent.

At the University of Cape Town, N isotope measurements were referenced to atmospheric N₂ using three inhouse organic standards: Choc, Merck Gel and Valine.

[table of contents | back to top]

Data Files



[table of contents | back to top]

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:<u>10.1021/ac00199a007</u> *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:<u>10.1021/ac020113w</u> *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 Methods

Knapp, A. N., Sigman, D. M., & Lipschultz, F. (2005). N isotopic composition of dissolved organic nitrogen and nitrate at the Bermuda Atlantic Time-series Study site. Global Biogeochemical Cycles, 19(1). doi:<u>10.1029/2004gb002320</u> *Methods*

Nydahl, F. (1978). On the peroxodisulphate oxidation of total nitrogen in waters to nitrate. Water Research, 12(12), 1123–1130. doi:10.1016/0043-1354(78)90060-x https://doi.org/10.1016/0043-1354(78)90060-X https://doi.org/10.1016/0043-1354(78)9060 https://doi.org/10.1016/0043-1354(78)9060 https://doi.org/10.1016/0043-1354 https://doi.org/10.1016/0043-1354 https://doi.org/10.1016/0043-1354 https://doi.org/10.1016 https://doi.org/10.1016 https:/

Ren, H., Sigman, D. M., Thunell, R. C., & Prokopenko, M. G. (2012). Nitrogen isotopic composition of planktonic foraminifera from the modern ocean and recent sediments. Limnology and Oceanography, 57(4), 1011–1024. doi:10.4319/lo.2012.57.4.1011

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:<u>10.1021/ac010088e</u> *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). Groundtruthing the planktic foraminifer-bound nitrogen isotope paleo-proxy in the Sargasso Sea. Geochimica et Cosmochimica Acta, 235, 463–482. doi:<u>10.1016/j.gca.2018.05.023</u> *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:<u>10.1002/rcm.7570</u> *Methods*

[table of contents | back to top]

Parameters

Parameter	Description	Units
cruise	Cruise identifier	unitless
ship	Ship name	unitless
tow	Tow number	unitless
date	Date; format: yyyy-mm-dd	unitless
time_starttow	Time at start of tow (UTC); format: HH:MM	unitless

time_endtow	Time at end of tow (UTC); format: HH:MM	unitless
species	The planktic foraminifer species measured with the following abbreviations: bul = G. bulloides; glu = G. glutinata; hir = G. hirsuta; inc = N. incompta; inf = G. inflata; pac = N. pachyderma; qui = T. quinqueloba; tru = G. truncatulinoides; uni = O. universa	unitless
type	The kind of foraminiferal organic matter (i.e., tissue or shell- bound) measured for N isotope composition	unitless
analysis_year	The year in which foraminifer samples were measured for N isotope composition. The measurement protocol differed slightly between the three analysis sessions (see Methods Section and Supplemental Text S1 of Smart et al. (2020) for more detail).	unitless
latitude	Latitude; positive values = North	decimal degrees
longitude	Longitude; positive values = East	decimal degrees
depth_tow	Depth of the tow	meters (m)
d15N_foram_avg	Average d15N. d15N is the nitrogen isotopic composition of a sample 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_foram_sd	Standard deviation of d15N_foram_avg	per mil vs AIR
d15N_foram_n	Number of replicate measurements of d15N_foram_avg	unitless
indiv_avg	Average number of individual foraminifer specimens combined to make a measurement	unitless
indiv_sd	Standard deviation of indiv_avg	unitless
indiv_n	Number of replicate measurements of indiv_avg	unitless
Ni_avg	Average nitrogen contents of foraminifera per individual	nanomoles per individual (nmol/indiv)
Ni_sd	Standard deviation of Ni_avg	nanomoles per individual (nmol/indiv)

Ni_n	Number of replicate measurements of Ni_avg	unitless
Nw_avg	Average nitrogen contents of foraminifera per milligram	nanomoles per milligram (nmol/mg)
Nw_sd	Standard deviation of Nw_avg	nanomoles per milligram (nmol/mg)
Nw_n	Number of replicate measurements of Nw_avg	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
conc_avg_nitrate	Concentration of nitrate in a seawater sample	micromolar (uM)
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
conc_avg_nitrate_nitrite	Concentration of nitrate+nitrite in a seawater sample	micromolar (uM)
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)
conc_PON_avg	Average concentration of PON. PON is the bulk (> 0.3 um) particulate organic nitrogen in surface waters filtered from the ship's underway intake during the net tow.	micromolar (uM)

conc_PON_sd	Standard deviation of PON concentration	micromolar (uM)
conc_PON_n	Number of replicate measurements of PON concentration	unitless
d15N_PON_avg	Average d15N of PON. 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_PON_sd	Standard deviation of d15N of PON	per mil vs AIR
d15N_PON_n	Number of replicate measurements of d15N of PON	unitless
d15N_zoop_avg	Average d15N of zooplankton. zoop refers to the bulk (i.e., <150-5000 um) zooplankton collected in the same net during the same tow as the foraminifera.	per mil vs AIR
d15N_zoop_se	Standard error of the d15N of zooplankton	per mil vs AIR
d15N_zoop_n	Number of replicate measurements of the d15N of zooplankton	unitless
ISO_DateTime_UTC_starttow	Date and time (UTC) of start of tow formatted to ISO 8601 standard; format: yyyy-mm-ddTHH:MM:SSZ	yyyy-MM- dd'T'HH:mm:ss'Z'
ISO_DateTime_UTC_endtow	Date and time (UTC) of end of tow formatted to ISO 8601 standard; format: yyyy-mm-ddTHH:MM:SSZ	unitless

Instruments

Dataset- specific Instrument Name	Sea-Bird conductivity-temperature depth sensor
Generic Instrument Name	CTD Sea-Bird
	IVDAWD SAA 3KA ATDAR SA3KIRA INSTRUMANTS IISTAA UDAAR (111). MARA INTARMATIAN TRAM SA3 KIRA 🗤 🗌

Dataset- specific Instrument Name	Thermo Scientific FLASH 2000
Generic Instrument Name	Elemental Analyzer
Generic Instrument Description	Instruments that quantify carbon, nitrogen and sometimes other elements by combusting the sample at very high temperature and assaying the resulting gaseous oxides. Usually used for samples including organic material.

Dataset- specific Instrument Name	Thermo MAT 253 mass spectrometer
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	Thermo Scientific Delta V Plus
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	200-um-mesh plankton net
Generic Instrument Name	Plankton Net
	A Plankton Net is a generic term for a sampling net that is used to collect plankton. It is used only when detailed instrument documentation is not available.

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).

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 (δ 15Ndb) 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 fbdel15N, 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 fbdel15N (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.

[table of contents | back to top]

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