

Nitrate N and O isotopes from the GP12 ("PANDORA") cruise in the South-West Pacific and Solomon Sea from June to August 2012 carried out as part of the international GEOTRACES program

Website: <https://www.bco-dmo.org/dataset/838914>

Data Type: Cruise Results

Version: 1

Version Date: 2021-01-27

Project

- » [Understanding the nitrogen isotopes of planktonic foraminifera: A modern Sargasso Sea study](#) (N Isotopes Foraminifera)
- » [Collaborative Research: US GEOTRACES PMT: Investigating geochemical tracers of the Pacific nitrogen cycle and budget](#) (PMT Nitrate)
- » [Collaborative Research: GEOTRACES Atlantic Section Nitrate Isotope Measurements \(GP12\)](#) (GT Atlantic Nitrate)

Program

- » [U.S. GEOTRACES](#) (U.S. GEOTRACES)

Contributors	Affiliation	Role
Rafter, Patrick	Princeton University	Principal Investigator
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Abstract

Nitrate N and O isotopes from the GP12 ("PANDORA") cruise in the South-West Pacific and Solomon Sea from June to August 2012 carried out as part of the international GEOTRACES program. This dataset was supported by NSF OCE-1060947, NSF OCE-1736652, NSF OCE-0960802, and the Grand Challenges Program of Princeton University.

Table of Contents

- [Coverage](#)
- [Dataset Description](#)
 - [Methods & Sampling](#)
 - [Data Processing Description](#)
- [Data Files](#)
- [Supplemental Files](#)
- [Related Publications](#)
- [Parameters](#)
- [Instruments](#)
- [Deployments](#)
- [Project Information](#)
- [Program Information](#)
- [Funding](#)

Coverage

Spatial Extent: N:-5.503 E:163 S:-14 W:149.999

Temporal Extent: 2012-07-02 - 2012-07-26

Methods & Sampling

Briefly, samples were acquired and kept frozen until analysis using the Denitrifier Method (Sigman et al. 2001; Casciotti et al. 2002) at Princeton University.

The following methods are further described in the [Intercalibration Report](#) (PDF) for this dataset (also provided under Supplemental Files).

Sampling and storage procedures followed the GEOTRACES cookbook: (1) seawater samples were collected from Niskin bottles into pre-rinsed square 60 mL high-density polyethylene (HDPE) bottles, (2) Each sample was filled to approximately $\frac{3}{4}$ the bottle height to prevent sample overflow during ice expansion, (3) Samples were stored immediately in upright position at -20°C. The one difference between the sampling for the PANDORA cruise and the GEOTRACES cookbook is that these samples were not filtered before freezing. As per the GEOTRACES cookbook, filtration is recommended, but prior tests showed no difference between filtered and non-filtered samples for nitrate isotope measurements (at least within 18 months of sampling).

Samples were analyzed by the Denitrifier Method (Casciotti et al., 2002; Sigman et al., 2001), with technical updates described by (Weigand et al., 2016). Specific protocols for these samples are described in (Marconi et al., 2015) and in detail along with extensive analysis of reference solution results in Weigand et al., 2016. All isotope analyses were performed on a MAT253 Thermo IRMS equipped with a custom-sample preparation system, described by Weigand et al. (2016). Nitrite was not removed from these samples, so they should be considered as possibly "Nitrate + Nitrite" measurements.

Raw data were calibrated to nitrate reference materials IAEA-NO3 and UGSS34, dissolved in low-nitrate seawater collected from the mixed layer at BATS. Samples were bracketed in nitrate concentration by the reference nitrate solutions. When nitrate reference solutions indicated a concentration trend in nitrate d18O, a correction was applied based on those results. These and other aspects of the data processing are described in detail by Weigand et al. (2016).

Data Processing Description

For blank values, detection limits, and internal and external consistency information, refer to the [Intercalibration Report](#) (PDF).

Reported standard deviation is either observed value for replicate analysis or average of this standard deviation (0.04 per mil for d15N and 0.09 per mil for d18O). One sample at very low nitrate concentration (<0.5 uM) has a much higher standard deviation for both d15N and d18O.

BCO-DMO Processing:

- renamed parameters;
- converted Start_Date_UTC field to format YYYY-MM-DD.

[[table of contents](#) | [back to top](#)]

Data Files

File
GP12_Nitrate.csv (Comma Separated Values (.csv), 3.20 KB) MD5:dee56d4d191f8cddd06878fd307aabe6
Primary data file for dataset ID 838914

[[table of contents](#) | [back to top](#)]

Supplemental Files

File
GP12 Nitrate N and O Isotopes Intercalibration Report filename: qs0dim__NITRATE_15_14_D_DELTA_BOTTLE-intercal-report.pdf (Portable Document Format (.pdf), 621.01 KB) MD5:ee01740de50c50ef4ee8d5ce6196b79a GEOTRACES Intercalibration Report for the GP12 (PANDORA) Nitrate N and O Isotope data reported by Patrick Rafter.

[[table of contents](#) | [back to top](#)]

Related Publications

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

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

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

[[table of contents](#) | [back to top](#)]

Parameters

Parameter	Description	Units
Station_ID	Station number	unitless
Start_Date_UTC	Date the event started (UTC); format: YYYY-MM-DD	unitless
Start_Time_UTC	Time the event started (no data)	unitless
End_Date_UTC	Date the event ended (no data)	unitless
End_Time_UTC	Time the event ended (no data)	unitless
Start_Latitude	Latitude the event started	degrees North
Start_Longitude	Longitude the event started	degrees East
End_Latitude	Latitude the event ended (no data)	degrees North
End_Longitude	Longitude the event ended (no data)	degrees East

Event_ID	Event number (no data)	unitless
Sample_ID	GEOTRACES sample number (no data)	unitless
Sample_Depth	Sample depth	meters (m)
NITRATE_15_14_D_DELTA_BOTTLE_qs0dim	Atom ratio of dissolved N isotopes in NITRATE expressed in conventional DELTA notation referenced to Air N2, samples may or may not have been filtered	per mil
SD1_NITRATE_15_14_D_DELTA_BOTTLE_qs0dim	One standard deviation of NITRATE_15_14_D_DELTA_BOTTLE_qs0dim	per mil
Flag_NITRATE_15_14_D_DELTA_BOTTLE_qs0dim	Quality flag for NITRATE_15_14_D_DELTA_BOTTLE_qs0dim (no data)	unitless
NITRATE_18_16_D_DELTA_BOTTLE_zhttuq	Atom ratio of dissolved O isotopes in NITRATE expressed in conventional DELTA notation referenced to {VSMOW}, samples may or may not have been filtered	per mil
SD1_NITRATE_18_16_D_DELTA_BOTTLE_zhttuq	One standard deviation of NITRATE_18_16_D_DELTA_BOTTLE_zhttuq	per mil
Flag_NITRATE_18_16_D_DELTA_BOTTLE_zhttuq	Quality flag for NITRATE_18_16_D_DELTA_BOTTLE_zhttuq (no data)	unitless

[[table of contents](#) | [back to top](#)]

Instruments

Dataset-specific Instrument Name	MAT253 Thermo IRMS
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	Isotope analyses were performed on a MAT253 Thermo IRMS
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	Niskin bottles
Generic Instrument Name	Niskin bottle
Dataset-specific Description	Seawater samples were collected from Niskin bottles
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.

[[table of contents](#) | [back to top](#)]

Deployments

GP12

Website	https://www.bco-dmo.org/deployment/838911
Platform	R/V L'Atalante
Start Date	2012-06-27
End Date	2012-08-07
Description	Cruise DOI: https://doi.org/10.17600/12010050 The main objectives of the French Pandora cruise (GP12 GEOTRACES section) that sailed in the South-West Pacific and through the Solomon Sea from June 27th and until August 7th (Nouméa-Nouméa, R/V Atalante) were: to provide a quasi-synoptic description of surface and subsurface circulation in the Solomon Sea and in the straits connecting that sea with the equatorial circulation, based on both hydrological and geochemical parameters; to deploy a series of moorings in the straits to obtain the temporal variability of the circulation; to evaluate water masses transformations and mixing; to document water/margins exchanges. See more information at: https://www.geotraces.org/geotraces-french-cruise-in-the-solomon-sea-suc... This cruise was supported by the LEFE program of Fr-CNRS/INSU, Fr-IRD and Fr-ANR-09-BLAN-0233 contract.

[[table of contents](#) | [back to top](#)]

Project Information

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 CO_2 . 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.

Collaborative Research: US GEOTRACES PMT: Investigating geochemical tracers of the Pacific nitrogen cycle and budget (PMT Nitrate)

NSF Award Abstract:

Nitrate is an important nutrient that marine plants and algae need for growth. It is abundant in deep ocean waters, but scarce in most sunlit surface waters. The purpose of this project is to better understand what controls the availability of nitrate in the deep ocean and its delivery to surface waters. Researchers from Stanford University, Princeton University, and Brown University will analyze the stable isotopes of seawater nitrate collected between Alaska and Tahiti in the Pacific Ocean. The data will provide information about the supply of nitrate to a large section of the Pacific Ocean and allow informed decisions on past and future changes in marine photosynthesis. This collaborative project will be carried under the GEOTRACES program, an international effort to understand the distribution of elements in the global ocean. This study will include undergraduate, graduate, and postdoctoral researchers at all three academic institutions. The investigators will develop a 1-day workshop for the Teachers as Scholars program, for middle and high school teachers at Princeton University. The workshop will focus on accessing and visualizing ocean data sets and other content available on the internet for project-based learning in the classroom. Investigators will also participate in teacher workshops offered each summer at Stanford University. Data from this project will be made available to the public through the Biological and Chemical Oceanography-Data Management Office (bco-dmo.org). The data will also be compiled in GEOTRACES data products that will be freely available.

The isotopic composition of nitrate in the ocean interior records biogeochemical and physical processes on the time scales of years, decades, centuries, and millennia, with the shallow subsurface and deep ocean recording shorter and longer time scales, respectively. These are meaningful time scales in the efforts to (1) understand

the feedbacks that structure the biogeochemistry of N in the ocean, ocean productivity, and the global carbon cycle, (2) reconstruct past changes in ocean biogeochemistry and carbon cycling, and (3) perhaps predict future changes. This proposal seeks to analyze the nitrate isotopes during the upcoming US GEOTRACES Pacific Meridional Transect (GP15) between Alaska and Tahiti. Nitrate isotopes provide critical constraints on the ocean N cycle and budget, especially in the Pacific Ocean where a variety of processes affect the distribution of nitrate and its supply to surface waters. This largely meridional section of nitrate isotope data will be broadly useful as part of the growing nitrate isotope dataset for the global ocean and for comparison to the many complementary geochemical data sets that will be generated as part of this GEOTRACES effort. In addition, nitrate isotopes in aerosols will be measured to support interpretations of nitrate isotopes in surface waters along the section. The proposed measurements will contribute to the investigation of three overarching questions: 1) What are the similarities and differences in N biogeochemistry among the different nutrient-rich regions in the Pacific basin: the Southern Ocean, equatorial Pacific, and subarctic North Pacific, and how do they affect nitrate supply to low-latitude surface waters? 2) What sources of nitrogen fuel export production in surface waters across the Pacific? 3) What are the roles in surface and subsurface processes in the distribution of nitrate isotopes in the ocean interior?

Collaborative Research: GEOTRACES Atlantic Section Nitrate Isotope Measurements (GP12) (GT Atlantic Nitrate)

NSF Award Abstract:

Nitrogen is one of the two major nutrients required universally by plankton in the ocean, and its availability can affect the ocean's ecology, productivity, and carbon cycle. While the cycling of fixed N in the ocean is in one sense emblematic of other nutrient cycles, it is also unique in that its largest input (N fixation) and output (denitrification) are biologically mediated, which renders the ocean N budget susceptible to complex biological feedbacks. It thus provides a platform for asking one of the core questions of global biogeochemical cycles: How is it that the actions of individual organisms and groups conspire with physicochemical conditions to produce a global Earth surface environment that has been continuously habitable for billions of years?

The dominant terms in the oceanic fixed N input/output budget are poorly characterized, and we focus our attention here on N fixation. Developing robust estimates of the global rate and distribution of N fixation from "direct" shipboard measurements of N fixing activity is complicated by the inherent spatial and temporal variability of this biologically mediated flux. Thus, geochemical approaches for estimating N fixation inputs have come to the forefront. Currently, nitrate stable isotope measurements, which could provide an integrative estimate of N fixation on a regional or basin scale, are sparse in the Atlantic, being focused primarily in the Sargasso Sea. The GEOTRACES program provides a platform to put these data into a broader context through the illumination of basin-scale patterns.

In this project researchers from Princeton University, Brown University, and the Woods Hole Oceanographic Institution will measure the $\delta^{15}\text{N}$ of nitrate in seawater and atmospheric samples collected as part of the GEOTRACES North Atlantic Section. Nitrate $\delta^{15}\text{N}$ is a GEOTRACES "core parameter" that will complement other measurements and will by itself provide important constraints on the oceanographic processes, including N fixation, lateral nitrate transport, low latitude N cycling, the effect of the North African upwelling regions on nutrient fluxes across the basin, and the exchange of fixed N with the Mediterranean. In addition to yielding such specific process-related insights, this work will provide one of the first cross-basin views of nitrate isotopes in the interior and will thus help to simply characterize the isotope signals of different interior water masses, including the Mode Waters, Antarctic Intermediate Water, Mediterranean Intermediate Water, Lower and Upper North Atlantic Deep Water, and Antarctic Bottom Water. Finally, the isotopic characterization of atmospheric nitrate deposition will inform our understanding of the N isotope budget and isotopic gradients of the North Atlantic. Combined, these measurements will yield insight into modern biogeochemical processes and will also provide first order background information for both modern physical oceanographic and paleoceanographic applications. As an example of the latter, studies of Atlantic sediments seek to reconstruct past changes in the rate of N fixation, based on the modern finding that N fixation appears to lower the $\delta^{15}\text{N}$ of thermocline nitrate in the Sargasso Sea. Progress in this paleoceanographic work relies on a more complete picture of nitrate $\delta^{15}\text{N}$ in the modern Atlantic.

Broader impacts: The broader impacts of the proposed study include the mentoring of a postdoctoral investigator and the inclusion of undergraduates in state-of-the-art research. The project will also provide a high-quality nitrate isotope data set for the North Atlantic for use by the broader community.

Program Information

U.S. GEOTRACES (U.S. GEOTRACES)

Website: <http://www.geotraces.org/>

Coverage: Global

GEOTRACES is a [SCOR](#) sponsored program; and funding for program infrastructure development is provided by the [U.S. National Science Foundation](#).

GEOTRACES gained momentum following a special symposium, S02: Biogeochemical cycling of trace elements and isotopes in the ocean and applications to constrain contemporary marine processes (GEOSECS II), at a 2003 Goldschmidt meeting convened in Japan. The GEOSECS II acronym referred to the Geochemical Ocean Section Studies To determine full water column distributions of selected trace elements and isotopes, including their concentration, chemical speciation, and physical form, along a sufficient number of sections in each ocean basin to establish the principal relationships between these distributions and with more traditional hydrographic parameters;

- * To evaluate the sources, sinks, and internal cycling of these species and thereby characterize more completely the physical, chemical and biological processes regulating their distributions, and the sensitivity of these processes to global change; and

- * To understand the processes that control the concentrations of geochemical species used for proxies of the past environment, both in the water column and in the substrates that reflect the water column.

GEOTRACES will be global in scope, consisting of ocean sections complemented by regional process studies. Sections and process studies will combine fieldwork, laboratory experiments and modelling. Beyond realizing the scientific objectives identified above, a natural outcome of this work will be to build a community of marine scientists who understand the processes regulating trace element cycles sufficiently well to exploit this knowledge reliably in future interdisciplinary studies.

Expand "Projects" below for information about and data resulting from individual US GEOTRACES research projects.

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-0960802
NSF Division of Ocean Sciences (NSF OCE)	OCE-1060947
NSF Division of Ocean Sciences (NSF OCE)	OCE-1736652