

# Porewater measurements of nitrate and nitrite concentration and N and O isotopic ratios (d15N and d18O) collected from sites 3 and 10 on the North Atlantic Long Core Cruise R/V Knorr KN223 from October to December 2014

**Website:** <https://www.bco-dmo.org/dataset/748792>

**Data Type:** Cruise Results

**Version:** 1

**Version Date:** 2018-10-26

## Project

» [Determining the rates of denitrification, nitrification, and nitrogen fixation using natural abundance isotope profiles in North Atlantic sediments](#) (North Atlantic Nitrate and Nitrite)

## Program

» [Center for Dark Energy Biosphere Investigations](#) (C-DEBI)

Contributors	Affiliation	Role
<a href="#">Buchwald, Carolyn</a>	Woods Hole Oceanographic Institution (WHOI)	Principal Investigator
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## Abstract

Porewater measurements of nitrate and nitrite concentration and N and O isotopic ratios (d15N and d18O) collected from sites 3 and 10 on the North Atlantic Long Core Cruise R/V Knorr KN223 from October to December 2014.

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## Coverage

**Spatial Extent:** N:14.4007 E:-50.6203 S:14.4 W:-50.6207

**Temporal Extent:** 2014-10-25 - 2014-12-02

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## Dataset Description

Porewater measurements of nitrate and nitrite concentration and N and O isotopic ratios (d15N and d18O) from sites 3 and 10 on the North Atlantic Long Core Cruise R/V Knorr KN223.

## Methods & Sampling

Samples were collected aboard the R/V Knorr using its long coring system in November of 2014 on cruise KN-223 in the North Atlantic. Samples used in this study came from two sediment coring sites located within 90m of each other at 50°37.25'W, 14°24.05'N, and 4455 m water depth. Porewaters were extracted at approximately 0.5m intervals from two long piston cores (30 and 34 m long) using Rhizon samplers (0.2 mm pore size) and either analyzed shipboard or frozen until analyses were conducted shore side.

Nitrate and nitrite concentrations were determined shipboard using ion chromatography with UV detection (D'Hondt et al., 2015). Isotopes were measured in the Wankel lab (Woods Hole Oceanographic Institution) using an Isoprime 100 isotope ratio mass spectrometer coupled to a modified TraceGas prep system similar to that described previously (McIlvin and Casciotti, 2011), which is used to flush, purify and cryogenically trap sample N<sub>2</sub>O from converted nitrate or nitrite samples. Nitrate isotopic composition was measured using the denitrifier method to convert nitrate to N<sub>2</sub>O, normalized to international reference materials (USGS 34, USGS 32, and USGS 35) (Sigman et al., 2001; Casciotti et al., 2002). Nitrite isotope measurements were made separately using the azide method for conversion of nitrite to N<sub>2</sub>O (McIlvin and Altabet, 2005), normalizing to previously calibrated Wankel isotope lab standards (WILIS 10, 11, and 20) (Buchwald et al., 2016). Where co-occurring nitrite concentrations were less than 5 times as high as nitrate, nitrite was removed by addition of sulfamic acid (Granger and Sigman, 2009) prior to the denitrifier method. In the deepest samples having measurable nitrate, where concentrations were very low, the N and O isotopic composition of nitrate was calculated by mass balance using analyses of the combined nitrate + nitrite pools by the denitrifier method, in which both nitrate and nitrite standards were also analyzed, together with nitrite isotope values from the azide-only measurements described previously (Casciotti and McIlvin, 2007).

## Data Processing Description

BCO-DMO Processing:

- modified parameter names to conform to BCO-DMO naming conventions (removed parentheses);
- converted original lat/lon values (degrees & decimal mins) to decimal degrees;
- replaced blank cells (no data) with "nd";
- combined data from both sites into one dataset.

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## Data Files

File
<b>porewater_nitrogen.csv</b> (Comma Separated Values (.csv), 14.09 KB) MD5:23d4fa000b9a513954cfbd35786b29b2
Primary data file for dataset ID 748792

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## Related Publications

Buchwald, C., Grabb, K., Hansel, C. M., & Wankel, S. D. (2016). Constraining the role of iron in environmental nitrogen transformations: Dual stable isotope systematics of abiotic NO<sub>2</sub>— reduction by Fe(II) and its production of N<sub>2</sub>O. *Geochimica et Cosmochimica Acta*, 186, 1–12. doi:[10.1016/j.gca.2016.04.041](https://doi.org/10.1016/j.gca.2016.04.041)  
*Methods*

Casciotti, K. L., & McIlvin, M. R. (2007). Isotopic analyses of nitrate and nitrite from reference mixtures and application to Eastern Tropical North Pacific waters. *Marine Chemistry*, 107(2), 184–201. doi:[10.1016/j.marchem.2007.06.021](https://doi.org/10.1016/j.marchem.2007.06.021)  
*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*

D'Hondt, S., Inagaki, F., Zarikian, C. A., Abrams, L. J., Dubois, N., Engelhardt, T., ... Ziebis, W. (2015). Presence of oxygen and aerobic communities from sea floor to basement in deep-sea sediments. *Nature Geoscience*, 8(4), 299–304. doi:[10.1038/ngeo2387](https://doi.org/10.1038/ngeo2387)

## *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*

McIlvin, M. R., & Altabet, M. A. (2005). Chemical Conversion of Nitrate and Nitrite to Nitrous Oxide for Nitrogen and Oxygen Isotopic Analysis in Freshwater and Seawater. *Analytical Chemistry*, 77(17), 5589–5595.

doi:[10.1021/ac050528s](https://doi.org/10.1021/ac050528s)

## *Methods*

McIlvin, M. R., & Casciotti, K. L. (2011). Technical Updates to the Bacterial Method for Nitrate Isotopic Analyses. *Analytical Chemistry*, 83(5), 1850–1856. doi:[10.1021/ac1028984](https://doi.org/10.1021/ac1028984)

## *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*

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## **Parameters**

Parameter	Description	Units
Site_Number	Site number where samples were collected	unitless
Latitude	Latitude of site; North = positive values	decimal degress
Longitude	Longitude of site; East = positive values	decimal degress
Depth_for_O2	Depth of sample for oxygen (O2) measurement	meters below seafloor (mbsf)
Oxygen	Oxygen concentration	micromolar (uM)
Depth_for_Nitrate_and_Nitrite	Depth of sample for nitrate and nitrite measurements	meters below seafloor (mbsf)
Nitrate	Nitrate concentration	micromolar (uM)
Nitrite	Nitrite concentration	micromolar (uM)
Depth_for_Nitrite_isotopes	Depth of sample for nitrite isotope measurements	meters below seafloor (mbsf)
d15N_Nitrite	d15N nitrite	per mil (‰)
d18O_Nitrite	d18O nitrite	per mil (‰)
Depth_for_Nitrate_isotopes	Depth of sample for nitrate isotope measurements	meters below seafloor (mbsf)
d15N_Nitrate	d15N nitrate	per mil (‰)
d18O_Nitrate	d18O nitrate	per mil (‰)
Depth_for_Ammonium	Depth of sample for ammonium measurements	meters below seafloor (mbsf)
Ammonium	Ammonium concentration	micromolar (uM)

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## Instruments

<b>Dataset-specific Instrument Name</b>	ion chromatography with UV detection
<b>Generic Instrument Name</b>	Ion Chromatograph
<b>Generic Instrument Description</b>	Ion chromatography is a form of liquid chromatography that measures concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently depending on species type and size. Ion chromatographs are able to measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulfate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range. (from <a href="http://serc.carleton.edu/microbelife/research_methods/biogeochemical/ic....">http://serc.carleton.edu/microbelife/research_methods/biogeochemical/ic....</a> )

<b>Dataset-specific Instrument Name</b>	Isoprime 100 isotope ratio mass spectrometer
<b>Generic Instrument Name</b>	Isotope-ratio Mass Spectrometer
<b>Dataset-specific Description</b>	Isoprime 100 isotope ratio mass spectrometer coupled to a modified TraceGas prep system
<b>Generic Instrument Description</b>	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).

<b>Dataset-specific Instrument Name</b>	R/V Knorr long coring system
<b>Generic Instrument Name</b>	Piston Corer
<b>Generic Instrument Description</b>	The piston corer is a type of bottom sediment sampling device. A long, heavy tube is plunged into the seafloor to extract samples of mud sediment. A piston corer uses a "free fall" of the coring rig to achieve a greater initial force on impact than gravity coring. A sliding piston inside the core barrel reduces inside wall friction with the sediment and helps to evacuate displaced water from the top of the corer. A piston corer is capable of extracting core samples up to 90 feet in length.

<b>Dataset-specific Instrument Name</b>	Rhizon samplers
<b>Generic Instrument Name</b>	Sediment Porewater Sampler
<b>Dataset-specific Description</b>	Rhizon samplers extract small volumes of pore water from soil and sediments. See: <a href="https://www.rhizosphere.com/">https://www.rhizosphere.com/</a>
<b>Generic Instrument Description</b>	A device that collects samples of pore water from various horizons below the seabed.

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## Deployments

## KN223

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/567408">https://www.bco-dmo.org/deployment/567408</a>
<b>Platform</b>	R/V Knorr
<b>Start Date</b>	2014-10-25
<b>End Date</b>	2014-12-02

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## Project Information

**Determining the rates of denitrification, nitrification, and nitrogen fixation using natural abundance isotope profiles in North Atlantic sediments (North Atlantic Nitrate and Nitrite)**

**Website:** <https://www.darkenergybiosphere.org/award/determining-the-rates-of-denitrification-nitrification-and-nitrogen-fixation-using-natural-abundance-isotope-profiles-in-north-pond-sediments/>

**Coverage:** North Pond, North Atlantic

### Project Abstract:

Deep-sea sediments in the oligotrophic ocean host a diverse array of microbes that are involved in multiple processes within the nitrogen cycle. Using measurements of nitrate and nitrite, and their stable isotopes (d15N and d18O) in sedimentary pore fluids, we have been developing approaches for determining the distribution and magnitude of key processes in the oligotrophic sediments of the North Atlantic. While concentration profiles alone indicate the production of nitrate through nitrification in the surface sediments and the reduction of the nitrate deeper in the absence of oxygen, the dual stable isotope profiles of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> demonstrate clear evidence of further complexity; specifically, that nitrite oxidation occurs deeper in the sediments as well, apparently in the absence of O<sub>2</sub>. A number of lines of evidence contribute to this refined understanding of the distribution of N cycling processes in these environments, including large differences in the nitrate and nitrite d15N, as well as the evolution of a greater than 1:1 relationship between the d15N and d18O of nitrate. We used a 1D inverse model that predicts the distribution and rates of different oxidative and reductive nitrogen cycling processes throughout these vertical profiles. Our analysis reveals that nitrate reduction and nitrite oxidation co-occur between 0 and 10 meters, and that the ratio of these processes changes in relation to the abundance of porewater oxygen. In the upper profile where dissolved oxygen is more abundant oxidative processes (e.g., nitrite re-oxidation) play an exceptionally large role, as reflected in the very high slope for the evolving relationship between d15N and d18O nitrate. Below the depth of oxygen penetration, while nitrate reduction becomes a substantially more important processes, a clear indication of oxidation remains – as reflected in the large difference between nitrate and nitrite d15N. All rates were predicted to be slow on the order of 0.1 mM per year, which was substantiated by d18O values of nitrite reflecting complete isotopic equilibration with water.

This project was funded by a [C-DEBI Postdoctoral Fellowship](#) to Carolyn Buchwald (advisor: Scott Wankel).

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## Program Information

**Center for Dark Energy Biosphere Investigations (C-DEBI)**

**Website:** <http://www.darkenergybiosphere.org>

**Coverage:** Global

The mission of the Center for Dark Energy Biosphere Investigations (C-DEBI) is to explore life beneath the

The mission of the Center for Dark Energy Biosphere Investigations (C-DEBI) is to explore life beneath the seafloor and make transformative discoveries that advance science, benefit society, and inspire people of all ages and origins.

C-DEBI provides a framework for a large, multi-disciplinary group of scientists to pursue fundamental questions about life deep in the sub-surface environment of Earth. The fundamental science questions of C-DEBI involve exploration and discovery, uncovering the processes that constrain the sub-surface biosphere below the oceans, and implications to the Earth system. What type of life exists in this deep biosphere, how much, and how is it distributed and dispersed? What are the physical-chemical conditions that promote or limit life? What are the important oxidation-reduction processes and are they unique or important to humankind? How does this biosphere influence global energy and material cycles, particularly the carbon cycle? Finally, can we discern how such life evolved in geological settings beneath the ocean floor, and how this might relate to ideas about the origin of life on our planet?

C-DEBI's scientific goals are pursued with a combination of approaches:

- (1) coordinate, integrate, support, and extend the research associated with four major programs—Juan de Fuca Ridge flank (JdF), South Pacific Gyre (SPG), North Pond (NP), and Dorado Outcrop (DO)—and other field sites;
- (2) make substantial investments of resources to support field, laboratory, analytical, and modeling studies of the deep subseafloor ecosystems;
- (3) facilitate and encourage synthesis and thematic understanding of submarine microbiological processes, through funding of scientific and technical activities, coordination and hosting of meetings and workshops, and support of (mostly junior) researchers and graduate students; and
- (4) entrain, educate, inspire, and mentor an interdisciplinary community of researchers and educators, with an emphasis on undergraduate and graduate students and early-career scientists.

Note: Katrina Edwards was a former PI of C-DEBI; James Cowen is a former co-PI.

#### **Data Management:**

C-DEBI is committed to ensuring all the data generated are publically available and deposited in a data repository for long-term storage as stated in their [Data Management Plan \(PDF\)](#) and in compliance with the [NSF Ocean Sciences Sample and Data Policy](#). The data types and products resulting from C-DEBI-supported research include a wide variety of geophysical, geological, geochemical, and biological information, in addition to education and outreach materials, technical documents, and samples. All data and information generated by C-DEBI-supported research projects are required to be made publically available either following publication of research results or within two (2) years of data generation.

To ensure preservation and dissemination of the diverse data-types generated, C-DEBI researchers are working with BCO-DMO Data Managers make data publicly available online. The partnership with BCO-DMO helps ensure that the C-DEBI data are discoverable and available for reuse. Some C-DEBI data is better served by specialized repositories (NCBI's GenBank for sequence data, for example) and, in those cases, BCO-DMO provides dataset documentation (metadata) that includes links to those external repositories.

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## **Funding**

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-0939564</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1433150</a>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1537485</a>

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