Measurements of Kr/Ar and N2/Ar ratios in stored dissolved gas samples collected in 1981 through the Transient Tracers in the Ocean (TTO) program North Atlantic Survey (NAS)

Website: https://www.bco-dmo.org/dataset/890427
Data Type: Cruise Results
Version: 1
Version Date: 2023-02-23

Project
» Collaborative Research: Probing the Ventilation Efficiency of the Deep Ocean with Conservative Dissolved Gas Tracers in Archived Samples (TTO NGs and O2)
» Collaborative Research: Novel constraints on air-sea gas exchange and deep ocean ventilation from high-precision noble gas isotope measurements in seawater (HPNGI)

Contributors	Affiliation	Role
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Abstract
This dataset includes measurements of Kr/Ar and N2/Ar ratios in stored dissolved gas samples collected in 1981 through the Transient Tracers in the Ocean (TTO) program. These data were used, along with new observations of heavy noble gas ratios (elemental and isotopic ratios) from the Bermuda Atlantic Time-series (BATS) on cruise 10391 (30 April 2022 - 05 May 2022), to model simulations of these tracers using the Transport Matrix Method (TMM). Together these new measurements and model simulations provide insight into physical processes governing gas exchange in the high-latitude regions of North Atlantic Deep Water formation, and a comparison of physical simulations of N2/Ar ratios to observations in TTO samples reveals excess N2 that arises from benthic denitrification in the deep North Atlantic.

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Coverage

Spatial Extent: **N**:49.5 **E**:-11 **S**:23.3 **W**:-70.4
Temporal Extent: 1981-04-01 - 1981-10-19

Methods & Sampling

Note: all methods are described in detail in the accompanying publication currently in final review at *Proceedings of the National Academy of Sciences.*

Samples were collected via the Transient Tracers in the Ocean (TTO) North Atlantic Survey (NAS) in 1981 via shipboard degassing of ~285-liter Gerard Barrel samples. The extraction technique is described in detail in Smethie and Mathiue (1986). Aliquots of archived gas from these samples were analyzed in the Seltzer and Jenkins Labs at Woods Hole Oceanographic Institution for noble gas elemental ratios and O2/Ar and N2/Ar ratios following techniques described in Seltzer et al. (2023).

The model simulations are available as a related dataset at BCO-DMO. See: https://www.bco-dmo.org/dataset/890293

Data Processing Description

Data Processing:
All data were processed using MATLAB. Codes are available upon request.

BCO-DMO Processing:
- renamed fields to comply with BCO-DMO naming conventions.

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Data Files

File
tto_nas_tanks.csv (Comma Separated Values (.csv), 1.11 KB) MD5:7d3245015fcae30e2a3050d1d0ce99d8 Primary data file for dataset ID 890427

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Related Publications

Seltzer, A. M., Nicholson, D. P., Smethie, W. M., Tyne, R. L., Le Roy, E., Stanley, R. H. R., Stute, M., Barry, P. H., McPaul, K., Davidson, P. W., Chang, B. X., Rafter, P. A., Lethaby, P., Johnson, R. J., Khatiwala, S., & Jenkins, W. J. (2023). Dissolved gases in the deep North Atlantic track ocean ventilation processes. Proceedings of the National Academy of Sciences, 120(11). https://doi.org/10.1073/pnas.2217946120
Results

Smethie, W. M., & Mathieu, G. (1986). Measurement of krypton-85 in the ocean. Marine Chemistry, 18(1), 17–33. https://doi.org/10.1016/0304-4203(86)90073-3
Methods

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Related Datasets

IsSourceOf

Seltzer, A. M., Barry, P., Jenkins, W. J., Khatiwala, S., Nicholson, D. P., Smethie Jr., W. M., Stanley, R., Stute, M.

(2023) **Model simulations of elemental and isotopic heavy noble gas ratios using the Transport Matrix Method (TMM).** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-02-21 doi:10.26008/1912/bco-dmo.890293.1 [view at BCO-DMO]
Relationship Description: The TTO data in dataset 890427 were used in the development of the model in dataset 890293.

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Parameters

Parameter	Description	Units
Station	TTO/NAS station number where sample was collected	unitless
Depth	Depth of sampling	meters (m)
Lat	Station latitude	degrees North
Lon	Station longitude	degrees East
delta_N2_to_Ar_raw	Δ(N2/Ar),raw: deviation of N2/Ar from solubility equilibrium before physical correction (‰, vs eq)	permil (0/00)
delta_N2_to_Ar_corr	Δ(N2/Ar),corr: deviation of N2/Ar from solubility equilibrium after physical correction (‰, vs eq)	permil (0/00)
O2_sat	O2 sat: oxygen concentration relative to solubility equilibrium originally measured in 1981	percent (%)
delta_O2_to_Ar	Δ(O2/Ar): deviation of O2/Ar ratio from solubility equilibrium measured in this study (% vs eq)	percent (%)
Mean_Age_K12	Mean age (K12): ideal mean age (yr) of nearest grid cell in Khatiwala et al., 2012 inversion	years
Mean_Age_H21	Mean age (H21): ideal mean age (yr) of nearest grid cell in Holzer et al., 2021 inversion	years
delta_Kr_to_Ar_raw	Δ(Kr/Ar),raw: deviation of measured Kr/Ar from solubility equilibrium (‰, vs eq)	permil (0/00)
delta_Kr_to_Ar_model	Δ(Kr/Ar),model: deviation of modeled Kr/Ar from solubility equilibrium (‰, vs eq)	permil (0/00)
delta_N2_to_Ar_model	Δ(N2/Ar),model: deviation of modeled N2/Ar from solubility equilibrium (‰, vs eq)	permil (0/00)

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Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	Gerard barrel
Dataset-specific Description	Samples were collected via the Transient Tracers in the Ocean (TTO) North Atlantic Survey (NAS) in 1981 via shipboard degassing of ~285-L Gerard Barrel samples
Generic Instrument Description	A barrel used to collect water samples in oceanography. It holds 250 liters of sea water.

Dataset-specific Instrument Name	Thermo MAT 253 Plus
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	A Thermo MAT 253 Plus (Seltzer Lab) was used for dynamic noble gas ratios.
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 MAT 253
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	A Thermo MAT 253 (Seltzer Lab) was used for N2, O2, Ar analysis.
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	quadrupole mass spectrometer
Generic Instrument Name	Quadrupole Mass Spectrometer
Dataset-specific Description	A custom quadrupole mass spectrometer (Jenkins lab) was used for static noble gas ratios.
Generic Instrument Description	A piece of apparatus that consists of an ion source, a mass-to-charge analyser, a detector and a vacuum system and is used to measure mass spectra. The detector is a quadrupole mass-to-charge analyser, which holds the ions in a stable orbit by an electric field generated by four parallel electrodes.

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Deployments

TTO

Website	https://www.bco-dmo.org/deployment/890471
Platform	R/V Knorr
Start Date	1981-04-01
End Date	1981-10-19
Description	The Transient Tracers in the Ocean (TTO) program, North Atlantic Study took place in 1981, with expeditions on R/V Knorr. It was comprised of the following legs, with dates in YYYY-MM-DD format. EXPOCODES correspond to their ID numbers in CCHDO (CLIVAR and Carbon Hydrographic Data Office): North Atlantic Study, 1981 Leg 1 (Woods Hole to Freeport): P. G. Brewer*, R. T. Williams. 1981-04-01 to 1981-04-13. EXPOCODE 316N19810401. Leg 2 (Freeport to Bermuda): J. L. Sarmiento*, R. T. Williams. 1981-04-16 to 1981-05-10. EXPOCODE 316N19810416. Leg 3 (Bermuda to Azores): L. Armi*. 1981-05-16 to 1981-06-14. EXPOCODE 316N19810516. Leg 4 (Azores to Glasgow): W. S. Broecker*, C. G. Rooth. 1981-06-19 to 1981-07-17. EXPOCODE 316N19810619. Leg 5 (Glasglow to Reykjavik): T. Takahashi*, J. H. Swift. 1981-07-21 to 1981-08-14. EXPOCODE 316N19810721. Leg 6 (Reykjavik to St. Johns): W. J. Jenkins*, P. B. Rhines. 1981-08-21 to 1981-09-17. EXPOCODE 316N19810821. Leg 7 (St. Johns to Woods Hole): P. G. Brewer*, W. M. Smethie. 1981-09-23 to 1981-10-19. EXPOCODE 316N19810923. More information can be found in the following publication: Brewer, P.G., Sarmiento, J.L., & Smethie, W.M. (1985). The Transient Tracers in the Ocean (TTO) program: The North Atlantic Study, 1981; The Tropical Atlantic Study, 1983. Journal of Geophysical Research, 90, 6903-6905. DOI: 10.1029/JC090IC04P06903 Additional cruise information and data are also available from CCHDO at https://cchdo.ucsd.edu/search?q=North%20Atlantic%20Study

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Project Information

Collaborative Research: Probing the Ventilation Efficiency of the Deep Ocean with Conservative Dissolved Gas Tracers in Archived Samples (TTO NGs and O2)

Coverage: Atlantic Ocean

NSF Award Abstract:

This award is funded in whole or in part under the American Rescue Plan Act of 2021 (Public Law 117-2).

The transfer of gases between the atmosphere and the interior of ocean is controlled by processes in the high latitudes, where deep waters are “formed” by the sinking of cold and/or salty surface waters. The processes that affect air-sea gas exchange during water mass formation play an important role in the uptake of carbon dioxide and other important gases by the ocean. Dissolved noble gases, which are not affected by chemistry or biology, are excellent tracers of the physics of air-sea gas exchange: their abundances in the ocean interior tell us about how efficient gas exchange was when water was last at the sea surface. Another tracer, the “triple oxygen isotope” (TOI) composition of dissolved oxygen (a measure of the relative abundances of oxygen-16, oxygen-17, and oxygen-18) is sensitive to both biology and physics. However, each of these important tracers of air-sea exchange remains understudied in the modern ocean. This project aims to make new state-of-the-art measurements of noble gases and TOIs in 100 archived gas samples from the North and South Atlantic. The methods developed in this project will also enable future research opportunities that take advantage of these valuable samples. The project will support the training of a PhD student and multiple undergraduates, while contributing to ongoing efforts to develop workshop and lecture materials for a new partnership between Woods Hole Oceanographic Institution (WHOI) and a nearby public high school that has a primarily underrepresented minority student body.

The primary objective of this project is to quantify the magnitude and spatial variability of two sets conservative tracers that are each independently sensitive to air-sea gas exchange at the time of deep-water formation: noble gases and TOIs. A deeper understanding of these tracers will provide insight into the physical mechanisms that regulate the efficiency of deep-ocean ventilation. Over recent decades, multiple studies have

consistently found undersaturation of the heavy noble gases (Ar, Kr, and Xe) in the deep ocean, with respect to their solubility equilibrium concentrations in seawater. However, while several theories exist, there is no consensus on why the heavy noble gases are undersaturated throughout the deep ocean nor any reason to suspect that a single process is responsible. The spatial variability in noble gas disequilibrium between the North and South Atlantic may provide key clues to this open question, given the vastly different mechanisms of northern and southern deep-water formation. However, to date, analytical limitations have limited the robust detection and quantification of inter water-mass differences in disequilibrium. TOIs may also provide insight into air-sea disequilibrium during deep-water formation, as the relative excess of oxygen-17 (with respect to the atmospheric oxygen isotope ratios and corrected for isotopic fractionation due to respiration) reflects the balance between air-sea exchange and photosynthesis. Together, noble gases and TOIs provide useful constraints to elucidate fundamental mechanisms. For example, sea-ice cover in regions of deep-water formation will simultaneously lead to undersaturation of noble gases and accumulation of photosynthetic oxygen (and thus excess oxygen-17). However, few high-quality measurements of TOI in the deep ocean exist, due to analytical challenges, despite the great potential of TOI as a conservative tracer of physics and biogeochemistry during deep-water formation. The proposed work will involve 100 measurements of archived dissolved gas samples that were extracted at sea in the 1980s and stored in robust tanks since collection. This project is the first effort to measure noble gases and TOI in the same deep-ocean samples across a wide spatial range, by consistently employing the same methodology and instrumentation to eliminate inter-laboratory biases. It involves measurements in three WHOI labs and makes use of state-of-the-art techniques for each independent tracer measurement. This work builds in redundancy to improve the accuracy of results by measuring all samples on multiple instruments, including pairs of adjacent stations, and carrying out extraction experiments with the original equipment used in the 1980s to collect these samples. For example, heavy noble gas elemental ratios will be measured independently on two separate instruments, and high-precision (order 0.01 permil) measurements of noble gas isotopes will be used to test and correct for sample integrity. Overall, this large set of archived gases offers a unique opportunity to better understand these tracers and explore the quantitative insight they may offer into outstanding questions about the deep-ocean ventilation.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

Collaborative Research: Novel constraints on air-sea gas exchange and deep ocean ventilation from high-precision noble gas isotope measurements in seawater (HPNGI)

Coverage: North Atlantic

NSF Award Abstract:
The proposed work brings together the fields of chemical oceanography, ocean modeling, and solid Earth geochemistry to develop the stable isotope composition of heavy noble gases dissolved in seawater as novel physical tracers of air-sea gas exchange. Noble gases represent ideal tools for quantifying physical processes due to the fact that they are chemically inert. Because argon (Ar), krypton (Kr), and xenon (Xe) isotope ratios have distinct solubility and diffusivity ratios, as recently quantified in laboratory experiments, they complement existing bulk noble gas measurements in seawater by adding new constraints with unique sensitivities. Precise constraints on air-sea exchange of inert gases are paramount to properly quantifying production, consumption, and physical transport of biogeochemically important gases (such as carbon dioxide and oxygen) as well as ventilation age tracers (such as sulfur hexafluoride and CFCs). Additionally, global circulation models (GCMs) routinely underestimate deep-ocean ventilation compared to noble gas observations. Introducing these new isotopic constraints into model simulations will help identify physical processes related to deep-water formation that require improvement in future GCM development. Because the overturning circulation is closely tied to projections of future climate, by both the transports of radiative gases and heat into the deep ocean, there is broad international interest in improving future model projections. Therefore, adding high-precision noble gas isotope measurements to the existing body of research on inert gases in seawater will provide valuable new constraints for both the marine biogeochemistry and physical oceanography communities. Education and training of a graduate student and postdoctoral scholar will contribute to the human resource base of the United States.

The proposed work will develop high-precision Ar, Kr, and Xe stable isotope ratios in seawater as new oceanographic tracers. Along with a 2018 pilot study, the proposed measurements represent the first high-precision Kr and Xe isotope ratio analyses in seawater. A key goal of this project is to test two specific

hypotheses for the observed undersaturation of Ar, Kr, and Xe throughout the deep ocean: (1) rapid cooling-induced gas uptake by the surface ocean during deep-water formation with insufficient time for equilibration before sinking, or (2) subsurface cooling caused by melting of glacial ice, leading to the dissolution of air bubbles trapped in ice. Whereas both of these non-mutually exclusive processes produce similar patterns of heavy noble gas undersaturation, the isotope ratios of these gases are well suited to distinguish the relative importance of each process. Specifically, theoretical predictions suggest a decrease in heavy-to-light isotope ratios from the kinetic fractionation associated with rapid surface ocean gas uptake, but an increase in these ratios from the input of gravitationally enriched glacial meltwater. Other goals include: (a) comparing observations to model simulations to identify successes and shortcomings of GCM representations of deep-water formation processes, and (b) a year-long time series of surface-ocean observations from the SIO pier to test models of isotopic fractionation associated with bubble injection and upwelling, with implications for the saturation of biogeochemically important gases. This work will improve upon a recent method for dissolved noble gas isotopic analysis by increasing sample sizes and refining purification techniques to achieve a >60% improvement in precision.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-2122427
NSF Division of Ocean Sciences (NSF OCE)	OCE-1923915

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