# Model simulations of elemental and isotopic heavy noble gas ratios using the Transport Matrix Method (TMM)

**Website**: https://www.bco-dmo.org/dataset/890293
**Data Type**: model results
**Version**: 1
**Version Date**: 2023-02-21

**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)



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**Abstract**
This dataset includes model simulations of the following tracers using the Transport Matrix Method (TMM): (i) 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), and (ii) 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. Together these 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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### 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.*

All model simulations were carried out using the University of Victoria Earth System Climate Model (UVic ESCM) via the Transport Matrix Method (TMM), using an updated version of the gas exchange model of Nicholson et al. (2016) to include noble gas isotopes, N2, and different gas exchange parameterizations. A full description is included in the accompanying paper (Seltzer et al., 2023).

The BATS data and TTO data are available as related datasets at BCO-DMO. See the following:
BATS - https://www.bco-dmo.org/dataset/890342
TTO - https://www.bco-dmo.org/dataset/890427

**Data Processing Description**

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

The data are provided here in both NetCDF (.nc) and MATLAB (.mat).

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## Data Files

| File |
|---|
| **UVic_TMM_output.nc** (NetCDF, 109.94 MB) MD5:382713b172d61b0486dd2549b279cc54<br>Primary data file for dataset ID 890293. Data are the sam as UVic_TMM_output.mat but in NetCDF format.<br><br>netcdf UVic_TMM_output {<br>dimensions:<br>lon = 100 ;<br>lat = 100 ;<br>depth = 19 ;<br>month = 12 ;<br>mon = 12 ;<br>variables:<br>double D136Xe_model(month, depth, lat, lon) ;<br>double D40Ar_model(month, depth, lat, lon) ;<br>double D86Kr_model(month, depth, lat, lon) ;<br>double DKrAr_model(month, depth, lat, lon) ;<br>double DN2Ar_model(month, depth, lat, lon) ;<br>double DXeAr_model(month, depth, lat, lon) ;<br>double month(mon) ;<br>double x(lon) ;<br>double y(lat) ;<br>double z(depth) ; |

| File |
| --- |
| } |
| Variable descriptions: |
| D136Xe_model: monthly climatologies of simulated 136Xe/129Xe solublity anomaly (in per mil; lon x lat x depth x month) |
| D40Ar_model: monthly climatologies of simulated 40Ar/36Ar solublity anomaly (in per mil; lon x lat x depth x month) |
| D86Kr_model: monthly climatologies of simulated 86Kr/82Kr solublity anomaly (in per mil; lon x lat x depth x month) |
| DKrAr_model: monthly climatologies of simulated Kr/Ar solublity anomaly (in per mil; lon x lat x depth x month) |
| DN2Ar_model: monthly climatologies of simulated N2/Ar solublity anomaly (in per mil; lon x lat x depth x month) |
| DXeAr_model: monthly climatologies of simulated Xe/Ar solublity anomaly (in per mil; lon x lat x depth x month) |
| month: month of year (1 to 12; Jan to Dec) |
| x: longitude (0 to 360 degrees) |
| y: latituide (-90 to 90 degrees) |
| z: depth (meters) |

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## Supplemental Files

| File | |
|---|---|
| **UVic_TMM_output.mat** | (MATLAB Data (.mat), 43.39 MB)<br>MD5:02babd5f11474b62e1729a271121e2f7 |
| Supplemental data file for dataset ID 890293. Data are the same as UVic_TMM_output.nc but in MATLAB Format.<br><br>Variable descriptions:<br><br>D136Xe_model: monthly climatologies of simulated 136Xe/129Xe solublity anomaly (in per mil; lon x lat x depth x month)<br><br>D40Ar_model: monthly climatologies of simulated 40Ar/36Ar solublity anomaly (in per mil; lon x lat x depth x month)<br><br>D86Kr_model: monthly climatologies of simulated 86Kr/82Kr solublity anomaly (in per mil; lon x lat x depth x month)<br><br>DKrAr_model: monthly climatologies of simulated Kr/Ar solublity anomaly (in per mil; lon x lat x depth x month)<br><br>DN2Ar_model: monthly climatologies of simulated N2/Ar solublity anomaly (in per mil; lon x lat x depth x month)<br><br>DXeAr_model: monthly climatologies of simulated Xe/Ar solublity anomaly (in per mil; lon x lat x depth x month)<br><br>month: month of year (1 to 12; Jan to Dec)<br><br>x: longitude (0 to 360 degrees)<br><br>y: latituide (-90 to 90 degrees)<br><br>z: depth (meters) | |

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## Related Publications

Nicholson, D. P., Khatiwala, S., & Heimbach, P. (2016). Noble gas tracers of ventilation during deep-water formation in the Weddell Sea. IOP Conference Series: Earth and Environmental Science, 35, 012019. doi:10.1088/1755-1315/35/1/012019
*Methods*

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*

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## Related Datasets

### IsDerivedFrom

Seltzer, A. M., Barry, P., Jenkins, W. J., Khatiwala, S., Nicholson, D. P., Smethie Jr., W. M., Stanley, R., Stute, M. (2023) **Elemental and isotopic noble gas ratios from the Bermuda Atlantic Time-series (BATS) on cruise 10391 on R/V Atlantic Explorer (AE2208) from 30 April 2022 to 05 May 2022.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-02-22 doi:10.26008/1912/bco-dmo.890342.1 [view at BCO-DMO]
*Relationship Description: The BATS data in dataset 890342 were used in the development of the model in dataset 890293.*

Seltzer, A. M., Barry, P., Jenkins, W. J., Khatiwala, S., Nicholson, D. P., Smethie Jr., W. M., Stanley, R., Stute, M. (2023) **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).** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2023-02-23 doi:10.26008/1912/bco-dmo.890427.1 [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 |
|---|---|---|
| D136Xe_model | monthly climatologies of simulated 136Xe/129Xe solublity anomaly (in per mil; lon x lat x depth x month) | per mil |
| D40Ar_model | monthly climatologies of simulated 40Ar/36Ar solublity anomaly (in per mil; lon x lat x depth x month) | per mil |
| D86Kr_model | monthly climatologies of simulated 86Kr/82Kr solublity anomaly (in per mil; lon x lat x depth x month) | per mil |
| DKrAr_model | monthly climatologies of simulated Kr/Ar solublity anomaly (in per mil; lon x lat x depth x month) | per mil |
| DN2Ar_model | monthly climatologies of simulated N2/Ar solublity anomaly (in per mil; lon x lat x depth x month) | per mil |
| DXeAr_model | monthly climatologies of simulated Xe/Ar solublity anomaly (in per mil; lon x lat x depth x month) | per mil |
| month | month of year (1 to 12; Jan to Dec) | unitless |
| x | longitude (0 to 360 degrees) | degrees |
| y | latituide (-90 to 90 degrees) | degrees |
| z | depth (meters) | meters |

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## Instruments

| | |
|---|---|
| **Dataset-specific Instrument Name** | NCAR Cheyenne supercomputer |
| **Generic Instrument Name** | High-Performance Computing Cluster |
| **Dataset-specific Description** | The TMM infrastructure developed by S. Khatiwala and D. Nicholson was implemented on the NCAR Cheyenne supercomputer. Cheyenne is a 5.34-petaflops, high-performance computer built for the National Center for Atmospheric Research (NCAR). The system was released for production work on January 12, 2017. The Cheyenne supercomputer features 145,152 Intel Xeon processor cores in 4,032 dual-socket nodes (36 cores/node) and 313 TB of total memory. |
| **Generic Instrument Description** | "High-Performance Computing" (HPC) refers to a class of evolving technologies that provide leading-edge computational capabilities, including scalable high-performance computers, high-end graphic systems, and high-speed networks. HPC may be used for molecular modeling, genome analysis, and image processing, among others. |

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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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