Noble gas isotope data from field campaigns sampling groundwater in Umatilla, Oregon during September 2020 and in Tucson, Arizona during November 2021

Project
» 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
Severinghaus, Jeffrey	University of California-San Diego (UCSD-SIO)	Principal Investigator
Ng, Jessica Yijun	University of California-San Diego (UCSD-SIO)	Student
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Abstract
This project developed a novel seawater and groundwater noble gas isotope extraction technique, building on an approach pioneered by Dr. Steve Emerson that involves equilibration of headspace and water followed by vacuum removal and disposal of almost all the water. Corrections are then made for the lost noble gas in the water, using precisely measured mass and volume. The method uses 6-liter stainless steel flasks with Nupro valves for improved leak-tightness. This extraction technique made it possible to measure neon as well as the heavier noble-gas isotopes, all from the same sample, providing a constraint on "excess air" using the neon. Field campaigns sampling groundwater were conducted in Oregon and Arizona. Data from these campaigns are deposited here.

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Coverage

Spatial Extent: **N**:46.05 **E**:-110.73 **S**:32.14 **W**:-119.81
Temporal Extent: 2020-09-15 - 2021-11-12

Methods & Sampling

Field campaigns to sample groundwater were conducted in Umatilla, Oregon, USA during September 2020 and in Tucson, Arizona, USA during November 2021. Water samples for dissolved noble gas isotope measurements were collected in 6-liter (L) pre-evacuated stainless steel flasks (Restek TO-can air sampling flasks sealed with a Swagelok SS-4H valve), leaving 1 L of headspace. The sample gases were equilibrated between the dissolved phase in the sample water and the gas phase in the headspace on an orbital shaker for at least 3 days at a constant known temperature. After the sample water was drained, the headspace gas was transferred and gettered to remove non-inert gases. The remaining gas sample was measured on a dynamic isotope ratio mass spectrometer (IRMS), and the measured isotope ratios were corrected using known

solubilities (Seltzer et al., 2019) and the recorded equilibration temperature to obtain the original isotope ratios of the water sample (Ng et al., 2023). Umatilla samples were stored for a year at room temperature prior to sampling. Tucson samples were stored for 2 weeks at room temperature prior to sampling.

Data Processing Description

Data Processing:
Corrections were made to account for 1) partitioning of the sample gas between the dissolved phase and the headspace and 2) matrix effects (ME) which are known to affect the apparent isotopic ratio of a trace gas in a mixture of gases. We empirically determine ME by measuring air and air-equilibrated water (AEW) standards and employing an optimization routine, such that squared deviations between measured AEW isotope ratios and known solubility equilibrium values are minimized.

BCO-DMO Processing:
- removed 'NaN' as a missing data identifier (missing data are blank/empty in the final csv file);
- renamed fields to comply with BCO-DMO naming conventions;
- converted the Sampling_date column to YYYY-MM-DD format.

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Data Files

File
noble_gas_isotopes.csv(Comma Separated Values (.csv), 5.71 KB) MD5:3a97ee00341980f950ebfe9f6e4862cf Primary data file for dataset ID 897484

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Related Publications

Ng, J., Tyne, R., Seltzer, A., Noyes, C., McIntosh, J., & Severinghaus, J. (2023). A new large-volume equilibration method for high-precision measurements of dissolved noble gas stable isotopes. Rapid Communications in Mass Spectrometry, 37(7). Portico. https://doi.org/10.1002/rcm.9471
Methods

Seltzer, A. M., Ng, J., & Severinghaus, J. P. (2019). Precise determination of Ar, Kr and Xe isotopic fractionation due to diffusion and dissolution in fresh water. Earth and Planetary Science Letters, 514, 156–165. https://doi.org/10.1016/j.epsl.2019.03.008
Methods

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Parameters

Parameter	Description	Units
State_ID	State identification number of well (Umatilla sites only)	unitless
Location	Location of sampling (Umatilla or Tucson)	unitless
Site	Name of well	unitless
Lat	Latitude of sampling location where positive values = North	decimal degrees
Lon	Longitude of sampling location where negative values = West	decimal degrees
Elevation_m	Elevation of sampling location in meters	meters (m)

Elevation_ft	Elevation of sampling location in feet	feet (ft)
Pressure_atm	Pressure	atmosphere (atm)
Mid_screen_depth_ft	Mid screen depth	feet (ft)
Screen_length_ft	Screen length	feet (ft)
Depth_to_water_ft	Depth to water	feet (ft)
Sampling_date	Date of sampling	unitless
NG_method	Method used for noble gas sampling and analysis; LVE refers to large volume equilibration method (Ng et al., 2022); CT means copper tube.	unitless
He	Helium	cubic centimeters per gram (cc/g)
He_err	Standard error for He	cubic centimeters per gram (cc/g)
Ne	Neon	cubic centimeters per gram (cc/g)
Ne_err	Standard error for Ne	cubic centimeters per gram (cc/g)
Ar	Argon	cubic centimeters per gram (cc/g)
Ar_err	Standard error for Ar	cubic centimeters per gram (cc/g)
Kr	Krypton	cubic centimeters per gram (cc/g)
Kr_err	Standard error for Kr	cubic centimeters per gram (cc/g)
Xe	Xenon	cubic centimeters per gram (cc/g)
Xe_err	Standard error for Xe	cubic centimeters per gram (cc/g)
dXe	d*Xe	per mil (‰)
dKr	d*Kr	per mil (‰)
d40_36_Ar	d40/36 Ar	per mil (‰)
d40_36_err	Standard error for d40_36_Ar	per mil (‰)
d38_36_Ar	d38/36 Ar	per mil (‰)
d38_36_err	Standard error for d38_36_Ar	per mil (‰)
d86_82_Kr	d86/82 Kr	per mil (‰)
d86_82_err	Standard error for d38_36_Ar	per mil (‰)
d86_83_Kr	d86/83 Kr	per mil (‰)

d86_83_err	Standard error for d86_83_Kr	per mil (‰)
d86_84_Kr	d86/84 Kr	per mil (‰)
d86_84_err	Standard error for d86_84_Kr	per mil (‰)
d136_129_Xe	d136/129 Xe	per mil (‰)
d136_129_err	Standard error for d136_129_Xe	per mil (‰)
d134_129_Xe	d134/129 Xe	per mil (‰)
d134_129_err	Standard error for d134_129_Xe	per mil (‰)
d132_129_Xe	d132/129 Xe	per mil (‰)
d132_129_err	Standard error for d132_129_Xe	per mil (‰)
WTD	Water table depth	meters (m)
WTD_err	Standard error for WTD	meters (m)

Instruments

Dataset-specific Instrument Name	MAT-253 dual inlet dynamic mass spectrometer
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	The gas sample was measured on a MAT-253 dual inlet dynamic mass spectrometer at the Scripps Institution of Oceanography.
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	MKS 122b-11993 100 Torr barotron
Generic Instrument Name	Pressure Sensor
Dataset-specific Description	The pressure of the purified noble gas sample was measured with an MKS 122b-11993 100 Torr barotron.
Generic Instrument Description	A pressure sensor is a device used to measure absolute, differential, or gauge pressures. It is used only when detailed instrument documentation is not available.

Project Information

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.

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1924394