Stable carbon isotope of dissolved inorganic carbon (δ13C-DIC) collected during the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) A16N cruises on R/V Ronald Brown between March and May 2023

Website: https://www.bco-dmo.org/dataset/942833
Data Type: Cruise Results
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Project
» Measurements of stable carbon isotopes on board GO-SHIP cruises in the South Atlantic Ocean to enhance our ability to quantify anthropogenic CO2 uptake rates by the ocean (South Atlantic Ocean δ13CDIC)

Contributors	Affiliation	Role
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Abstract
These data include the stable carbon isotope of dissolved inorganic carbon (δ13C-DIC) collected during the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) A16N cruise in 2023. The cruise was divided into two legs and all aboard the R/V Ronald H. Brown between dates 2023-03-06 and 2023-05-09 in the North Atlantic Ocean. An automated, efficient, and high-precision method for ship-based δ13C-DIC analysis based on Cavity Ring-Down Spectroscopy (CRDS) was used. Stable isotopes of carbon can be used as a "signature" to identify fossil fuel-derived carbon dioxide in the atmosphere and ocean. These data were collected by Dr. Wei-Jun Cai's group of the University of Delaware.

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Coverage

Location: North Atlantic Ocean A16N line
Spatial Extent: **N**:63.3007 **E**:-19.9813 **S**:-5.9988 **W**:-29.0094
Temporal Extent: 2023-03-09 - 2023-05-08

Methods & Sampling

Sampling:

During the ship-based repeated hydrographic observations, discrete seawater samples for δ13C-DIC were collected according to procedures outlined in the PICES Special Publication, Guide to Best Practices for Ocean CO2 Measurements from a profiling Conductivity, Temperature, and Depth (CTD) instrument paired with Niskin bottles. One or two duplicate samples were taken at each station. Pre-combusted (550 degrees Celsius for 4 hours) 250-milliliter (mL) borosilicate glass bottles were rinsed three times with the sample seawater before being filled from the bottom, allowing it to overflow for approximately twice the time needed to fill the bottle to the top. Bottles were capped and left in the room for about 30 minutes (to bring cold deep-water samples to near room temperature). Then, 1 mL of water was extracted from each bottle to allow thermal expansion, and 50 microliters (µL) of saturated HgCl2 solution was added to poison biological activities. Sample bottles were sealed with Apiezon-L grease, and stoppers were fixed with rubber bands and clips. The samples were stored at room temperature for at least 24 hours before onboard analysis or in coolers for transporting back to the home laboratory.

Analysis:
A G2131-i Isotope and Gas Concentration CRDS Analyzer (Picarro, USA) was employed along with an AS-D1 δ13C-DIC Analyzer (Apollo SciTech, USA) for sample injection, CO2 extraction, instrument control, and data acquisition in δ13C-DIC measurements. The analytical procedure began with drawing 0.7 mL of phosphoric acid brine (2% vol./vol. H3PO4 with 7% wt./vol. NaCl) into a 10 mL syringe by a digital syringe pump (Precision ≤ 0.05%, Tecan, USA) coupled to a 12-port valve and followed up by injection of the acid brine into the reactor. This step also cleaned residues from the previous cycle. While this pre-acid was bubbled in the reactor with a CO2-free air stream, an additional 0.9 mL of the acid brine was drawn into the syringe, followed by a 6.6 mL sample (or standard). The excess of acid brine ensured that all DIC in the sample could completely convert to CO2. Once a stable baseline of near zero CO2 was reached in the reactor and the CO2 detector, the sample and acid brine in the syringe were injected into the reactor at a controlled low speed to allow the acid brine to clear the sample DIC attached to the syringe wall into the reactor, where all carbonate species were converted to CO2. The CO2 was extracted and carried to the CRDS analyzer at a rate of 60 mL-1 by CO2-free compressed air from a 40-liter (L) cylinder. The CRDS concurrently reported CO2 concentration (12CO2 + 13CO2) and δ13C-CO2 values at 1 Hz for about 500 seconds, with data similarly captured by the AS-D1's data processing and control module. The analytical cycle would complete when CO2 levels drop below a set threshold (i.e., the deviation between 15 successive data points of CO2 reading was less than 5 parts per million (ppm) above the initial baseline), followed by a 120 second purge with carrier gas before the next cycle. Measurements occur under room temperature (20 ± 1 degree Celsius), each lasting about 13 minutes.

During the cruise, a total of 3890 samples were collected from 3518 Niskin bottles, corresponding to 10.6% duplicate rate. Of these, 2875 samples were analyzed onboard, while the rest were analyzed ashore within 3 months.

Data Processing Description

Due to the logistical complexities of implementing standard gas setups on a ship, we did not adopt the built-in δ13C-CO2 calibration program of the G2131-i CRDS system. Instead, leveraging multiple in-house standards with pre-calibrated δ13C-DIC values facilitated the correction of δ13Cmean inaccuracies. Throughout the analytical period, in-house standards were sub-sampled into 12-mL glass vials weekly and then sent to the UC Davis Stable Isotope Facility for δ13C-DIC analysis. In their approach, DIC in water was converted to headspace CO2 using phosphoric acid and analyzed using headspace equilibration technique with a Thermo Scientific GasBench II and Thermo Finnigan Delta Plus XL isotope-ratio mass spectrometer (IRMS). The δ13C-DIC values, obtained through Gasbench-IRMS method at the facility, were utilized to calibrate the CRDS measurements of δ13C-DIC.

To balance the need for frequent calibrations with the onboard sample processing efficiency, a calibration using one of the three in-house standards was conducted following analysis of every eight seawater samples. This procedure ensured each standard was assessed a minimum of three times daily. We calculated the CO2 concentration-weighted mean δ13C-CO2 (δ13Cmean) for each analysis by incorporating both raw δ13C-CO2 (δ13Craw) data and net CO2 concentration (CO2net) readings from the CRDS at every time point. The δ13Cmean values for each in-house standard, derived from itsadjacent measurements, were used in a time-based linear regression model to track the instrumental drift and estimate the value of the standard’s δ13C signal (δ13Cest) at the time of each sample measurement. This enabled the establishment of a separate three-point calibration curve (R2 > 0.999) for each measurement, incorporating the δ13Cest and the exact δ13C-DIC values of three in-house standards.

In our approach, each sample or reference material was subjected to a minimum of two and up to four consecutive measurements to achieve the preset relative standard deviation (RSD) of 0.001 for the net integration area and 0.06 for the CO_2-weighted mean of δ13C-CO_2. From these measurements, we selected two "valid" rounds that met our precision criteria, and the final DIC concentrations and δ13C-DIC results were always reported as an average of these two valid rounds. In addition, CRM Batch #197, #199, #201, #202, and #206 were randomly included in the sample sequence as quality checks for δ13C-DIC analysis.

Based on our previous study, the method's uncertainty is 0.03‰ for the δ13C-DIC value (1σ). The GO-SHIP A16N cruise in 2023 analyzed 320 replicate samples from 150 CTD stations. Excluding 15 pairs of abnormal data with a δ13C-DIC difference greater than 0.2‰, the mean absolute differences was 0.06 ± 0.05‰ for δ13C-DIC (1σ, n = 305), which was within 2σ of the overall uncertainty of the method.

BCO-DMO Processing Description

- Imported original file "GO-SHIP_A16N_2023_d13C_checked.xlsx" into the BCO-DMO system.
- Flagged "-999.00" as a missing data value (missing data are empty/blank in the final csv file).
- Renamed fields to comply with BCO-DMO naming conventions.
- Created the date-time column in ISO 8601 format.
- Saved final file as "942833_v1_go-ship_a16n_2023_d13c_dic.csv".

Problem Description

Some δ13C-DIC values reported are suspected to be inconsistent with historical values, and are accordingly labeled with a QC flag of 3. See flag definitions at: https://doi.org/10.3389/fmars.2021.705638

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Related Publications

Sun, Z., Li, X., Ouyang, Z., Featherstone, C., Atekwana, E. A., Hussain, N., & Cai, W. (2024). Simultaneous onboard analysis of seawater dissolved inorganic carbon (DIC) concentration and stable isotope ratio (δ13C-DIC). Limnology and Oceanography: Methods. Portico. https://doi.org/10.1002/lom3.10642
Methods

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Parameters

Parameter	Description	Units
EXPOCODE	EXPOCODE of the cruise	unitless
SECT_ID	Section ID of the cruise	unitless
ISO_DateTime_UTC	Date and time (UTC) of sample collection in ISO 8601 format	unitless
DATE	Date of sample collection	unitless
TIME_UTC	UTC Time of sample collection	unitless
STATION	Station number where seawater samples were collected	unitless
NISKIN	Niskin bottles number	unitless
LATITUDE	Latitude of the station	decimal degrees
LONGITUDE	Longitude of the station; negative values = West	decimal degrees
DEPTH	Water depth of the sample	meters (m)
DELC13	δ13C-DIC; values are expressed relative to the reference standard Vienna PeeDee Belemnite (V-PDB)	per mil (‰)
DELC13_FLAG	Quality flag of δ13C-DIC: 2 = acceptable; 3 = questionable; 6 = median of replicates; 9 = missing value.	unitless

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Instruments

Dataset-specific Instrument Name	AS-D1 δ13C-DIC Analyzer (Apollo SciTech, USA)
Generic Instrument Name	Apollo AS-D1 DIC and d13C-DIC Analyzer
Dataset-specific Description	A G2131-i Isotope and Gas Concentration CRDS Analyzer (Picarro, USA) was employed along with an AS-D1 δ13C-DIC Analyzer (Apollo SciTech, USA) for sample injection, CO2 extraction, instrument control, and data acquisition in δ13C-DIC measurements.
Generic Instrument Description	The AS-D1 is an instrument designed to prepare natural water samples for Dissolved Inorganic Carbon (DIC) and delta13C analysis and provide the user with the analyses outputs. It has features that are specifically useful for seawater and coastal water samples. The instrument provides the user with DIC values (micromol per kg) and the delta13C content of the DIC (per mille). It consists of a digital syringe pump for delivery of reagent and samples, a mass flow controller to regulate flow rate, a CO2 stripping reactor, and an electronic cooling system to remove moisture. The AS-D1 does not measure the sample but is designed to send the gas to a different analyzer. This second instrument then sends the measurements back to the AS-D1 after analysis. The AS-D1 then calculates the desired DIC and delta13C outputs. This instrument is designed for automatic sampling from multiple bottles. It can be used in laboratories on shore or at sea. The instrument was created to be paired with the Picarro G-2131i Carbon Isotope Analyser, however, other models that measure the isotopic ratio of CO2 may be compatible. The precision is +/- 0.1 % for DIC of seawater and +/- 0.07 % for DIC-delta13C. Sample volume is 1-7 milliliters per analysis, and sample time is under 12 minutes. Additional information from the manufacturer is available at: https://apolloscitech.com/dicdelta.html

Dataset-specific Instrument Name	G2131-i Isotope and Gas Concentration CRDS Analyzer (Picarro, USA)
Generic Instrument Name	Gas Analyzer
Dataset-specific Description	A G2131-i Isotope and Gas Concentration CRDS Analyzer (Picarro, USA) was employed along with an AS-D1 δ13C-DIC Analyzer (Apollo SciTech, USA) for sample injection, CO2 extraction, instrument control, and data acquisition in δ13C-DIC measurements.
Generic Instrument Description	Gas Analyzers - Instruments for determining the qualitative and quantitative composition of gas mixtures.

Dataset-specific Instrument Name	10-liter Niskin bottles
Generic Instrument Name	Niskin bottle
Dataset-specific Description	10 L Niskin bottles were used to collect discrete seawater samples for δ13C-DIC measurements.
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.

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Deployments

33RO20230306

Website	https://www.bco-dmo.org/deployment/942847
Platform	NOAA Ship Ronald H. Brown
Report	https://cchdo.ucsd.edu/data/38324/33RO20230306_do.pdf
Start Date	2023-03-06
End Date	2023-04-07
Description	More information is available at https://cchdo.ucsd.edu/cruise/33RO20230306

33RO20230413

Website	https://www.bco-dmo.org/deployment/942849
Platform	NOAA Ship Ronald H. Brown
Report	https://cchdo.ucsd.edu/data/41351/33RO20230413_do.pdf
Start Date	2023-04-13
End Date	2023-05-09
Description	More information is available at https://cchdo.ucsd.edu/cruise/33RO20230413

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Project Information

Measurements of stable carbon isotopes on board GO-SHIP cruises in the South Atlantic Ocean to enhance our ability to quantify anthropogenic CO2 uptake rates by the ocean (South Atlantic Ocean δ13CDIC)

NSF Award Abstract:
Rising carbon dioxide concentrations in the atmosphere, global climate change, and the sustainability of the Earth's biosphere are of great scientific and societal concern. Approximately one-quarter of fossil fuel emissions of carbon dioxide emitted each year are absorbed by the oceans, and it is important to understand where and how fast this process occurs. Stable isotopes of carbon can be used as a "signature" to identify fossil fuel-derived carbon dioxide in the atmosphere and ocean. The investigators have developed a new method for measuring the stable carbon isotope composition of dissolved carbon dioxide rapidly and precisely while at sea. They will measure several thousand samples on two research expeditions to the South Atlantic Ocean. They will compare their measurements to ones made in the same locations approximately ten years earlier, and determine the amount of carbon dioxide absorbed over that time period. The proposed research will enhance ocean carbon research infrastructure, general science education, and public awareness of climate change and environmental issues. The investigators plan to enhance diversity in earth sciences by recruiting underrepresented minority students in the research and have a graduate and an undergraduate student involved in all phases of this project. The team, including the students, will actively disseminate the research results in international, national, regional, local education and outreach activities, and in peer-review journals.

In the South Atlantic Ocean, anthropogenic CO2 uptake rates are high and variable as mode and intermediate waters are formed and are sensitive to climate changes. The carbon-13 Suess effect makes delta13C-CO2 in the atmosphere a clearly defined endmember and delta13C-DIC in the ocean a powerful tracer to independently estimate anthropogenic CO2 uptake and storage in the ocean. The team has developed a precise, rapid, and sea-going method to simultaneously measure dissolved inorganic carbon (DIC) concentration (to plus or minus 2 micromol per kilogram) and stable carbon isotope composition (delta13C-DIC) (to plus or minus 0.03 permil) by combining a CO2 extraction device with a Cavity Ring-Down

Spectroscopy (CRDS) isotope analyzer. They will use this method aboard GO-SHIP cruises A13.5 and A16S to analyze about 1000 samples onboard the ship and 2000 samples on land for each cruise. Extensive evaluation and comparison of this method with the traditional isotope ratio mass spectrometry (IRMS)-based method will be done. The PIs hypothesize that the formation and the strength of mode and intermediate waters have a strong influence on the lateral transport of anthropogenic carbon and thus the decadal variability of the water column anthropogenic carbon inventory change. As a result, the change in inventory has both meridional and zonal trends, and therefore a combination of A13.5 and A16S will better represent the basin-wide changes. Two objectives will be achieved in testing this hypothesis: (1) Demonstrate that precise and accurate delta13C-DIC data, comparable in quality to IRMS-based data, can be collected via the CRDS-based method, and that large numbers of samples can be analyzed onboard ships and back home with high spatial resolution comparable to other GO-SHIP level 1 parameters such as DIC; (2) Assess the spatial variations and temporal changes of the anthropogenic carbon uptake and storage rates in the South Atlantic Ocean. In particular, the PIs will compare estimated anthropogenic carbon inventories independently from delta13C-DIC and DIC observations from transect A13.5 (2022 vs. 2010 and earlier data) in the eastern basin with those of transect A16S (2024 vs. 2013 and earlier data) in the western basin. They will also compare the basin-wide water column anthropogenic 13C-DIC inventory with the surface ocean anthropogenic 13CO2 uptake flux estimated from air-sea carbon isotope disequilibrium, the difference being anthropogenic carbon carried by lateral transport.

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-2123768

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