Bottle data from R/V Endeavor cruise EN665 in the Gulf of Maine, conducted April 7-12, 2021

Website: https://www.bco-dmo.org/dataset/884424
Data Type: Cruise Results
Version: 1
Version Date: 2022-11-29

Project
» Biogenic Calcium Carbonate Solubilities and Reaction Rates by Lab and Field Saturometry (Calcite Saturometer)

Contributors	Affiliation	Role
Subhas, Adam V.	Woods Hole Oceanographic Institution (WHOI)	Principal Investigator
Rauch, Shannon	Woods Hole Oceanographic Institution (WHOI BCO-DMO)	BCO-DMO Data Manager

Abstract
This dataset is the bottle data for Cruise EN665 on the R/V Endeavor in the Gulf of Maine, conducted April 7-12, 2021. Included are the CTD rosette data along with nutrient and carbonate chemistry analyses (DIC, TA, and d13C-DIC). Data were collected and analyzed by PI Subhas.

Table of Contents

Coverage

Spatial Extent: **N**:43.4936333 **E**:-67.8296833 **S**:42.3413667 **W**:-69.6683
Temporal Extent: 2021-04-07 - 2021-04-12

Methods & Sampling

These data were collected on R/V Endeavor cruise EN665 from three stations in the Wilkinson and Jordan Basins of the Gulf of Maine (approximately 42.6 North, 69.6 West, depth 0-260 meters). Water samples were collected using Niskin bottles on the CTD rosette.

Nutrients:
Nutrient samples were collected directly from Niskin bottles using clean 60-milliliter (mL) plastic syringes. Samples were then passed through a 25-millimeter (mm) 0.2-micron filter (either polycarbonate or PTFE) into clean, 60-mL HDPE bottles. Bottles were rinsed 3 times with filtered water before filling and capping. Bottles were then frozen at -20 degrees Celsius for approximately 30 days until analysis. Analyses were performed at the WHOI Nutrient Analytical Facility on a SEAL Analytical AA3 HR following established procedures.

Total Alkalinity, Dissolved Inorganic Carbon (DIC), and d13C-DIC:
Samples for total alkalinity (TA), dissolved inorganic carbon (DIC), and d13C-DIC were collected simultaneously. Water from the Niskins was passed through a 0.45-micron cartridge filter and all bubbles were removed from

the line. Ground-glass stoppered 250-mL were rinsed 3 times with flowing, filtered seawater and then filled. Each sample bottle was left to overflow for approximately double the amount of time it took to fill the bottle. Excess water was gently dumped out to leave a ~2-3 mL headspace below the ground glass fitting. Following collection, samples were poisoned with 100 microliters of saturated mercuric chloride solution. Bottles were sealed with a greased stopper (Apiezon-L). A rubber band was placed over the stopper to ensure sample closure. Samples were stored cool and in the dark prior to analysis at the Woods Hole Oceanographic Institution.

DIC and d13C analyses were performed first immediately after opening the bottle. DIC and d13C-DIC were determined simultaneously using an Apollo AS-D1 analyzer connected to a Picarro G-2121i cavity ringdown system on a 5 mL sample of seawater. Samples were run in at least triplicate and calibrated against seawater Certified Reference Materials. Isotopic values were calibrated against an in-house seawater standard that was intercalibrated against known solid materials (NBS-19, IAEA-C2, and NBS-20). Intercalibration was performed on the same Picarro instrument using an Automate-Liaison front-end unit. Total alkalinity was determined using an open-system Gran titration on 5-mL samples in triplicate, using a Metrohm 805 Dosimat and a robotic Titrosampler, calibrated against seawater Certified Reference Materials.

pH:
pH samples were measured on the total scale with pure meta cresol purple indicator (mCP) at 25C +/- 0.1C on an Agilent 8453 spectrophotometer. A subset of the samples (18 out of 30 total) was used to derive the R-value perturbation by the indicator, for which all of the samples were then corrected.

Data Processing Description

Data Quality Flags:
Quality flags were applied according to the definitions described in Jiang et al., 2022, as follows:
0 = interpolated data;
1 = not evaluated / quality unknown;
2 = acceptable;
3 = questionable;
4 = known bad;
6 = median of replicates;
9 = missing value.

BCO-DMO Processing:
- replaced "NaN" with "nd" ("no data");
- converted date to ISO 8601 format;
- added column for date-time in UTC;
- renamed fields to comply with BCO-DMO naming conventions;
- converted longitude values from positive degrees West to negative degrees East;
- replaced the wrong cruise ID of EN669 with EN665.

[table of contents | back to top]

Data Files

File
en665_bottle.csv (Comma Separated Values (.csv), 6.87 KB) MD5:58ff055e1b860972214dce3b7fa85ea0 Primary data file for dataset ID 884424

[table of contents | back to top]

Related Publications

Clayton, T. D., & Byrne, R. H. (1993). Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Research Part I: Oceanographic

Research Papers, 40(10), 2115–2129. doi:10.1016/0967-0637(93)90048-8
Methods

Dickson, A.G.; Sabine, C.L. and Christian, J.R. (eds) (2007) Guide to best practices for ocean CO2 measurement. Sidney, British Columbia, North Pacific Marine Science Organization, 191pp. (PICES Special Publication 3; IOCCP Report 8). DOI: https://doi.org/10.25607/OBP-1342
Methods

Jiang, L.-Q., Pierrot, D., Wanninkhof, R., Feely, R. A., Tilbrook, B., Alin, S., Barbero, L., Byrne, R. H., Carter, B. R., Dickson, A. G., Gattuso, J.-P., Greeley, D., Hoppema, M., Humphreys, M. P., Karstensen, J., Lange, N., Lauvset, S. K., Lewis, E. R., Olsen, A., ... Xue, L. (2022). Best Practice Data Standards for Discrete Chemical Oceanographic Observations. Frontiers in Marine Science, 8. https://doi.org/10.3389/fmars.2021.705638
Methods

[table of contents | back to top]

Related Datasets

IsRelatedTo

Allen, K. A., Subhas, A. V., Woods, M. (2024) **Carbonate chemistry analyses (total alkalinity, DIC, and d13C of DIC) from discrete bottle samples and CTD data from 12 stations sampled during R/V Endeavor cruise EN669 in the Gulf of Maine during August 2021.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2024-04-17 doi:10.26008/1912/bco-dmo.915709.1 [view at BCO-DMO]
Relationship Description: A complementary dataset from the same year in the same region.

[table of contents | back to top]

Parameters

Parameter	Description	Units
Cruise_ID	cruise identifier	unitless
STNNBR	station number	unitless
LATITUDE	latitude	decimal degrees North
LONGITUDE	longitude (negative values = West)	decimal degrees East
CASTNO	cast number	unitless
ISO_DateTime_Local	date and time in local time zone (US Eastern) in ISO 8601 format	unitless
ISO_DateTime_UTC	date and time (UTC) in ISO 8601 format	unitless
DEPTH	depth	meters (m)
CTDTMP	CTD temperature	degrees Celsius
CTDSAL	CTD salinity	unitless
CTDOXY	CTD oxygen	micromoles per kilogram
NO2_NO3	nitrate + nitrite	micromoles per kilogram
NH4	ammonia	micromoles per kilogram
PHSPHT	phosphate	micromoles per kilogram
SILCAT	silicate	micromoles per kilogram
NITRIT	nitrite	micromoles per kilogram
ALKALI	total alkalinity	micromoles per kilogram
ALKALI_SD	total alkaliniy measurement standard deviation	micromoles per kilogram
ALKALI_W_FLAG	total alkalinity quality flag	unitless
PH_TOT	pH, total scale at surface pressure and measurement temperature	unitless
PH_TOT_SD	pH, total scale measurement standard deviation	unitless
PH_TMP	pH, total scale measurement temperature	degrees Celsius
TCARBN	dissolved inorganic carbon	micromoles per kilogram
TCARBN_SD	dissolved inorganic carbon measurement standard deviation	micromoles per kilogram
TCARBN_W_FLAG	dissolved inorganic carbon quality flag	unitless
DELC13	delta-13C of DIC	permil vs. PDB
DELC13_SD	delta-13C of DIC measurement standard deviation	permil vs. PDB
DELC13_W_FLAG	delta-13C of DIC quality flag	unitless
SIGMA_T	density at surface pressure	kilograms per cubic meter
CTDOXY_SAT	CTD oxygen saturation value	micromoles per kilogram
XMISS	CTD beam transmission	percent
FLUOR	CTD fluorescence	milligrams per cubic meter
PAR	CTD photosynthetically active radiation	unitless

[table of contents | back to top]

Instruments

Dataset-specific Instrument Name	Apollo AS-D1 DIC and d13C-DIC analyzer unit
Generic Instrument Name	Apollo AS-D1 DIC and d13C-DIC Analyzer
Dataset-specific Description	DIC-d13C was determined using an Apollo AS-D1 DIC and d13C-DIC analyzer unit, connected to a Picarro G-2121i Cavity Ringdown Spectrometer.
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	Titrosampler
Generic Instrument Name	Automatic titrator
Dataset-specific Description	Total alkalinity was determined using an open-system Gran titration on 5-mL samples in triplicate, using a Metrohm 805 Dosimat and a robotic Titrosampler, calibrated against seawater Certified Reference Materials.
Generic Instrument Description	Instruments that incrementally add quantified aliquots of a reagent to a sample until the end-point of a chemical reaction is reached.

Dataset-specific Instrument Name	Picarro G-2121i Cavity Ringdown Spectrometer
Generic Instrument Name	Cavity enhanced absorption spectrometers
Dataset-specific Description	DIC-d13C was determined using an Apollo AS-D1 DIC and d13C-DIC analyzer unit, connected to a Picarro G-2121i Cavity Ringdown Spectrometer.
Generic Instrument Description	Instruments that illuminate a sample inside an optical cavity, typically using laser light, and measure the concentration or amount of a species in gas phase by absorption spectroscopy. Techniques include cavity ring-down spectroscopy (CRDS) and integrated cavity output spectroscopy (ICOS).

Dataset-specific Instrument Name	SeaBird SBE-911+
Generic Instrument Name	CTD Sea-Bird SBE 911plus
Generic Instrument Description	The Sea-Bird SBE 911 plus is a type of CTD instrument package for continuous measurement of conductivity, temperature and pressure. The SBE 911 plus includes the SBE 9plus Underwater Unit and the SBE 11plus Deck Unit (for real-time readout using conductive wire) for deployment from a vessel. The combination of the SBE 9 plus and SBE 11 plus is called a SBE 911 plus. The SBE 9 plus uses Sea-Bird's standard modular temperature and conductivity sensors (SBE 3 plus and SBE 4). The SBE 9 plus CTD can be configured with up to eight auxiliary sensors to measure other parameters including dissolved oxygen, pH, turbidity, fluorescence, light (PAR), light transmission, etc.). more information from Sea-Bird Electronics

Dataset-specific Instrument Name	
Generic Instrument Name	Metrohm 805 Dosimat
Dataset-specific Description	Total alkalinity was determined using an open-system Gran titration on 5-mL samples in triplicate, using a Metrohm 805 Dosimat and a robotic Titrosampler, calibrated against seawater Certified Reference Materials.
Generic Instrument Description	The Metrohm 805 Dosimat is a dispensing instrument for titrating and dosing operations in the laboratory. The 805 Dosimat is controlled by Touch control or PC control software. The instrument controls the dosing of liquids, which are attached via an exchange unit. Metrohm recommends using the Metrohm 806 Exchange units which come with 1, 5, 10, 20, or 50 milliliter (mL) dosing cylinders. The instrument can read and overwrite data from the exchange unit. It has a resolution of 20,000 steps per cylinder volume and a dosing/filling time of 18 seconds. The 805 Dosimat and the corresponding 806 Exchange Unit are suitable as a buret not only for simply dosing auxiliary solutions but also for titrations. Additional information is available from the instrument manufacturer: https://www.metrohm.com/en_au/products/2/8050/28050010.html

Dataset-specific Instrument Name	Niskin bottles
Generic Instrument Name	Niskin bottle
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.

Dataset-specific Instrument Name	SEAL Analytical AA3 HR
Generic Instrument Name	Seal Analytical AutoAnalyser 3HR
Dataset-specific Description	Nutrients were determined at the WHOI Nutrient Analytical Facility on a SEAL Analytical AA3 HR following established procedures.
Generic Instrument Description	A fully automated Segmented Flow Analysis (SFA) system, ideal for water and seawater analysis. It comprises a modular system which integrates an autosampler, peristaltic pump, chemistry manifold and detector. The sample and reagents are pumped continuously through the chemistry manifold, and air bubbles are introduced at regular intervals forming reaction segments which are mixed using glass coils. The AA3 uses segmented flow analysis principles to reduce inter-sample dispersion, and can analyse up to 100 samples per hour using stable LED light sources.

[table of contents | back to top]

Deployments

EN665

Website	https://www.bco-dmo.org/deployment/884430
Platform	R/V Endeavor
Start Date	2021-04-07
End Date	2021-04-12
Description	See more information from the Rolling Deck to Repository (R2R): https://www.rvdata.us/search/cruise/EN665

[table of contents | back to top]

Project Information

Biogenic Calcium Carbonate Solubilities and Reaction Rates by Lab and Field Saturometry (Calcite Saturometer)

NSF Award Abstract:
The ocean actively exchanges carbon dioxide with the atmosphere and is currently absorbing about a third of the carbon dioxide humans emit through fossil fuel burning. Because carbon dioxide is acidic, ocean pH drops as it takes up carbon dioxide, a process known as "ocean acidification". Ocean acidification negatively affects the health of marine ecosystems by making it harder for organisms to grow their calcium carbonate shells. Yet, the dissolution of these calcium carbonate shells in the deep ocean helps neutralize the carbon dioxide we emit as humans. The extent to which this process takes place is a function of the solubility of marine calcium carbonate. This project will evaluate the temperature and pressure effects on the stability of biologically produced calcium carbonate minerals. The results from this study will allow us to better predict where, how much, and how fast, carbon dioxide will be neutralized and stored in the world's ocean. We will also investigate the ways in which small changes in the chemical composition of calcium carbonate shells - such as the incorporation of magnesium - influence their stability. This project will also conduct micro-computed tomography scans of microorganisms' shells to better visualize them in 3-dimensional detail. We will print these 3-dimensional scans for use as educational tools in the classroom and in the Woods Hole Visitor Center. In addition, professional development workshops for high school teacher on ocean acidification and the

importance of marine calcification will be held yearly.

The ocean is the ultimate repository for most of anthropogenic carbon dioxide emissions, which in turn is making ocean chemistry less favorable for biogenic carbonate precipitation through the process of ocean acidification. Ocean acidification decreases seawater pH but dissolution of primarily biogenic carbonate minerals has the capacity to buffer this acidification and over thousands of years push whole-ocean pH and atmospheric carbon dioxide to their preindustrial values. Unfortunately, the relationship between seawater chemistry, carbonate mineral solubility, and the kinetics that govern carbonate dissolution and precipitation are not fully understood. Currently, it is clear that relationships based solely on inorganic calcite are insufficient to describe the cycling of biogenic calcites in the ocean. This project will conduct a systematic determination of the solubilities and reaction kinetics of the three most common biogenic carbonates (coccoliths, foraminifera, and pteropods), both in the laboratory and in the field, using spectrophotometric pH saturometry. The saturometer incubates calcium carbonate with seawater in a closed system. During each run, the change in pH within the saturometer traces the progression of calcium carbonate dissolution/precipitation as the system approaches equilibrium. The saturometer therefore has the potential to link mechanistic interpretations of mineral dissolution/precipitation kinetics to measurements of solubility in a single experiment. The spectrophotometric pH method uses well-calibrated indicator dyes, allows solubility and data to be tied to modern pH calibrations and reference materials, and can be used in the laboratory or deployed on a hydrowire at sea. Field experiments will be conducted at multiple depths, elucidating in-situ controls on solubility and kinetics, as well as the sensitivity of biogenic calcite solubility to temperature and pressure. Experiments will be conducted from both sides of equilibrium, allowing for robust determinations of inorganic and biogenic solubilities.

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.

[table of contents | back to top]

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1923998

[table of contents | back to top]