# 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

Website: https://www.bco-dmo.org/dataset/915709

**Data Type**: Cruise Results

Version: 1

Version Date: 2024-04-17

#### **Project**

» <u>CAREER: Gulf of Maine Temperature Trends and Variability from the early Holocene to the Present</u> (GoM Temperature Trends)

Contributors	Affiliation	Role
Allen, Katherine A.	University of Maine	Principal Investigator
Subhas, Adam V.	Woods Hole Oceanographic Institution (WHOI)	Co-Principal Investigator
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#### **Abstract**

This dataset includes seawater properties observed during cruise EN669 on the R/V Endeavor in the Gulf of Maine, conducted in August 2021 by PI Katherine Allen and the shipboard science party. Included are data from twelve CTD/Niskin rosette casts at twelve different stations accompanied by carbonate chemistry analyses (total alkalinity, DIC, and d13C of DIC) from discrete bottle samples collected during each cast. Bottle samples were analyzed by Adam Subhas at the Woods Hole Oceanographic Institution after the cruise was complete. Data from CTD casts were collected by the Endeavor's shipboard scientific party. These Gulf of Maine seawater observations provide constraints on growth conditions of synchronously collected foraminifera, enabling geochemical paleo-proxies to be assessed and refined for regional paleoceanographic reconstructions.

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## Coverage

**Spatial Extent**: N:44.2444 E:-65.9087 S:40.8734 W:-69.756

**Temporal Extent**: 2021-08-04 - 2021-08-11

## Methods & Sampling

These data were collected on R/V Endeavor cruise EN669 from 12 stations across the Gulf of Maine. Water samples were collected using Niskin bottles on the CTD rosette. Equipment included a Seabird Scientific

SBE9plus CTD equipped with a transmissometer, oxygen, and fluorescence sensors.

#### 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-milliliter (mL) bottles 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.

#### **BCO-DMO Processing Description**

- Imported the first sheet of the original file "EN669\_CTD\_Bottle\_BCODMO.xlsx" from into the BCO-DMO system.
- Removed the empty column (column M in Excel file).
- Renamed fields to comply with BCO-DMO naming conventions.
- Created the ISO DateTime UTC column by converting the julian date (TimeJ) column to ISO 8601 format.
- Saved the final file as "915709 v1 en669 bottle.csv".

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#### **Data Files**

#### File

**915709\_v1\_en669\_bottle.csv**(Comma Separated Values (.csv), 45.55 KB)

MD5:01c3141137b3499bdd17bf0a30a734cb

Primary data file for dataset ID 915709, version 1

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## **Related Datasets**

#### IsRelatedTo

Rolling Deck To Repository. (2023). *CTD (Conductivity, Temperature, Depth) data collected during research cruise EN669 using a SeaBird SBE-911+ instrument system onboard the platform RV Endeavor* (Version 1) [Data set]. Rolling Deck to Repository (R2R) Program. https://doi.org/10.7284/146161

Subhas, A. V. (2022) **Bottle data from R/V Endeavor cruise EN665 in the Gulf of Maine, conducted April 7-12, 2021.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2022-11-29 doi:10.26008/1912/bco-dmo.884424.1 [view at BCO-DMO] Relationship Description: A complementary dataset from the same year in the same region.

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# **Parameters**

Parameter	Description	Units
CTD_Cast	Cast number from cruise EN669	unitless
Niskin	Bottle number on Niskin rosette	unitless
PotTemp	Potential temperature used in carbsys calculations	degrees Celsius
Sal	Salinity value used in carbsys calculations	unitless
Depthm	Depth used in carbsys calculations	meters (m)
DIC_Bottle	Niskin bottle number from which DIC water sample was taken	unitless
DICumolkg	Dissolved inorganic carbon	micromoles per kilogram seawater
d13Cpermil	delta carbon isotope value vs PDB	permille vs PDB
talkumolkg	Total alkalinity	micromoles per kilogram seawater
DICsd	1 standard deviation, dissolved inorganic carbon measurement	micromoles per kilogram seawater
d13Csd	1 standard deviation, delta carbon isotope measurement	permille vs PDB
talksd	1 standard deviation, total alkalinity measurement	micromoles per kilogram seawater
Scan	Scan number (24 scans/second)	unitless
TimeJ	Julian time	days
TimeS	Duration (seconds)	seconds
PrDM	Pressure digiquartz (meters)	meters (m)
T090C	Primary temperature (degrees C)	degrees Celsius

T190C	Secondary temperature (degrees C)	degrees Celsius
T2_T190C	Difference between primary and secondary temperature	degrees Celsius
COS_m	Primary conductivity S/m	Siemens/meter
C1S_m	Secondary conductivity (S/m)	Siemens/meter
C2_C1S_m	Difference between primary and secondary conductivity	Siemens/meter
V0	Voltage of transmissometer	volts (V)
CStarAt0	Attenuation (1/m)	1/meter
CStarTr0	Beam transmission (%)	percent
V1	Voltage of fluorometer	volts (V)
FIECO_AFL	Flourometer Eco Chl a (mg/m3)	milligrams per cubic meter
V2	Altimeter voltage	volts (V)
AltM	Altimeter (m)	meters (m)
V3	Par sensor voltage	volts (V)
V4	Primary oxygen voltage	volts (V)
Sbeox0V	Primary oxygen voltage	volts (V)
V5	Secondary oxygen voltage	volts (V)
Sbeox1V	Secondary oxygen voltage	volts (V)
Par	Photosynthetically available radiation - on the ctd (umol photons/m2/s)	micromoles photons per meter- squared per second

Cpar	Corrected PAR (umol photons/m2/s)	micromoles photons per meter- squared per second
Spar	Surface photosynthetically available radiation - on the ship (umol photons/m2/s)	micromoles photons per meter- squared per second
Pumps	on or off (on=1)	unitless
Latitude	latitude in degrees north	decimal degrees
Longitude	longitude in degrees east	decimal degrees
DepSM	Depth saltwater meters	meters (m)
Sal00	Salinity - calc using primary T and primary cond.	unitless
Sal11	Salinity - calc using secondary T and secondary cond.	unitless
Sigma_E00	Density - calc using primary T and primary cond.	kilograms per cubic meter (minus 1000)
Sigma_E11	Density - calc using secondary T and secondary cond.	kilograms per cubic meter (minus 1000)
Sbox0Mm_Kg	Seabird oxygen (umol/kg) primary sensor	micromoles per kilogram seawater
Sbox1Mm_Kg	Seabird oxygen (umol/kg) secondary sensor	micromoles per kilogram seawater
OxsolMm_Kg	Oxygen saturation (Garcia and Gordon, μmol/kg)	micromoles per kilogram seawater
OxsatMm_Kg	Oxygen (Weiss, umol/kg)	micromoles per kilogram seawater
Potemp090C	Potential temperature (ITS90, degrees C) primary	degrees Celsius
Potemp190C	Potential temperature (ITS90, degrees C) secondary	degrees Celsius
SvCM	Sound velocity (Chen-Millero, m/s) primary	meters per second
SvCM1	Sound velocity (Chen-Millero, m/s) secondary	meters per second

Dz_dtM	Descent rate (m/s)	meters per second
Gpa	Geopotential anomaly (J/kg)	Joules per kilogram
Nbin	Number of bins in a row	unitless
Flag	Quality control; 0 = ok, 1 = problem	unitless
ISO_DateTime_UTC	Date and time (UTC) in ISO 8601 format	unitless

## Instruments

Dataset- specific Instrument Name	Apollo AS-D1 analyzer
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.
	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: <a href="https://apolloscitech.com/dicdelta.html">https://apolloscitech.com/dicdelta.html</a>

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
Dataset- specific Description	Water samples were collected using Niskin bottles on the CTD rosette. Equipment included a Seabird Scientific SBE9plus CTD equipped with a transmissometer, oxygen, and fluorescence sensors.
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	Metrohm 805 Dosimat
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	lunit It had a recolution of 70 000 ctone her cylinder volume and a decina/tilling time of 19

Dataset- specific Instrument Name	Niskin bottles
Generic Instrument Name	Niskin bottle
Dataset- specific Description	Water samples were collected using Niskin bottles on the CTD rosette.
	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.
	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.

Dataset- specific Instrument Name	Titrosampler
Generic Instrument Name	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	Titrators are instruments that incrementally add quantified aliquots of a reagent to a sample until the end-point of a chemical reaction is reached.

# **Deployments**

**EN669** 

Website	https://www.bco-dmo.org/deployment/915761
Platform	R/V Endeavor
Start Date	2021-08-03
End Date	2021-08-12
Description	More information is available in R2R: <a href="https://www.rvdata.us/search/cruise/EN669">https://www.rvdata.us/search/cruise/EN669</a> Start/End: Narragansett, Rhode Island

## **Project Information**

CAREER: Gulf of Maine Temperature Trends and Variability from the early Holocene to the Present (GoM Temperature Trends)

Coverage: Gulf of Maine, USA

#### NSF Award Abstract:

The Gulf of Maine supports a highly productive marine ecosystem extending from Cape Cod to Nova Scotia. Ocean temperatures in this region are sensitive to changes in the relative influx of colder currents from the north and warmer currents from the south, which are ultimately linked to the greater regional and global ocean-atmosphere circulation. From 2004 to 2013, the Gulf of Maine warmed faster than 99% of the world's oceans, but the processes driving recent temperature change here are not fully understood. A deeper understanding of oceanographic trends on time scales beyond instrumental records (older than ~100 years) can elucidate the causes of change, determine whether abrupt changes have happened in the past, and shed light on environmental impacts on past coastal communities. This project brings together a multi-disciplinary team of researchers and Native American students in New England, who will conduct a 10-day research expedition in the Gulf and delve into the region's past using geochemical evidence buried in ancient marine sediments. Results and research experiences of students will be shared with the broader community via development of an innovative multi-media online storytelling environment and through partnership with local schools. The project has the potential to enhance long-term environmental prediction and planning in an area where human populations and ocean ecosystems have been interlinked for millennia.

Long-term records of ocean temperature and seawater oxygen isotope composition (d180) will be reconstructed from the magnesium to calcium ratio (Mg/Ca) and d180 of fossil foraminiferal calcite derived from a suite of sediment cores from the Gulf of Maine and Scotian Shelf and Slope. High-resolution (~100 to 200-year interval) records will extend from the start of the Holocene  $\sim 11,600$  years ago to the present, providing insight into long-term temperature trends as well as any abrupt changes. In addition to traditional whole-shell geochemical analysis, micro-analysis of individual foraminiferal specimens will be conducted to provide complementary data for assessing environmental variability. A research cruise in the Gulf of Maine will provide sediment-core and plankton-tow material as well as hydrographic data for refinement and regional calibration of the geochemical proxies. One key goal is to test and extend the Mg/Ca-temperature calibration for a common high-latitude foraminifer species, Neogloboquadrina incompta. In parallel with paleoceanographic research, artifacts from coastal archaeological sites will be radiocarbon-dated to refine the chronology of fishing practices in the region. In particular, the beginning and end of intensive sword-fishing in coastal communities will be re-dated and reassessed in light of new paleotemperature data. All work will be carried out by a team of high school, undergraduate, and graduate students who will gain both technical and communications training in partnership with the Wabanaki Center and the New Media and Internet Technologies Lab at the University of Maine. In addition to developing online narratives that can be widely shared, high school students will practice presenting their research verbally to different groups, including at national meetings. A diverse team of women and men, including a member of the Penobscot Nation, will collaborate to guide and mentor students through the scientific process and to help them develop a voice that can effectively reach diverse audiences.

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-1847742

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