Carbonate chemistry data for shipboard ocean alkalinity enhancement (OAE) experiments in the North Atlantic on R/V Atlantic Explorer cruise AE2320 in September 2023

Website: https://www.bco-dmo.org/dataset/963736
Data Type: experimental, Cruise Results
Version: 1
Version Date: 2025-06-12

Project
» OCE-PRF: Towards Quantifying Calcium Carbonate Sediment Dissolution During Marine Diagenesis (Marine CaCO3 and ocean chemistry)

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Abstract

To explore mineral formation due to alkalinity addition, we present results from shipboard experiments in which an aqueous solution of NaOH was added to unfiltered seawater collected from the surface ocean in the Sargasso Sea. Alkalinity addition ranged from 500 to 2000 micromoles per kilogram (µmol.kg-1) and the carbonate chemistry was monitored through time by measuring total alkalinity (TA) and dissolved inorganic carbon (DIC), which were used to calculate Ω. The amount of precipitate and its minerology were determined throughout the experiments. Mineral precipitation took place in all experiments over a timescale of hours to days. The dominant mineralogy of precipitate is aragonite with trace amounts of calcite and brucite. Aragonite crystallite size increases and its micro-strain decreases with time, consistent with Ostwald ripening. This dataset contains carbonate chemistry data that include TA and DIC measurements, precipitation rates from the shipboard experiments, and precipitation rates calculated in the same way (by changes in alkalinity through time) for the study of Moras et al. (2022) and precipitation rate data from Mucci et al. (1989).

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Coverage

Location: North Atlantic Ocean
Spatial Extent: **Lat**:31.6667 **Lon**:-64.1667
Temporal Extent: 2023-09-06 - 2023-09-11

Methods & Sampling

Experiments involved the addition of NaOH solution prepared by weighing ACS grade NaOH in the lab prior to the cruise (R/V Atlantic Explorer AE2320) in a plastic Falcon tube that was capped and sealed with parafilm tape. During the cruise, DI water was added to make up stock NaOH solutions with a final concentration of 1 M. The NaOH solution was pipetted into the seawater filled bags through the Luer-fitted stopcock. Because NaOH contributes only alkalinity but not DIC, seawater in the experiments was out of equilibrium with the atmosphere, which was intended to simulate conditions immediately following alkalinity addition to seawater during OAE deployments.

In total, 5 experiments were conducted. The first experiment (experiment A) was a control with no alkalinity addition. In the second, third, and fourth experiments (B, C, and D), alkalinity was enhanced by 500, 1000, and 2000 micromoles per kilogram (µmol/kg) respectively. The fifth experiment (E) represents a set of "sacrificial" time series experiments whereby 9 bags were prepared similar to other experiments and alkalinity was enhanced by 1000 µmol/kg in each one of them, but each bag was sequentially opened and filtered in order to evaluate the precipitate mineralogy through time. In experiment E, water samples for TA and DIC measurements were taken only at the end of the experiment. The experiments were run for approximately 5 days.

Two separate 12-milliliter (mL) seawater samples were taken from bags through time, one for DIC and one for TA. Each of these samples was subsequently modified in order to test recently proposed best practices for carbonate chemistry sampling techniques (Schulz et al., 2023). These proposed techniques were designed to retain the original DIC and TA values at the time of sampling while decreasing Ω in the sample container to avoid mineral precipitation during sample storage. For DIC samples, adding an acid to a sample in a completely sealed vessel with no headspace neutralizes a proportion of the previously added alkalinity and thus decreases Ω while retaining all the DIC inside the vial. Similarly, for TA samples, bubbling CO2 into the sample increases the DIC, and thus decreases Ω without changing the TA. As such, Ω can be lowered in both samples to prevent mineral precipitation during sample storage in a way that allows for the accurate determination of DIC and TA (Schulz et al., 2023). We note that these techniques only work for conservative carbonate system parameters (i.e. DIC and TA), and not for non-conservative parameters such as pCO2 or pH.

The 12 mL aliquot taken for DIC was passed through a 0.2 micrometer (µm) filter into a gas-tight borosilicate vial (CHROMONE, NJ, USA), poisoned with 2.4 microliters (µL) of saturated HgCl2, and then acidified by adding a pre-calculated volume of 0.075 M HCl using a glass syringe through the plastic vial septum to titrate the initially added alkalinity. The amount of HCl added was 80, 160, 400, and 160 µl for samples taken from experiments B, C, D, and E, respectively. The 12 mL TA aliquot was filtered (0.2 µm filter), and then bubbled with pure CO2 using a nylon tubing with a stainless steel needle for 30 seconds to increase its DIC without changing TA, followed by poisoning with HgCl2. A gas regulator was used to maintain a constant CO2 flow rate and to prevent over-bubbling. The DIC and TA samples were returned to the lab where they were kept in cool and dark conditions until analysis, which took place within 2 months.

TA was determined using an open-system Gran titration on weighed 5 mL samples in duplicate using a Metrohm 805 Dosimat, with a 1 mL burette, and an 855 robotic Titrosampler. An 0.04 M HCl titrant was used to first acidify the sample to a pH of 3.9 before continuing to a pH of 3.25, dosing at 0.02 mL increments. The analyses were calibrated using in-house seawater standards that were run every 15 samples, to assess titrant and electrode drifts throughout the day. A nonlinear least-squares method was used to determine TA as outlined in the Best Practices guide (Dickson et al., 2007).

DIC was determined using an Apollo LI-5300A connected to a Li-COR CO2 analyzer, with CO2 extracted from a 1.5 mL sample volume by adding 0.8 mL of 3% phosphoric acid. Once opened, the sample lines were inserted to the base of the vial and sealed with parafilm tape to limit gas exchange. Before each analysis, 0.75 mL of sample and 0.8 mL of acid is drawn into the sample syringe to flush out any prior remnants from the system. After the flush, the 1.5 mL sample is drawn into the calibrated syringe and injected into the reaction chamber, where resulting CO2 is carried by a zero CO2 air stream to the Li-COR CO2 analyzer. Samples were run in triplicates. The instrument was calibrated twice daily against an in-house seawater standard that were intercalibrated against seawater Certified Reference Materials (Dickson batch #187).

The saturation state with respect to aragonite (Ω_A) throughout the experiments was calculated using PyCO2 1.8.1 (Humphreys et al., 2022), the Python version of the original CO2SYS program (Lewis et al., 1998) using the carbonic acid dissociation constants of Mehrbach et al. (1973) refitted by Dickson and Millero (1987). The Ω_A calculations used a corrected concentration of Ca to account for changes induced by CaCO3 precipitation.

Data Processing Description

The rate of mineral precipitation was calculated from the changes in TA through time for our expeirments as well as those of Moras et al. (2022). For comparison, rate data from the study of Mucci et al. (1989) who conducted similar mineral precipitation experiments.

BCO-DMO Processing Description

- Imported sheet 1 of original file "Hashim et al OAE resaerch data_carbonate chemistry.xlsx" into the BCO-DMO system.
- Flagged "NA" 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 date columns to YYYY-MM-DD format.
- Saved the final file as "963736_v1_carbonate_chemistry.csv".
- Converted sheet 2 of original file "Hashim et al OAE resaerch data_carbonate chemistry.xlsx" to CSV format and saved as "963736_v1_precip_rate_vs_omega.csv".

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Data Files

File
963736_v1_carbonate_chemistry.csv(Comma Separated Values (.csv), 5.66 KB) MD5:9ea530ca229a4bd25cd4a5782d912fe2 Primary data file for dataset ID 963736, version 1

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Supplemental Files

File
963736_v1_precip_rate_vs_omega.csv(Comma Separated Values (.csv), 4.16 KB) MD5:faf447b051d7222f1d5b0ca143e058ab Supplemental file for dataset ID 963736, version 1. Precipitation rate vs. Omega.

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Related Publications

Dickson, A. G., & Millero, F. J. (1987). A comparison of the equilibrium constants for the dissociation of

carbonic acid in seawater media. Deep Sea Research Part A. Oceanographic Research Papers, 34(10), 1733–1743. doi:10.1016/0198-0149(87)90021-5
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

Hashim, M., Marx, L., Klein, F., Dean, C., Burdige, E., Hayden, M., McCorkle, D., & Subhas, A. (2025). Mineral Formation during Shipboard Ocean Alkalinity Enhancement Experiments in the North Atlantic. https://doi.org/10.5194/egusphere-2025-988
Results

Mehrbach, C., Culberson, C. H., Hawley, J. E., & Pytkowicx, R. M. (1973). Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. Limnology and Oceanography, 18(6), 897–907. doi:10.4319/lo.1973.18.6.0897
Methods

Moras, C. A., Bach, L. T., Cyronak, T., Joannes-Boyau, R., & Schulz, K. G. (2022). Ocean alkalinity enhancement – avoiding runaway CaCO3 precipitation during quick and hydrated lime dissolution. Biogeosciences, 19(15), 3537–3557. https://doi.org/10.5194/bg-19-3537-2022
Methods

Mucci, A., Canuel, R., & Zhong, S. (1989). The solubility of calcite and aragonite in sulfate-free seawater and the seeded growth kinetics and composition of the precipitates at 25°C. Chemical Geology, 74(3–4), 309–320. https://doi.org/10.1016/0009-2541(89)90040-5
Methods

Schulz, K. G., Bach, L. T., & Dickson, A. G. (2023). Seawater carbonate chemistry considerations for ocean alkalinity enhancement research: theory, measurements, and calculations. State of the Planet, 2-oae2023, 1–14. https://doi.org/10.5194/sp-2-oae2023-2-2023
Methods

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Parameters

Parameter	Description	Units
Experiment_name	name of the experiment (A through D)	unitless
TA_addition	the amount of alkalinity added in micromoles	micromoles (umol)
Start_day	experiment start date	unitless
Start_time	experiment start time	unitless
End_day	experiment end date	unitless
End_time	experiment end time	unitless
Duration	experiment duration in hours	hours (h)
measured_TA	measured TA	micromoles per kilogram (umol/kg)
TA_std	standard deviation of TA	micromoles per kilogram (umol/kg)
measured_DIC	measured DIC	micromoles per kilogram (umol/kg)
DIC_std	standard deviation of DIC	micromoles per kilogram (umol/kg)
calculated_DIC	calculated DIC from TA assuming that precipitation of CaCO3 (TA:DIC of 2:1)	micromoles per kilogram (umol/kg)
calculated_CaCO3_precipitate	amount of CaCO3 precipitated calculated from changes in TA	milligrams per kilogram (mg/kg)

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Instruments

Dataset-specific Instrument Name	Li-COR CO2 analyzer
Generic Instrument Name	CO2 Analyzer
Dataset-specific Description	Apollo LI-5300A connected to a Li-COR CO2 analyzer
Generic Instrument Description	Measures atmospheric carbon dioxide (CO2) concentration.

Dataset-specific Instrument Name	Apollo LI-5300A
Generic Instrument Name	Inorganic Carbon Analyzer
Dataset-specific Description	Apollo LI-5300A connected to a Li-COR CO2 analyzer
Generic Instrument Description	Instruments measuring carbonate in sediments and inorganic carbon (including DIC) in the water column.

Dataset-specific Instrument Name	Metrohm 805 Dosimat
Generic Instrument Name	Metrohm 805 Dosimat
Dataset-specific Description	TA was determined using an open-system Gran titration on weighed 5 mL samples in duplicate using a Metrohm 805 Dosimat, with a 1 mL burette, and an 855 robotic Titrosampler.
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

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Deployments

AE2320

Website	https://www.bco-dmo.org/deployment/963695
Platform	R/V Atlantic Explorer
Start Date	2023-09-04
End Date	2023-09-11
Description	See additional information from R2R: https://www.rvdata.us/search/cruise/AE2320

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Project Information

OCE-PRF: Towards Quantifying Calcium Carbonate Sediment Dissolution During Marine Diagenesis (Marine CaCO3 and ocean chemistry)

NSF Award Abstract:
OCE-PRF Towards Quantifying Calcium Carbonate Sediment Dissolution During Marine Diagenesis The goal of the project is to investigate dissolution of calcium carbonate (CaCO3) in sediments below the seafloor and

determine its importance to the chemistry of seawater. This project uses sediment samples and chemical data collected from different parts of the ocean during the past five decades by scientific ocean drilling programs. Sediment dissolution of carbonate can lessen the impact of ocean acidification, the process that causes the pH of the ocean to decrease due to the uptake of carbon dioxide (CO2) from the atmosphere. Ocean acidification threatens the survival of marine organisms, such as oysters, clams, and coral reefs, which could alter marine food chains and food supply to humans. By improving understanding of carbonate dissolution in the ocean, results from this project will enable better predictions of the effects of ocean acidification on marine organisms. This will advance the progress of science and contribute to the knowledge that can inform public policy. In addition, understanding carbonate sediment dissolution serves other important purposes. For example, dissolution can create small spaces between sediments that may get filled with groundwater once sediments convert to rocks over millions of years. Thus, understanding the occurrence and spatial distribution of spaces within rocks may help determine the volume and movement of groundwater in subsurface aquifers. This project provides support for a postdoctoral research fellow and research training opportunities for students through the Summer Student Fellowship and Woods Hole-wide Partnership Education Programs at the Woods Hole Oceanographic Institution.

Carbonate mineral dissolution is an integral part of the alkalinity and carbon cycles in the ocean and is expected to play an increasingly significant role in mediating changes in ocean chemistry as atmospheric CO2 continues to rise. The goal of this project is to provide thermodynamic constraints necessary for quantifying carbonate sediment dissolution in marine diagenetic environments. Specifically, the CaCO3 saturation state of pore fluids will be calculated in 365 globally distributed sites from previous scientific ocean drilling expeditions using a specially developed Pitzer ion activity model which is particularly useful for calculating activity coefficients in high ionic strength solutions such as those that characterize most diagenetic environments. These calculations will be substantiated with geochemical and textural analyses of sediment samples from four representative sites to identify the specific diagenetic processes (e.g., dissolution, precipitation, and recrystallization) and document the conditions responsible for their occurrence and prevalence. The immediate advantage of calculating the saturation state of pore fluids is that such data can be used to estimate carbonate sediment dissolution below the seafloor and quantify its contribution to the alkalinity and carbon cycles, which will lead to more accurate predictions of the consequences of ocean acidification. Another benefit of the global saturation state dataset is that it will improve our understanding of authigenic carbonate precipitation and its link to the carbon cycle over Earth history, which has been proposed as a significant sink for carbon. Furthermore, by complementing the thermodynamic calculations with textural and geochemical analyses, this project will parse out various diagenetic processes and identify the sedimentological and geochemical conditions responsible for their occurrence. Such knowledge is crucial for evaluating the impact of diagenesis on the carbonate-hosted paleoenvironmental proxies. Collectively, this project will pave the way towards a mechanistic understanding of carbonate diagenesis. This will provide important constraints on the oceanic alkalinity cycle, carbon burial rates, and geochemical proxies, which ultimately help us better understand the future of our ocean system in the context of climate change.

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-2205984

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