Water column data from the Cocos Ridge (Eastern Equatorial Pacific) acquired during cruise SR2113 between November - December 2021

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Project
» Collaborative Research: New approaches to study calcium carbonate dissolution on the sea floor and its impact on paleo-proxy interpretations (CDISP 2021)

Contributors	Affiliation	Role
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Abstract
These data include water column parameters and carbonate chemistry measurements from the Cocos Ridge in the Eastern Equatorial Pacific. This cruise was aboard the R/V Sally Ride between 2021-11-20 and 2021-12-20. Instruments used were a CTD profiler, spectrophotometer, and Picarro cavity ring-down spectrometer. These data contributed to our understanding of the carbonate chemistry system in this region, particularly the water depth location of the calcite saturation horizon. Xuewu Liu and Kalla Fleger, members of the Robert Byrne lab at University of South Florida, measured alkalinity and pH; Nick Rollins and Jaclyn Cetiner, members of the Will Berelson lab at University of Southern California, measured DIC and delta 13C of DIC.

Table of Contents

Coverage

Spatial Extent: **N**:6.78487 **E**:-85.59988 **S**:5.35008 **W**:-88.26095
Temporal Extent: 2021-12-02 - 2021-12-17

Methods & Sampling

There were 5 stations were sampled with only station 5 getting 2 casts to get a higher resolution in the mid-shallow water column.

Samples for pH analysis were collected first in the rosette sampling sequence. Seawater samples were collected from the Niskin bottles directly into 10-cm glass cylindrical optical cells (~30 mL volume) using a section of silicone tubing (~15 cm long). One end of the silicone tubing was first attached to the nipple of the Niskin bottle. The nipple was pushed in to initiate flow, and the silicone tubing was squeezed to eliminate air bubbles. The other end of the silicone tubing was attached to the optical cell, which was agitated to eliminate any residual bubbles. After ~15 seconds of sample flow, the cell was capped at one end with a Teflon stopper. The silicone tubing was then detached from the optical cell, and, with the water still flowing, the other cap was rinsed and used to seal the optical cell. Samples collected this way are not exposed to the atmosphere, and each cell was flushed with at least three cell volumes of seawater. The samples were collected and taken into the lab, where the outside of the cell was rinsed with tap water to eliminate salt build-up. The cells were dried thoroughly, and the optical windows were cleaned with Kimwipes immediately before measurement. Samples were thermostatted at 25 ºC (±0.05 °C) in a custom-made, 36-position cell warmer.

Seawater samples for total alkalinity (AT) were collected directly after pH samples from the Niskin bottles into clear 300 mL BOD borosilicate glass (Fisher Scientific) bottles as described in Section 3.4 of Liu et al. (2015).

Silicone tubing, connected directly to the Niskin, was inserted into the bottom of the bottle. Each bottle was rinsed three times with seawater with approximately one-third of the sample bottle volume. Sample bottles were overflowed for at least one complete volume (300 mL). The silicone tubing was squeezed to eliminate air bubbles, and care was taken to ensure no air bubbles were trapped in the bottle. While filling the bottle, the sample temperature was measured (t_s) using a Fisher Scientific Traceable Digital Thermometer (±0.05℃). Sample temperature is required to ascertain sample volume and convert it to sample mass. Once all bubbles dissipated, sample caps were rinsed, and the tubing, while water still flowed, was slowly removed, and the sample was sealed by inserting the bottle cap. Seawater in the flange area was eliminated, and the bottleneck area was dried with a Kimwipe.

In the ship's laboratory, the outside of each bottle was carefully rinsed with tap water, and the bottle surface was wiped clean with Kimwipes to remove any salt build-up. Samples were left to equilibrate to room temperature. Samples were not poisoned with HgCl2. When the samples warmed, seawater was forced into the flanged bottleneck. Care was taken to ensure no sample loss—the bottle was maintained upright, and water within the flanged neck was not wiped away as the sample warmed.

DIC and delta13C of DIC were analyzed with a Picarro Cavity Ring-Down Spectrometer (G2131-i) with Liaison autosampler; the detailed methodology is described in Subhas et al. (2015). These measurements were made on board the ship. Dickson seawater CRM was used as the standard for DIC; pre-weighed optical calcite powder was used as the standard for delta13C. Exetainer vials were pre-acidified and pre-weighed in the lab prior to the cruise. After the vials were filled with 3-5 mL of porewater and analyzed on the cruise, the stored vials were weighed again in the lab to obtain the sample mass. Results using this methodology were corrected by normalizing to measured values of Dickson seawater CRM. Uncertainty (1sigma) for replicate DIC and delta13C measurements were ±23 umol/kg and ±0.15 per mille (VPDB), respectively. DIC uncertainty was higher than reported in our previous studies (e.g., Subhas et al., 2015) likely due to mass determination: ship-board analysis necessitated weighing after analysis, but there was uncertainty in precisely how much sample mass may be removed during the analysis. Additionally, lower sample volume (5 mLs, instead of 7-8 mLs in our previous studies) may have added error.

The pH of each sample was determined on an Agilent 8453 spectrophotometer setup with a custom-made temperature-controlled cell holder. Only the tungsten lamp was turned on. The UV lamp was turned off to prevent photodegradation of organic matter in the samples by UV light. A custom macro program running on Agilent UV-Visible ChemStation Software Rev. B.04.01 was used to guide the measurements and data

processing. The macro automated the procedures of sample input information, blank and sample scans, quality control, and data archiving. The quality control steps included checking the baseline shift after dye injection and monitoring the standard deviation of multiple scans. Absorbance blanks were taken for each sample, and 10 µL of purified m-cresol purple (10 mmol kg-1) was added for the analysis. pHT(total scale) was calculated according to Müller and Rehder (2018).

The salinity and temperature dependence is provided in Table 1 of Müller and Rehder (2018). The temperature and salinity dependence of $e1$ and $e3/e2$ are given in Eq. (6-7) of Muller and Rehder (2018). Sample temperature was then measured using a Fisher Scientific Traceable Digital Thermometer (±0.05°C). These equations are applicable for samples between temperature ($278.15 \leq T \leq 308.15$) and salinity ($0 \leq S \leq 40$). In all our measurements at sea, $T \approx 298.15$ K. Water column salinity was measured using a Sea-Bird Electronics CTD sensor. Duplicate pH samples, collected from discrete samples taken from Niskin bottles ($N=12$), displayed a standard deviation of 0.001.

The automated spectrophotometric alkalinity system consists of a stir plate with an anchoring bottle holder and a Metrohm Dosimat 665. The bottle holder is configured so that optical fibers, connected either to an Ocean Optics LS-1 tungsten halogen light source with a blue filter or an Ocean Optics USB4000 spectrophotometer, are positioned about 1 cm above the bottom of the bottle (configuration shown in Liu et al. 2015, Fig 1). The spectrophotometer and Dosimat are connected to a portable computer equipped with custom software that controls acid delivery from the titrator and monitors absorbances. The software is programmed to control the rate and sequence of acid titration and record sample input, absorbance ratios, and acid volumes.

DIC and delta13C of DIC were analyzed with a Picarro Cavity Ring-Down Spectrometer (G2131-i) with Liaison autosampler.

Data Processing Description

The absorbance ratio of the indicator dye used was adjusted to $R = 1.6$ (pH ~ 7.9) in the laboratory before the cruise. Small changes in sample pH (measurement perturbations; Clayton and Byrne, 1993) are created by the addition of titrant to samples. Dye perturbation was previously quantified using samples collected from profiles over a range of pH values. For each perturbation determination, ΔpH was defined as ΔpH = pHfinal – pHinitial, where pHinitial is the total scale pH taken after a single titrant addition, and pHfinal is the total scale pH after a second titrant addition.

An equation developed using this perturbation data was used to correct pH measurements: $pH^0\_T = -0.0042 \cdot pH - 0.0326$ (1.3). Where pH is the raw pHT measurement and pH0 is the perturbation-corrected pHT measurement.

All spectrophotometric pH measurements were tentatively flagged if the baseline shifted more than 0.002 absorbance units. A series of five spectra were averaged for each determination, and samples were rerun if the overall standard deviations were higher than 0.0004. This process was repeated until the standard deviation of multiple readings was within 0.0004. Absorbance values were saved so that the quality criteria could be evaluated in the future.

Perturbation-corrected pHT measurements were reported along with their associated quality-control flags. pHT was reported at the measurement temperature of approximately 25 ºC, with the exact measurement temperature specified as an average of temperature measurements at the beginning and end of each set of samples.

The spectrophotometric AT measurement titration procedure is outlined in Liu et al. (2015).

The sample bottle thermostatted to room temperature (~24°C) was wiped clean and placed inside the bottle holder on the stir plate. The bottle cap was removed, and excess seawater that may have moved into the flanged bottleneck was rinsed into the sample bottle with a small amount (1–2 mL) of MilliQ water. A small stir bar was added to the bottle, and the acid tube from the Dosimat titrator was inserted just below the sample liquid's surface to ensure that the HCl was well mixed with the seawater before reaching the light path at the lower part of the bottle.

After a reference absorbance was recorded, 0.1 mL of 10 mM bromocresol purple BCP stock solution ($R \sim 0.3$) was added and mixed. Acid was then delivered to the sample bottle, with the rate of acid addition being guided by continuous spectrophotometric monitoring of the seawater pH. The titrations were terminated at $R = 0.070$ (pHT ~ 4.2).

A plastic syringe was used to remove ~60 mL of the acidified sample so that the sample did not overflow and to decrease purging time. A fritted glass purging tube was placed into the bottle, positioning it above the light path, and the sample was purged of CO2 with N2 until R stabilized (i.e., ± 0.002 units in 1 min). The final solution temperature was measured and used with the absorbance ratio to calculate the final pHT of the sample.

Spectrophotometric measurements of AT were calculated using the following equation: $A_T = \{[HCl]_{AV} \cdot V_A - [H^+]_{ASW} \cdot M_{ASW}\}/M_{SW}$ (2.1). Where $[HCl]_{AV}$ is the HCl concentration of the acid titrant in volumetric units, and V_A is the volume of the added acid titrant (mL).

M_{SW} is the sample mass obtained from volumetric measurements and solution densities (SOP 12, Dickson et al., 2007). Sample bottles were calibrated (as a function of temperature) in the laboratory prior to the cruise following methods outlined in Section 3.2 in Liu et al. (2015). On board the ship, sample fill temperature was used to calculate the mass of the collected seawater (SOP 12, Dickson et al., 2007): $M_{SW}(t_s) = V(t_s) \cdot \rho(sw, t_s)$ (2.2)

where seawater density ($\rho(sw, t_s)$) as a function of salinity and temperature was calculated according to Millero and Poisson (1981), and $V(t_s)$ is the volume of the sample at fill temperature (SOP 12, Dickson et al., 2007, Liu et al., 2015, Eqs. 7 – 11).

The gravimetric M_A term ($M_{ASW} = M_{SW} + M_A$) was calculated by measuring the added volume and density (σ_A) of the acid ($M_A = V_A \, \sigma_A$).

The acid concentration ($[HCl]_{AV}$) was determined by titrating the acid with a seawater Certified Reference Material (CRM) with known AT and solved for $[HCl]_{AV}$ in Eq. (2.1). CRM Batch #197 was obtained from Dr. Andrew Dickson of the Scripps Institution of Oceanography and used throughout this cruise (Salinity = 33.529; AT = 2256.77 ± 0.90 µmol kg-1).

The titrant acid (0.2 N) was prepared from concentrated HCl and adjusted to an ionic strength of 0.7 M using NaCl. $[HCl]_{AV}$ was calculated to be 0.1934 N at 23°C ($N = 7$).

The $[H^+]_{ASW}$ term in Eq. (2.1) provides proton concentrations directly in terms of total moles per kg of seawater (pHT = $-\log[H^+]_{ASW}$). Solution pHT was measured spectrophotometrically from absorbance ratio measurements (R) at $\lambda 2A$ and $\lambda 1A$ (Liu et al., 2015; Hudson-Heck et al., 2021): $pH_T = -\log(K^T_2 \cdot e_2) + \log((R - e_1)/(1 - R e_4))$ (2.3).

Where is the indicator's equilibrium constant, and the symbols e_1, e_2, and e_4 refer to indicator molar absorbance ratios at wavelengths $\lambda 1$ and $\lambda 2$. Sample pH was calculated using the indicator bromocresol purple (BCP). Absorbances were measured using at $\lambda 1$ = 432 nm and $\lambda 2$ = 589 nm, and an additional wavelength of 700 nm ($\lambda 3$) to correct for baseline changes (). The remaining terms in Eq. (2.3) can be calculated using equations from Hudson-Heck et al. (2021) over a range of salinity from 0 to 40 and temperatures from 278.15 to 308.15K.

- $e_1 = 0.00049$ (2.4a).
- $e_4 = -7.101 \cdot 10^{-3} + 7.674 \cdot 10^{-5} \cdot T + 1.361 \cdot 10^{-5} \cdot S$ (2.4b).
- $-\log(K^T_2 \cdot e_2) = 4.981 - 0.1729 \cdot S^{0.5} + 0.09406 \cdot S + 0.373 S^{1.5} + 0.000907 \cdot S^2 + 310.1/T - 17.03 S^{1.5}/T - 0.058 S^{1.5} \cdot \ln(T) - 0.0005658 S^{0.5} T$ (2.4c)"

The sample pH was calculated using the recorded R value and the final measured temperature.

The acid concentration of the titrant was calibrated using a CRM (Batch 197, certified AT value: 2256.77 ± 0.90 µmol kg-1). At the start of the cruise and for each CTD cast, a CRM was titrated before or after analyzing collected samples to check acid concentration. A total of 7 CRMs were measured, with an average $[HCl]_{AV}$ of 0.1934 ± 0.0001 N and measured AT value of 2256.77 ± 1.03 µmol kg-1.

For each CTD cast, duplicates were collected from two Niskin bottles. The average standard deviation of the duplicates was 0.53 µmol kg-1 ($N=12$). All sample data was saved so that the quality criteria could be evaluated in the future. AT measurements were reported along with their associated quality-control flags.

Omega_calcite was calculated from pH and Total Alkalinity using CO2SYS (MATLAB v3.1.1) (Lewis and Wallace, 1998), using the total pH scale and K1, K2 constants from Hansson (1972, 1973) and Mehrbach et al. (1973), refit by Dickson and Millero (1987).

Data Files

File
925367_v1_watercolumn.csv(Comma Separated Values (.csv), 18.16 KB) MD5:56e3fbd0f3bcd49f76e54e9d95a0a212 Primary data file for dataset ID 925367, version 1

[ ]

Related Publications

Liu, X., Byrne, R. H., Lindemuth, M., Easley, R., & Mathis, J. T. (2015). An automated procedure for laboratory and shipboard spectrophotometric measurements of seawater alkalinity: Continuously monitored single-step acid additions. Marine Chemistry, 174, 141–146. doi:10.1016/j.marchem.2015.06.008
Methods

Subhas, A. V., Rollins, N. E., Berelson, W. M., Dong, S., Erez, J., & Adkins, J. F. (2015). A novel determination of calcite dissolution kinetics in seawater. Geochimica et Cosmochimica Acta, 170, 51–68. https://doi.org/10.1016/j.gca.2015.08.011
Methods

Submitted to GCA: Cetiner J. E. P., Berelson W. M., Rollins N. E., Liu X., Pavia, F. J., Waldeck, A. R., Dong S., Fleger, K., Barnhart H. A., Quinan, M., Wani, R., Rafter, P. A., Jacobson, A. D., Byrne R. H. and Adkins J. F. Carbonate dissolution fluxes in deep-sea sediments as determined from in situ porewater profiles in a transect across the saturation horizon
Results

[ ]

Parameters

Parameter	Description	Units
Station	Station identifier	unitless
Cast	Cast number	unitless
Date	Date of CTD cast	unitless
Start_Time	Start time of CTD cast. US Central Time (UTC-6) timzone.	unitless
ISO_DateTime_UTC	Start date time of cast in ISO format, UTC timezone	unitless
Latitude	Station latitude	decimal degrees
Longitude	Station longitude	decimal degrees
Water_Column_Depth	Water column depth	meters (m)
Pressure	Pressure	decibars (db)
Temperature	Temperature	degrees Celcius (C)
Salinty	Salinity	parts per thousand (ppt)
Oxygen	Dissolved Oxygen	micromoles per kilogram (umol/kg)
Alkalinity	Total Alkalinity	micromoles per kilogram (umol/kg)
pH	pH (lab, "input")	total pH scale
DIC	Dissolved Inorganic Carbon (DIC)	micromoles per kilogram (umol/kg)
d13C_DIC	delta 13C of DIC	per mil (0/00)
Omega_calcite	Omega with respect to calcite, calcite saturation state, calculated with Total Alkalinity and pH	unitless

Instruments

Dataset-specific Instrument Name	
Generic Instrument Name	CTD Sea-Bird
Dataset-specific Description	Water column salinity was measured using a Sea-Bird Electronics CTD sensor.
Generic Instrument Description	A Conductivity, Temperature, Depth (CTD) sensor package from SeaBird Electronics. This instrument designation is used when specific make and model are not known or when a more specific term is not available in the BCO-DMO vocabulary. Refer to the dataset-specific metadata for more information about the specific CTD used. More information from: http://www.seabird.com/

Dataset-specific Instrument Name	
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	
Generic Instrument Name	Spectrometer
Dataset-specific Description	DIC and delta13C of DIC were analyzed with a Picarro Cavity Ring-Down Spectrometer (G2131-i) with Liaison autosampler.
Generic Instrument Description	A spectrometer is an optical instrument used to measure properties of light over a specific portion of the electromagnetic spectrum.

Dataset-specific Instrument Name	
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	The pH of each sample was determined on an Agilent 8453 spectrophotometer setup with a custom-made temperature-controlled cell holder. Only the tungsten lamp was turned on. The UV lamp was turned off to prevent photodegradation of organic matter in the samples by UV light. A custom macro program running on Agilent UV-Visible ChemStation Software Rev. B.04.01 was used to guide the measurements and data processing. The macro automated the procedures of sample input information, blank and sample scans, quality control, and data archiving. The quality control steps included checking the baseline shift after dye injection and monitoring the standard deviation of multiple scans. Absorbance blanks were taken for each sample, and 10 µL of purified m-cresol purple (10 mmol kg-1) was added for the analysis. pHT(total scale) was calculated according to Müller and Rehder (2018).
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

Deployments

SR2113

Website	https://www.bco-dmo.org/deployment/925232
Platform	R/V Sally Ride
Start Date	2021-11-20
End Date	2021-12-20

Project Information

Collaborative Research: New approaches to study calcium carbonate dissolution on the sea floor and its impact on paleo-proxy interpretations (CDISP 2021)

Coverage: Cocos Ridge, Eastern Equatorial Pacific

NSF Award Abstract:
The uptake of anthropogenic CO2 by the ocean will eventually be mitigated by the dissolution of CaCO3 on the sea floor. Dissolution is an important component of the carbon cycle in models used for climate projections though the relative importance of where it occurs (water column versus sediments) and the rates and processes involved are not fully understood. This ambitious field and laboratory study is designed to advance our knowledge of the important factors that control carbonate dissolution/ preservation in deep ocean sediments. Using a novel tracer approach and multiple in situ sampling strategies, the project will investigate sea floor dissolution rates, their kinetic controlling factors, the depth in sediments at which dissolution occurs, the role that oxidation of particulate organic carbon plays, and the ramifications of solid phase alteration for the use of geochemically-based paleoceanographic proxies. The project will foster further development of benthic lander technology and yield key information relating sea floor conditions to carbonate dissolution rate, thereby helping to constrain the rate at which the ocean can neutralize the impacts of ocean acidification. Graduate and undergraduate students will be trained and the research team will use film and animation to bring

this work to a broader audience through a collaboration with the Los Angeles Natural History Museum.

The research team has developed a new approach to quantify calcium carbonate dissolution rates based on 13-C labeled carbonate substrates, a technique which is significantly more sensitive than traditional approaches based on alkalinity and/or calcium measurements. This has opened a range of new opportunities and insights into the governing mechanisms and rates of calcium carbonate dissolution, a challenging and long-standing geochemical problem. Carbonate dissolution rates on the sea floor will be directly assessed by benthic chamber flux measurements of alkalinity and calcium as well as pore water models of TCO2 and alkalinity and their isotopic composition. The potential impacts of organic carbon remineralization will be measured through oxygen and nutrient flux determinations, pore water gradients and modeling. Labeled 13C-enriched calcite will serve as a tracer of near surface dissolution processes when added to benthic chambers and of down-core dissolution processes using 13C-labeled rods inserted into the sediment column. These in situ experiments of labeled carbonate dissolution will be the first of their kind. To complement these measurements, the team will continue development of a rhizon-based pore water sampler that works on a multi-corer at all ocean depths. Field experiments will be conducted at sea at 4-6 sites in a transect through water column supersaturation to undersaturation between Panama and the Galapagos. Dissolution rate measurements, coupled with analyses of cation/Ca ratios in CaCO3 foraminiferal shells will help calibrate the impact of dissolution on paleo-proxy interpretations. Further, analyses of sediment calcite and aragonite fractions will help explain net dissolution and sediment response with time. The results from this study should help to better parameterize sediment variables in ocean-climate models (GCMs), which has important implications for predicting the consequences of ocean acidification and the modeling of paleoceanographic records. The methodologies and new techniques will surely be adopted by other researchers, therefore impacting the larger geochemical community.

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-1834475