In situ porewater data from the Cocos Ridge (Eastern Equatorial Pacific) acquired during cruise SR2113 between November - December 2021

Website: https://www.bco-dmo.org/dataset/925487
Data Type: Other Field Results
Version: 1
Version Date: 2024-06-21

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

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Abstract
These data include porewater measurements with a focus on carbonate chemistry 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 novel in situ porewater sampler, spectrophotometer, Liaison autosampler coupled to a Picarro cavity ring-down spectrometer, Inductively Coupled Plasma - Mass Spectrometer, and Inductively Coupled Plasma - Optical Emission Spectrometer. These data contributed to our understanding of the carbonate chemistry system in this region, particularly regarding carbonate dissolution in deep-sea sediments. 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; Matt Quinan of the Berelson lab measured silica; Jaclyn Cetiner (USC) and Frank Pavia (Caltech) measured manganese. Jaclyn Cetiner (USC) and Anna Waldeck (Northwestern) measured calcium and strontium.

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Coverage

Spatial Extent: **N**:6.78487 **E**:-86.59988 **S**:4.81197 **W**:-88.26095
Temporal Extent: 2021-12-02 - 2021-12-14

Methods & Sampling

Porewater pH samples were collected in 3-mL capacity gas-tight borosilicate glass syringes with triple O-ring seals. A 2 – 2.5 mL volume was drawn from each coil into a syringe. 1 mL of sample was added to a cuvette for AT measurements and the remaining 1 mL was used for pH measurements. To each sample, 4 μL of 2 mM mCP ($R \simeq 1.2$) was added using a 10 μL Eppendorf Research pipette fitted with thin Teflon tubing at the end of the pipette tip. The sample with added dye was capped and thoroughly mixed, then housed in a custom-made cell warmer and thermostatted to 20°C (±0.05 °C). During the sampling process, care was taken to ensure that samples were not exposed to the atmosphere and that there was no entrapment of air bubbles within the syringe.

For small volume total alkalinity (AT) measurements, 1 mL of sample was pipetted directly into a semi-micro cuvette (1-cm pathlength, Fisher Cat 14-955-127) with a syringe or an Eppendorf Research pipette. Samples were covered with a polyethylene cuvette stopper (Cat. S29264) and placed inside a semi-submerged cuvette tray thermostated to a set temperature (e.g., 20°C) in a large-capacity water bath (Lauda Ecoline RE 120 water bath).

DIC and d13C 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 d13C. 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 (1σ) for replicate DIC and d13C measurements were ±23 µmol/kg and ±0.15‰ (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.

Porewater dissolved manganese [Mn] was analyzed at Caltech by ICP-MS (inductively coupled plasma - mass spectrometry) using an Agilent 8800 triple-quadrupole instrument. In situ porewater samples were stored in acid-cleaned HDPE bottles and acidified using 6M distilled HCl. After at least one week, 1 mL aliquots were diluted 10:1 in distilled 5% HNO3 for ICP-MS analysis. Concentrations of [Mn] were determined via calibration to multi-element commercial ICP-MS standards, matrix-matched to samples by addition to artificial seawater and diluted in 5% HNO3, identically to the samples. Blanks were assessed by analysis of both pure 5% nitric acid and artificial seawater with no metal standard added. ICP-MS measurements were made in MS/MS mode using He as a carrier gas in the collision cell. The detection limit was 0.03 µmol/kg [Mn].

Porewater calcium, strontium, and sodium were measured at Northwestern University using a Thermo iCap7600 ICP-OES (inductively coupled plasma - optical emission spectrometer). In order to capture signals from high- to low-abundance cations ([Na] and [Sr], respectively), samples were diluted 1:100, by mass, with trace metal clean 3% HNO3. Each sample was weighed, diluted, and analyzed in five replicates. Samples were

run in randomized order to account for any instrumental drift not corrected through standard bracketing. Cation concentrations were based on counts per second using two wavelengths from each cation (Ca393.366, Ca396.847, Sr407.771, Sr421.552, Na588.995, and Na589.592 nm). The two wavelengths for each element produced virtually identical results but were averaged, nonetheless. Calibration standards were synthetic mixtures of 1000 ppm cation solutions (Mg, Sr, Na, Ca, and K) diluted in 5% HNO3 to match expected sample concentrations. Calibration standards were used to correct for instrumental drift within a single run by interpolating between standards run at the beginning and end of the run. Blank measurements were made on HNO3 and were included in the calibration curve to account for instrumental blank. IAPSO standard seawater was used to adjust for drift across multiple days. Between 3-8 IAPSO standards were measured every run; the IAPSO average in a single run was normalized to the IAPSO average for all runs. This normalization was applied to all porewater samples. In this manner, samples analyzed on different days were normalized to a single measured IAPSO average. [Ca] and [Sr] were normalized to [Na]; all stations had a CTD measured salinity of 34.6 ppt; salinity was converted to [Na] using a seawater Na:salinity ratio of 10.781 g/kg:35 ppt (Pilson, 1998). IAPSO seawater measurements had the following one standard error spreads: ± 0.026 mmol/kg Ca, ± 0.56 µmol/kg Sr, and 1.5 mmol/kg Na.

Porewater silica was measured at USC. A spectrophotometric molybdenum blue method, modified from Parsons et al. (1984), was used to determine the concentration of silicic acid (H4SiO4 or DSi) in the pore water samples. Filtered pore water samples collected on the cruise were stored at 4°C and transported back to USC for analysis. Standards were made via dilution of 1,000 ppm Si standard solution (Aqua Solutions) in DSi free artificial seawater. The precision of this method, determined by duplicate analyses, was 1.3% for samples with DSi concentrations > 20 µM (< 20 µM analytical precision = 13.1%).

Instruments:

The pH and total alkalinity (AT) of porewater samples were measured using a multiparameter CO2 instrument named mvMICA (minimal volume Multiparameter-Inorganic Carbon Analyzer). The mvMICA is a dual parameter system engineered to simultaneously measure AT with sample volumes as low as 0.5 mL and pH with 1 and 1.5 mL (Fleger et al., *in prep*). The mvMICA configuration consisted of pH and AT channels encased in a thermoregulating water bath. Optical fibers connected channels to a custom tungsten halogen light source and Ocean Optics USB4000 spectrophotometers. Spectrophotometers were housed in a small refrigerator regulated to 18°C. The spectrophotometers were connected to a portable computer with custom software that monitors and records absorbances and sample information. The encased water bath had a lid with openings for AT sample input, CO2 gas tubing, and two Luer lock ports for pH sample input and output.

The submerged pH channel was affixed to the bottom of the case. The pH optical cell consisted of a gas impermeable PEEK tubing (1/8 in OD, 1/16 in ID) with T-connectors on either side to control sample throughput and extend fiber-optical leads within the cell.

The pH and AT of porewater samples were measured using the mvMICA (see section 3.2). Small-volume spectrophotometric AT measurements were made by directly purging the sample with CO2 gas (Fleger et al., in prep) and monitoring the absorbances until equilibration was reached.

A semi-micro disposable cuvette has a small volume whereby 1 mL of sample fills the cell to more than 50% of the cell height. A mounted cuvette holder secured the AT cuvette inside the mvMICA. The holder was positioned so that the top of the cuvette (~0.5 cm) was above the water bath level, but sample volume remained equilibrated to bath temperature. Optical fibers are positioned just above the bottom of the cuvette. The purging tube assembly includes a CO2 equilibration tube that fits into the cuvette cover and is secured to control the positioning of the purging tube without obstructing the light path. Before purging the sample, water-saturated 10% CO2 gas was pre-equilibrated to 20°C by passing through a two-meter-long copper coil immersed in a thermostated water bath.

DIC and d13C of DIC were analyzed with a Picarro Cavity Ring-Down Spectrometer (G2131-i) with Liaison autosampler.

Porewater dissolved manganese [Mn] was analyzed by ICP-MS (inductively coupled plasma - mass spectrometry) using an Agilent 8800 triple-quadrupole instrument.

Porewater calcium, strontium, and sodium were measured using a Thermo iCap7600 ICP-OES (inductively coupled plasma - optical emission spectrometer).

Porewater silica was measured on a spectrophotometer.

Data Processing Description

Measurements of sample pH made using the mvMICA were made on the total scale (i.e., pHT = – log[H+]T). Spectrophotometric pH was measured using the indicator meta Cresol Purple (mCP).

At the beginning of each set of samples, surface seawater without indicator was injected into the submerged optical cell to obtain a reference spectrum. Due to volume limitations, fresh surface seawater collected from the ship's underway system was used as a reference, as it had properties similar to porewater samples. After a reference spectrum was taken, a syringe with sample and dye was quickly mixed and injected into the pH cell through the Luer lock port of the pH channel. The input port was checked for bubbles before sample injection to prevent bubble entrapment. The exit port, a two-way Luer shutoff valve, was closed immediately after sample injection. After thermal equilibration of the sample was reached (usually 1 minute), the signal stabilized, and absorbance measurements were obtained at 434, 578, and 730 nm. The pHT was calculated according to Müller and Rehder (2018).

Measurements made using the mvMICA were conducted at 20°C. A Fisher Scientific Traceable Digital Thermometer (±0.05°C) monitored the water bath temperature. The bottom water salinity was measured by the CTD for each station and used in calculations as sample salinity.

Duplicate pH samples were collected at each station. Replicate pH measurements of fill water had an average standard deviation of 0.0023 ($N = 8$). The measurement of pH is calibration-free. With the small sample volume measurements, dye perturbation was not considered. All absorbance measurements were tentatively flagged if the baseline shifted more than 0.005 absorbance units or if there were visible signal issues. Absorbance values were saved so that the quality criteria could be evaluated in the future. In the data set, pHT measurements were reported along with their associated quality-control flags. The pHT was reported at the measurement temperature of 20ºC.

Sample AT was measured spectrophotometrically after equilibrating with CO_2 gas using bromocresol purple (BCP) as indicator dye. Samples were inserted into the 1-cm cuvette holder partially submerged inside the mvMICA. After the lid was closed, a reference (baseline) spectrum was obtained. Absorbances were measured using at $\lambda_1 = 432$ nm and $\lambda_2 = 589$ nm, and an additional wavelength of $\lambda_3 = 700$ nm to correct for baseline changes. 10 μL of 2 mM BCP stock solution ($R \simeq 1$) was added to the cuvette with an Eppendorf pipette.

The cuvette cover with its attached CO_2 equilibration tube and vent port cutouts was placed on the cuvette, and CO_2 bubbling was initiated. The CO_2 concentration used in AT measurements for this cruise was measured to be 20% using an onboard Picarro Cavity Ring-Down Spectrometer (G2131-i) with a Liaison autosampler. CO_2 was bubbled through the upper portion of the spectrophotometric cell while absorbance measurements were monitored. Once stabilized (~ 4 minutes), R was recorded along with temperature and sample information. BCP absorbance ratios are then used to calculate AT (µmol kg-1) using the equation:

$$\log(A_T + [H+]_T) = \log(K_0 \cdot K'_1) + E + pH_T \qquad (4.1)$$

where pHT = –log[H+]T on the total pH scale and is measured spectrophotometrically using Eqs. (2.3) and (2.4) (Clayton and Byrne, 1993; Liu et al., 2011; Hudson-Heck et al., 2021).

The K_0 term in Eq. 4.1 is the Henry's law constant (K_0), which is calculated as a function of temperature and salinity as $273.15 \leq T \leq 313.15$ K and $0 \leq S \leq 40$ (Weiss, 1974, Millero, 1995)

$$\ln(K_0) = -60.2409 + 93.4517(100/T) + 23.3585 \cdot \ln(T/100) + S[0.023517 – 0.023656(T/100) + 0.0047036(T/100)^2] \qquad (4.4)$$

The dissociation constant of carbonic acid, , is calculated using the characterization of Roy et al. (1993) ($5 \leq S \leq 45$ and $273.15 \leq T \leq 318.15$ K).

$$\ln(K'_1) = 2.83655 – 2307.1266/T – 1.5529423 \cdot \ln(T) + (-0.20760841 – 4.0484/T) \cdot S^{0.5} + 0.08468345S – 0.00654208S^{1.5} + \ln(1-0.001005S) \qquad (4.5)$$

E is a temperature-dependent empirical constant that includes known constants and the fugacity of CO_2 (fCO2). The constant is determined by measuring the absorbances of a certified reference material (CRM) after equilibration with CO_2. The procedure for determining E is outlined in section 4.4.

The calibration constant, E, in Eq. (4.1) was determined using a standard CRM with a well-characterized AT (Batch # 197). 1 mL of CRM was pipetted into a 1-cm pathlength cuvette. The same measurement procedure

outlined in section 4.3 was followed. After equilibration, absorbance ratios were used with the known AT value of the CRM to calculate E using the equation:

$$E = \log(A_T + [H+]_T) - \log(K'_1 \cdot K_0) - pH_T \tag{4.6}$$

The calibration constant, E, was determined to be -1.180 with a standard deviation of 0.003 (N = 54).

The AT of CRMs was measured using the mvMICA at the beginning and end of each set and after every 10 – 15 samples to monitor instrument performance and check the calibration constant. The calibration constant, E, was determined at the start of each sample set and used in Eq (4.1) to calculate sample AT. The average AT of CRM batch #197 (Salinity = 33.529; certified AT value: 2256.77 ± 0.90 µmol kg-1) using the average calibration constant (-1.180 ±0.003) was measured to be 2256.81 ± 13.87 µmol kg-1 (N = 54).

Duplicate samples were collected at each station. All absorbance measurements were tentatively flagged if the baseline shifted more than 0.005 absorbance units or if there were visible signal issues. Absorbance values were saved so that the quality criteria could be evaluated in the future. AT measurements and associated quality-control flags were reported in the data set. The AT was reported at the measurement temperature of 20ºC.

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).

BCO-DMO Processing Description

* Added latitude, longitude and date to the dataset

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Data Files

File
925487_v1_porewater.csv (Comma Separated Values (.csv), 21.18 KB) MD5:84936b4c7b793551631ee4279f8388e9 Primary data file for dataset ID 925487, version 1

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Supplemental Files

File
IAPSO seawater standards filename: IAPSO_JC.csv   (Comma Separated Values (.csv), 664 bytes) MD5:5b5ee2e216067b22e67886d4f71e1c39 IAPSO seawater standards, supplemental to the porewater data. Added two extra columns to the IAPSO sheet to indicate sample ID and run number.

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Related Publications

Cetiner, J. E. P., Berelson, W. M., Rollins, N. E., Barnhart, H. A., Liu, X., Dong, S., Byrne, R. H., & Adkins, J. F. (2022). Novel device to collect deep-sea porewater in situ: A focus on benthic carbonate chemistry. Limnology and Oceanography: Methods, 21(2), 82–97. Portico. https://doi.org/10.1002/lom3.10530
Methods

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., & 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

Fleger et al, in prep: Fleger, K., Liu, X., Berelson, W.M., Cetiner J.E.P., Adkins, J.F., Byrne, R.H. Total alkalinity measurements on very small samples by spectrophotometric pH observations and equilibration with CO2. Limnol Oceanogr-Meth. In Prep
Methods

Hansson, 1972: Hansson I. (1972) An analytical approach to the carbonate system in sea water. Göteborgs universitet. https://hdl.handle.net/http://hdl.handle.net/2077/11464
Methods

Hansson, I. (1973). A new set of acidity constants for carbonic acid and boric acid in sea water. Deep Sea Research and Oceanographic Abstracts, 20(5), 461–478. https://doi.org/10.1016/0011-7471(73)90100-9
Methods

Hudson-Heck, E., Liu, X., & Byrne, R. H. (2021). Purification and Physical–Chemical Characterization of Bromocresol Purple for Carbon System Measurements in Freshwaters, Estuaries, and Oceans. ACS Omega, 6(28), 17941–17951. https://doi.org/10.1021/acsomega.1c01579
Methods

Lewis, E., Wallace, D., & Allison, L. J. (1998). Program developed for CO2 system calculations (No. ORNL/CDIAC-105). Brookhaven National Lab., Dept. of Applied Science, Upton, NY (United States); Oak Ridge National Lab., Carbon Dioxide Information Analysis Center, TN (United States). doi: 10.2172/639712
Methods

Liu, X., Patsavas, M. C., & Byrne, R. H. (2011). Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements. Environmental Science & Technology, 45(11), 4862–4868. doi:10.1021/es200665d
Methods

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

Millero, F. J. (1995). Thermodynamics of the carbon dioxide system in the oceans. Geochimica et Cosmochimica Acta, 59(4), 661–677. doi:10.1016/0016-7037(94)00354-o https://doi.org/10.1016/0016-7037(94)00354-O
Methods

Müller, J. D., & Rehder, G. (2018). Metrology of pH Measurements in Brackish Waters—Part 2: Experimental Characterization of Purified meta-Cresol Purple for Spectrophotometric pHT Measurements. Frontiers in Marine Science, 5. doi:10.3389/fmars.2018.00177
Methods

Parsons, T. R., Maita, Y., & Lalli, C. M. (1984). *A Manual of Chemical and Biological Methods for Seawater Analysis.* Pergamon Press. https://doi.org/10.25607/OBP-1830
Methods

Pilson M. E. Q. (1998) An Introduction to the Chemistry of the Sea., Prentice Hall. https://isbnsearch.org/isbn/0132589710
Methods

Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., Millero, F. J., Campbell, D. M. (1993). The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. Marine Chemistry, 44(2-4), 249-267. doi:10.1016/0304-4203(93)90207-5
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

Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Marine Chemistry, 2(3), 203–215. doi:10.1016/0304-4203(74)90015-2
Methods

Parameters

Parameter	Description	Units
Sample_ID	Sample Identifier	unitless
Station	Station identifier	unitless
Date	Sampling date in ISO format	unitless
Lat	Latitude of sampling location, south is negative	decimal degrees
Lon	Longitude of sampling location, west is negative	decimal degrees
Water_Column_Depth	Water column depth	meters (m)
Sediment_Depth	Sediment depth	centimeters (cm)
Alkalinity	Total Alkalinity	micromoles per kilogram (umol/kg)
pH	pH (in situ, "output" of CO2SYS)	total pH scale
Silica	Silicic acid (H4SiO4)	micromolar (uM)
DIC	Dissolved Inorganic Carbon (DIC)	micromoles per kilogram (umol/kg)
d13C_DIC	delta 13C of DIC	per mil (0/00)
Manganese	Mn +2 (Manganese ion concentration)	micromoles per kilogram (umol/kg)
Calcium	Ca +2 (Calcium ion concentration)	millimoles per kilogram (mmol/kg)
Strontium	Sr +2 (Strontium ion concentration)	micromoles per kilogram (umol/kg)
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	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	Porewater dissolved manganese [Mn] was analyzed by ICP-MS (inductively coupled plasma - mass spectrometry) using an Agilent 8800 triple-quadrupole instrument.
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset-specific Instrument Name	Thermo iCap7600 ICP-OES
Generic Instrument Name	Inductively Coupled Plasma Optical Emission Spectrometer
Dataset-specific Description	Porewater calcium, strontium, and sodium were measured using a Thermo iCap7600 ICP-OES (inductively coupled plasma - optical emission spectrometer).
Generic Instrument Description	Also referred to as an Inductively coupled plasma atomic emission spectroscope (ICP-AES). These instruments pass nebulised samples into an inductively-coupled gas plasma (8-10000 K) where they are atomised and excited. The de-excitation optical emissions at characteristic wavelengths are spectroscopically analysed. It is often used in the detection of trace metals.

Dataset-specific Instrument Name	minimal volume Multiparameter-Inorganic Carbon Analyzer
Generic Instrument Name	Multi-parameter Inorganic Carbon Analyzer
Dataset-specific Description	Multiparameter CO2 instrument named mvMICA (minimal volume Multiparameter-Inorganic Carbon Analyzer). The mvMICA is a dual parameter system engineered to simultaneously measure AT with sample volumes as low as 0.5 mL and pH with 1 and 1.5 mL. The mvMICA configuration consisted of pH and AT channels encased in a thermoregulating water bath.
Generic Instrument Description	The Multi-parameter Inorganic Carbon Analyzer (MICA) developed in the USF/College of Marine Science is an autonomous multi-parameter flow-through CO2 system capable of simultaneously measuring pH, carbon dioxide fugacity (fCO2), atmospheric carbon dioxide partial pressure (pCO2), and the total dissolved inorganic carbon (DIC) of natural water. Multiparameter Inorganic Carbon Analyzer (MICA)

Dataset-specific Instrument Name	custom tungsten halogen light source and Ocean Optics USB4000 spectrophotometer
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	Optical fibers connected channels to a custom tungsten halogen light source and Ocean Optics USB4000 spectrophotometers. Spectrophotometers were housed in a small refrigerator regulated to 18°C. The spectrophotometers were connected to a portable computer with custom software that monitors and records absorbances and sample information. The encased water bath had a lid with openings for AT sample input, CO2 gas tubing, and two Luer lock ports for pH sample input and output.
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.

Dataset-specific Instrument Name	
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	Picarro Cavity Ring-Down Spectrometer (G2131-i) with Liaison autosampler.
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.

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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

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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.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1834475

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