Diel variability in discrete samples of reef seawater temperature, salinity, dissolved inorganic carbon, pH, and stable carbon isotopes from Willemstad, Curaçao from February 2023 to May 2025

Website: https://www.bco-dmo.org/dataset/986726
Data Type: Other Field Results
Version: 1
Version Date: 2025-11-25

Project
» Collaborative Research: Reconstructions of Southern Caribbean Climate Variability using Contemporaneous and Co-Located Corals and Speleothems (P4Climate Curacao)

Program
» Paleo Perspectives on Present and Projected Climate (P4CLIMATE)

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Abstract
These data capture bihourly variability in the carbonate chemistry parameters of dissolved inorganic carbon (DIC), pH, and seawater stable carbon isotopes (δ13CDIC) measured from discrete bottle samples of seawater collected from Piscadera (Willemstad), Curaçao during 36-hour field campaigns in February 2023, March 2024, November 2024, and May 2025. In-situ water temperature of each sample was captured via Onset HOBO deployable sensors deployed at the sampling location. DIC concentrations, pH (total scale), and sample salinity were measured via coupled coulometric titration, spectrophotometry, and salinometry, respectively. δ13CDIC was measured via isotope ratio mass spectrometry (IRMS). Monitoring carbon cycling in shallow water coral reef ecosystems on diel-to-seasonal timescales directly informs our understanding of natural and externally-forced changes to reef metabolism, structure, function, and ultimately stability. These data help establish gradients in modern Southern Caribbean coral reef metabolism and were collected by a team of researchers associated with an NSF P4Climate-supported award on Southern Caribbean climate change studies.

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Coverage

Location: Southern Caribbean Sea
Spatial Extent: **Lat**:12.1221 **Lon**:-68.969188
Temporal Extent: 2023-02-11 - 2025-05-23

Methods & Sampling

Seawater samples were collected via a hand-triggered Niskin sampler at an average depth of 1 meter from the pier of the Caribbean Research and Management of Biodiversity (CARMABI) field laboratory located in Piscadera, Curaçao in February 2023, March 2024, November 2024, and May 2025. Benthic coverage in this zone is ~15% live coral, ~5% crustose coralline algae (CCA), ~30% turf algae, ~10% fleshy macroalgae, and ~40% carbonate sands (de Bakker et al., 2016; The Waitt Institute, 2017). During each field campaign, discrete Niskin casts were subsampled for DIC and $\delta^{13}C_{DIC}$ at a 2-hour frequency for 36 hours to capture the characteristic diel variation in the reef biogeochemistry. Briefly, following the protocols of Dickson et al. (2007), samples for DIC were transferred from the Niskin without exposure to the atmosphere into a 300 milliliter (mL) borosilicate glass BOD bottle. A ~3 mL aliquot of water from each Niskin cast was injected into a pre-flushed (He) 12 mL Labco Exetainer vial preloaded with phosphoric acid (H_3PO_4) for $\delta^{13}C$ analyses. All DIC water samples were poisoned immediately onsite with 150 microliters (µL) of a saturated mercuric chloride ($HgCl_2$) solution as a biocide and stoppered with greased (Apiezon-L) glass caps for laboratory analyses. As a complement to these discrete bottle samples, sea surface temperature was measured at each sampling time via moored submersible sensors at the sampling location.

Total DIC in micromoles per kilogram (µmol kg^{-1}), pH (total scale), and salinity of each sample were measured via coupled coulometric and spectrophotometric determination (MODICA, UIC). $\delta^{13}C_{DIC}$ of samples was determined via isotope ratio mass spectrometry (Delta V with GasBench II, ThermoScientific) at Vanderbilt University. Samples were analyzed with the ThermoCalcite and VU Coral in-house carbonate standards, both of which are referenced to the IAEA602 and NBS019 standards. Two additional in-house standards, VU Marble and Pol2, are also run as unknowns in each run. Corrections were conducted using the USGS LIMS for Light Stable Isotopes data reduction scheme (Coplen, 1998). The $^{13}C/^{12}C$ ratio of each sample is expressed in del (δ) notation in per mil (‰) units relative to Vienna Pee Dee Belemnite (VPDB), which is defined to have a $\delta^{13}C$ value equal to 0 and an absolute $^{13}C/^{12}C$ ratio equal to 0.0112372 (Allison et al., 1995). Long-term precision of DIC measurements, based on repeated assessments of certified reference materials, is ± 4 µmol kg^{-1} (1σ). Long-term precision of $\delta^{13}C_{DIC}$ measurements, based on repeat measurements of VU Marble, is ± 0.07‰ (1σ) VPDB.

Data Processing Description

For DIC, reported concentrations were corrected online using Dickson CRM batch 187, which was run as a bracketing standard during each set of analyses. Long-term precision of DIC measurements, based on repeated assessments of certified reference materials, is ± 4 µmol kg^{-1} (1σ).

For δ13C, samples were analyzed with the ThermoCalcite and VU Coral in-house carbonate standards, both of which are referenced to the IAEA602 and NBS019 standards. Two additional in-house standards, VU Marble and Pol2, are also run as unknowns in each run. Reported values were corrected using the USGS LIMS for Light Stable Isotopes data reduction scheme (Coplen, 1998). Long-term precision of $\delta^{13}C_{DIC}$ measurements, based on repeat measurements of VU Marble, is ± 0.07‰ (1σ) VPDB.

BCO-DMO Processing Description

- Imported original file "Curaçao δ13C-DIC BCO-DMO_Reformatted.csv" into the BCO-DMO system.
- Re-named fields to comply with BCO-DMO naming conventions.
- Added columns for site latitude and longitude.
- Saved the final file as "986726_v1_curacao_diel_carbonate_chemistry.csv".

Problem Description

Samples CP21, CP26, CP38, CP78 were compromised during DIC analyses, and as a result, all values for these time points were removed from the dataset.

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Parameters

Parameter	Description	Units
Date_Time_UTC	Station timestamp (UTC) in ISO 8601 format	unitless
Sample_Name	Sample ID number - Curaçao Project = CP and # is sample index	unitless
Temperature_C	In-situ sea surface temperature at time of sample collection	degrees Celsius
Salinity_PSU	Salinity of sample	unitless
pH_totalscale	Sample pH at time of analyses in a 20°C water bath	unitless
d13C_permil	Sample ?13C of DIC	per mil
d13C_Uncertainty_permil	Internal precision of individual sample ?13C measurements	per mil
DIC_umol_kg	Concentration of dissolved inorganic carbon in each sample	micromoles per kilogram seawater
Site_Lat	Latitude of sample collection site	decimal degrees
Site_Lon	Longitude of sample collection site	decimal degrees

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Instruments

Dataset-specific Instrument Name	Wheaton 300 mL BOD borosilicate glass bottles with stoppers
Generic Instrument Name	Bottle
Dataset-specific Description	Water samples from each Niskin cast were transferred without exposure to the atmosphere to 300 ml Wheaton borosilicate glass BOD bottles and immediately poisoned with saturated mercuric chloride for dissolved inorganic carbon analyses.
Generic Instrument Description	A container, typically made of glass or plastic and with a narrow neck, used for storing drinks or other liquids.

Dataset-specific Instrument Name	UIC 5017O coulometer
Generic Instrument Name	CO2 Coulometer
Dataset-specific Description	The MODICA system was coupled to a UIC 5017O coulometer for the coulometric determination of DIC.
Generic Instrument Description	A CO2 coulometer semi-automatically controls the sample handling and extraction of CO2 from seawater samples. Samples are acidified and the CO2 gas is bubbled into a titration cell where CO2 is converted to hydroxyethylcarbonic acid which is then automatically titrated with a coulometrically-generated base to a colorimetric endpoint.

Dataset-specific Instrument Name	ThermoScientific Delta V with GasBench II
Generic Instrument Name	Isotope-ratio Mass Spectrometer
Dataset-specific Description	δ13CDIC of samples was determined via isotope ratio mass spectrometry (Delta V with GasBench II, ThermoScientific).
Generic Instrument Description	The Isotope-ratio Mass Spectrometer is a particular type of mass spectrometer used to measure the relative abundance of isotopes in a given sample (e.g. VG Prism II Isotope Ratio Mass-Spectrometer).

Dataset-specific Instrument Name	General Oceanics 8L and 2.5L Niskin bottles
Generic Instrument Name	Niskin bottle
Dataset-specific Description	Dissolved seawater samples were collected using either 8L or 2.5L General Oceanics Niskin bottles.
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	Onset HOBO U2OL-0x depth logger
Generic Instrument Name	Onset HOBO U20L water level logger series
Dataset-specific Description	In-situ sea surface temperatures at the sampling location were monitored during each diel field campaign with an Onset HOBO U2OL-0x depth logger with temperature sensor (manufacturer stated accuracy ± 0.44°C).
Generic Instrument Description	The HOBO U20L is designed for monitoring changing water levels in a variety of applications including tidal areas, streams, lakes, wetlands, and groundwater. It outputs pressure, water level, and temperature data. The instrument can record samples, sensor measurements at each logging interval, and events data, occurrences such as a bad battery or host connected. The samples are recorded as absolute pressure values, which are later converted to water level readings using software. Absolute pressure is atmospheric pressure plus water head. The deployment of an additional HOBO U20L at the surface can be used to compensate for barometric pressure changes. Each instrument is individually calibrated. They require a coupler and optic base station or HOBO waterproof shuttle to connect to a computer. The instrument is operated with a 3.6 V lithium battery. This series contains 3 models, U20L-01, U20L-02, and U20L-04, with different operation ranges, calibrated ranges, and burst pressures. The pressure sensor is temperature compensated between 0 and 40 degrees Celsius (C), and calibrated between 69 and a maximum of 400 kPa (depending on the model). Its accuracy is within 0.3 % of the full scale for absolute pressure, and 0.1 % FS for water level readings. The temperature sensor operates between -20 and 50 degrees C, with an accuracy of 0.44 deg C, and a resolution of 0.1 deg C. The drift is 0.1 deg C per year.

Dataset-specific Instrument Name	GasBench II, ThermoScientific
Generic Instrument Name	Thermo-Fisher Scientific Gas Bench II
Dataset-specific Description	δ13CDIC of samples was determined via isotope ratio mass spectrometry (Delta V with GasBench II, ThermoScientific).
Generic Instrument Description	An on-line gas preparation and introduction system for isotope ratio mass spectrometry that is designed for high precision isotope and molecular ratio determination of headspace samples, including water equilibration, carbonates and atmospheric gases. The instrument allows for the use of a dual viscous flow inlet system of repetitive measurements of sample and standard gas on a continuous flow isotope ratio mass spectrometer (CF-IRMS) system. The sample volume is the sample vial (instead of a metal bellows), and the reference gas volume is a pressurized gas tank. The instrument consists of a user programmable autosampler, a gas sampling system, a maintenance-free water removal system, a loop injection system, an isothermal gas chromatograph (GC), an active open split interface, a reference gas injection system with three reference ports, and one or two optional LN2 traps for cryofocusing. The gas sampling system includes a two port needle which adds a gentle flow of He into the sample vial, diluting and displacing sample gas. Water is removed from the sample gas through diffusion traps. The loop injector aliquots the sample gas onto the GC column, which separates the molecular species. The reference gas injection system allows accurate referencing of each sample aliquot to isotopic standards. The system can be used with several options including a carbonate reaction kit that allows injection of anhydrous phospohric acid into sample vials. Note "Finnigan GasBench-II" is the previous brand name of this instrument.

Dataset-specific Instrument Name	UIC MODICA
Generic Instrument Name	UIC Multifunction Dissolved Inorganic Carbon Analyzer (MODICA)
Dataset-specific Description	Total DIC (µmol kg-1), pH (total scale), and salinity of each BOD bottle sample were measured using a UIC Multifunction Dissolved Inorganic Carbon Analyzer (MODICA) equipped with a spectrophotometric pH sensor and built-in salinometer. The MODICA system was coupled to a UIC 5017O coulometer for the coulometric determination of DIC.
Generic Instrument Description	MODICA was jointly developed by UIC INC. and AlphaZeta Sciences LLC. MODICA is a multidetector, multichannel-capable dissolved inorganic carbon analyzer. In addition to measuring DIC, MODICA can also provide spectrophotometric pH readings from the same sample as an option. More information: https://www.uicinc.com/modica-a-multifunction-dissolved-inorganic-carbon...

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Project Information

Collaborative Research: Reconstructions of Southern Caribbean Climate Variability using Contemporaneous and Co-Located Corals and Speleothems (P4Climate Curacao)

Coverage: Curacao, Dutch Caribbean

NSF Award Abstract:
Historical and ancient climate data from paleoclimate proxy records can provide the long-term climate context

necessary to support coastal Caribbean communities in preparing for, adapting to, and/or mitigating the numerous impacts of anthropogenic climate change. This project will study coral and speleothem carbonates from reef ecosystems and cave environments on the island of Curaçao in the arid Southern Caribbean. Geochemical analyses and dating of these carbonates will be used to generate records of local temperature and aridity that span the interval as Earth warmed from the Last Glacial Maximum (~20 thousand years ago) to present. Coupling these geochemical analyses with monitoring of modern reef and cave environments and numerical modeling will help determine the extent to which Caribbean Sea climates have varied in the past and the role that they play in mediating global climate on seasonal to glacial-interglacial timescales. The proposed research presents a unique opportunity to develop and apply integrated approaches to understand coeval archives of terrestrial and marine climate variability at a single, relatively understudied location. Broader impacts of this research include the dissemination of major findings through community-influenced geoscience curricula development and tiered mentorship opportunities for students from the K-12 through postdoctoral levels. For example, the research will support research exchange opportunities for University of Curaçao students through a targeted cross-institutional partnership with the Caribbean Research and Management of Biodiversity (CARMABI) foundation, in which undergraduate students will work on the Georgia Tech and Vanderbilt campuses where they will be integrated into a diverse, multi-institutional team of PIs, postdocs, and graduate and undergraduate students.

Anthropogenic climate change in the Caribbean Sea is projected to extend seasonal warm periods, increase the frequency and intensity of heavy rainfall events, and increase periods of prolonged drought. Paleoclimate records from speleothem and coral carbonates from the wet tropical Northern and Western Caribbean have provided context for these projections by illustrating the relevant climate drivers and teleconnections over the past several thousand years. However, equally extensive and informative records are notably absent from the arid Southern Caribbean. This project will develop precisely dated, co-located coral and speleothem proxy temperature and hydroclimate records from Curaçao, synthesize these records with other regional and global proxies, and make transformative progress in the understanding of how carbonate minerals in terrestrial and marine ecosystems record past environmental change in this region. Trace element-to-calcium ratios (i.e. Sr/Ca, Mg/Ca, Ba/Ca, etc.) and traditional stable isotopes ($\delta^{18}O$, $\delta^{13}C$, etc.) from actively-precipitating stalagmites, drip waters, modern coral skeletons, and seawater will be further integrated with proxy system models and instrumental data to fingerprint the dominant drivers of terrestrial and marine climate on seasonal to decadal timescales. This understanding will be applied to jointly interpret speleothem and coral proxy records of hydroclimate and SST and develop a comprehensive picture of seasonal to millennial climate evolution since the last deglaciation. This work includes the development of optimal U-Th dating techniques to jointly analyze speleothem and coral carbonates, active seawater and cave monitoring, and the development and application of novel geochemical proxies, including new methods for the analysis of the calcium isotope quantitative precipitation proxy in speleothems via collision cell multi-collector ICP-MS. This award is co-funded by the Division of Earth Sciences and Division of Atmospheric and Geospace Sciences by way of the Paleo Perspectives on Present and Projected Climate Program, as well as the Division of Earth Sciences funds for support of projects that increase research capabilities, capacity and infrastructure at a wide variety of institution types, as outlined in the GEO EMBRACE DCL.

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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Program Information

Paleo Perspectives on Present and Projected Climate (P4CLIMATE)

Website: https://new.nsf.gov/funding/opportunities/paleo-perspectives-present-projected-climate

excerpt from https://new.nsf.gov/funding/opportunities/paleo-perspectives-present-projected-climate (Accessed on 2024-09-04):

Synopsis:

Much can be learned about the climate system using existing historical observations and models of current climate, but those records and models do not reflect the range of climate behavior on multi-decadal to

millennial time scales, or capture tipping points, thresholds, and other key features of the climate system. For that, data from geological records or other environmental archives are required.

The PALEO PERSPECTIVES ON PRESENT AND PROJECTED CLIMATE (P4CLIMATE) competition is a coordinated paleoclimate science initiative that is funded by the National Science Foundation (NSF) Divisions of Atmospheric and GeoSpace Sciences (AGS), Earth Sciences (EAR), Ocean Sciences (OCE), and Office of Polar Programs (OPP) in the Geosciences (GEO) Directorate. The annual P4CLIMATE competition supports the scientific objectives of the National Science Foundation by fostering interdisciplinary research and synthesis of climate data.

The goal of the interdisciplinary P4CLIMATE solicitation is to utilize observational and modeling studies to provide paleo perspectives addressing the two research themes: 1) Past Regional and Seasonal Climate; and 2) Past Climate Forcing, Sensitivity, and Feedbacks.

OPP will accept proposals to this solicitation A) with and without fieldwork in the Arctic, and B) only without fieldwork in the Antarctic. Proposals that have fieldwork in Antarctica should be submitted to the annual solicitation for proposals that have fieldwork in Antarctica.

Program Solictiation:
NSF 22-612: Paleo Perspectives on Present and Projected Climate (P4CLIMATE)

Full Proposal Target Date(s):

October 20, 2022

October 20, Annually Thereafter

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Funding

Funding Source	Award
NSF Division of Earth Sciences (NSF EAR)	EAR-2303297
NSF Division of Earth Sciences (NSF EAR)	EAR-2303298
NSF Division of Earth Sciences (NSF EAR)	EAR-2303299
NSF Division of Earth Sciences (NSF EAR)	EAR-2303300

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