Open cell and single-step method for total alkalinity titrations from samples collected on R/V Mirai cruises MR23-06C and MR23-07 in the North Pacific and Western Arctic from September to November 2023

Website: https://www.bco-dmo.org/dataset/957527
Data Type: Cruise Results, experimental
Version: 2
Version Date: 2025-07-29

Project
» US GEOTRACES GP17-OCE and GP17-ANT: Inorganic Carbon Cycling in the South Pacific and Southern Oceans by Direct Measurement (GP17-OCE and GP17-ANT Inorganic Carbon)
» Collaborative Research: Opening the black box of oxygen deficient zone biogeochemistry through integrative tracers (O2 Deficient Zone Tracers)

Contributors	Affiliation	Role
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Abstract
Duplicate samples were collected for total alkalinity on two cruises in 2023 aboard the R/V Mirai (MR23-06C and MR23-07) in order to compare two different methods of total alkalinity titrations: the open cell with non-linear least squares fitting and single step with spectrophotometric endpoint detection. Measurements of dissolved inorganic carbon and pH on the total scale were also made as quality control checks. GLODAPv2 hinted at a potential offset between laboratories in the Pacific Ocean. We hypothesized that if non-negligible amounts of organic alkalinity were present, the different methods could be titrating different amounts leading to differences between the methods. The results show that any offset is within the uncertainty of the analytical precision and presence of organic alkalinity in open ocean waters remains inconclusive.

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Coverage

Spatial Extent: **N**:77.0399 **E**:-143.0531 **S**:27.5003 **W**:179.4858
Temporal Extent: 2023-09-07 - 2023-11-01

Dataset Description

Version 2 (the current version) contains the following changes from version 1:
- Corrections to a small number of values where, rather than giving the average of two duplicates, the value of one replicate was given (Column 16, flags 6, for cruise MR23-07).
- The addition of column Final_pHt_for_Single_Step_method_TA.

Methods & Sampling

Samples were collected from the CTD rosette following best practices (Dickson et al., 2007). Samples for single-step total alkalinity (TA) titrations were collected in 100-milliliter (mL) borosilicate glass bottles, and samples for open cell titrations were collected in 250-mL borosilicate glass bottles. Samples were poisoned with 0.04% HgCl2 and a precise headspace of ~1% was created using a pipette. Bottles were sealed with ground glass stopper, and apiezon L grease and a rubber band and plastic hose clamp were used to keep the stopper in place.

The TA measured on board was measured by single-step titration with spectrophotometric endpoint detection using bromocresol green following the methods of Yao and Byrne (1998). The duplicate samples were shipped to the laboratory at Massachusetts Institute of Technology (MIT) in Cambridge, MA, USA for analysis using an open cell titration and non-linear least squares fitting as described in Dickson et al. (2003). DIC for both shipboard and land-based analysis was done by acidification and coulometric detection following best practices methods (Dickson et al. 2007).

Land-based pH on the total scale (pHt) at 20 degrees Celsius was done using a custom-built instrument similar to Carter et al. (2013) and purified meta-cresol purple indicator.

Instrumentation:
The shipboard TA analysis by single step titration was done using spectrophotometry with a single acid addition procedure using a custom-made system (Nippon ANS, Inc., Japan).

Land-based TA was performed with a custom-designed titration designed and built by the laboratory of Andrew G. Dickson (University of California, San Diego) as described in Dickson et al. (2003).

Shipboard DIC was determined using an automated TCO2 analyzer (Nippon ANS, Inc., Japan) with coulometric detection.

Land-based DIC was determined by a custom dissolved inorganic carbon extraction with coulometric detection built by the National Oceanographic and Atmospheric Administration Pacific Marine Laboratory and is a modern version of the original SOMMA system (Johnson et al. 1992).

Land-based pHt was measured at 20 degrees Celsius with a custom system designed and built by the Woosley laboratory consisting of a Kloehn syringe pump and Agilent 8453 spectrophotometer and controlled using LabView Software.

Data Processing Description

Certified reference material (CRM) provided by Andrew Dickson (UCSD) were used for all TA and DIC measurements. For shipboard analysis, Batch 209 was used. For laboratory analysis, batch 216 was used.

For single-step TA, the values were adjusted according to the ratio of the mean measured CRM value and the certified value. For open cell TA, no adjustment was made to the CRM.

For laboratory pHt, TRIS buffer made in house according to Paulsen and Dickson (2020) was used as an accuracy and precision check.

BCO-DMO Curation Notes

Version 1:
(version date 2025-03-25)
- Imported original file "TA Comparison Submit to BCODMO.xlsx" into the BCO-DMO system.

- Marked "-999", "-999.0000", and "-999.000" as missing data values (missing data are empty/blank in the final csv file).
- Renamed fields to comply with BCO-DMO naming conventions.
- Created date-time UTC column in ISO 8601 format.
- Saved final file as "957527_v1_ta_comparison.csv".

Version 2:
(version date 2025-07-29)
- Imported revised file "TA Comparison Submit to BCODMO.xlsx" into the BCO-DMO system.
- Marked "-999", "-999.0000", and "-999.000" as missing data values (missing data are empty/blank in the final csv file).
- Renamed fields to comply with BCO-DMO naming conventions.
- Created date-time UTC column in ISO 8601 format.
- Rounded Total_Alkalinity_Open_Cell_Method, Final_pHt_for_Single_Step_method_TA, and Lab_pHt to 4 decimal places.
- Saved final file as "957527_v2_ta_comparison.csv".

Problem Description

WOCE quality flags were used (2 = good, 3 = questionable, 4 = bad, 5 = lost, 6 = average of two duplicates, 9 = not sampled).

For laboratory based DIC and pHt, two flags were assigned: an 'analytical quality flag' indicating quality of the actual analytical analysis and a 'storage quality flag' indicating if changes did or are suspected to have occurred between time of collection and time of analysis in the lab.

For the storage flag the meanings are: loss/gain of CO2 was suspected (3) or confirmed (4). 2 means no change a sample during storage.

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Data Files

File	
957527_v2_ta_comparison.csv	(Comma Separated Values (.csv), 47.36 KB) MD5:2a91cddd2df39a342df0b32071a27515
Primary data file for dataset ID 957527, version 2	

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Related Publications

Carter, B. R., Radich, J. A., Doyle, H. L., & Dickson, A. G. (2013). An automated system for spectrophotometric seawater pH measurements. Limnology and Oceanography: Methods, 11(1), 16–27. doi:10.4319/lom.2013.11.16
Methods

Dickson, A. G., Afghan, J. D., & Anderson, G. C. (2003). Reference materials for oceanic CO2 analysis: a method for the certification of total alkalinity. Marine Chemistry, 80(2), 185–197. https://doi.org/10.1016/S0304-4203(02)00133-0
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

Johnson, K. M. (1992). Single-operator multiparameter metabolic analyzer (SOMMA) for total carbon dioxide (C{sub T}) with coulometric detection. Operator`s manual. Office of Scientific and Technical Information

(OSTI). https://doi.org/10.2172/10194787
Methods

Paulsen, M., & Dickson, A. G. (2020). Preparation of 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS) pHT buffers in synthetic seawater. Limnology and Oceanography: Methods, 18(9), 504–515. Portico. https://doi.org/10.1002/lom3.10383
Methods

Woosley, R.J., J.A. Bruno, D. Neithardt, Z.A. Wang, N. Fujiki, and A. Murata. (submitted, 2025) Comparison of open cell and single-step total alkalinity titration methods and implications for organic alkalinity. Limnol. Ocenogr. Meth.
Results

Yao, W., & Byrne, R. H. (1998). Simplified seawater alkalinity analysis. Deep Sea Research Part I: Oceanographic Research Papers, 45(8), 1383–1392. https://doi.org/10.1016/s0967-0637(98)00018-1 https://doi.org/10.1016/S0967-0637(98)00018-1
Methods

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Related Datasets

IsRelatedTo

Fujiwara, A. , Hatta, M. , Murata, A. , Uchida, H. , Fujiki, N., 2023, CTD and routinely analyzed biogeochemical parameters in samples collected during R/V Mirai MR23-06C cruise, 0.00, Arctic Data archive System (ADS), Japan, https://ads.nipr.ac.jp/dataset/A20241108-002

Katsumata, K. 2023. Hydrographic data from cruise 49NZ20231006. Accessed from CCHDO https://cchdo.ucsd.edu/cruise/49NZ20231006

Woosley, R., Neithardt, D., Bruno, J. A. (2025) **Total alkalinity from an experiment testing the suitability of high-density polyethylene (HDPE) for collection and long-term storage of total alkalinity samples using laboratory-manipulated oligotrophic Atlantic surface water.** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2025-04-03 doi:10.26008/1912/bco-dmo.957694.1 [view at BCO-DMO]

Woosley, R., Neithardt, D., Lahn, L. (2025) **Total alkalinity determined through experiments comparing usage of high-density polyethylene (HDPE) and borosilicate glass bottles for collection and storage of water samples collected on the GEOTRACES GP17-OCE cruise (R/V Roger Revelle RR2214).** Biological and Chemical Oceanography Data Management Office (BCO-DMO). (Version 1) Version Date 2025-04-02 doi:10.26008/1912/bco-dmo.957644.1 [view at BCO-DMO]

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Parameters

Parameter	Description	Units
Cruise	Cruise identification number	unitless
sample_ID	Sample identifier composed of formula (Station"*1000)+("Cast"*100)+("Niskin")"	unitless
Station	Station number	unitless
Cast	Cast identifier	unitless

NiskinBottle_No	Niskin bottle identifier	unitless
Date	Station occupation date	unitless
Time	Station occupation time (UTC)	unitless
ISO_DateTime_UTC	Station occupation date and time (UTC) in ISO8601 format	unitless
LATITUDE	Latitude	degrees North
LONGITUDE	Longitude	degrees East
CTD_Salinity	Practical salinity as measured by the CTD	unitless
CTD_Salinity_flag	WOCE QC flagging scheme	unitless
Bottle_Salinity	Practical salinity measured from the niskin bottle	unitless
Bot_Sal_flag	WOCE QC flagging scheme	unitless
CTD_Pressure	Pressure	decibars (db)
Total_Alkalinity_Single_Step_method	Total alkalinity as measured using the single-step titration method	micromoles per kilogram of seawater (umol/kg_sw)
Total_Alkalinity_Single_Step_Method_flag	WOCE QC flagging scheme	unitless
Final_pHt_for_Single_Step_method_TA	pHt (total scale) measured at the end of the titration for the single step method of Total Alkalinity	total scale
Total_Alkalinity_Open_Cell_Method	Total alkalinity as measured using the open cell method	micromoles per kilogram of seawater (umol/kg_sw)
Total_Alkalinity_Open_Cell_Method_Flag	WOCE QC flagging scheme	unitless
Ship_DIC	Dissolved inorganic carbon measured on board the ship	micromoles per kilogram of seawater (umol/kg_sw)

Ship_DIC_flag	WOCE QC flagging scheme	unitless
Lab_DIC	Dissolved inorganic carbon measured in the laboratory	micromoles per kilogram of seawater (umol/kg_sw)
Lab_DIC_analytical_flag	WOCE QC flagging scheme	unitless
Lab_DIC_Storage_flag	WOCE QC flagging scheme	unitless
Ship_pHt	pH on the total scale measured on the ship	total scale
Ship_pHt_flag	WOCE QC flagging scheme	unitless
Ship_pH_Temp	Temperature of ship pHt analysis	degrees Celsius
Lab_pHt	pH on the total scale measured in the laboratory	total scale
Lab_pHt_analytical_flag	WOCE QC flagging scheme	unitless
Lab_pHt_storage_flag	WOCE QC flagging scheme	unitless
Lab_pHt_temp	Temperature of lab pHt anaysis	degrees Celsius
CTDTEMP	Temperature measured by the CTD sensor	degrees Celsius
CTDTEMP_Flag	WOCE QC flagging scheme	unitless
O2	Dissolved oxygen	micromoles per kilogram of seawater (umol/kg_sw)
O2_flag	WOCE QC flagging scheme	unitless
DOC	Dissoloved organic carbon	micromoles per kilogram of seawater (umol/kg_sw)
DOC_flag	WOCE QC flagging scheme	unitless
NO3	Dissolved nitrate	micromoles per kilogram of seawater (umol/kg_sw)

NO3_flag	WOCE QC flagging scheme	unitless
NO2	Dissolved nitrite	micromoles per kilogram of seawater (umol/kg_sw)
NO2_flag	WOCE QC flagging scheme	unitless
Si	Dissolved silicate	micromoles per kilogram of seawater (umol/kg_sw)
Si_flag	WOCE QC flagging scheme	unitless
PO4	Dissolved phosphate	micromoles per kilogram of seawater (umol/kg_sw)
PO4_flag	WOCE QC flagging scheme	unitless
NH4	Dissolved ammonium	micromoles per kilogram of seawater (umol/kg_sw)
NH4_flag	WOCE QC flagging scheme	unitless
fDOM	Florescent dissolved organic carbon	RU
fDOM_flag	WOCE QC flagging scheme	unitless

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Instruments

Dataset-specific Instrument Name	Agilent 8453 spectrophotometer
Generic Instrument Name	Agilent 8453 UV-visible spectrophotometer
Dataset-specific Description	Land-based pHt was measured at 20 degrees Celsius with a custom system designed and built by the Woosley laboratory consisting of a Kloehn syringe pump and Agilent 8453 spectrophotometer and controlled using LabView Software.
Generic Instrument Description	The Agilent 8453 spectrophotometer is a laboratory optical instrument for chemical analysis to extract spectral information in the ultraviolet (UV) and visible light. The instrument radiates a single light beam by optically combining two source lamps: a deuterium-discharge lamp for the UV wavelength range and a tungsten lamp for the visible and short wave near-infrared (SWNIR) wavelength range. The beam passes through the sample, is focused and dispersed within the spectrograph lens, slit and grating, and reaches the diode array in the form of a spectral image. The diode array samples a wavelength range of 190 to 1100 nm at a mean sampling interval of 0.9 nm. The nominal spectral slit width is 1 nm and the stray light is less than 0.03%.

Dataset-specific Instrument Name	TCO2 analyzer (Nippon ANS, Inc., Japan)
Generic Instrument Name	CO2 Analyzer
Dataset-specific Description	Shipboard DIC was determined using an automated TCO2 analyzer (Nippon ANS, Inc., Japan) with coulometric detection.
Generic Instrument Description	Measures atmospheric carbon dioxide (CO2) concentration.

Dataset-specific Instrument Name	a modern version of the original SOMMA system
Generic Instrument Name	Single Operator Multi-parameter Metabolic Analyzer
Dataset-specific Description	Land-based DIC was determined by a custom dissolved inorganic carbon extraction with coulometric detection built by the National Oceanographic and Atmospheric Administration Pacific Marine Laboratory and is a modern version of the original SOMMA system (Johnson et al. 1992).
Generic Instrument Description	Single Operator Multi-parameter Metabolic Analyzer (SOMMA) which was manufactured at the University of Rhode Island and standardized at the Brookhaven National Laboratory.

Dataset-specific Instrument Name	custom-designed titration
Generic Instrument Name	Titrator
Dataset-specific Description	The shipboard TA analysis by single step titration was done using spectrophotometry with a single acid addition procedure using a custom-made system (Nippon ANS, Inc., Japan). Land-based TA was performed with a custom-designed titration designed and built by the laboratory of Andrew G. Dickson (University of California, San Diego) as described in Dickson et al. (2003).
Generic Instrument Description	Titrators are instruments that incrementally add quantified aliquots of a reagent to a sample until the end-point of a chemical reaction is reached.

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Deployments

MR23-06C

Website	https://www.bco-dmo.org/deployment/957530
Platform	R/V Mirai
Report	https://www.godac.jamstec.go.jp/darwin_cruise/metadata/d73ac6eb-52b4-4235-bab4-122d01efc7cd/MR23-06C_summary_eng.pdf
Start Date	2023-08-25
End Date	2023-10-04
Description	More information is available from JAMSTEC at https://www.godac.jamstec.go.jp/darwin_cruise/view/metadata?key=MR23-06C... (DOI: 10.17596/0003983)

MR23-07

Website	https://www.bco-dmo.org/deployment/957531
Platform	R/V Mirai
Report	https://cchdo.ucsd.edu/cruise/49NZ20231006
Start Date	2023-10-06
End Date	2023-11-08
Description	More information is available from JAMSTEC at https://www.godac.jamstec.go.jp/darwin_cruise/view/metadata?key=MR23-07&... (DOI: 10.17596/0003829)

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Project Information

US GEOTRACES GP17-OCE and GP17-ANT: Inorganic Carbon Cycling in the South Pacific and Southern Oceans by Direct Measurement (GP17-OCE and GP17-ANT Inorganic Carbon)

Coverage: South Pacific and Amundsen Sea

NSF Award Abstract

The oceans help to slow climate change by absorbing about a quarter of the carbon dioxide (CO2) produced by burning of fossil fuels and other human activities. The Pacific and Southern Oceans are known to take up and store significant amounts of anthropogenic CO2, but many questions regarding the amount, variability, and biogeochemical and ecological impacts remain unanswered. This research will focus on answering some of those questions in two areas of the Pacific by analyzing samples for total CO2, total alkalinity, and pH on two GEOTRACES cruises, GP17-OCE and GP17-ANT. The project will support several undergraduate student researchers and create educational modules on ocean acidification for general public and K-12 students.

On the GP17-OCE expedition in the south Pacific, sub-decadal scale variability in the uptake of CO2 and resulting decrease in pH (termed ocean acidification) will be examined by comparing data collected on this expedition with data from prior occupations of the line in 1991, 2005 and 2014. An extended multilinear regression technique will be used to separate natural variability from human induced changes. The second expedition, GP17-ANT, covers the Amundsen Sea, an area with few prior carbon measurements. This sea is perennially ice-covered with several seasonal polynyas (areas of open water surrounded by sea ice) and exhibits complex water circulation making the contribution to the global carbon cycle uncertain. The data collected from this expedition will examine several hypotheses regarding how carbon is taken up, mixed, and recirculated in the region, how glacial ice melt, sea ice, and biological productivity influence the carbon cycle, and provide baseline measurements against future data to determine changes in the carbon cycle of the region over time. Both expeditions will leverage the myriad of other parameters being measured, particularly trace metals such as iron and zinc, to examine how cycling of carbon and trace metals are interlinked through pH.

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.

Collaborative Research: Opening the black box of oxygen deficient zone biogeochemistry through integrative tracers (O2 Deficient Zone Tracers)

Coverage: eastern tropical North Pacific ocean

NSF abstract:

The oxygen deficient zones are regions in the ocean where dissolved oxygen disappears. These regions harbor unique ecosystems only found in waters without oxygen, and they are important for Earth’s climate. Specifically, the production of nitrogen gas by two microbial processes, anammox and denitrification can control how productive the oceans are. Yet how much each process shapes ocean chemistry within these areas remains unknown. This project aims to study the oxygen deficient waters of the eastern tropical North Pacific ocean to better understand the mechanisms shaping marine nitrogen and carbon chemistry. Through this work, the project will train undergraduate and graduate students at three universities. The project aims to broaden participation in and understanding of ocean sciences by developing public videos about the methods used and the science behind the project.

The investigators will conduct a research cruise in the eastern tropical North Pacific ocean, the largest oxygen deficient zone. They will measure many nutrients including inorganic carbon and nitrogen and natural abundance stable isotopes of nitrogen compounds. They will use these patterns to establish how the major reactions work together to control nitrogen cycling and gaseous nitrogen production. In addition, a high-resolution model of the ocean will reveal the influence of ocean mixing, set the timescales for reactions, and enable synthesis of the measurements into a global context. The work will determine how the input of oxygen through mixing controls chemistry, and it will distinguish between the processes restricted to the permanently anoxic core vs. those that tolerate (or are enhanced by) occasional oxygenation. Overall, the project will provide new information about nitrogen cycling pathways (anammox, denitrification, and nitrite oxidation) across the region and link the resulting isotopic signals to the global nitrogen budget.

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-2148468
NSF Division of Ocean Sciences (NSF OCE)	OCE-2342986

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