Scripps Institution of Oceanography Technical Report

Time-Series of Inorganic Carbon Measurements on Surface Ocean Water near Bermuda and Hawaii, 1983-2023.

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Abstract

Time series measurements of dissolved inorganic carbon (DIC), titration alkalinity (ALK, also abbreviated as TA) and the $^{13}C/^{12}C$ ratio of the DIC are presented for surface ocean sampled near Bermuda and Hawaii. The concentration of DIC is determined by vacuum extraction of acidified seawater followed by manometric assay of the evolved CO_2. ALK is determined by potentiometric titration. The CO_2 gas extracted from the samples is analyzed with isotope ratio mass spectrometry (IRMS) to determine the reduced $^{13}C/^{12}C$ ratio ($\delta^{13}C$) of the DIC. The in-situ temperature, salinity, DIC and ALK are used to calculate the partial pressure of CO_2 (pCO_2) and the pH_T of the samples. In the 4 decades of this study, trends in DIC and $\delta^{13}C$ records are seen to track rising CO_2 in the atmosphere at all locations. Calculated pCO_2 and pH_T also exhibit trends expected from the uptake of atmospheric CO_2.

Introduction

Since the 1980s, the Scripps Institution of Oceanography has collaborated to maintain time-series measurements of the ocean carbon parameters in surface waters at sites in near Bermuda (Hydrostation S (32°10'N, 64°30'W), Bermuda Atlantic Time Series (BATS 31°40'N 64°10'W), and near Hawaii (Hawaiian Ocean Time-series (HOT station ALOHA[1] (22.45°N 158°W)). These measurements are a component of a wider suite of parameters (physical, chemical and biological dynamics of carbon) that have been tracked over time at these sites (Bates and Johnson, 2020, Bates et al., 2014, Bates 2007, Karl et al., 2021, Dore et al., 2009, and references therein). Both time series are located in subtropical gyres, which cover a large fraction of the ocean surface and are important as global sinks for atmospheric CO_2. Tracing this uptake and the associated ocean acidification through direct measurements is a major goal of the Scripps CO_2 program.

Throughout its history, the Scripps program has focused on measuring three variables: dissolved inorganic carbon (DIC), titration alkalinity (ALK), and the reduced $^{13}C/^{12}C$ ratio of the DIC ($\delta^{13}C$). This technical report summarizes details of the seawater analyses covering samples collected through 2023. From DIC and ALK we also calculate the partial pressure of CO_2 in the seawater (pCO_2), and pH_T[2], which are sensitive measures of the uptake of CO_2 and acidification.

[1] (A Long-term Oligotrophic Habitat Assessment)

[2] $pH_T = -\log \{ [H] * (1 + S_T/K(HSO_4) \}$ = pH on the total scale (Dickson 2007).

Methods

1. Seawater sampling

This study has relied on seawater sample collected by personnel from the Bermuda Institute of Ocean Sciences (BIOS) and University of Hawai'i at Manoa. Sampling occurs approximately once a month. From 1983, at Station S and from 1989 at BATS until Sept. 2005 two pairs of one-liter Pyrex reagent bottles were filled with seawater drawn from 10 liter Niskin bottles tripped at approximately 2 and 10 meter depths. Each sample was promptly poisoned with 100 µl of saturated $HgCl_2$ solution and then sealed with a greased stopper. After Sept. 2005 pairs samples were collected in 500ml bottles at 10 m depths only. At Station ALOHA, beginning in 1988 until July 2003, two pairs of Pyrex one-liter reagent bottles were filled with seawater drawn from 10 liter Niskin bottles tripped at approximately 5 and 25 meter depths, also poisoned and sealed with greased stoppers. After July 2003 samples were collected at 5 m only. After May 2004 samples were collected in 500ml bottles. For a description of the 500ml sampling bottles and exhaustive description of the Keeling lab sampling methodology refer to Guenther et al. 1994, page 118. For a detailed description of the recommended sampling techniques for seawater CO_2 samples in general refer to PICES special publication 3 - Guide for best practices of seawater CO_2 measurements, Chapter 4, SOP 1 (Dickson et al., 2007).

2. DIC measurement

DIC is measured by vacuum extraction of the acidified seawater sample and manometric analysis of the liberated CO_2 gas, as described in Lueker et al., 1998 and Gunther et al.,1994. The procedure for DIC measurement is essentially the same as that used to quantify the DIC of seawater certified reference materials (CRMs, Dickson 2010). The DIC measurements have relied on four separate manometers over their history, starting with original constant-volume mercury-column manometer (CMM) (see Keeling et al., 2016 for a detailed description), also originally used to calibrate measurement of CO_2 mole fraction in air for the Scripps CO_2 program. The measurements then used a commercially manufactured Ruska model XR38 manometer (Guenther et al., 1994), which was subsequently replaced by either of two electronic constant-volume manometers (ECMI, and ECMII) fabricated by David Moss, which are still in service. Descriptions of the ECM manometers are provided in Appendix 1.

All manometers have been calibrated by introducing known molar amounts of CO_2 prepared externally to the manometer. The “manometer standards” have been either prepared using a series of “plenums” (known volumes filled with CO_2 at a measured pressure and temperature, see Box 1), or prepared using the “small volume” of the CMM, effectively using CMM as a transfer instrument. Since the early 1990s, the ECMI has been the work-horse instrument for measuring seawater samples. The calibration of ECMI has relied on plenums filled in a controlled temperature bath with pressure measured using a Ruska deadweight tester. Currently, the procedure involves first introducing the manometric standard into ECM II, then refreezing the CO_2 into flame-sealed glass tubes, and later introducing the CO_2 into ECM I.

Beginning in 2020 Guy Emanuele made repairs and upgrades to the ECM I. Subsequently the results of previous plenum calibrations (analyzed from November 2011 to November 2024) were re-evaluated, and adjustments to DIC analyses results were applied for manometer analyses after November 1, 2021, as shown in table 1. The adjustments were calculated as an apparent change in the manometer volume. An adjustment for the first period (11/1/2011-

10/31/2020) was not applied since it would result in an insignificant change in the data (0.012% or 0.25 μmol kg^{-1} for a DIC value of 2000 μmol kg^{-1})[3]. Thus, the data previously reported for DIC (samples through 2017) on the Scripps CO_2 website remain unchanged.

The reason(s) for the apparent volume shift in the ECM I may be related to regreasing of the glass stopcock or repairs and adjustments made to the fans or temperature controls during instrument refurbishments.

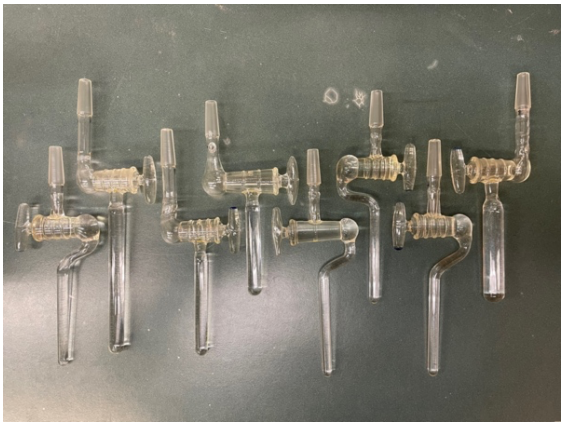
ALK Measurement

ALK analyses are performed using the same method as that used to certify seawater reference materials (CRMs) for total alkalinity (Dickson et al., 2003). The technique employs a two-stage, potentiometric, open-cell titration using coulometrically analyzed hydrochloric acid. The equivalence point is evaluated from titration points in the pH region 3.0–3.5 using a least-squares procedure that corrects for the reactions with sulfate and fluoride ions. Batches of hydrochloric acid are repeatedly re-analyzed over several years to verify the constancy of the method for calibration of the HCl.

Box 1:

Gas plenums

The photograph shows eight glass plenums of different volumes. The volumes are determined by filling with Hg or H_2O in a temperature controlled environment and weighing. The plenums are used to transfer a known amount of CO_2 into the manometers in order to calibrate the manometer volumes. The CO_2 amount is prepared by filling the plenum with pure CO_2 from a gas cylinder in a temperature controlled bath to a pressure established by a "dead weight tester". After filling, the plenums are closed and the quantity of CO_2 is transferred into the manometer for analyses. Early calibrations of the constant volume mercury-column CMM) were performed by filling plenums to the room air pressure measured with a Hg barometer located in the laboratory (Gunther and Keeling, 1986).



[3] imprecision in manometric DIC measurements is typically 0.7 μmol kg^{-1} (Dickson 2010)

$\delta^{13}C$ Measurement

From 1978 till 1992 the $\delta^{13}C$ measurements were made on a VG Sira mass spectrometer at the Centrum voor Isotopen Onderseok (CIO) at the University of Groningen, where CO_2 extracted from the Scripps flasks was sent for analysis. From 1992 to 2000 the measurements were made on a Prism mass spectrometer in the lab of Professor Martin Wahlen at Scripps. From 2000 onwards the $\delta^{13}C$ measurements were made by the Scripps CO_2 program on an Optima Mass Spectrometer. After a long hiatus in seawater isotope analyses from 2004 to 2015, we made new isotope standards and checked them for consistency with previous calibration standards by analyzing duplicates of previously determined seawater sample pairs, as detailed in Brooks (2020, Chapter 2) (see also Lueker et al., 2020). We currently calibrate our $\delta^{13}C$ analyses with three different pure CO_2 gas aliquots stored in FOTs:

1) **GEA4** consisting of several hundred aliquots of CO_2 in FOTs prepared in the 1990s from pure Na_2CO_3 dissolved in seawater, acidified, and extracted under vacuum.
2) **2342** consisting of aliquots CO_2 that are periodically extracted from an N265 Aluminum cylinder containing a CO_2 in N_2 gas mixture, currently at 700psi. The CO_2 was originally extracted from a sample of Coral from Palmyra atoll in the equatorial Pacific.
3) **DCS1** initially 189 aliquots of CO_2 in FOTs from a 5 liter flask of pure CO_2 extracted from a sample of Dover Chalk. The remaining CO_2 gas is stored in the 5 liter flask and is available for future extractions.

Database Description

The data are presented on the Scripps CO_2 Program website https://scrippsco2.ucsd.edu/data/seawater_carbon/ocean_time_series.html under file names BERM.CSV (Hydrostation S), BATS.CSV (BATS) and HAWI.CSV (HOT station ALOHA). The data are tabulated by sample date (DATE)(format yyyymmdd), sample date expressed as a decimal year (DDATE), latitude (LAT), longitude (LONG), sample depth (Z) (nominal or actual), salinity (SAL), and temperature (TEMP), as shown in the following example. We report either the pair averages (when available), or single bottle values of the $\delta^{13}C$ (ISO), DIC (AVGDIC) and ALK (AVGALK). An example from HAWI.CSV is shown below.

DATE	DDATE	LAT	LONG	Z	SAL	TEMP	ISO	AVGDIC	AVGALK
19881202	1988.923	22.75	157.97	1	34.984	25.62	1.49	1954.77	2306.08
19881202	1988.923	22.75	157.97	26	34.991	25.56	1.54	1954.23	2304.47
19890108	1989.024	22.8	157.97	3	35.03	24.63	1.47	1963.1	2303.87
19890108	1989.024	22.8	157.97	38	35.028	24.63	1.6	1963.64	2299.31
19890327	1989.238	22.78	157.9	5	34.639	24.36	1.65	1945.83	2280.73
19890327	1989.238	22.78	157.9	28	34.682	24.33	1.66	1946.47	2283.31

Scripps data corresponding to samples collected from 1983-2002 (2001 for HOT) were previously archived at the Carbon Dioxide Information Analysis Center (CDIAC) (https://data.globalchange.gov/organization/carbon-dioxide-information-analysis-center) and referenced in previous studies (Bacastow et al., 1996, Gruber et al., 1998, 1999, 2002, Brix et al., 2004, Keeling et al., 2004). Data from 2002 to 2017 (2016 for HOT) were published on the

Scripps website in 2020, and described in Mariella Brooks' Ph.D. thesis (2020). From November 2020 to 2024, with support from the Schmidt Ocean Institute (SOI), we analyzed additional samples collected from 2017 to 2023. For this data release, previous data through 2017 were revisited to correct minor discrepancies and missing values, and new results for samples collected through 2023 were added to the website.

Synthesis and Discussion

Extending over decades, our time-series document the rise in DIC and decrease in $\delta^{13}C$ expected from increasing fossil fuel CO_2 emissions into the atmosphere. The data also display interannual variability due to changing conditions in the subtropical ocean gyres that have been linked to the North Atlantic Oscillation (NAO), Pacific Decadal Oscillation (PDO), and the El Nino -Southern Oscillation (ENSO) in previous studies (Gruber et al., 2002, Dore et al., 2009, Bates and Johnson, 2020, Brooks, 2020). Here we briefly describe the long-term trends compared to the changes in the atmosphere.

To observe the trends in DIC and ALK we normalize the data to a constant salinity of 35 to remove the effects of precipitation and evaporation (sDIC, sALK). We fit the sDIC and $\delta^{13}C$ data to a simple harmonic seasonal cycle to illustrate the average seasonality and also reveal interannual variability expressed as residuals. We find similar trends in sDIC at all locations, (Table 3) close to values reported previously (Figures 1a-1c) (Bates and Johnson 2020, Brooks, 2020). The sALK data (Figure 3) do not show a seasonal cycle or statistically significant trends over time at either site, however they do indicate shifting values possibly related ocean to gyre transport or meteorological variability (Dore et al., 2003, Bates and Johnson 2020, Brooks, 2020).

The annual trends in the $\delta^{13}C$ of DIC at HOT, Hydrostation S, and BATS are all nearly the same, and are also similar to the air sampled at our station at sea level on Hawaii (KUM) and for clean background air sampled at La Jolla (Figures 2a-2c)(Table 3).

Trends in pCO_2 and pH_T.

The partial pressure of CO_2 in the sampled seawater (pCO_2) and the pH_T varies as functions of the in-situ temperature, DIC, ALK, and to a lesser extent salinity, nutrients, and other minor chemical components (Dickson et al. 2007). We calculate the pCO_2 and pH_T using a CO2CALC program (Robbins et al., 2010, Orr et al., 2015) in excel spreadsheet form https://github.com/jamesorr/CO2SYS-Excel (James Orr version in Excel 2024). We used the set of equilibrium constants recommended in the program (Table 2) (see also Dickson et al., 2007). We calculate pH_T and pCO_2 for stations HOT and BATS (BERM is very similar to BATS as shown in Figures 1-3) at the reported in-situ temperature and salinity, neglecting the inorganic nutrients which, given the low concentrations at these locations, have an insignificant effect on the calculations[4].

The trends in pCO_2 seen at BATS and HOT closely follow the trends of rising CO_2 seen in the atmosphere (Figure 4). The pCO_2 at HOT lies almost always below atmospheric CO_2 resulting in net flux of CO_2 into the ocean (Dore et al., 2009). At BATS, given the larger seasonal cycle of the ocean temperature, pCO_2 exceeds the atmospheric CO_2 during warmer summer months. At

[4] We also performed the calculations of pCO_2 and pH using the measured nutrient concentrations reported for HOT and BATS stations and confirmed the results had no significant difference in the computed trends.

this time the surface mixed layer shoals, and the CO_2 flux is reduced. Hence the majority of the year the CO_2 flux is also into the ocean. Both locations are sinks for atmospheric CO_2 and the trends in pCO_2 equal or slightly exceed the increasing CO_2 in the atmosphere.

pH_T

We compute the surface ocean pH_T ($pH_T = -\log \{ [H] * (1 + S_T/K(HSO_4) \}$ = pH expressed on the total scale (Dickson 2007, Lueker et al., 2000)) at the in-situ temperature and pressure. We find nearly identical trends in pH_T for both locations, -0.0021 yr^{-1} at HOT and -0.0020 yr^{-1} at BATS. (Figure 5).

Summary

Our time-series of DIC, ALK, and $\delta^{13}C$ at Station "S", BATS, and HOT station ALOHA comprise the longest continuing records of these ocean carbon parameters. The results quantify the uptake of increasing atmospheric CO_2 and corresponding reduction in the $\delta^{13}C$ ratio at these locations. Calculated pCO_2 levels at HOT and BATS suggest the air-sea flux of CO_2 is the primary cause of the upward trend in DIC. Calculated pH_T trends of -0.021 per decade are nearly identical in both locations, documenting the degree of ongoing ocean acidification in the subtropical gyres.

Acknowledgements

The Scripps inorganic carbon time series were initiated by C David Keeling in the 1980s and maintained with his leadership until his passing in 2005, after which they were continued under the leadership of Andrew Dickson and Ralph Keeling. This study could not exist without the cooperation and diligent efforts over several decades of our colleagues at the Hawaiian Ocean Time Series at the University of Hawaii at Manoa and the Bermuda Institute of Ocean Sciences, who have provided logistic support and the seawater samples for this study. Several members of the Keeling and Dickson Labs at Scripps have also contributed to this effort over the 40+ years of our study, including Peter Guenther, Elizabeth Stewart, Alane Bollenbacher, Steve Piper, George Anderson, Daniela Nestory, Kelly Battaile, and many others. Since 2020 funding for the ocean carbon time series has been provided by the Schmidt Ocean Institute (SOI) https://schmidtocean.org/.

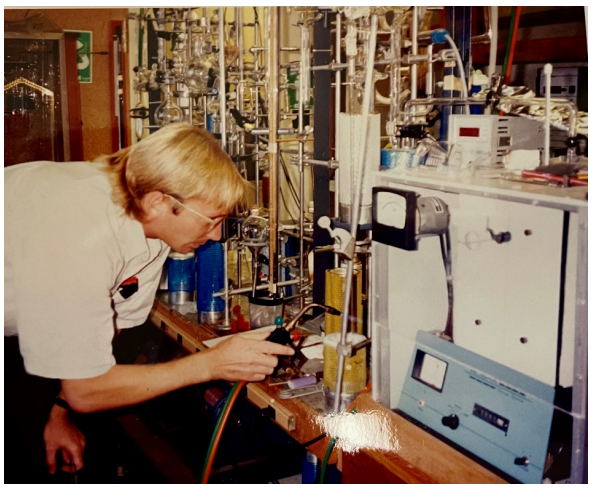


Figure 1. Ruska model XR38 quartz spiral manometer circa 1990. (photo credit Tim Lueker).

Table 1. Adjustments made to ECM-1 DIC by analyses date.

ECM-1 Analysis dates	Avg. ECM-1 volume computed from plenums	Std. dev. of avg.	Resulting change in DIC for a value of 2000 µmol kg^{-1}*
Previous value	8.77971	Nominally assigned	
11/1/2011 – 10/31/2020	8.77862	.00348 (n=52)	0.25
11/1/2020 – 10/31/2023	8.76735	.00436 (n=33)	2.82
11/1/2023 – 10/31/2024	8.75859	.00955 (n=17)	4.82

Table 2. Equilibrium constant expressions and details of the pCO_2 and pH_T calculations.

Constants	Source
K_1,K_2	Lueker et al., 2000
$KHSO_4$	Dickson, 1990
KHF	Perez and Fraga, 1987
pH_T scale	Total scale (mol/kg – SW)
$[B]_T$ value	Lee et al., 2010
T and S	EOS – 80 *

Table 3. Trends in sDIC, $\delta^{13}C$, pCO_2, and pH for the Stations. Results for this study and Brooks (2020) including atmospheric CO_2 measured at Cape Kumukahi HI and La Jolla CA.

Trends in	HOT 1989-2023	Brooks HOT 1989-2016	Atm CO_2 (KUM)[5]	Hydros. S 1983-2023	BATS 1989-2023	Brooks S-BATS 1989-2017	Atm CO_2 LJO[6]
sDIC µmol kg^{-1}/yr^{-1}	1.16	1.21		1.00	1.09	1.07	
$\delta^{13}C$ ‰ yr^{-1}	-0.0276	-0.0259	-0.0258	-0.0266	-0.0264	-0.0264	-0.0268
pCO_2 µatm yr^{-1}	2.21		2.03		2.06		2.05
pH_T yr^{-1}	-0.0021				-0.0020		

[5] Air sampled at Cape Kumukahi until 2018, after at Kahaki Park HI.

[6] Air sampled at La Jolla CA, has a similar latitude to Bermuda sites (32.9° N vs. 32.2°N Sta. S or 31.7°N BATS).

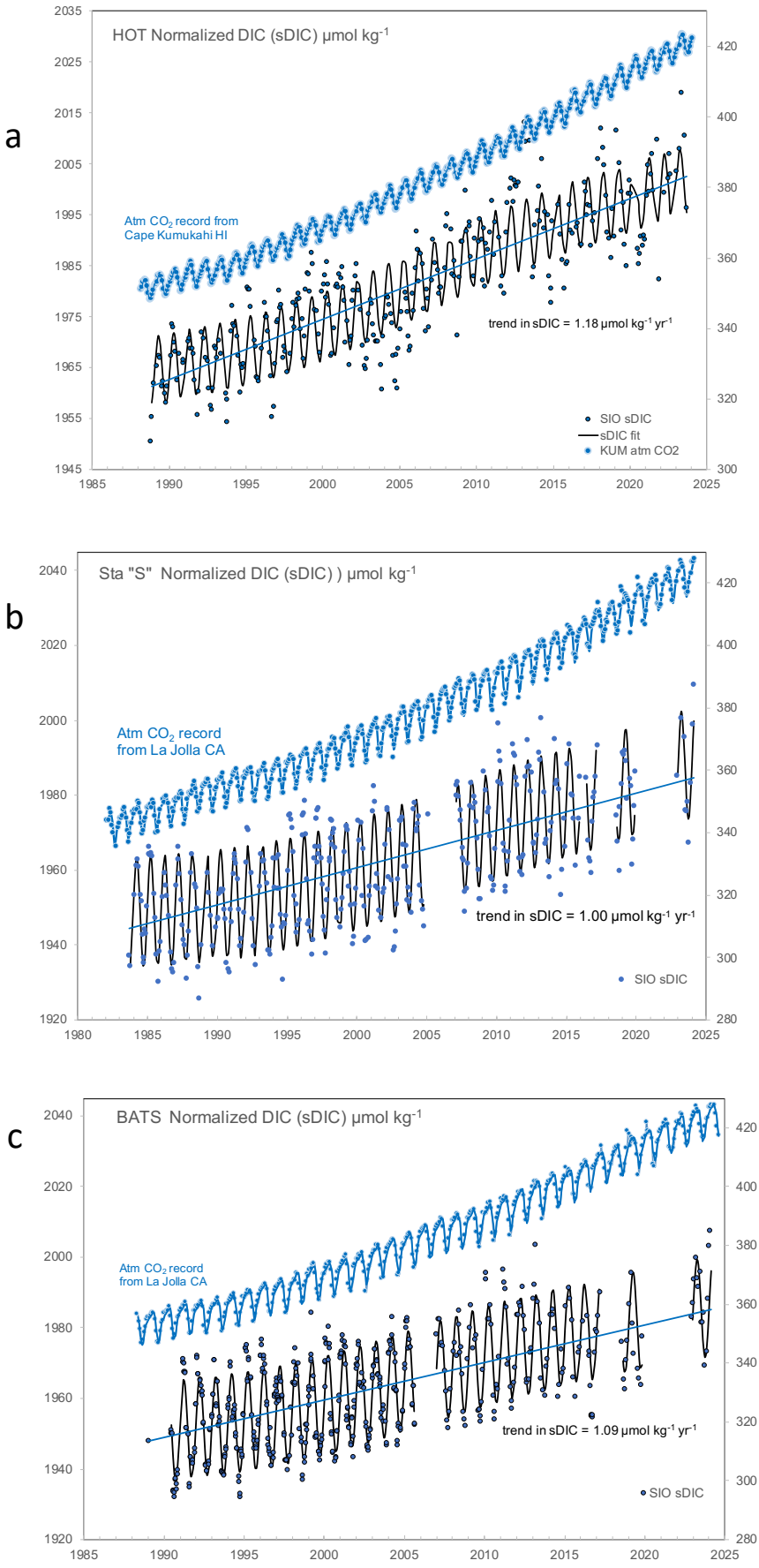


Figure 1. sDIC (µmol kg^{-1}) from seawater sampled at HOT station ALOHA shown with CO_2 from air sampled at sea level at Cape Kumukahi on Hawaii (a) Hydrostation S (b) and BATS (c) shown with CO_2 from air sampled at La Jolla CA. The seawater data shown in dark blue were fit to a 2 harmonic function to obtain an average seasonal cycle, shown with a linear fit to the averaged seasonal cycles.

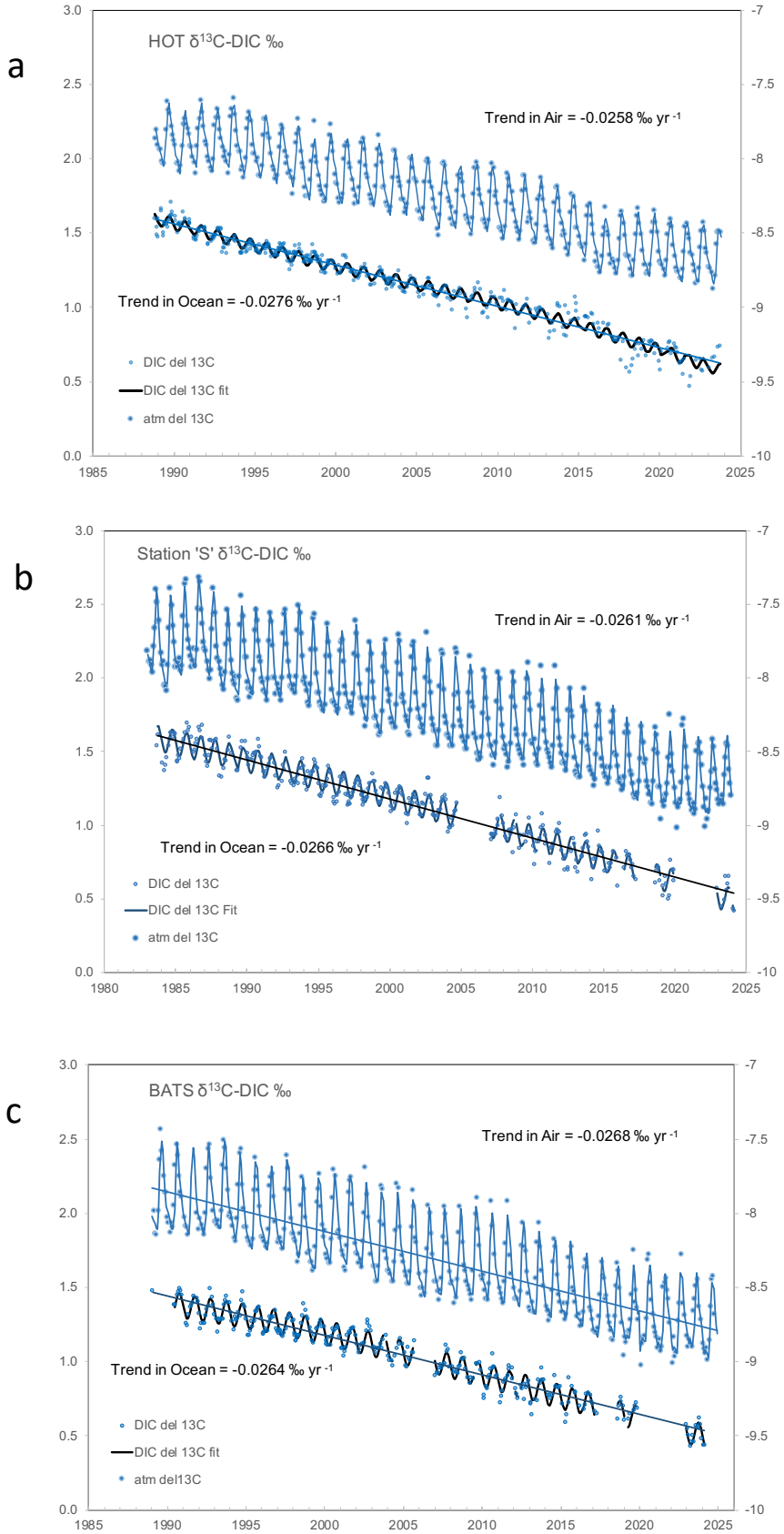


Figure 2. δ^{13}C-DIC from seawater sampled at HOT station ALOHA (a) shown with the record of δ^{13}C in CO_2 from air sampled at sea level at Cape Kumukahi on Hawaii, Hydrostation S (b) and BATS (c) shown with the record of δ^{13}C in CO_2 from air sampled at La Jolla CA. The seawater data, shown in dark blue, were fit to a 2 harmonic function to obtain an average seasonal cycle. The trend in δ^{13}C-DIC at HOT is -0.0276 ‰ yr^{-1}, 0.0266 ‰ yr^{-1} at S, and 0.0264 ‰ yr^{-1} at BATS.

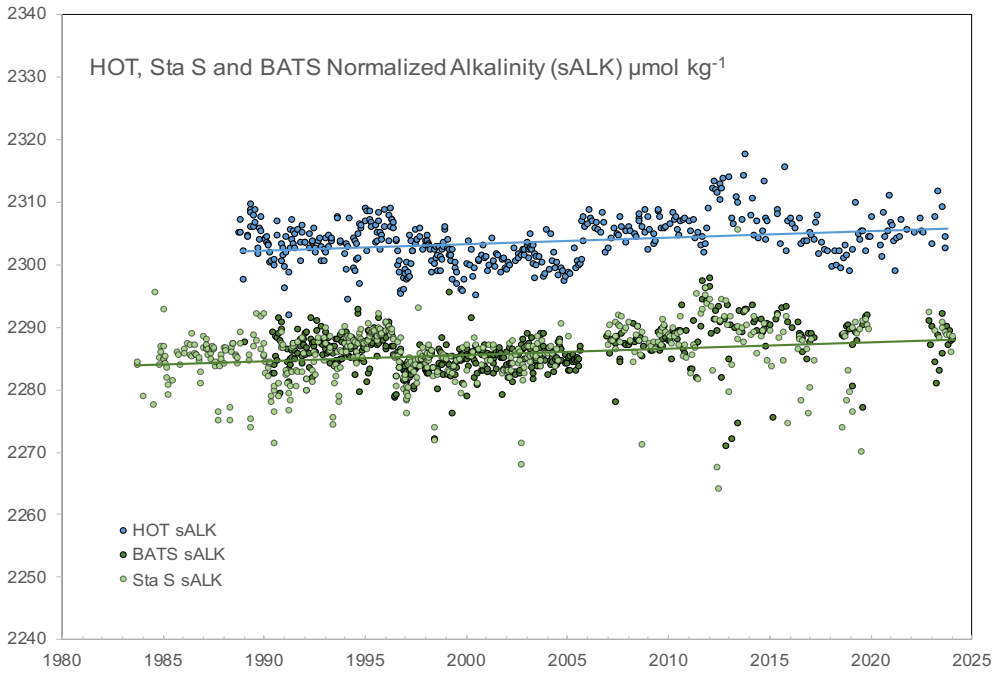
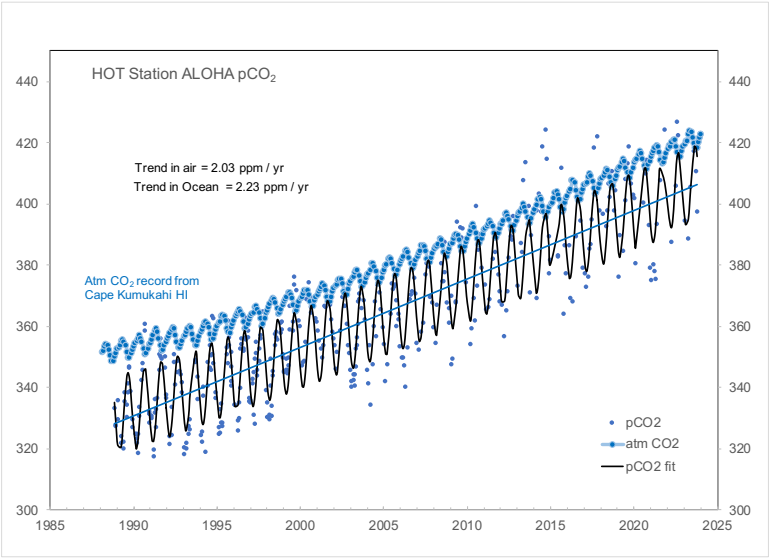


Figure 3. Normalized alkalinity (sALK) at HOT station ALOHA and Station S and BATS. All data normalized to salinity = 35.

a



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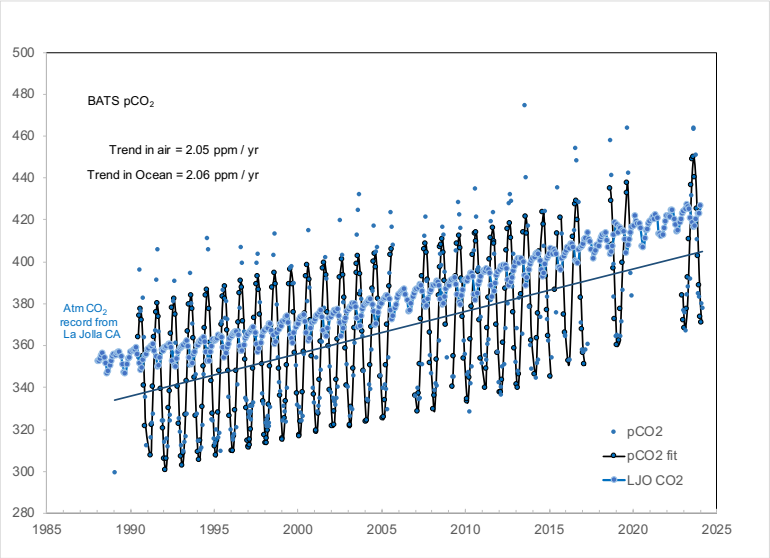
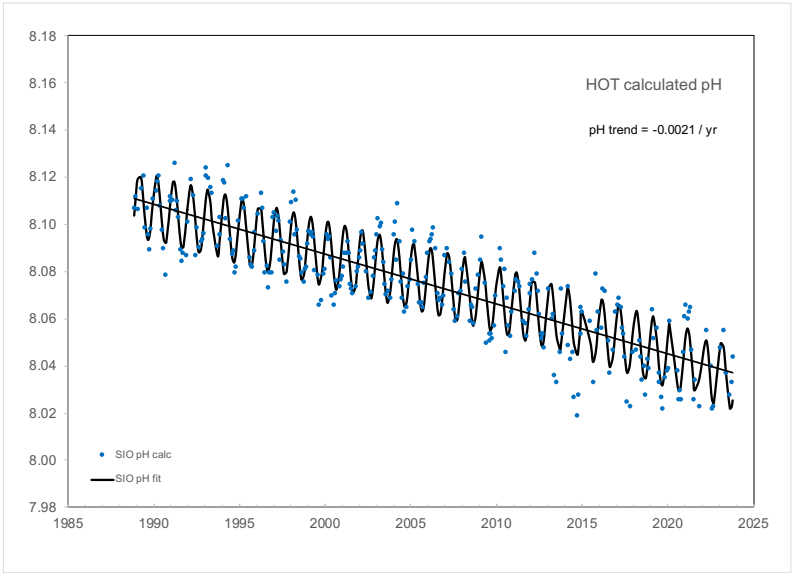


Figure 4. Calculated pCO_2 of seawater sampled at HOT Station ALOHA shown with CO_2 from air sampled at Cape Kumukahi (a) and at BATS shown with CO_2 from air sampled at La Jolla CA. (b). The trends in pCO_2 at HOT of 2.23 ppm yr^{-1} and at BATS of 2.05 ppm yr^{-1} agree closely to the rising CO_2 in the air over the same period.

a



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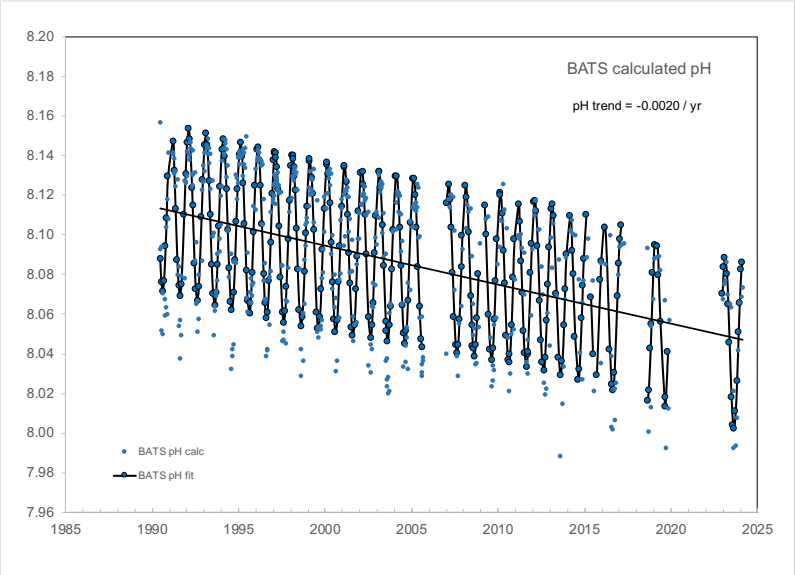


Figure 5. Calculated pH_T at HOT and BATS, with equal y axes to compare the magnitude of the seasonal cycles. The trend of pH_T at HOT a) is -0.0021 yr^{-1} and at BATS (b) is -0.0020 yr^{-1}.

References

Bacastow, R.B., Keeling, C.D., Lueker, T.J., Wahlen, M., 1996. The ^{13}C Suess effect in the world surface oceans and its implication for oceanic uptake of CO_2: Analysis of observations at Bermuda. Global Biogeochemical Cycles 10, 335–346.

Bates, N., Johnson, R. 2020 Acceleration of ocean warming, salinification, deoxygenation and acidification in the surface subtropical North Atlantic Ocean. Nature communications earth and environment https://doi.org/10.1038/s43247-020-00030-5

Bates, N., Astor, Y., Church, M., Currie, K., Dore, J., Gonaález-Dávila, M., Lorenzoni, L., Muller-Karger, F., Olafsson, J., Santa-Casiano, M., 2014. A Time-Series View of Changing Ocean Chemistry Due to Ocean Uptake of Anthropogenic CO_2 and Ocean Acidification. Oceanography 27, 126–141. https://doi.org/10.5670/oceanog.2014.16

Bates, N.R., 2007. Interannual variability of the oceanic CO_2 sink in the subtropical gyre of the North Atlantic Ocean over the last 2 decades. Journal of Geophysical Research 112. https://doi.org/10.1029/2006JC003759.

Brix, H., Gruber, N., Keeling, C.D., 2004. Interannual variability of the upper ocean carbon cycle at station ALOHA near Hawaii. Global Biogeochemical Cycles 18. https://doi.org/10.1029/2004GB002245.

Brooks, M., 2020. Time-series of stable isotopes in dissolved inorganic carbon of surface seawater near Bermuda and Hawaii. Ph.D. Thesis University of California, San Diego.

Dickson, A.G., 1990. Standard potential of the reaction: $AgCl(s) + 1/2H_2(g) = Ag(s) + HCl(aq)$, and and the standard acidity constant of the ion HSO_4 in synthetic sea water from 273.15 to 318.15 K. Journal of Chemical Thermodynamics 113–127.

Dickson, A.G., Afghan, J.D., Anderson, G.C., 2003. Reference materials for oceanic CO_2 analysis: a method for the certification of total alkalinity. Marine Chemistry 80, 185–197. https://doi.org/10.1016/S0304-4203(02)00133-0.

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to Best Practices for Ocean CO_2 Measurements. PICES Special Publication 3, 191 pp.

Dickson A.G. 2010 STANDARDS FOR OCEAN MEASUREMENTS Oceanography , Vol. 23, No. 3 https://www.jstor.org/stable/10.2307/24860884

Dore, J.E., Lukas, R., Sadler, D.W., Church, M.J., Karl, D.M., 2009. Physical and biogeochemical modulation of ocean acidification in the central North Pacific. Proceedings of the National Academy of Sciences 106, 12235–12240.

Dore, J.E., Lukas, R., Sadler, D.W., Karl, D.M., 2003. Climate-driven changes to the atmospheric CO_2 sink in the subtropical North Pacific Ocean. Nature 424, 754–757. https://doi.org/10.1038/nature01885.

Doran, H. E., & Quilkey, J. J. (1972). Harmonic analysis of seasonal data: some important properties. American Journal of Agricultural Economics, 54, volume 4, part 1, 646-651.

Gruber, N., Keeling, C.D., Bacastow, R.B., Guenther, P.R., Lueker, T.J., Wahlen, M., Meijer, H.A.J., Mook, W.G., Stocker, T.F., 1999. Spatiotemporal patterns of carbon-13 in the global surface oceans and the oceanic Suess Effect. Global Biogeochemical Cycles 13, 307–335. https://doi.org/10.1029/1999GB900019.

Gruber, N., Keeling, C.D., Bates, N.R., 2002. Interannual Variability in the North Atlantic Ocean Carbon Sink. Science 298.

Gruber, N., Keeling, C.D., Stocker, T.F., 1998. Carbon-13 constraints on the seasonal inorganic carbon budget at the BATS site in the northwestern Sargasso Sea. Deep-Sea Research I 45, 673–717.

Guenther, P., and C.D. Keeling. 1986. *Scripps Reference Gas Calibration System for Carbon Dioxide-in-Nitrogen and Carbon Dioxide-in-Air Standards: Results of the Manometric Volume Reanalysis of 1986*. A report prepared for the environmental monitoring program of the World Meteorological Organization.

Guenther, Peter R., Keeling, Charles D., and Guy Emanuele, III. 1994. Oceanic $C0_2$ Measurements for the WOCE Hydrographic Survey in the Pacific Ocean, 1990-1991: Shore Based Analyses, S.I.O. Reference Series No. 94-28.

Kavanaugh, M.T., Church, M.J., Davis, C.O., Karl, D.M., Letelier, R.M., Doney, S.C., 2018. ALOHA From the Edge: Reconciling Three Decades of in Situ Eulerian Observations and Geographic Variability in the North Pacific Subtropical Gyre. Frontiers in Marine Science 5. https://doi.org/10.3389/fmars.2018.00130.

Karl, D.M., Ricardo M. Letelier, Robert R. Bidigare, Karin M. Björkman, Matthew J. Church, John E. Dore, Angelicque E. White, 2021. Seasonal-to-decadal scale variability in primary production and particulate matter export at Station ALOHA Progress in Oceanography, Vol. 195 102563 https://doi.org/10.1016/j.pocean.2021.102563

Keeling, C.D., Brix, H., Gruber, N., 2004. Seasonal and long-term dynamics of the upper ocean carbon cycle at Station ALOHA near Hawaii. Global Biogeochemical Cycles 18. https://doi.org/10.1029/2004GB002227

Keeling, R.F., P.R. Guenther, S.J. Walker, and D. Moss. Scripps Reference Gas Calibration System for Carbon Dioxide-in-Nitrogen and Carbon Dioxide-in-Air Standards: Revision of 2012, Scripps Institution of Oceanography: 2016. https://scrippsco2.ucsd.edu/assets/publications/manometry_report_scripps_ref_gas_calibration_revision_of_2012_pub_2016.pdf

Kitack Lee, Tae-Wook Kim, Robert H. Byrne, Frank J. Millero, Richard A. Feely, Yong-Ming Liu, The universal ratio of boron to chlorinity for the North Pacific and North Atlantic oceans. Geochimica et Cosmochimica Acta 74 (2010) 1801–1811 doi:10.1016/j.gca.2009.12.027

Lueker, T.J., Dickson, A.G., Keeling, C.D., 2000. Ocean pCO_2 calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2: validation based on laboratory measurements of CO_2 in gas and seawater at equilibrium. Marine Chemistry 105–119.

Lueker, T.J., Keeling, C.D., Guenther, P.R., Wahlen, M., 1998. Inorganic carbon variations in surface ocean water near Bermuda (SIO Technical Report). UC San Diego: Scripps Institution of Oceanography. https://escholarship.org/uc/item/8742p2nb

Lueker, T., Keeling, R., Bollenbacher, A., Walker, S., Morgan, E., Brooks, M. 2020. Calibration Methodology for the Scripps $^{13}C/^{12}C$ and $^{18}O/^{16}O$ stable Isotope program 1992-2018

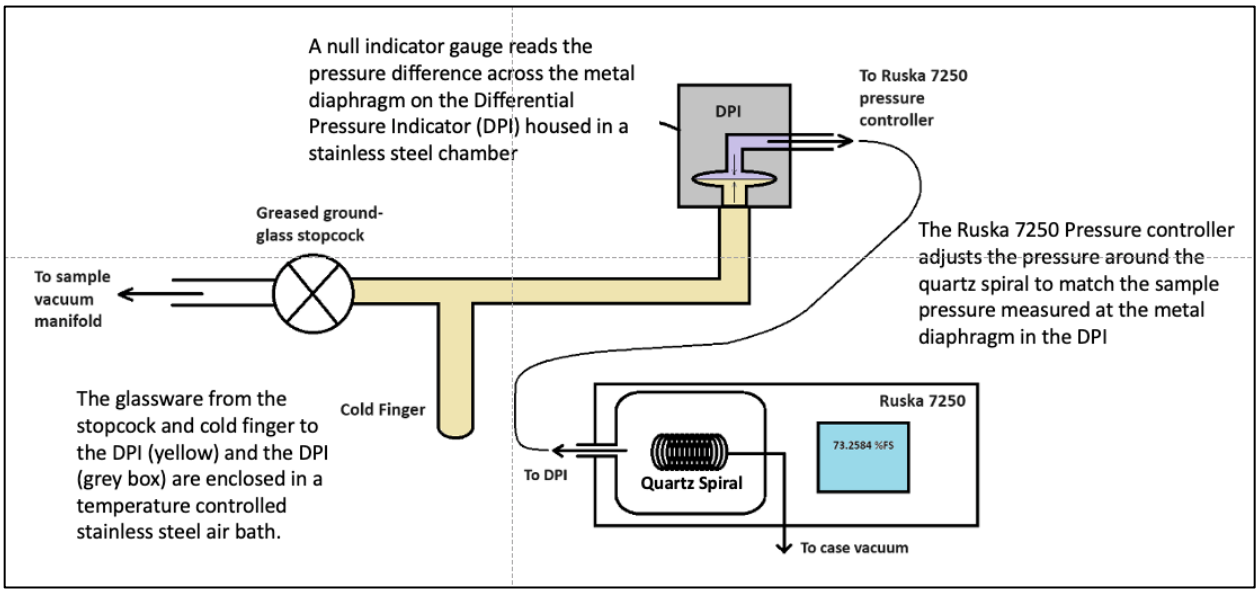
Orr, J. C., Epitalon, J.-M., and Gattuso, J.-P.: Comparison of ten packages that compute ocean carbonate chemistry, Biogeosciences, 12, 1483–1510, https://doi.org/10.5194/bg-12-1483-2015, 2015.

Perez, F. F., and Fraga, F.:Association constant of fluoride and hydrogen ions in seawater, Mar. Chem., 21, 161–168, 1987.

Robbins, L.L., Hansen, M.E., Kleypas, J.A., and Meylan, S.C., 2010, CO_2calc—A user-friendly seawater carbon calculator for Windows, Max OS X, and iOS (iPhone): U.S. Geological Survey Open-File Report 2010–1280, 17 p.

Appendix 1. Descriptions of the Electronic Constant-Volume Manometers.

ECM I

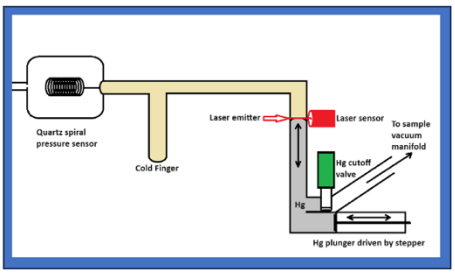


- The manometer volume is defined with a greased ground glass stopcock. Apiezon H grease is used on the stopcock (high temperature formulation).
- The contained volume is approximately 8.9 cc.
- The air bath is set to 40°C.
- The pressure exerted by the thawed CO_2 sample is balanced against pressure controlled by a Rusksa Model 7250 pressure controller at a differential pressure indicator (DPI). The DPI is stainless steel and rated to withstand up to 1500 psi.
- A computer measures the deflection of the stainless-steel diaphragm of the DPI to locate the balancing point.
- The computer will continually adjust the balancing pressure to keep the DPI centered.
- The Ruska 7250 uses a quartz spiral to determine its control pressure.
- The interior of the quartz spiral is held at a constant vacuum in this configuration. The case pressure is varied using a supply of N_2 and a vacuum pump to match the sample pressure, and is determined by the flexing of the quartz spiral.
- The final pressure is recorded once a stable rate of decay is achieved, usually around six to eight minutes after thawing the CO_2. The DIC is determined by the average of the last five pressure and temperatures recorded before the operator terminates the run.
- The temperature is measured using a calibrated 2.2 kOhm thermistor wired directly to an Agilent 34970A Digital Volt Meter.

ECM II

The mercury, manometer volume, quartz spiral and the case containing the Quartz spiral are inside a temperature controlled bath (blue box). The spiral case is evacuated with a vacuum pump.

The glassware from the Mercury to the interior of the Quartz Spiral makes up the volume of the manometer



The pressure is determined by measuring the flex (movement) of the quartz spiral. Once the temperature has stabilized the pressure measurement is stable for an indefinite period.

- The Quartz spiral is filled with the sample CO_2 and is part of manometer cell volume.
- The spiral case is held at a constant vacuum (less than 10 mtorr).
- The manometer cell volume, approximately 8.4 cc, is defined by a Hg column (yellow shading).
- The Hg column height is adjusted to a fixed point determined by a laser sensor (The sensor has not been moved since it was set in place in 2011).
- Hg control is provided via a plunger driven by a stepper motor under computer control.
- The procedure for adjusting the Hg column height cutoff is
    - Hg is raised to just below the cutoff point, which is defined as the point that the transmittance reaching the sensor drops to about 50%.
    - Hg is raised in large increments (2000 steps) until the beam is broken.
    - Hg is lowered in medium increments (100 steps) until beam is fully restored, then backed off another 500 steps.
    - Hg is then raised in small increments (50 steps) until beam drops below 50% transmittance.
- The Hg cutoff is always approached from below to maintain consistent meniscus shape.
- Hg height always set after CO_2 has thawed.
- The temperature bath is set to 30°C.
- The final CO_2 pressure measurement is taken during the one minute following 16 minutes of elapsed time after the final setting of the Hg column height. The 16 minute interval insures the stability of the manometer temperature environment. Ten readings of 6 second intervals are averaged to obtain the final pressure.
- The temperature is read from a Hart “super thermistor” wired directly to the Agilent 34970A DVM.