

Cruise: WS22281

Ship: R/V Walton Smith

Expo Code: 33WA20221008

Funding Project Title: Expanding near-shore carbonate measurements along the East-coast and Gulf of Mexico through multiple collaborations

Funding Project ID: 21403

Dates: October 8th-October 14th, 2022

Chief Scientist: Ian Smith

Equipment: CTD-Niskin and Flow-Through (FT)

Total number of stations: 55

Location: Southwest Florida Gulf of Mexico coastal region

Samples were collected for Dr. Leticia Barbero for the Ocean Acidification Program during the South Florida Project (SFP) water quality cruises in the SW Gulf of Mexico lead by Dr. Chris Kelble.

Sample Collection

The discrete samples were collected from the CTD-Niskin/rosette and Flow-Through system onboard the R/V Walton Smith by Ian Smith, Rachel Cohn and Alexandra Fine. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

55 locations, 81 samples each 500-ml, 7 duplicate samples.

Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by: Charles Featherstone, Patrick Mears and Alison MacLeod

pH:

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Analyzed by Patrick Mears and Alison MacLeod

Sample Analysis

DIC:

Instrument ID	Date	Certified CRM ($\mu\text{mol/kg}$)	CRM Value ($\mu\text{mol/kg}$)	CRM Offset ($\mu\text{mol/kg}$)	Blank (Counts)	Avg. Sample Analysis Time
AOML 5	10/26/2022	2025.17	2024.53	0.64	12	10
AOML 5	11/2/2022	2025.17	2025.41	0.24	24	9
AOML 5	11/7/2022	2025.17	2025.74	0.57	13	9
AOML 6	10/26/2022	2025.17	2028.65	3.48	12	11
AOML 6	10/31/2022	2025.17	2023.8	1.37	13	10
AOML 6	11/7/2022	2025.17	2024.96	0.96	12	11

Analysis date: 10/26/2022

Coulometer used: DICE-CM5017O-AOML 5

Blanks: 12.0 counts/min

CRM # 617 was used and with an assigned value of (includes both DIC and salinity):

Batch 194, c: 2025.17 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 5: offset 0.64 $\mu\text{mol/kg}$ (2024.53 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 10, 8 and 12 min.

Analysis date: 11/2/2022

Coulometer used: DICE-CM5017O-AOML 5

Blanks: 24.0 counts/min

CRM # 319 was used and with an assigned value of (includes both DIC and salinity):

Batch 194, c: 2025.17 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 5: offset 0.24 $\mu\text{mol/kg}$ (2025.41 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 7 and 11 min.

Analysis date: 11/7/2022

Coulometer used: DICE-CM5017O-AOML 5

Blanks: 12.6 counts/min

CRM # 597 was used and with an assigned value of (includes both DIC and salinity):

Batch 194, c: 2025.17 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 5: offset 0.57 $\mu\text{mol/kg}$ (2025.74 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 8 and 12 min.

Analysis date: 10/26/2022

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 479 was used and with an assigned value of (includes both DIC and salinity):

Batch 194, c: 2025.17 $\mu\text{mol/kg}$, S: 33.361

CRM values measured: AOML 6: offset 3.48 $\mu\text{mol/kg}$ (2028.65 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 11, 9 and 12 min.
 Analysis date: 10/31/2022
 Coulometer used: DICE-CM5017O-AOML 6
 Blanks: 12.5 counts/min
 CRM # 105 was used and with an assigned value of (includes both DIC and salinity):
 Batch 194, c: 2025.17 $\mu\text{mol/kg}$, S: 33.361
 CRM values measured: AOML 6: offset 1.37 $\mu\text{mol/kg}$ (2023.8 $\mu\text{mol/kg}$).
 Average run time, minimum run time, maximum run time: 10, 8 and 12 min.

Analysis date: 11/7/2022
 Coulometer used: DICE-CM5017O-AOML 6
 Blanks: 12.0 counts/min
 CRM # 425 was used and with an assigned value of (includes both DIC and salinity):
 Batch 194, c: 2025.17 $\mu\text{mol/kg}$, S: 33.361
 CRM values measured: AOML 6: offset 0.96 $\mu\text{mol/kg}$ (2024.96 $\mu\text{mol/kg}$).
 Average run time, minimum run time, maximum run time: 11, 8 and 13 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.81 (0.18-2.5) and average STDEV of 0.58 (0.13-1.77).

Sample ID	DIC ($\mu\text{mol/kg}$)	Average	STDEV	Difference
450112	1996.5			
450112	1996.0	1996.27	0.31	0.44
490112	2099.5			
490112	2099.1	2099.30	0.35	0.49
510112	2119.2			
510112	2119.6	2119.41	0.27	0.38
57.30112	1988.6			
57.30112	1988.4	1988.51	0.20	0.28
CAL20112	1977.6			
CAL20112	1977.4	1977.49	0.13	0.18
CAL10112	2013.2			
CAL10112	2015.7	2014.42	1.77	2.50
TB40112	2026.36			
TB40112	2024.9	2025.66	1.00	1.42

Average	0.58	0.81
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CRM, salinity and HgCl₂ correction applied: Salinity correction was applied using TSG salinity.

Remarks

The volume correction was applied due to added HgCl₂ (Measured DIC*1.00037).
The first CRM of each cell was used for a CRM correction.

The DIC instruments were stable: the gas loop and CRM values did not change significantly throughout the life span of each cell.

DIC samples were analyzed on new coulometers 50170 from UIC. Inc.

pH:

Analysis date: 10/26/2022, 10/31/2022, 11/2/2022, 11/7/2022
No CRMs were analyzed before sample analysis.

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

Sample ID	Sample BTL #	Salinity	Analysis T (°C)
TB100101	1	36.132	19.989
TB100112	2	36.023	19.982
410112	3	33.932	19.987
450112	4	35.171	19.987
450112	5	35.171	19.982
490112	6	32.729	19.988
490112	7	32.729	19.988
510112	8	33.083	19.99
510112	9	33.083	20.001
580112	10	36.900	19.999
57.30112	11	36.782	20.002
57.30112	12	36.782	19.998
57.20112	13	36.159	19.994
57.10112	14	33.662	20.012
540112	15	30.295	20.004
550112	16	30.707	20.016

560112	17	31.465	20.015
570112	18	32.251	20.011
600112	19	34.060	20.008
650112	20	36.290	20.015
680112	125	37.255	20.089
700000	126	37.356	20.083
20112	401	35.514	20.164
MR0101	402	35.491	20.152
MR0112	403	35.501	20.164
UK_OFF0000	404	35.563	20.161
UK_MID0000	406	34.921	20.163
UK_IN0000	407	34.091	20.167
70112	408	35.201	20.151
100112	409	36.309	20.155
160112	410	35.692	20.162
21/LK0101	411	35.590	20.158
21/LK0112	412	35.539	20.166
WS0112	413	35.697	20.165
WS0101	414	35.697	20.075
KW10112	415	35.116	20.079
KW20101	416	34.958	20.094
KW20112	417	34.948	20.084
KW40101	418	35.460	20.078
KW40112	419	35.375	20.081
300101	420	35.415	20.079
300112	421	35.397	20.086
310112	422	35.511	20.08
330112	423	34.111	20.09
CAL50101	424	34.964	20.088
CAL50112	425	34.964	20.093
CAL40101	426	34.856	20.093
CAL40112	427	34.857	20.096
CAL30101	428	34.289	20.103
CAL30112	429	34.062	20.096
CAL20112	430	32.299	20.104
CAL10112	431	30.666	20.099
CAL10112	432	30.666	19.985
CAL20112	433	32.299	19.989
RP10112	434	34.641	19.998
RP20112	435	33.536	20.002
RP30112	436	33.165	20

RP40101	437	35.431	20.005
RP40112	438	32.942	19.996
GP50101	439	35.686	19.998
GP50112	440	35.659	20.001
BG40101	441	35.530	20.01
BG40112	442	33.716	19.997
BG30101	443	35.868	19.994
BG30112	444	30.870	20
BG20112	445	32.544	19.994
BG10112	446	32.697	20.001
V10112	447	34.530	20.011
V50101	448	36.022	20.006
V50112	449	34.489	20.017
V90101	450	36.183	20.013
V90112	451	35.600	20.016
AMI90101	452	36.176	19.991
AMI90112	453	35.784	19.981
AMI50101	454	35.983	19.987
AMI50112	455	35.987	19.989
AMI10112	456	34.748	19.989
TB10112	457	34.837	19.99
TB40101	458	36.038	19.985
TB40112	459	36.029	19.999
TB40112	460	36.029	19.999

Reproducibility: pH @ 20°C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0028 (0.0003– 0.0082) and an average STDEV of 0.0020 (0.0002 – 0.0058).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	450112	4	8.158	8.160	0.0022	0.0031
HP Agilent 8453	450112	5	8.161			
HP Agilent 8453	490112	6	8.004	8.003	0.0012	0.0017
HP Agilent 8453	490112	7	8.002			
HP Agilent 8453	510112	8	8.090	8.086	0.0058	0.0082
HP Agilent 8453	510112	9	8.082			
HP Agilent 8453	57.30112	11	8.112	8.110	0.0023	0.0033
HP Agilent 8453	57.30112	12	8.109			
HP Agilent 8453	CAL20112	430	8.203	8.203	0.0002	0.0003
HP Agilent 8453	CAL20112	431	8.203			
HP Agilent 8453	CAL10112	432	8.112	8.113	0.0014	0.0020
HP Agilent 8453	CAL10112	433	8.114			
HP Agilent 8453	TB40112	459	8.195	8.194	0.0008	0.0011
HP Agilent 8453	TB40112	460	8.194			
Average					0.0020	0.0028

Reproducibility: pH @ 25°C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0028 (0.0002-0.0082) and an average STDEV of 0.0020 (0.0002-0.0058).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	450112	4	8.082	8.083	0.0022	0.0030
HP Agilent 8453	450112	5	8.085			
HP Agilent 8453	490112	6	7.929	7.929	0.0012	0.0017
HP Agilent 8453	490112	7	7.928			
HP Agilent 8453	510112	8	8.015	8.010	0.0058	0.0082
HP Agilent 8453	510112	9	8.006			

HP Agilent 8453	57.3011	11	8.036	8.035	0.0023	0.0032
HP Agilent 8453	57.3011	12	8.033			
HP Agilent 8453	CAL20112	430	8.126	8.126	0.0002	0.0002
HP Agilent 8453	CAL20112	431	8.126			
HP Agilent 8453	CAL10112	432	8.036	8.037	0.0013	0.0019
HP Agilent 8453	CAL10112	433	8.038			
HP Agilent 8453	TB40112	459	8.118	8.118	0.0008	0.0011
HP Agilent 8453	TB40112	460	8.117			
Average					0.0020	0.0028

Remarks

The equations of Liu et al, 2011 formulated using the purified m-cresol purple indicator was used to determine pH of the samples. pH samples were analyzed at 20⁰C at Full Scale (pH 0-14). The pH was reported at 20⁰C and 25⁰C.

Temperature for each sample was measured before analysis using a Hart Scientific Fluke 1523 reference thermometer.

Approximately 80 mL of sample was extracted from each DIC sample bottle by automatic syringe before DIC analysis to determine the pH.

Talk:

Analysis date: 10/28/2022, 11/01/2022, 11/03/2022, 11/08/2022, and 11/10/2022

Titration system used: Open cell

Batch 194, CRM #479 Salinity = 33.361, cert. TA = 2169.83 μmol/kg.

Batch 194, CRM #105 Salinity = 33.361, cert. TA = 2169.83 μmol/kg.

Batch 194, CRM #319 Salinity = 33.361, cert. TA = 2169.83 μmol/kg.

Batch 194, CRM #597 Salinity = 33.361, cert. TA = 2169.83 μmol/kg.

Batch 194, CRM #425 Salinity = 33.361, cert. TA = 2169.83 μmol/kg.

On 10/28/2022 CRM #479 was analyzed before and after sample analysis on System 2.

On 11/01/2022 CRM #105 was analyzed before and after sample analysis on System 2.

On 11/03/2022 CRM #319 was analyzed before and after sample analysis on System 2.

On 11/08/2022 CRM #597 was analyzed before and after sample analysis on System 2.

On 11/10/2022 CRM #425 was analyzed before and after sample analysis on System 2.

The TA for the water samples was corrected using the daily averaged ratios between the certified and measured values of the CRMs run on system 2 cells. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	\Delta CRM
2	10/28/2022	09:29:57	479	2170.58	0.75
2	10/28/2022	18:19:41	479	2170.77	0.94
2	11/1/2022	09:10:49	105	2166.78	3.05
2	11/1/2022	17:36:18	105	2171.32	1.49
2	11/3/2022	09:02:33	319	2170.56	0.73
2	11/3/2022	17:49:37	319	2171.64	1.81
2	11/8/2022	10:12:59	597	2170.19	0.36
2	11/8/2022	16:46:33	597	2168.25	1.58
2	11/10/2022	12:05:25	425	2165.96	3.87
2	11/10/2022	17:44:30	425	2168.11	1.72

Reproducibility: (# samples and average difference): 7 duplicate samples were collected, one duplicate pair was discarded due to one being significantly different from calculated TA values using the other carbonate parameters. The average difference of 3.25(0.92 – 6.58) and an average STDEV of 2.29 (0.65 – 4.65).

Station	Sample ID	TA (umol/kg)	Average	STDEV	Difference
45	450112	2347.68			
45	450112	2344.73	2346.2	2.08	2.95
49	490112	2345.61			
49	490112	2352.19	2348.9	4.65	6.58
57.3	57.30112	2294.27			
57.3	57.30112	2295.22	2294.7	0.67	0.95
CAL2	CAL20112	2320.09			
CAL2	CAL20112	2317.46	2318.7	1.85	2.62
CAL1	CAL10112	2327.67			

CAL1	CAL10112	2322.17	2324.9	3.88	5.49
TB4	TB40112	2381.23			
TB4	TB40112	2380.31	2380.7	0.65	0.92
Average				2.29	3.25

Remarks

The average of the CRMs were used to adjust the values of the samples for each day.

The measured TA value for one of the duplicates with Sample ID 510112 was determined to be a bad measurement through comparison with other parameters and is not reported.

Samples taken around Shark River, (Stations 54, 55, 56, 57) have high TA values that are a consistent feature present in past cruises and should be considered real features.

Comments

The latitude, longitude, date, and time reported with the DIC, pH and TAlk measurements were taken from the sample field log. The field log values are provided for reference; no post-cruise assurance of accuracy has been done to this data. The Niskin bottles are approximately one-half meter above the CTD sensors on the rosette. Therefore, Temp and Sal are bin-averaged CTD values representing the next shallower depth from that recorded by the CTD (CTD Depth) at the time the Niskin bottles were fired with the exception of the surface values, which are the same as the CTD Depth values (as per the log sheet).

The Sample ID is the station number, cast number and niskin number.

Corresponding UW pCO₂ data can be found at the following website
<http://www.aoml.noaa.gov/ocd/ocdweb/occ.html>

Nutrients:

Analysis Date: 10/25/2022

Nutrient samples were analyzed using a Seal Analytical high-resolution digital colorimeter auto-analyzer 3 (AA3). A series of standards for each method were run before sample analysis to obtain a calibration curve for data reduction. Method 353.4 was used to determine the concentration of nitrate and nitrite for each station (Zhang et al., 1997b). This method used automated, gas-segmented, continuous

flow colorimetry for the analysis of nitrate and nitrite. Samples were first passed through a copper-coated cadmium reduction column. Nitrate was reduced to nitrite in a buffer solution. The nitrite was then determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a color azo dye. The absorbance measured at 550 nm is linearly proportional to the concentration of nitrite + nitrate in the sample. Nitrate concentrations are obtained by subtracting nitrite values, which have been separately determined without the cadmium reduction procedure, from the nitrite + nitrate values.

Method 365.5 was used to determine the concentration of orthophosphate for each station (Zimmermann and Keefe, 1997; Zhang et al., 2001). This method used automated colorimetric and continuous flow analysis for the determination of low-level orthophosphate concentrations. Ammonium molybdate and antimony potassium tartrate react in an acidic medium with orthophosphate to form an antimony-phospho-molybdate complex. This complex was reduced to a blue-colored complex by ascorbic acid. The absorbance measured at 880 nm is proportional to the phosphate concentration in the sample.

Method 366.0 was used to determine the concentration of soluble silica for each station (Zhang and Berberian, 1997). This method used automated, gas-segmented, continuous flow colorimetry for the analysis of dissolved silicate concentration. In this method, β -molybdosilicic acid was formed by the reaction of the silicate contained in the sample with molybdate in acidic solution. The β -molybdosilicic acid was then reduced by ascorbic acid to form molybdenum blue. The absorbance of the molybdenum blue, measured at 550 nm, is linearly proportional to the concentration of silicate in the sample.

Zhang, J.-Z. and Berberian, G.A. (1997). Determination of dissolved silicate in estuarine and coastal waters by gas segmented flow colorimetric analysis, *U.S. Environmental Protection Agency, (EPA Method 366.0)*, EPA-600-R-97-072.

Zhang, J.-Z., Fischer, C.J. and Ortner, P.B. (2001). Continuous flow analysis of phosphate in natural waters using hydrazine as a reductant. *Intern. J. Environ. Anal. Chem.* 80(1): 61-73.

Zimmermann, C.F., and C.W. Keefe (1997). Determination of orthophosphate in estuarine and coastal waters by automated colorimetric analysis. *U.S. Environmental Protection Agency (EPA method 365.5)*, EPA-600-R-97-072.

Zhang, J.-Z., Ortner, P.B. and Fischer, C.J. (1997b). Determination of nitrate and nitrite in estuarine and coastal waters by gas segmented continuous flow colorimetric analysis. *U.S. Environmental Protection Agency (EPA Method 353.4)*, EPA-600-R-97-072.

Operation Manual (2008), AutoAnalyzer 3 high resolution, Seal Analytical. *Publication No. MB7-31EN-02*, (February 2008).

Remarks

No remarks.

Chlorophyll and Phaeophytin:
Analysis Date: 10/20/2022

Chlorophyll-a concentrations are determined via a standardized filtration-extraction method using a 60:40 mixture of 90% acetone and dimethyl sulfoxide. The fluorescence of each sample is measured before and after acidification in order to correct for phaeophytin on a TD-700 fluorometer. Samples are stored in the dark at -80°C until analysis. A sample duplicate is analyzed with each sample.

Shoaf, W.T. and Lium, B.W. (1976). Improved extraction of chlorophyll-a and b from algae using dimethyl sulfoxide. *Limnology and Oceanography* 21: 926-928.

EPA Method 445 (1997) In vitro determination of chlorophyll-a in marine and freshwater algae by fluorescence.