Cruise: WS23011
Ship: R/V Walton Smith
Expo Code: 33WA20230111
Funding Project Title: Expanding near-shore carbonate measurements along the East-coast and Gulf of Mexico through multiple collaborations
Funding Project ID: 21403
Dates: January 11th – January 18th, 2023
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 and Rachel Cohn. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
55 locations,79 samples each 500-ml, 7 duplicate samples.
Sample ID#: CAL10101, etc.; Station name/number, cast number and Niskin bottle number.
PI: Dr. Rik Wanninkhof
Analyzed by: Patrick Mears and Alison MacLeod

pH:
55 locations, 79 samples each 500-ml, 7 duplicate samples.
Sample_ID#: #: CAL10101, etc.; Station name/number, cast number and Niskin bottle number.
PI: Dr. Rik Wanninkhof
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Sample_ID#: #: CAL10101, etc.; Station name/number, cast number and Niskin bottle number.
PI: Dr. Rik Wanninkhof
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Sample Analysis
DIC:

Instrument ID	Date	Certified CRM (µmol/kg)	CRM Value (µmol/kg)	CRM Offset (µmol/kg)	Blank (Counts)	Avg. Sample Analysis Time
AOML 5	2/6/2023	2024.96	2028.58	3.62	30	8
AOML 5	2/8/2023	2024.96	2027.49	2.53	17	9
AOML 6	2/6/2023	2024.96	2025.74	3.76	12	11
AOML 6	2/8/2023	2024.96	2028.65	2.63	22	9

Analysis date: 2/6/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 29.2 counts/min
CRM # 489 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 5: offset 3.62 µmol/kg (2024.53 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 2/8/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 16.7 counts/min
CRM # 584 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 5: offset 2.53 µmol/kg (2025.41 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 12 min.

Analysis date: 2/6/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.6 counts/min
CRM # 466 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 5: offset 0.57 µmol/kg (2025.74 µmol/kg).
Average run time, minimum run time, maximum run time: 11, 10 and 13 min.

Analysis date: 2/8/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 519 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 6: offset 3.48 µmol/kg (2028.65µmol/kg).

Average run time, minimum run time, maximum run time: 9, 7 and 12 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.90 (0.08-2.14) and average STDEV of 0.63 (0.06-1.51).

Sample ID	DIC (µmol/kg)	Average	STDEV	Difference
AMI10112	2178.4			
AMI10112	2180.0	2179.17	1.13	1.60
BG10112	2140.5			
BG10112	2141.3	2140.92	0.54	0.77
RP10112	2126.6			
RP10112	2127.1	2126.85	0.40	0.56
CAL10112	2251.5			
CAL10112	2249.3	2250.38	1.51	2.14
450112	2128.8			
450112	2128.4	2128.59	0.32	0.45
600112	2129.6			
600112	2129.5	2129.58	0.06	0.08
650112	2805.1			
650112	2804.5	2804.82	0.47	0.66
Average			0.63	0.90

CRM, salinity and $HgCl_2$ correction applied: Salinity correction was applied using TSG salinity.

Remarks

On 2/6/2023 the primary water bath for temperature control was not turned on, affecting Sample IDs: RP10112, CAL10112, CAL20112, CAL30101, CAL30112, CAL40101, CAL40112, CAL50101, CAL501112, 330112. These stations are flagged 3 due to the temperature of the sample not being controlled and accurately measured.

The volume correction was applied due to added $HgCl_2$ (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 5017O from UIC. Inc.

pH:

Analysis date: 2/6/2023 and 2/8/2023
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 (^{0}C)
160112	1	34.917	19.899
21/LK0101	2	36.199	19.91
21/LK0112	3	35.986	19.913
WS0101	4	36.006	19.921
WS0112	5	36.012	19.914
KW10112	6	35.199	19.92
KW20101	7	35.394	19.915
KW20112	8	35.395	19.914
KW40101	9	35.854	19.911
KW40112	10	35.855	19.914
300101	11	36.087	19.917
300112	12	36.088	19.913
TB10112	13	34.490	19.913
TB40101	14	36.171	19.912
TB40112	15	36.267	19.916
AMI90101	16	36.309	19.909
TB100000	17	36.227	19.909
AMI90112	18	36.283	19.913
AMI50101	19	36.190	19.908
AMI50112	20	36.252	19.91
AMI10112	401	33.545	19.912
AMI10112	402	33.545	19.916
V10112	403	35.003	19.921
V50101	404	36.192	19.913

V50112	405	36.192	19.918
V90101	406	36.286	19.912
V90112	407	36.286	19.918
GP50101	408	36.254	19.912
GP50112	409	36.244	19.904
BG40101	410	36.307	19.911
BG40112	411	36.308	19.91
RP40101	412	36.278	19.917
RP40112	413	36.278	19.92
BG30101	414	35.641	19.915
BG30112	415	35.641	19.912
BG20112	416	35.426	19.911
BG10112	417	33.818	19.912
BG10112	418	33.818	19.914
RP30112	419	35.603	19.912
RP20112	420	35.616	19.915
RP10112	421	34.771	19.866
RP10112	422	34.771	19.87
CAL10112	423	31.928	19.878
CAL10112	424	31.928	19.873
CAL20112	425	34.735	19.87
CAL30101	426	35.291	19.873
CAL30112	427	35.287	19.883
CAL40101	428	35.548	19.869
CAL40112	429	35.544	19.876
CAL50101	430	36.048	19.87
CAL50112	431	36.041	19.867
330112	432	35.459	19.88
310112	433	35.990	19.88
410112	434	34.967	19.873
450112	435	35.361	19.877
450112	436	35.361	19.886
490112	437	32.686	19.881
510112	438	33.906	19.874
57.10112	439	34.967	19.878
570112	440	33.808	19.872
560112	441	33.165	19.88
550112	442	32.536	19.877
540112	443	29.703	19.878
57.20112	444	35.713	19.866
57.30112	445	35.610	19.873

580112	446	35.812	19.874
600112	447	34.976	19.864
600112	448	34.976	19.872
650112	449	31.448	19.877
650112	450	31.448	19.87
680112	451	34.222	19.913
100112	452	33.051	19.903
70112	453	35.584	19.905
UK OFF0000	454	35.788	19.909
UK MID0000	455	35.813	19.912
UK IN0000	456	35.978	19.915
MR0101	457	36.066	19.902
MR0112	458	35.832	19.901
20112	459	36.047	19.907

Reproducibility: pH @ 20^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0018 (0.0004– 0.0039) and an average STDEV of 0.0013 (0.0003 – 0.0028).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	AMI10112	401	7.993	7.992	0.0019	0.0027
HP Agilent 8453	AMI10112	402	7.991			
HP Agilent 8453	BG10112	417	7.948	7.946	0.0028	0.0039
HP Agilent 8453	BG10112	418	7.944			
HP Agilent 8453	RP10112	421	7.948	7.950	0.0023	0.0033
HP Agilent 8453	RP10112	422	7.951			
HP Agilent 8453	CAL10112	423	7.934	7.934	0.0003	0.0004
HP Agilent 8453	CAL10112	424	7.934			
HP Agilent 8453	450112	435	7.998	7.997	0.0006	0.0009
HP Agilent 8453	450112	436	7.997			
HP Agilent 8453	600112	447	8.099	8.099	0.0003	0.0004
HP Agilent 8453	600112	448	8.099			
HP Agilent 8453	650112	449	7.926	7.927	0.0007	0.0010
HP Agilent 8453	650112	450	7.927			
Average					0.0013	0.0018

Reproducibility: pH @ 25^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0018 (0.0003-0.0032) and an average STDEV of 0.0013 (0.0003-0.0027).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	AMI10112	401	7.919	7.917	0.0019	0.0027
HP Agilent 8453	AMI10112	402	7.916			
HP Agilent 8453	BG10112	417	7.874	7.872	0.0027	0.0038
HP Agilent 8453	BG10112	418	7.870			
HP Agilent 8453	RP10112	421	7.874	7.876	0.0023	0.0032
HP Agilent 8453	RP10112	422	7.877			
HP Agilent 8453	CAL10112	423	7.861	7.860	0.0003	0.0004
HP Agilent 8453	CAL10112	424	7.860			
HP Agilent 8453	450112	435	7.923	7.923	0.0006	0.0009
HP Agilent 8453	450112	436	7.922			
HP Agilent 8453	600112	447	8.023	8.023	0.0003	0.0004
HP Agilent 8453	600112	448	8.023			
HP Agilent 8453	650112	449	7.852	7.853	0.0007	0.0010
HP Agilent 8453	650112	450	7.853			
Average					0.0013	0.0018

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 20^0C at Full Scale (pH 0-14). The pH was reported at 20^0C and 25^0C.

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: 2/7/2023 and 2/9/2023
Titration system used: Open cell
Batch 195, CRM # 489 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM # 584 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM # 466 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM # 590 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.

On 2/7/2023 CRM #489 was analyzed before and after sample analysis on System 1.
On 2/9/2023 CRM #584 was analyzed before and after sample analysis on System 1.
On 2/7/2023 CRM #466 was analyzed before and after sample analysis on System 2.
On 2/9/2023 CRM #590 was analyzed before and after sample analysis on System 2.

Unless it is otherwise noted in the remarks section, the TA for the water samples were 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	|ΔCRM|
1	2/7/2023	09:04:48	489	2209.66	3.85
1	2/7/2023	19:45:44	489	2213.74	0.23
1	2/9/2023	11:40:05	584	2226.73	13.22
1	2/9/2023	19:34:19	584	2210.21	6.7
2	2/7/2023	09:02:33	466	2223.15	9.64
2	2/7/2023	17:49:37	466	2214.03	0.52
2	2/9/2023	10:12:59	590	2219.42	5.91
2	2/9/2023	16:46:33	590	2218.75	5.24

Reproducibility: (# samples and average difference): 7 duplicate samples were collected, two duplicate pairs were discarded due to one sample being significantly different from calculated TA values using the other carbonate parameters. The average difference of 8.05(5.17 – 13.23) and an average STDEV of 2.18 (3.65 – 9.35).

Station	Sample ID	TA (umol/kg)	Average	STDEV	Difference
BG1	BG10112	2366.62			
BG1	BG10112	2373.31	2369.97	4.72	6.69
CAL1	CAL10112	2490.67			
CAL1	CAL10112	2497.58	2494.13	4.88	6.91
45	450112	2387.13			
45	450112	2392.30	2389.71	3.65	5.17
60	600112	2434.85			
60	600112	2426.6	2430.72	5.83	8.25
65	650112	3066.8			
65	650112	3053.57	3060.18	9.35	13.23
Average				2.18	8.05

Remarks

On 2/7/2023 on System 2, the ending CRM was used to adjust the values due to equipment issues being present near the beginning of the sample run. The average of the CRMs were used to adjust the values of the samples for the other days for both systems.

On 2/7/2023, System 2 was having equipment difficulties, as a result one of the duplicates on Station ID RP10112 was lost.

One of the duplicate samples on Station ID AMI10112 is very far off from the calculated value and is not included.

Only one of the duplicate for BG10112 and 450112 are reported in the final data set due to the value being questionable.

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: 2/8/2023, 2/9/2023, 2/15/2023

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: 2/8/2023, 2/9/2023, 2/15/2023

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^{0}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.