Cruise: WS22022
Ship: R/V Walton Smith
Expo Code: 33WA20220122
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 22nd - January 28th, 2022
Chief Scientist: Chris Kelble
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 Cohen. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
55 locations, 80 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 and Patrick Mears

pH:
55 locations, 80 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 and Patrick Mears

TAlk:
55 locations, 80 samples each 500-ml, 7 duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dismey Sosa-Rodriguez

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	03/07/2022	2025.17	2026.41	1.24	23.0	7
AOML 5	03/09/2022	2025.17	2025.34	0.17	30.0	8
AOML 6	03/07/2022	2025.17	2026.66	1.49	17.4	7
AOML 6	03/09/2022	2025.17	2029.18	4.01	12.0	7

Analysis date: 03/07/2022
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 23.0 counts/min
CRM #277 was used and with an assigned value of (includes both DIC and salinity):
Batch 194, c: 2025.17 µmol/kg, S: 33.361
CRM values measured: AOML 5: offset 1.24 µmol/kg (2026.41 µmol/kg).
Average run time, minimum run time, maximum run time: 7, 7 and 8 min.

Analysis date: 03/09/2022
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 30.0 counts/min
CRM #64 was used and with an assigned value of (includes both DIC and salinity): Batch 194, c: 2025.17 µmol/kg, S: 33.361
CRM values measured: AOML 5: offset 0.17 µmol/kg (2025.34 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 9 min.

Analysis date: 03/07/2022
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 17.4 counts/min
CRM #1185 was used and with an assigned value of (includes both DIC and salinity):
Batch 194, c: 2025.17 µmol/kg, S: 33.361
CRM values measured: AOML 6: offset 1.49 µmol/kg (2026.66 µmol/kg).
Average run time, minimum run time, maximum run time: 7, 7 and 10 min.

Analysis date: 03/09/2022
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM #78 was used and with an assigned value of (includes both DIC and salinity):
Batch 194, c: 2025.17 µmol/kg, S: 33.361
CRM values measured: AOML 6: offset 4.01 µmol/kg (2029.18 µmol/kg).
Average run time, minimum run time, maximum run time: 7, 7 and 9 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.16 (0.20-4.49) and average STDEV of 0.82 (0.14-3.17).

Station #	Sample Bottle #	Sample ID	DIC (μmol/kg)	Average	STDEV	Difference
CAL2	125	CAL20112	2146.5			
CAL2	126	CAL20112	2146.3	2146.4	0.14	0.20
CAL10	127	CAL10112	2208.6			
CAL10	128	CAL10112	2209.8	2209.2	0.82	1.16
V5	156	V50112	2107.1			
V5	157	V50112	2106.6	2106.9	0.36	0.51
57.1	276	57.10112	2161.6			
57.1	277	57.10112	2166.1	2163.9	3.17	4.49
TB10	2069	TB100112	2098.7			
TB10	2070	TB100112	2098.9	2098.8	0.14	0.20
41	2071	410112	2179.3			
41	2072	410112	2179.7	2179.5	0.32	0.46
49	2074	490112	2410.5			
49	2075	490112	2409.3	2409.9	0.79	1.12
Average					0.82	1.16

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

Remarks

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

pH:

Analysis date: 03/07/2022 and 03/09/2022
No CRMs was 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)
20112	103	34.421	19.967
MR0101	110	36.234	19.994
MR0112	111	36.204	20.015
CAL50101	113	35.607	19.974
330112	114	35.176	19.988
310112	115	36.017	19.976
CAL50112	116	35.607	19.978
CAL40101	117	35.181	19.979
CAL40112	118	35.180	19.981
CAL30101	119	34.800	19.974
CAL30112	120	34.788	19.984
CAL20112	125	33.481	20.004
CAL20112	126	33.481	20.006
CAL10112	127	30.660	20.013
CAL10112	128	30.660	20.001
RP10112	129	34.295	19.999
RP20112	130	34.675	20.035
RP30112	131	35.005	20.047
RP40101	132	35.633	20.078
RP40112	133	35.441	20.047
GP50101	134	36.074	20.066
GP50112	135	36.055	20.086
BG40101	136	35.615	20.116
UK-OFF0000	138	36.161	20.019
70112	139	35.237	20.023
UK-IN0000	140	36.286	19.998
UK-MID0000	141	36.227	20.012
100112	142	35.084	20.045
160112	143	35.399	20.067
21-LK0101	144	36.172	20.054
21-LK0112	145	36.179	20.06
WS0101	146	36.239	20.083
WS0112	147	36.240	20.096
KW10112	148	36.009	20.109
BG40112	149	35.419	20.123

BG30101	150	34.941	20.118
BG30112	151	34.541	20.086
KW20101	152	36.094	20.11
BG20112	152	34.468	20.119
BG10112	153	34.417	20.121
V10112	154	33.902	20.161
V50101	155	35.753	20.208
V50112	156	35.702	20.175
V50112	157	35.702	20.235
V90101	158	36.322	20.199
V90112	159	36.323	20.199
AMI90101	160	36.272	20.222
KW20112	197	36.096	20.098
KW40101	198	36.316	20.118
KW40112	199	36.317	20.127
300101	200	36.372	20.139
300112	201	36.373	20.192
550112	273	32.127	19.954
560112	274	32.956	19.958
570112	275	33.882	19.961
57.10112	276	35.294	19.969
57.10112	277	35.294	19.977
57.20112	278	35.763	19.973
580112	279	36.247	19.982
57.30112	280	35.946	20.171
600101	281	35.328	19.942
650112	282	31.755	19.94
680112	284	35.042	19.939
700000	285	34.437	19.941
AMI90112	2062	36.275	19.946
AMI50000	2063	35.477	19.96
AMI10112	2064	33.276	19.966
TB10112	2065	32.971	19.969
TB40101	2066	35.431	19.965
TB40112	2067	35.432	19.976
TB100101	2068	35.754	19.983
TB100112	2069	35.756	19.974
TB100112	2070	35.756	19.947
410112	2071	35.483	19.936
410112	2072	35.483	19.949
450112	2073	35.559	19.936

490112	2074	33.221	19.945
490112	2075	33.221	19.943
510112	2076	34.958	19.958
540112	2077	31.369	19.951

Reproducibility: pH @ 20^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.00286 (0.00096 – 0.00636) and an average STDEV of 0.00202 (0.00068 – 0.00228).

Instrument	Sample ID	Bottle #	pH @20 ^{0}C	Average	STDEV	Difference
HP Agilent 8453	CAL20112	125	7.96468			
HP Agilent 8453	CAL20112	126	7.96756	7.96612	0.00204	0.00289
HP Agilent 8453	CAL10112	127	7.93884			
HP Agilent 8453	CAL10112	128	7.94257	7.94071	0.00264	0.00374
HP Agilent 8453	V50112	156	8.06460			
HP Agilent 8453	V50112	157	8.06481	8.06470	0.00015	0.00021
HP Agilent 8453	57.10112	276	8.01399			
HP Agilent 8453	57.10112	277	8.01133	8.01266	0.00189	0.00267
HP Agilent 8453	TB100112	2069	8.08041			
HP Agilent 8453	TB100112	2070	8.07718	8.07879	0.00228	0.00323
HP Agilent 8453	410112	2071	7.95593			
HP Agilent 8453	410112	2072	7.95497	7.95545	0.00068	0.00096
HP Agilent 8453	490112	2074	7.99088			
HP Agilent 8453	490112	2075	7.99724	7.99406	0.00449	0.00636
Average					0.00202	0.00286

Reproducibility: pH @ 25^0C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.00362 (0.00095 – 0.00628) and an average STDEV of 0.00230 (0.00067 – 0.00444).

Instrument	Sample ID	Bottle #	pH @25 ^{0}C	Average	STDEV	Difference
HP Agilent 8453	CAL201012	125	7.89049			
HP Agilent 8453	CAL201012	126	7.89333	7.89191	0.00201	0.00285
HP Agilent 8453	CAL101012	127	7.86509			

HP Agilent 8453	CAL10112	128	7.86877	7.86693	0.00260	0.00368
HP Agilent 8453	V50112	156	7.93915			
HP Agilent 8453	V50112	157	7.93652	7.93784	0.00186	0.00264
HP Agilent 8453	57.10112	276	8.00495			
HP Agilent 8453	57.10112	277	8.00175	8.00335	0.00226	0.00320
HP Agilent 8453	TB100112	2069	8.00495			
HP Agilent 8453	TB100112	2070	8.00175	8.00335	0.00226	0.00320
HP Agilent 8453	410112	2071	7.88175			
HP Agilent 8453	410112	2072	7.88080	7.88128	0.00067	0.00095
HP Agilent 8453	490112	2074	7.91638			
HP Agilent 8453	490112	2075	7.92266	7.91952	0.00444	0.00628
Average					0.00230	0.00326

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: 03/02/2022, 03/08/2022 and 03/10/2022
Titration system used: Open cell

Batch 178, CRM #333 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.
Batch 194, CRM #277 Salinity = 33.361, cert. TA = 2169.83 µmol/kg.
Batch 194, CRM #64 Salinity = 33.361, cert. TA = 2169.83 µmol/kg.
Batch 194, CRM #161 Salinity = 33.361, cert. TA = 2169.83 µmol/kg.
Batch 194, CRM #362 Salinity = 33.361, cert. TA = 2169.83 µmol/kg.
Batch 194, CRM #78 Salinity = 33.361, cert. TA = 2169.83 µmol/kg.

On 03/02/2022 CRM #333 was analyzed before and after sample analysis on System 1.
On 03/02/2022 CRM #161 was analyzed before and after sample analysis on System 2.
On 03/08/2022 CRM #277 was analyzed before and after sample analysis on System 1.
On 03/08/2022 CRM #362 was analyzed before and after sample analysis on System 2.
On 03/10/2022 CRM #64 was analyzed before and after sample analysis on System 1.
On 03/10/2022 CRM #78 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 1 and 2 cells. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	Difference
1	03/02/2022	10:41:17	333	2213.93	2.60
1	03/02/2022	18:43:38	333	2215.99	0.54
1	03/08/2022	11:40:05	277	2167.46	2.37
1	03/08/2022	17:42:57	277	2172.85	3.02
1	03/10/2022	09:25:12	64	2173.00	3.17
1	03/10/2022	16:33:10	64	2174.85	5.02
2	03/02/2022	10:37:44	161	2169.10	0.73
2	03/02/2022	18:58:53	161	2169.59	0.24
2	03/08/2022	11:48:52	362	2169.26	0.57
2	03/08/2022	17:58:07	362	2171.94	2.11
2	03/10/2022	08:50:58	78	2170.13	0.30
2	03/10/2022	16:27:11	78	2167.40	2.43

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 2.54 (0.16 – 5.15) and an average STDEV of 1.80 (0.11 – 3.64).

Station	Sample ID	Sample Bottle #	TA (µmol/kg)	Average	STDEV	Difference
CAL2	CAL20112	125	2363.84			
CAL2	CAL20112	126	2368.99	2366.4	3.64	5.15

CAL1	CAL10112	127	2409.41			
CAL1	CAL10112	128	2409.25	2409.3	0.11	0.16
V5	V50112	156	2381.99			
V5	V50112	157	2384.66	2383.3	1.89	2.68
57.1	57.10112	276	2418.29			
57.1	57.10112	277	2416.15	2417.2	1.51	2.13
TB10	TB100112	2069	2377.96			
TB10	TB100112	2070	2374.51	2376.2	2.44	3.46
41	410112	2071	2403.39			
41	410112	2072	2404.94	2404.2	1.10	1.56
49	490112	2074	2377.86			
49	490112	2075	2380.53	2379.2	1.89	2.67
Average					1.80	2.54

Remarks

None

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.

Sample bottle #192 for station RP1 was lost-no carbon data available.

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

Nutrients:
Analysis Date: 02/04/2022

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).

Chlorophyll and Phaeophytin:
Analysis Date: 02/10/2022

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 -80^0C 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.