Cruise: WS21212
Ship: R/V Walton Smith
Expo Code: 33WA20210731
Funding Project Title: Near-Shore Carbonate Sampling
Funding Project ID: Near-Shore-OA
Dates: July 31st – August 6th, 2021
Chief Scientist: Ian Smith
Equipment: CTD-Niskin and Flow-Through (FT)
Total number of stations: 58
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 Alex Fine. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

58 locations, 87 samples each 500-ml, 8 duplicate samples.
Sample ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Denis Pierrot, Dr. Leticia Barbero and Charles Featherstone

pH:

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TAlk:

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Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero and 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	08/16/2021	1952.65	1955.00	2.35	12	7
AOML 5	08/17/2021	1952.65	1951.36	1.29	12	8
AOML 6	08/16/2021	1952.65	1954.04	1.39	12	9
AOML 6	08/17/2021	1952.65	1954.98	2.33	12	8

Analysis date: 08/16/2021
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 1175 was used and with an assigned value of (includes both DIC and salinity):
Batch 178, c: 1952.65 µmol/kg, S: 33.782
CRM values measured: AOML 5: offset 2.35 µmol/kg (1955.00 µmol/kg).
Average run time, minimum run time, maximum run time: 7, 7 and 7 min.

Analysis date: 08/17/2021
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 874 was used and with an assigned value of (includes both DIC and salinity):
Batch 178, c: 1952.65 µmol/kg, S: 33.782
CRM values measured: AOML 5: offset 1.29 µmol/kg (1951.36 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 08/16/2021
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 625 was used and with an assigned value of (includes both DIC and salinity):
Batch 178, c: 1952.65 µmol/kg, S: 33.782
CRM values measured: AOML 6: offset 1.39 µmol/kg (1954.04 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 7 and 12 min.

Analysis date: 08/17/2021
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 934 was used and with an assigned value of (includes both DIC and salinity):
Batch 178, c: 1952.65 µmol/kg, S: 33.782
CRM values measured: AOML 6: offset 2.33 µmol/kg (1954.98 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 11 min.

Reproducibility: (# samples and average difference): 6 duplicate samples were collected with an average difference of 2.33 (0.11-11.84) and average STDEV of 1.64 (0.08-8.37).

Sample ID	DIC (µmol/kg)	Average	Difference	STDEV
CW301012	2009.6			
CW301012	2010.4	2010.0	0.86	0.61

CW401012	2056.3			
CW401012	2056.8	2056.5	0.48	0.34
TB40101	2086.7			
TB40101	2074.9	2080.8	11.84	8.37
AMI10101	2097.6			
AMI10101	2095.9	2096.7	1.72	1.22
4901012	2577.8			
4901012	2580.0	2578.9	2.23	1.57
5501012	2052.7			
5501012	2051.6	2052.2	1.13	0.80
57.301012	2040.9			
57.301012	2041.1	2041.0	0.23	0.16
6501012	1977.1			
6501012	1977.0	1977.0	0.11	0.08
Average			2.33	1.64

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

DIC samples were analyzed on new coulometers 5017O from UIC. Inc.

No DIC sample for bottle 198. The glass stopper broke off in the neck of the bottle.

pH:

Analysis date: 08/16/2021 and 08/17/2021
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)
201012	1	36.173	21.205
MR0101	2	36.202	21.264
MR01012	3	36.106	21.198
UK-OFF0000	4	35.887	21.197
UK-MID0000	5	35.872	21.308
UK-IN0000	6	36.122	21.326
701012	7	36.294	21.417
1001012	8	37.528	21.548
1601012	9	36.214	21.591
21-LK0101	10	36.247	21.643
21-LK01012	11	36.187	21.882
WS0101	12	36.218	22.111
WS01012	13	36.248	20.646
KW101012	14	35.674	21.378
KW20101	15	36.081	21.439
KW201012	16	36.120	21.102
KW40101	17	36.141	21.837
KW401012	18	36.214	21.613
300101	19	36.138	21.623
3001012	20	36.247	21.87
3101012	21	36.153	22.145
3301012	22	35.435	21.729
CAL50101	23	36.049	22.307
CAL501012	24	35.844	22.457
CAL40101	25	35.715	22.819
CAL401012	26	35.584	21.145
CAL30101	27	35.500	21.156
CAL301012	28	34.634	21.234
CAL201012	29	34.220	21.343
CAL101012	30	33.443	21.388
RP101012	31	34.795	21.521
RP201012	32	34.733	21.625
RP301012	33	34.725	21.671
RP40101	34	36.243	21.751
RP401012	35	35.284	22.028

GP50101	36	36.300	19.668
GP501012	37	36.219	20.871
BG40101	38	36.281	21.772
BG401012	39	35.606	21.351
BG30101	40	36.152	21.489
BG30105	81	36.156	22.007
BG301012	82	34.695	21.172
BG201012	83	34.596	22.044
BG101012	84	28.795	21.835
CW101012	85	34.446	22.602
CW201012	86	35.608	22.031
CW301012	87	35.651	22.161
CW301012	88	35.651	22.644
CW401012	89	35.925	21.52
CW401012	90	35.925	21.759
TB101012	91	35.007	21.948
TB40101	92	36.321	22.492
TB40101	93	36.321	22.610
TB401012	94	36.244	22.591
TB100101	95	36.339	22.689
TB1001012	96	36.322	21.237
AMI90101	97	36.181	21.909
AMI901012	98	36.285	22.273
AMI50101	99	36.324	22.498
AMI501012	100	36.243	22.648
AMI10101	173	35.343	19.981
AMI10101	174	35.343	20.025
V101012	175	35.032	20.074
V50101	176	36.251	20.085
V501012	177	35.675	20.090
V90101	178	36.283	20.105
V901012	179	36.350	20.455
4101012	180	34.448	21.497
4501012	181	35.741	19.854
4901012	182	33.212	19.886
4901012	183	33.212	19.900
5101012	184	36.002	19.921
5401012	185	36.420	22.187
5501012	186	36.482	22.522
5501012	187	36.482	22.613
5601012	188	36.229	22.674

5701012	189	36.086	22.853
57.10101	190	36.041	21.617
57.201012	191	36.146	22.137
57.301012	192	36.352	22.470
57.301012	193	36.352	22.620
5801012	194	36.127	22.693
6001012	195	36.240	20.015
6501012	196	36.108	20.050
6501012	197	36.108	20.094
6801012	198	36.059	20.099
700000	199	34.791	20.106

Reproducibility: pH @ 20^0C (# samples and average difference): 8 duplicate samples were collected with an average difference of 0.01457 (0.00063 – 0.02495) and an average STDEV of 0.01030 (0.00045 – 0.01764).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	CW301012	87	8.233183			
HP Agilent 8453	CW301012	88	8.235208	8.23420	0.00143	0.00203
HP Agilent 8453	CW401012	89	8.146218			
HP Agilent 8453	CW401012	90	8.151572	8.14890	0.00379	0.00535
HP Agilent 8453	TB40101	92	8.120385			
HP Agilent 8453	TB40101	93	8.145332	8.13286	0.01764	0.02495
HP Agilent 8453	AMI10101	173	8.199251			
HP Agilent 8453	AMI10101	174	8.124197	8.16172	0.05307	0.07505
HP Agilent 8453	4901012	182	7.942850			
HP Agilent 8453	4901012	183	7.941621	7.94224	0.00087	0.00123
HP Agilent 8453	5501012	186	8.037002			
HP Agilent 8453	5501012	187	8.036368	8.03668	0.00045	0.00063
HP Agilent 8453	57.301012	192	8.149337			
HP Agilent 8453	57.301012	193	8.144533	8.14693	0.00340	0.00480
HP Agilent 8453	6501012	196	8.085586			
HP Agilent 8453	6501012	197	8.088060	8.08682	0.00175	0.00247
Average					0.01030	0.01457

Reproducibility: pH @ 25^{0}C (# samples and average difference): 8 duplicate samples were collected with an average difference of 0.01879 (0.00122 – 0.07446) and an average STDEV of 0.01329 (0.00086 – 0.05265).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	CW301012	87	8.156459			
HP Agilent 8453	CW301012	88	8.158479	8.15747	0.00143	0.00202
HP Agilent 8453	CW401012	89	8.070192			
HP Agilent 8453	CW401012	90	8.075501	8.07285	0.00375	0.00531
HP Agilent 8453	TB40101	92	8.0445590			
HP Agilent 8453	TB40101	93	8.0692921	8.05693	0.01749	0.02473
HP Agilent 8453	AMI10101	173	8.1227823			
HP Agilent 8453	AMI10101	174	8.0483262	8.08555	0.05265	0.07446
HP Agilent 8453	4901012	182	7.8686641			
HP Agilent 8453	4901012	183	7.8674461	7.86806	0.00086	0.00122
HP Agilent 8453	5501012	186	7.8886428			
HP Agilent 8453	5501012	187	7.9240137	7.90633	0.02501	0.03537
HP Agilent 8453	57.301012	192	8.0733019			
HP Agilent 8453	57.301012	193	8.0685361	8.07092	0.00337	0.00477
HP Agilent 8453	6501012	196	8.010179			
HP Agilent 8453	6501012	197	8.012633	8.01141	0.00174	0.00245
Average					0.01329	0.01879

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

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: 08/18/2021 and 08/20/2021
Titration system used: Open cell
Batch 178, CRM #1175 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.
Batch 178, CRM #874 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.
Batch 178, CRM #625 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.
Batch 178, CRM #934 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.

On 08/18/2021 CRM #1175 was analyzed before sample analysis on System 1 and 2.
On 08/18/2021 CRM #625 was analyzed after sample analysis on System 1 and 2.
On 08/20/2021 CRM #874 was analyzed before sample analysis on System 1 and 2.
On 08/20/2021 CRM #934 was analyzed after sample analysis on System 1 and 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	|ΔCRM|
1	08/18/2021	09:22:17	1175	2217.07	0.54
1	08/18/2021	22:14:56	625	2215.44	1.09
1	08/20/2021	10:47:44	874	2220.26	3.73
1	08/20/2021	18:00:17	934	2222.40	5.87
2	08/18/2021	10:32:41	1175	2216.07	0.46
2	08/18/2021	21:47:50	625	2211.47	5.06
2	08/20/2021	09:27:19	874	2212.01	4.52
2	08/20/2021	17:21:59	934	2212.99	3.54

Reproducibility: (# samples and average difference): 8 duplicate samples were collected with an average difference of 6.15 (0.99 – 12.15) and an average STDEV of 4.35 (0.70 – 8.59).

Station	**Sample ID**	**TA (umol/kg)**	**Average**	**Difference**	**STDEV**
CW3	CW301012	2408.9			
CW3	CW301012	2396.7	2402.8	12.15	8.59
CW4	CW401012	2387.5			
CW4	CW401012	2388.5	2388.0	0.99	0.70

TB4	TB40101	2404.3			
TB4	TB40101	2415.3	2409.8	11.00	7.78
AMI10	AMI10101	2407.6			
AMI10	AMI10101	2416.3	2411.9	8.74	6.18
49	4901012	2819.5			
49	4901012	2829.0	2824.2	9.44	6.67
55	5501012	2324.9			
55	5501012	2322.0	2323.5	2.97	2.10
57.3	57.301012	2371.1			
57.3	57.301012	2372.1	2371.6	1.05	0.74
65	6501012	2267.6			
65	6501012	2264.8	2266.2	2.86	2.02
Average				6.15	4.35

Remarks

Sample bottle #15 was broken and sample lost-No TA result.

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: 08/16/2021 and 08/17/2021

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: ****No chlorophyll samples for this cruise

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.