

**Cruise:** WS21278  
**Ship:** R/V Walton Smith  
**Expo Code:** 33WA20211005  
**Funding Project Title:** Near-Shore Carbonate Sampling  
**Funding Project ID:** Near-Shore-OA  
**Dates:** October 5<sup>th</sup> – October 10<sup>th</sup>, 2021  
**Chief Scientist:** Chris Kelble  
**Equipment:** CTD-Niskin and Flow-Through (FT)  
**Total number of stations:** 56  
**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 Chris Kelble and Alex Fine. The date and time listed in the data file are UTC when each sample bottle was collected.

#### **DIC:**

56 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: Dr. Leticia Barbero and Charles Featherstone

#### **pH:**

56 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: Dr. Leticia Barbero and Charles Featherstone

#### **Talk:**

56 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: Dr. Leticia Barbero and Dismey Sosa-Rodriguez

### **Sample Analysis**

#### **DIC:**

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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
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AOML 5	10/13/2021	1952.65	1954.61	1.96	15	8
AOML 5	10/15/2021	1952.65	1949.02	3.63	15	10
AOML 6	10/13/2021	1952.65	1961.59	8.94	12	8
AOML 6	10/15/2021	1952.65	1958.99	6.34	12	10

Analysis date: 10/13/2021

Coulometer used: DICE–CM5017O-AOML 5

Blanks: 15.0 counts/min

CRM # 757 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 5: offset 1.96  $\mu\text{mol/kg}$  (1954.61  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 10/15/2021

Coulometer used: DICE–CM5017O-AOML 5

Blanks: 15.0 counts/min

CRM # 575 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 5: offset 3.63  $\mu\text{mol/kg}$  (1949.02  $\mu\text{mol/kg}$ ).

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

Analysis date: 10/13/2021

Coulometer used: DICE–CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 1058 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 6: offset 8.94  $\mu\text{mol/kg}$  (1961.59  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 8, 7 and 11 min.

Analysis date: 10/15/2021

Coulometer used: DICE–CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 512 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65  $\mu\text{mol/kg}$ , S: 33.782

CRM values measured: AOML 6: offset 6.34  $\mu\text{mol/kg}$  (1958.99  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 10, 7 and 13 min.

**Reproducibility:** (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.60 (0.09-2.08) and average STDEV of 0.42 (0.07-1.47).

Sample ID	DIC		Average	STDEV	Difference
	( $\mu\text{mol/kg}$ )				
3301012	2119.6				
3301012	2119.5	2119.57	0.07		0.10

BG201012	2116.2			
BG201012	2116.4	2116.31	0.16	0.23
AMI50101	2069.3			
AMI50101	2069.2	2069.23	0.07	0.09
AMI101012	1983.6			
AMI101012	1983.0	1983.32	0.38	0.54
4101012	2224.3			
4101012	2226.3	2225.31	1.47	2.08
5601012	2100.3			
5601012	2099.4	2099.83	0.61	0.86
6501012	1983.0			
6501012	1983.3	1983.19	0.21	0.30
Average			0.42	0.60

CRM, salinity and HgCl<sub>2</sub> correction applied: Salinity correction was applied using TSG salinity.

### **Remarks**

The volume correction was applied due to added HgCl<sub>2</sub> (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: 10/13/2021 and 10/15/2021  
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 (°C)
201012	1	35.339	20.135
MR0101	2	35.013	20.156
MR01012	3	34.995	20.147
UK-IN0000	4	35.415	20.147
UK-MID0000	5	35.346	20.142
UK-OFF0000	6	35.013	20.149
9.501012	7	35.338	20.156
701012	8	34.998	20.136
1001012	9	35.12	20.129
1601012	10	36.447	20.143
21-LK0101	11	35.363	20.133
21-LK01012	12	35.283	20.14
WS0101	13	35.046	20.14
WS01012	14	35.04	20.139
22.50000	15	34.927	20.147
KW101012	16	36.33	20.145
KW20101	17	36.037	20.145
KW201012	18	36.023	20.149
KW40101	19	36.369	20.152
KW401012	20	36.291	20.15
300101	21	36.371	20.14
3001012	22	36.36	20.136
3101012	23	36.252	20.143
3301012	24	35.048	20.15
3301012	25	35.048	20.146
CAL50101	26	36.244	20.034
CAL501012	27	36.244	20.01
CAL40101	28	36.08	19.993
CAL401012	29	36.08	20.004
CAL30101	30	35.877	20.021
CAL301012	31	35.879	20.021
CAL201012	32	35.045	20.023
CAL101012	33	32.347	20.011
RP101012	34	37.765	20.035
RP201012	35	33.698	20.046
RP301012	36	34.99	20.05
RP40101	37	35.926	20.057
RP401012	38	35.908	20.053

GP50101	39	36.236	20.059
GP501012	40	36.254	20.049
BG40101	81	36.019	20.134
BG401012	82	36.009	19.991
BG30101	83	35.394	19.996
BG301012	84	25.247	20.016
BG201012	85	32.798	20.005
BG201012	86	32.798	20.005
BG101012	87	30.773	20.013
V101012	88	34.373	20.007
V50101	89	36.065	20.027
V501012	90	36.004	20.025
V90101	91	36.201	20.026
V901012	92	36.01	20.021
AMI90101	93	36.13	20.04
AMI901012	94	35.799	20.047
AMI50101	95	36.022	20.055
AMI50101	96	36.022	20.059
AMI101012	97	34.833	20.059
AMI101012	98	34.833	20.071
TB101012	99	33.598	20.06
TB40101	100	35.947	20.086
TB401012	173	35.953	20.142
TB100101	174	36.035	20.143
TB1001012	175	35.685	20.161
4101012	176	32.169	20.157
4101012	177	32.169	20.137
4501012	178	36.406	20.135
4901012	179	32.837	20.137
5101012	180	35.267	20.139
5501012	181	34.023	20.142
5401012	182	33.775	20.136
5601012	183	34.75	20.149
5601012	184	34.75	20.142
5701012	185	34.692	20.139
57.101012	186	35.19	20.151
57.201012	187	36.363	20.151
57.301012	188	36.641	20.141
5801012	189	36.595	20.143
6001012	190	36.883	20.153
6501012	191	36.801	20.142

6501012	192	36.801	20.153
6801012	193	36.164	20.143

**Reproducibility:** pH @ 20°C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0086 (0.00008 – 0.04192) and an average STDEV of 0.0061 (0.00006 – 0.02965).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	3301012	24	8.101689			
HP Agilent 8453	3301012	25	8.101771	8.10173	0.00006	0.00008
HP Agilent 8453	BG201012	85	8.061407			
HP Agilent 8453	BG201012	86	8.061110	8.06126	0.00021	0.00030
HP Agilent 8453	AMI50101	95	8.140758			
HP Agilent 8453	AMI50101	96	8.144581	8.14267	0.00270	0.00382
HP Agilent 8453	AMI101012	97	8.234443			
HP Agilent 8453	AMI101012	98	8.242767	8.23860	0.00589	0.00832
HP Agilent 8453	4101012	176	8.056908			
HP Agilent 8453	4101012	177	8.056483	8.05670	0.00030	0.00043
HP Agilent 8453	5601012	183	8.107483			
HP Agilent 8453	5601012	184	8.102407	8.10495	0.00359	0.00508
HP Agilent 8453	6501012	191	8.102972			
HP Agilent 8453	6501012	192	8.061047	8.08201	0.02965	0.04192
Average					0.0061	0.0086

**Reproducibility:** pH @ 25°C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0085 (0.00008 – 0.04157) and an average STDEV of 0.0060 (0.00006 – 0.02939).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	3301012	24	8.02603			
HP Agilent 8453	3301012	25	8.02612	8.02607	0.00006	0.00008
HP Agilent 8453	BG201012	85	7.98616			
HP Agilent 8453	BG201012	86	7.98587	7.98602	0.00020	0.00029
HP Agilent 8453	AMI50101	95	8.06476			

HP Agilent 8453	AMI50101	96	8.06855	8.06665	0.00268	0.00379
HP Agilent 8453	AMI101012	97	8.15775			
HP Agilent 8453	AMI101012	98	8.16601	8.16188	0.00584	0.00825
HP Agilent 8453	4101012	176	7.98161			
HP Agilent 8453	4101012	177	7.98119	7.98140	0.00030	0.00042
HP Agilent 8453	5601012	183	8.03175			
HP Agilent 8453	5601012	184	8.02672	8.02923	0.00355	0.00502
HP Agilent 8453	6501012	191	8.02745			
HP Agilent 8453	6501012	192	7.98588	8.00666	0.02939	0.04157
Average					0.0060	0.0085

### **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<sup>0</sup>C at Full Scale (pH 0-14). The pH was reported at 20<sup>0</sup>C and 25<sup>0</sup>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: 11/10/2021 and 11/15/2021

Titration system used: Open cell

Batch 178, CRM #1118 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.

Batch 178, CRM #1058 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.

Batch 178, CRM #512 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.

Batch 178, CRM #757 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.

On 11/10/2021 CRM #1118 was analyzed before sample analysis on System 1 and 2.

On 11/10/2021 CRM #1058 was analyzed after sample analysis on System 1 and 2.

On 11/15/2021 CRM #512 was analyzed before and after sample analysis on System 1.

On 11/15/2021 CRM #757 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	ΔCRM
1	11/10/2021	11:55:13	1118	2192.03	24.50
1	11/10/2021	18:38:40	1058	2215.33	1.20
1	11/15/2021	08:41:17	512	2195.12	21.41
1	11/15/2021	12:06:56	512	2194.77	21.76
2	11/10/2021	11:55:04	1118	2190.95	25.58
2	11/10/2021	18:37:29	1058	2216.49	0.04
2	11/15/2021	08:39:01	757	2200.10	16.43
2	11/15/2021	11:43:32	757	2202.22	14.31

**Reproducibility:** (# samples and average difference): 7 duplicate samples were collected with an average difference of 6.89 (2.32 – 16.72) and an average STDEV of 4.87 (1.64 – 11.82).

Station	Sample ID	TA	Average	STDEV	Difference
		(umol/kg)			
33	3301012	2392.98			
33	3301012	2388.31	2390.6	3.30	4.66
BG2	BG201012	2365.36			
BG2	BG201012	2360.54	2362.9	3.40	4.81
AMI5	AMI50101	2412.83			
AMI5	AMI50101	2410.51	2411.7	1.64	2.32
AMI1	AMI101012	2336.39			
AMI1	AMI101012	2344.39	2340.4	5.65	8.00
41	4101012	2506.26			
41	4101012	2503.67	2505.0	1.83	2.58
56	5601012	2428.21			
56	5601012	2419.06	2423.6	6.47	9.14



65	6501012	2232.94			
65	6501012	2249.66	2241.3	11.82	16.72
Average				4.87	6.89

### **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.

Corresponding UW pCO<sub>2</sub> data can be found at the following website  
<http://www.aoml.noaa.gov/ocd/ocdweb/occ.html>

### **Nutrients:**

**Analysis Date:** 10/21/2021 and 11/04/2021

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,  $\beta$ -molybdosilicic acid was formed by the reaction of the silicate contained in the sample with molybdate in acidic solution. The  $\beta$ -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**

Nitrate + Nitrite – gain was too high and results were unusable and marked as -999 for sample bottles 1-13.

### **Chlorophyll and Phaeophytin:**

**Analysis Date:** 11/02/2021 and 11/18/2021

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.