

**Cruise:** WS21338

**Ship:** R/V Walton Smith

**Expo Code:** 33WA20211204

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

**Funding Project ID:** 21403

**Dates:** December 4<sup>th</sup> – December 10<sup>th</sup>, 2021

**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, 82 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, 82 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, 82 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	02/23/2022	1952.65	1959.56	6.91	23.0	7
AOML 5	02/28/2022	2025.17	2027.64	2.47	12.0	7
AOML 6	02/23/2022	1952.65	1962.68	10.03	12.0	9
AOML 6	02/28/2022	1952.65	1955.09	2.44	12.0	10

Analysis date: 02/23/2022

Coulometer used: DICE-CM50170-AOML 5

Blanks: 23.0 counts/min

CRM # 632 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 6.91 μmol/kg (1959.56 μmol/kg).

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

Analysis date: 02/28/2022

Coulometer used: DICE-CM50170-AOML 5

Blanks: 12.0 counts/min

CRM # 161 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 2.47 μmol/kg (2027.64 μmol/kg).

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

Analysis date: 02/23/2022

Coulometer used: DICE-CM50170-AOML 6

Blanks: 12.0 counts/min

CRM # 1185 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 10.03 μmol/kg (1962.68 μmol/kg).

Average run time, minimum run time, maximum run time: 9, 7 and 13 min.

Analysis date: 02/28/2022

Coulometer used: DICE-CM50170-AOML 6

Blanks: 12.0 counts/min

CRM # 333 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 2.44 μmol/kg (1955.09 μmol/kg).

Average run time, minimum run time, maximum run time: 10, 8 and 14 min.

**Reproducibility:** (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.84 (0.05-2.44) and average STDEV of 0.60 (0.04-1.72).

Station #	Sample Bottle #	Sample ID	DIC (μmol/kg)	Average	STDEV	Difference
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KW2	15	KW20101	2032.5				
KW2	16	KW20101	2035.0	2033.8	1.72	2.44	
BG1	26	BG10112	2085.2				
BG1	27	BG10112	2084.5	2084.9	0.46	0.65	
AMI5	36	AMI50112	2096.9				
AMI5	37	AMI50112	2096.7	2096.8	0.12	0.16	
TB10	39	TB10112	2162.0				
TB10	40	TB10112	2161.9	2161.9	0.04	0.05	
CAL10	92	CAL10112	2192.4				
CAL10	93	CAL10112	2191.4	2191.9	0.75	1.07	
45	179	450112	2118.9				
45	180	450112	2118.4	2118.7	0.32	0.45	
58	190	580112	2097.8				
58	191	580112	2098.9	2098.3	0.78	1.10	
Average					0.60	0.84	

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

### **pH:**

Analysis date: 02/23/2022 and 02/28/2022  
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 (°C)
20112	1	35.837	19.945
MR0101	2	36.245	19.950
MR0112	3	36.281	19.960
UK-OFF0000	4	36.263	19.954
UK-MID0000	5	36.154	19.951
UK-IN0000	6	35.936	19.947
70112	7	35.501	19.955
100101	8	35.783	19.954
160112	9	35.374	19.950
WS0101	10	36.192	19.947
WS0112	13	36.172	19.946
21-LK0101	11	36.137	19.950
21-LK0112	12	35.931	19.952
KW10112	14	36.546	19.939
KW20101	15	36.475	19.934
KW20101	16	36.475	19.941
KW20112	17	36.375	19.941
KW40101	18	36.329	19.945
KW40112	19	36.191	19.937
300101	20	36.238	19.951
BG40101	21	36.195	19.943
BG40112	22	36.226	19.942
BG30101	23	35.670	19.944
BG30112	24	34.966	19.956
BG20112	25	34.206	19.958
BG10112	26	33.765	19.959
BG10112	27	33.765	19.956
V10112	28	34.658	19.958
V50101	29	36.172	19.953
V50112	30	36.211	19.939
V90101	31	36.188	19.957
V90112	32	36.197	19.955
AMI90101	33	36.086	19.955
AMI90112	34	36.188	19.947
AMI50101	35	35.822	19.937
AMI50112	36	36.037	19.944
AMI50112	37	36.037	19.949
AMI10112	38	34.039	19.944
TB10112	39	33.343	19.942
TB10112	40	33.343	19.955

300112	81	36.243	19.920
310112	82	35.949	19.931
330112	83	34.876	19.935
CAL50101	84	35.614	19.927
CAL50112	85	35.550	19.932
CAL40101	86	35.425	19.933
CAL40112	87	35.369	19.940
CAL30101	88	34.789	19.946
CAL30112	89	34.480	19.933
CAL20101	90	34.533	19.936
CAL20112	91	33.692	19.937
CAL10112	92	31.809	19.936
CAL10112	93	31.809	19.968
RP10112	94	34.620	19.959
RP20112	95	34.474	19.961
RP30112	96	34.969	19.962
RP40101	97	36.214	19.981
RP40112	98	36.155	19.969
GP50101	99	36.226	19.972
GP50112	100	36.194	19.981
TB40101	174	35.500	19.922
TB40112	175	35.111	19.924
TB100101	176	35.754	19.938
TB100112	177	36.162	19.938
410112	178	35.093	19.942
450112	179	35.236	19.935
450112	180	35.236	19.943
490000	181	32.156	19.948
510112	182	33.817	19.939
540112	183	30.046	19.933
550112	184	31.086	19.968
560112	185	31.778	19.964
570112	186	32.682	19.957
57.10112	187	34.138	19.970
57.20112	188	35.403	19.961
57.30112	189	35.787	19.980
580112	190	35.731	19.983
580112	191	35.731	19.972
600112	192	34.568	19.972
650112	193	31.908	19.975
680112	194	32.897	19.945

700000                      195                      33.005                      19.948

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**Reproducibility:** pH @ 20<sup>0</sup>C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.00387 (0.00012 – 0.01707) and an average STDEV of 0.00274 (0.00009 – 0.01207).

Instrument	Sample ID	Bottle #	pH @20 <sup>0</sup> C	Average	STDEV	Difference
HP Agilent 8453	KW20101	15	8.083157			
HP Agilent 8453	KW20101	16	8.100230	8.09169	0.01207	0.01707
HP Agilent 8453	BG10112	26	8.010127			
HP Agilent 8453	BG10112	27	8.012144	8.01114	0.00143	0.00202
HP Agilent 8453	AMI50112	36	8.099556			
HP Agilent 8453	AMI50112	37	8.095448	8.09750	0.00290	0.00411
HP Agilent 8453	TB10112	39	7.986376			
HP Agilent 8453	TB10112	40	7.988861	7.98762	0.00176	0.00248
HP Agilent 8453	CAL10112	92	7.913859			
HP Agilent 8453	CAL10112	93	7.913372	7.91362	0.00034	0.00049
HP Agilent 8453	450112	179	8.030922			
HP Agilent 8453	450112	180	8.030136	8.03053	0.00056	0.00079
HP Agilent 8453	580112	190	8.057904			
HP Agilent 8453	580112	191	8.058027	8.05797	0.00009	0.00012
Average					0.00274	0.00387

**Reproducibility:** pH @ 25<sup>0</sup>C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.00383 (0.00012 – 0.01692) and an average STDEV of 0.00271 (0.00009 – 0.01197).

Instrument	Sample ID	Bottle #	pH @25 <sup>0</sup> C	Average	STDEV	Difference
HP Agilent 8453	KW20101	15	8.007722			
HP Agilent 8453	KW20101	16	8.024646	8.01618	0.01197	0.01692
HP Agilent 8453	BG10112	26	7.935450			
HP Agilent 8453	BG10112	27	7.937434	7.93644	0.00140	0.00198

HP Agilent 8453	AMI50112	36	8.023935				
HP Agilent 8453	AMI50112	37	8.019859	8.02190	0.00288	0.00408	
HP Agilent 8453	TB10112	39	7.911930				
HP Agilent 8453	TB10112	40	7.914378	7.91315	0.00173	0.00245	
HP Agilent 8453	CAL10112	92	7.840418				
HP Agilent 8453	CAL10112	93	7.839940	7.84018	0.00034	0.00048	
HP Agilent 8453	450112	179	7.955946				
HP Agilent 8453	450112	180	7.955166	7.95556	0.00055	0.00078	
HP Agilent 8453	580112	190	7.982659				
HP Agilent 8453	580112	191	7.982781	7.98272	0.00009	0.00012	
Average					0.00271	0.00383	

### **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: 02/24/2022 and 03/02/2022

Titration system used: Open cell

Batch 178, CRM #632 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.

Batch 178, CRM #333 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.

Batch 178, CRM #1185 Salinity = 33.782, cert. TA = 2216.53 µmol/kg.

Batch 194, CRM #161 Salinity = 33.361, cert. TA = 2169.83 µmol/kg.

On 02/24/2022 CRM #632 was analyzed before and after sample analysis on System 1.

On 02/24/2022 CRM #1185 was analyzed before and after sample analysis on System 2.

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.

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	02/24/2022	11:01:36	632	2204.14	12.39
1	02/24/2022	16:56:57	632	2204.41	12.43
1	03/02/2022	10:41:17	333	2213.93	2.60
1	03/02/2022	18:43:38	333	2215.99	0.54
2	02/24/2022	10:53:04	185	2222.69	6.16
2	02/24/2022	16:58:39	185	2221.11	4.58
2	03/02/2022	10:37:44	161	2169.10	0.67
2	03/02/2022	18:58:33	161	2169.59	0.24

**Reproducibility:** (# samples and average difference): 7 duplicate samples were collected with an average difference of 4.74 (0.08 – 14.04) and an average STDEV of 3.35 (0.60 – 9.93).

Station	Sample ID	Sample Bottle #	TA (µmol/kg)	Average	STDEV	Difference
KW2	KW20101	15	2322.7			
KW2	KW20101	16	2323.6	2323.2	0.60	0.85
BG1	BG10112	26	2305.4			
BG1	BG10112	27	2319.5	2312.4	9.93	14.04
AMI5	AMI50112	36	2371.6			
AMI5	AMI50112	37	2377.0	2374.3	3.84	5.42
TB1	TB10112	39	2367.5			
TB1	TB10112	40	2377.5	2372.5	7.07	10.00
CAL1	CAL10112	92	2387.9			
CAL1	CAL10112	93	2386.5	2387.2	1.02	1.44
45	450112	179	2374.1			
45	450112	180	2375.5	2374.8	0.95	1.34



58	580112	190	2373.8			
58	580112	191	2373.7	2373.7	0.06	0.08
Average					3.35	4.74

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

**Nutrients:**

**Analysis Date:** 12/17/2021

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,  $\beta$ -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).

### **Chlorophyll and Phaeophytin:**

**Analysis Date:** 01/06/2022

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  $-80^{\circ}\text{C}$  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.