

**Cruise:** WS19322  
**Ship:** R/V Walton Smith  
**Dates:** November 18<sup>th</sup> – September 24<sup>th</sup>, 2019  
**Expocode:** 33WA20191118  
**Chief Scientist:** Dr. Chris Kelble  
**Equipment:** CTD and Flow-Through (FT)  
**Total number of stations:** 34  
**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/rosette and Flow-Through system onboard the R/V Walton Smith by Ian Smith and Charles Featherstone. The date and time listed in the data file are UTC when each sample bottle was collected.

**DIC:**

34 locations, 59 samples each 500-ml, 6 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:**

34 locations, 59 samples each 500-ml, 6 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:**

34 locations, 59 samples each 500-ml, 6 duplicate samples.  
 Sample\_ID#: 90101, etc.; Station, cast number and Niskin bottle number  
 PI: Dr. Rik Wanninkhof  
 Analyzed by: Charles Featherstone and Patrick Mears

**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	12/03/2019	2017.88	2022.24	4.36	20.0	9
AOML 5	12/04/2019	2017.88	2017.92	0.04	20.0	7

AOML 6	12/03/2019	2017.88	2022.03	4.15	12.0	7
AOML 6	12/04/2019	2017.88	2023.09	5.21	12.0	10

Analysis date: 12/03/2019

Coulometer used: DICE–CM5011-AOML 5

Blanks: 20.0 counts/min

CRM # 724 was used and with an assigned value of (includes both DIC and salinity):

Batch 150, c: 2017.88  $\mu\text{mol/kg}$ , S: 33.343

CRM values measured: AOML 5: offset 4.36  $\mu\text{mol/kg}$  (2022.24  $\mu\text{mol/kg}$ ).

Average run time, minimum run time, maximum run time: 9, 8 and 12 min.

Analysis date: 12/04/2019

Coulometer used: DICE–CM5011-AOML 5

Blanks: 30.0 counts/min

CRM # 413 was used and with an assigned value of (includes both DIC and salinity):

Batch 150, c: 2017.88  $\mu\text{mol/kg}$ , S: 33.343

CRM values measured: AOML 5: offset 0.04  $\mu\text{mol/kg}$  (2017.92  $\mu\text{mol/kg}$ ).

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

Analysis date: 12/03/2019

Coulometer used: DICE–CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 1037 was used and with an assigned value of (includes both DIC and salinity):

Batch 150, c: 2017.88  $\mu\text{mol/kg}$ , S: 33.343

CRM values measured: AOML 6: offset 4.15  $\mu\text{mol/kg}$  (2022.03  $\mu\text{mol/kg}$ ).

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

Analysis date: 12/04/2019

Coulometer used: DICE–CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 971 was used and with an assigned value of (includes both DIC and salinity):

Batch 150, c: 2017.88  $\mu\text{mol/kg}$ , S: 33.343

CRM values measured: AOML 6: offset 5.21  $\mu\text{mol/kg}$  (2023.09  $\mu\text{mol/kg}$ ).

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

**Reproducibility:** (# samples and average difference): 6 duplicate samples were collected with an average difference 0.75  $\mu\text{mol/kg}$  (0.14 – 1.46) and an average STDEV of 0.53 (0.10 – 1.03).

Station	Sample ID	DIC		Difference	STDEV
		$\mu\text{mol/kg}$	Average		
22.5	11	2041.71			
22.5	12	2040.40	2041.05	1.31	0.92
CAL5	27	2054.23			
CAL5	28	2054.09	2054.16	0.14	0.10

CAL1	32	2193.05			
CAL1	33	2191.58	2192.32	1.46	1.03
RP3	40	2044.57			
RP3	41	2043.81	2044.19	0.76	0.54
V5	55	2054.27			
V5	56	2053.98	2054.12	0.29	0.20
57.2	78	2044.67			
57.2	79	2044.15	2044.41	0.52	0.37
Average				0.75	0.53

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 on AOML 6 were analyzed on a new coulometer 5017-O from UIC. Inc.

### **pH:**

Analysis date: 12/03/2019 and 12/04/2019

A CRM was analyzed before sample analysis.

12/03/2019, Batch 150, CRM #790, pH = 7.9378

12/04/2019, Batch 150, CRM #662, pH = 7.9386

Spectrophotometer used: HP Agilent 8453

### **Temperature and salinity of pH samples analyzed**

<b>Station</b>	<b>Sample ID</b>	<b>Bottle #</b>	<b>Temperature °C</b>	<b>Salinity</b>
CRM150_790	CRM150_790	790	20.035	33.343
CRM150_662	CRM150_662	662	20.028	33.343
6.5	1	1	20.062	36.178
MR	2	2	20.060	36.207
MR	3	3	20.065	36.286

UK-OFF	4	4	20.069	36.327
UK-MID	5	5	20.068	36.215
UK-IN	6	6	20.061	36.247
21-LK	7	7	20.072	36.310
21-LK	8	8	20.063	36.310
WS	9	9	20.074	36.313
WS	10	10	20.068	36.297
22.5	11	11	20.064	36.345
22.5	12	12	20.073	36.345
KW3	13	13	20.059	36.898
30	14	14	20.054	36.628
30	15	15	20.049	36.610
33	16	16	20.042	35.526
33	17	17	20.054	35.524
CAL6	21	21	20.070	36.370
CAL6	22	22	20.074	36.369
CAL5	26	26	20.069	35.520
CAL5	27	27	20.066	35.520
CAL5	28	28	20.072	35.520
CAL3	29	29	20.061	34.750
CAL3	30	30	20.064	34.740
CAL1	31	31	20.070	32.800
CAL1	32	32	20.060	32.780
CAL1	33	33	20.069	32.780
RP1	34	34	20.062	34.810
RP1	35	35	20.059	34.280
RP2	36	36	20.039	35.010
RP2	37	37	20.047	34.010
RP2	38	38	20.052	34.790
RP3	39	39	20.053	35.525
RP3	40	40	20.044	35.523
RP3	41	41	20.045	35.523
RP4	42	42	20.058	35.890
RP4	43	43	20.064	35.891
GP5	44	44	20.070	35.947
GP5	45	45	20.044	35.949
BG4	46	46	20.049	35.926
BG4	47	47	20.051	35.926
BG3	48	48	20.051	35.708
BG3	49	49	20.051	35.711

BG2	50	50	20.049	35.397
BG2	51	51	20.043	35.397
V1	52	52	20.054	33.808
V1	53	53	20.045	33.812
V5	54	54	20.058	35.630
V5	55	55	20.044	35.630
V5	56	56	20.049	35.630
V9	57	57	20.054	35.890
V9	58	58	20.072	35.890
TB10	62	62	20.055	36.025
TB10	63	63	20.056	36.024
TB6	70	70	20.046	31.487
41	71	71	20.055	35.110
41	72	72	20.062	35.120
54	73	73	20.057	31.160
54	199	199	20.053	31.160
55	74	74	20.047	32.780
56	75	75	20.045	33.740
57	76	76	20.051	34.400
57.1	77	77	20.038	35.720
57.2	78	78	20.038	36.020
57.2	79	79	20.048	36.020
57.3	80	80	20.053	35.819

**Reproducibility:** (# samples and average difference): 6 duplicate samples were collected with an average difference 0.0013 (0.0002– 0.0021) and an average STDEV of 0.0009 (0.0001 – 0.0015) .

Instrument	Sample ID	Bottle #	pH @20deeg C	Average	STDEV	Difference
HP Agilent 8453	2250000	11	8.1607			
HP Agilent 8453	2250000	12	8.1586	8.1597	0.0015	0.0021
HP Agilent 8453	CAL50103	27	8.1155			
HP Agilent 8453	CAL50103	28	8.1142	8.1149	0.0009	0.0012
HP Agilent 8453	CAL10102	32	8.0634			
HP Agilent 8453	CAL10102	33	8.0636	8.0635	0.0001	0.0002
HP Agilent 8453	RP30103	40	8.1193			
HP Agilent 8453	RP30103	41	8.1188	8.1191	0.0003	0.0004

HP Agilent 8453	V50103	55	8.1277			
HP Agilent 8453	V50103	56	8.1256	8.1266	0.0015	0.0021
HP Agilent 8453	5720102	78	8.0876			
HP Agilent 8453	5720102	79	8.0860	8.0868	0.0011	0.0016
Average					0.0009	0.0013

### **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 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: 12/05/2019 and 12/06/2019

Titration system used: Open cell

Batch 150, CRM #413 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

Batch 150, CRM #343 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

Batch 150, CRM #662 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

Batch 150, CRM #489 Salinity = 33.343, cert. TA = 2214.71 μmol/kg.

On 12/05/2019 CRM #413 was analyzed before and after sample analysis on System 1.

On 12/06/2019 CRM #343 was analyzed before and after sample analysis on System 1.

On 12/05/2019 CRM #662 was analyzed before and after sample analysis on System 2.

On 12/06/2019 CRM #489 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	12/05/2019	10:41:39	413	2216.16	1.45
1	12/05/2019	17:52:59	413	2220.38	5.67

1	12/06/2019	10:13:47	343	2213.49	1.25
1	12/06/2019	18:32:02	343	2213.30	1.41
2	12/05/2019	10:45:56	662	2204.22	10.49
2	12/05/2019	17:43:05	662	2209.48	4.62
2	12/06/2019	09:41:55	489	2211.44	3.27
2	12/06/2019	18:10:35	489	2204.27	9.83

**Reproducibility:** (# samples and average difference): 6 duplicate samples were collected with an average difference 2.73 (0.01 – 4.93) and an average STDEV of 1.93 (00.01 – 3.49).

Station	Sample ID	TA ( $\mu\text{mol/kg}$ )	Average	Difference	STDEV
22.5	11	2382.86	2385.04	4.36	3.08
22.5	12	2387.22			
CAL5	27	2359.29	2361.33	4.08	2.88
CAL5	28	2363.37			
CAL1	32	2470.02	2470.03	0.01	0.01
CAL1	33	2470.03			
RP3	40	2357.27	2359.74	4.93	3.49
RP3	41	2362.20			
V5	55	2358.16	2358.52	0.72	0.51
V5	56	2358.88			
57.2	78	2339.58	2338.45	2.25	1.59
57.2	79	2337.33			
			Average	2.73	1.93

### **Remarks**

### **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 bottle number for the discrete samples.

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:** November 26<sup>th</sup>, 2019 and December 3<sup>rd</sup>, 2019

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).

#### UPDATE:

Between March and June of 2021, all of the data for the discrete samples was put into a uniform format. The supporting information was checked for accuracy, especially the expocode, date, time, and positions.

Additionally, pH results were recalculated to 20 and 25 degrees Celsius.