**Cruise:** WS19322
**Ship:** R/V Walton Smith
**Expo Code:** 33WA20191118
**Dates:** November 18th – September 24th, 2019
**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 µmol/kg, S: 33.343
CRM values measured:  AOML 5: offset 4.36 µmol/kg (2022.24 µmol/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 µmol/kg, S: 33.343
CRM values measured:  AOML 5: offset 0.04 µmol/kg (2017.92 µmol/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 µmol/kg, S: 33.343
CRM values measured:  AOML 6: offset 4.15 µmol/kg (2022.03 µmol/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 µmol/kg, S: 33.343
CRM values measured:  AOML 6: offset 5.21 µmol/kg (2023.09 µmol/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 µmol/kg (0.14 – 1.46) and an average STDEV of 0.53 (0.10 – 1.03).

| Station | Sample ID | DIC µmol/kg | Average | Difference | STDEV |
|---|---|---|---|---|---|
| 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 HgCl2 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 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

| Station     | Sample ID   | Bottle # | Temperature $^0$C | Salinity |
|-------------|-------------|----------|-------------------|----------|
| 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 0.00134 (0.00006– 0.00223) and an average STDEV of 0.00095 (0.00004 – 0.00157).

| Station | Sample ID | pH Value | Average | Difference | STDEV |
|---|---|---|---|---|---|
| 22.5 | 11 | 8.15972 | 8.1586 | 0.00223 | 0.00157 |
| 22.5 | 12 | 8.15750 | | | |
| | | | | | |
| CAL5 | 27 | 8.11446 | 8.1138 | 0.00133 | 0.00094 |
| CAL5 | 28 | 8.11313 | | | |
| | | | | | |
| CAL1 | 32 | 8.06248 | 8.0625 | 0.00006 | 0.00004 |
| CAL1 | 33 | 8.06254 | | | |
| | | | | | |
| RP3 | 40 | 8.11862 | 8.1184 | 0.00046 | 0.00032 |

| | | | | | |
|---|---|---|---|---|---|
| RP3 | 41 | 8.11816 | | | |
| V5 | 55 | 8.12704 | 8.1259 | 0.00221 | 0.00156 |
| V5 | 56 | 8.12483 | | | |
| 57.2 | 78 | 8.08700 | 8.0861 | 0.00175 | 0.00124 |
| 57.2 | 79 | 8.08525 | | | |
| | | | Average | 0.00134 | 0.00095 |

## 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 $25^0$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: 12/05/2019 and 12/06/2019
Titration system used: Open cell
Batch 150, CRM #413 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #343 Salinity = 33.343, cert. TA = 2214.71µmol/kg.

Batch 150, CRM #662 Salinity = 33.343, cert. TA = 2214.71µmol/kg.
Batch 150, CRM #489 Salinity = 33.343, cert. TA = 2214.71µmol/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 | $|\Delta CRM|$ |
|---|---|---|---|---|---|
| 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 (μmol/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 pCO2 data can be found at the following website
http://www.aoml.noaa.gov/ocd/ocdweb/occ.html

**Nutrients:**
**Analysis Date:** November 26th, 2019 and December 3rd, 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, 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).