

Cruise: WS23259

Ship: R/V Walton Smith

Expo Code: 33WA20230916

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

Funding Project ID: 21403

Dates: September 16th - September 22nd, 2023

Chief Scientist: Ian Smith

Equipment: CTD-Niskin and Flow-Through (FT)

Total number of stations: 54

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, Rachel Cohn and Tyler Christian. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:

54 locations, 80 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, Patrick Mears and Alison MacLeod

pH:

54 locations, 80 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, Patrick Mears and Alison MacLeod

Talk:

54 locations, 80 samples each 500-ml, 7 duplicate samples.

Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number

PI: Dr. Rik Wanninkhof

Analyzed by Patrick Mears and Alison MacLeod

Sample Analysis

DIC:

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
AOML 5	11/1/2023	2028.23	2031.98	3.75	21	9
AOML 5	11/6/2023	2028.23	2031.85	3.62	30	8
AOML 6	11/1/2023	2028.23	2030.52	2.29	20	12
AOML 6	11/6/2023	2028.23	2030.58	2.35	16	11

Analysis date: 11/1/2023

Coulometer used: DICE–CM5017O-AOML 5

Blanks: 21.0 counts/min

CRM # 423 was used and with an assigned value of (includes both DIC and salinity):

Batch 204, c: 2028.23 $\mu\text{mol/kg}$, S: 33.494

CRM values measured: AOML 5: offset 3.75 $\mu\text{mol/kg}$ (2031.98 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 9, 7 and 11 min.

Analysis date: 11/6/2023

Coulometer used: DICE–CM5017O-AOML 5

Blanks: 30.0 counts/min

CRM # 1014 was used and with an assigned value of (includes both DIC and salinity):

Batch 204, c: 2028.23 $\mu\text{mol/kg}$, S: 33.494

CRM values measured: AOML 5: offset 3.62 $\mu\text{mol/kg}$ (2031.85 $\mu\text{mol/kg}$).

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

Analysis date: 11/1/2023

Coulometer used: DICE–CM5017O-AOML 6

Blanks: 19.9 counts/min

CRM # 022 was used and with an assigned value of (includes both DIC and salinity):

Batch 204, c: 2028.23 $\mu\text{mol/kg}$, S: 33.494

CRM values measured: AOML 5: offset 2.29 $\mu\text{mol/kg}$ (2030.52 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 12, 9 and 17 min.

Analysis date: 11/6/2023

Coulometer used: DICE–CM5017O-AOML 6

Blanks: 16.0 counts/min

CRM # 777 was used and with an assigned value of (includes both DIC and salinity):

Batch 204, c: 2028.23 $\mu\text{mol/kg}$, S: 33.494

CRM values measured: AOML 6: offset 2,35 $\mu\text{mol/kg}$ (2030.58 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 11, 9 and 14 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.47 (0.93-2.94) and average STDEV of 1.04 (0.66-2.08).

Sample ID	DIC (μmol/kg)	Average	STDEV	Difference
100112	1883.0	1884.1	1.64	2.31
100112	1885.3			
KW40112	2032.6	2033.2	0.93	1.32
KW40112	2033.9			
310112	1972.5	1971.7	1.04	1.47
310112	1971.0			
V10112	2061.8	2062.3	0.72	1.02
V10112	2062.8			
TB10112	2004.7	2005.1	0.66	0.93
TB10112	2005.6			
450112	1773.5	1772.9	0.82	1.16
450112	1772.3			
57.20112	1986.9	1985.5	2.08	2.94
57.20112	1984.0			
Average			1.04	1.47

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.

pH:

Analysis date: 11/1/2023 and 11/6/2023

No CRMs were 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	35.288	20.021
MR0101	2	35.825	20.018
MR0112	3	35.154	20.031
UK_OFF0000	4	34.988	20.032
UK_MID0000	5	34.945	20.039
UK_IN0000	6	35.024	20.037
70112	7	35.498	20.036
100112	8	36.914	20.034
100112	9	36.914	20.037
160112	10	37.415	20.038
21/LK0101	11	35.816	20.036
21/LK0112	12	34.923	20.029
WS0101	13	35.030	20.036
WS0112	14	34.907	20.041
KW10112	15	34.642	20.043
KW20101	16	34.816	20.038
KW20112	17	34.705	20.041
KW40101	18	35.424	20.04
KW40112	19	35.419	20.04
KW40112	20	35.419	20.048
300101	21	35.610	20.061
300112	22	35.635	20.056
310112	23	37.166	20.065
310112	24	37.166	20.066
330112	25	37.194	20.061
CAL10112	26	35.739	20.071
CAL20112	27	36.402	20.07
CAL30101	28	36.960	20.077
CAL30112	29	36.859	20.067
CAL40101	30	37.126	20.063

CAL40112	31	37.126	20.074
CAL50101	32	36.892	20.065
CAL50112	33	36.893	20.073
RP10112	34	36.007	20.077
RP20112	35	36.246	20.083
RP30112	36	36.431	20.089
BG10112	37	34.365	20.068
BG20112	38	35.688	20.068
BG30101	39	36.589	20.068
BG30112	40	36.570	20.066
RP40101	81	36.643	20.023
RP40112	82	36.620	20.026
BG40101	83	36.691	20.037
BG40112	84	36.628	20.039
GP50101	85	36.412	20.029
GP50112	86	36.432	20.028
V90101	87	36.358	20.035
V90112	88	36.323	20.027
V50101	89	36.720	20.033
V50112	90	36.718	20.03
V10112	91	36.431	20.033
V10112	92	36.431	20.037
AMI10112	93	36.696	20.037
AMI50101	94	37.020	20.029
AMI50112	95	37.014	20.037
AMI90101	96	36.450	20.039
AMI90112	97	36.179	20.036
TB100101	98	36.887	20.042
TB100112	99	36.893	20.041
TB40101	100	37.051	20.063
TB40112	173	37.052	20.061
TB10112	174	36.339	20.072
TB10112	175	36.339	20.058
410112	176	36.731	20.06
450112	177	38.262	20.061
450112	178	38.262	20.064
490112	179	33.818	20.064
510112	180	37.430	20.078
540112	181	35.604	20.069
550112	182	35.900	20.066
560112	183	37.624	20.074

570112	184	37.469	20.077
57.10112	185	37.297	20.067
57.20112	186	37.779	20.079
57.20112	187	37.779	20.078
57.30112	188	37.441	20.079
580112	189	36.396	20.078
600112	190	37.235	20.075
650112	191	37.999	20.072
680112	192	37.827	20.068

Reproducibility: pH @ 20°C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0022 (0.000– 0.012) and an average STDEV of 0.0015 (0.000 – 0.008).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	100112	8	8.111	8.105	0.008	0.012
HP Agilent 8453	100112	9	8.100			
HP Agilent 8453	KW40112	19	8.149	8.151	0.003	0.004
HP Agilent 8453	KW40112	20	8.153			
HP Agilent 8453	310112	23	8.106	8.104	0.002	0.003
HP Agilent 8453	310112	24	8.103			
HP Agilent 8453	V10112	91	8.020	8.020	0.001	0.001
HP Agilent 8453	V10112	92	8.021			
HP Agilent 8453	TB10112	174	8.087	8.088	0.001	0.001
HP Agilent 8453	TB10112	175	8.089			
HP Agilent 8453	450112	177	8.010	8.010	0.000	0.000
HP Agilent 8453	450112	178	8.010			
HP Agilent 8453	57.20112	186	8.098	8.096	0.003	0.004
HP Agilent 8453	57.20112	187	8.094			
Average					0.0015	0.0022

Reproducibility: pH @ 25⁰C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.0022 (0.000-0.012) and an average STDEV of 0.0015 (0.000-0.008).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	100112	8	8.036	8.030	0.008	0.012
HP Agilent 8453	100112	9	8.024			
HP Agilent 8453	KW40112	19	8.073	8.075	0.003	0.004
HP Agilent 8453	KW40112	20	8.077			
HP Agilent 8453	310112	23	8.030	8.029	0.002	0.003
HP Agilent 8453	310112	24	8.027			
HP Agilent 8453	V10112	91	7.945	7.945	0.001	0.001
HP Agilent 8453	V10112	92	7.946			
HP Agilent 8453	TB10112	174	8.012	8.013	0.001	0.001
HP Agilent 8453	TB10112	175	8.013			
HP Agilent 8453	450112	177	7.935	7.935	0.000	0.000
HP Agilent 8453	450112	178	7.935			
HP Agilent 8453	57.20112	186	8.023	8.021	0.003	0.004
HP Agilent 8453	57.20112	187	8.019			
Average					0.0015	0.0022

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 20⁰C at Full Scale (pH 0-14). The pH was reported at 20⁰C and 25⁰C.

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: 11/2/2023, 11/3/2023 and 11/7/2023

Titration system used: Open cell

Batch 204, CRM #423 Salinity = 33.494, cert. TA = 2202.12 $\mu\text{mol/kg}$.

Batch 204, CRM #022 Salinity = 33.494, cert. TA = 2202.12 $\mu\text{mol/kg}$.

Batch 204, CRM #777 Salinity = 33.494, cert. TA = 2202.12 $\mu\text{mol/kg}$.

Batch 204, CRM #542 Salinity = 33.494, cert. TA = 2202.12 $\mu\text{mol/kg}$.

Batch 204, CRM #1014 Salinity = 33.494, cert. TA = 2202.12 $\mu\text{mol/kg}$.

On 11/2/2023 CRM #423 was analyzed before and after sample analysis on System 1.

On 11/3/2023 CRM #022 was analyzed before and after sample analysis on System 1.

On 11/7/2023 CRM #777 was analyzed before and after sample analysis on System 1.

On 11/3/2023 CRM #542 was analyzed before and after sample analysis on System 2.

On 11/7/2023 CRM #1014 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 2 cells. The following table shows the CRM measurements for each day and cell.

Cell System	Date	Time	Bottle #	TA	$ \Delta\text{CRM} $
1	11/2/2023	09:37:01	423	2207.9	5.78
1	11/2/2023	18:59:17	423	2206.83	4.71
1	11/3/2023	08:20:51	22	2199.94	-2.18
1	11/3/2023	12:32:33	22	2205.26	3.14
1	11/7/2023	10:32:34	777	2200.61	-1.51
1	11/7/2023	18:27:16	777	2206.23	4.11
2	11/3/2023	09:29:20	542	2204.39	2.27
2	11/3/2023	12:16:05	542	2205.73	3.61
2	11/7/2023	09:45:47	1014	2204.69	2.57
2	11/7/2023	18:11:41	1014	2207.01	4.89

Reproducibility: (# samples and average difference): 7 duplicate samples were collected, three duplicate pairs were discarded due to one being significantly different from calculated TA values using the other carbonate parameters. The average difference of 8.26(1.81 – 11.62) and an average STDEV of 5.84 (1.28 – 8.21).

Sample ID	Bottle #	TA umol/kg	Average	STDEV	Difference
KW40112	19	2372.45	2367.52	6.98	9.87
KW40112	20	2362.58			
V10112	91	2334.37	2328.56	8.21	11.62
V10112	92	2322.75			
TB10112	174	2293.41	2298.29	6.90	9.75
TB10112	175	2303.16			
450112	177	2012.33	2011.43	1.28	1.81
450112	178	2010.52			
Average				5.84	8.26

Remarks

The average of the CRMs were used to adjust the values of the samples for each day.

The measured TA value for one of the duplicates with Sample ID 57.20112 was determined to be a bad measurement through comparison with other parameters and is not reported.

The measured TA value for one of the duplicates with Sample ID 100112 was determined to be a bad measurement through comparison with other parameters and is not reported.

The measured TA value for the duplicates from station 31 were determined to be a bad measurement through comparison with other parameters and is not reported in the statistics, and the average value is reported as a flag 3 in the dataset.

Samples taken around Shark River, (Stations 54, 55, 56, 57) have high TA values that are a consistent feature present in past cruises and should be considered real features.

The TA system 2 was not running well on 11/2/2023 and was not used to run samples. Both TA systems show problems with instrumentation in the analysis.

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: To be added at a later date

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 flow 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

No remarks.

Chlorophyll and Phaeophytin:

Analysis Date: To be added at a later date

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.