Cruise: WS22337
Ship: R/V Walton Smith
Expo Code: 33WA20221203
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 3rd – December 9th 2022
Chief Scientist: Ian Smith
Equipment: CTD-Niskin and Flow-Through (FT)
Total number of stations: 60
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 Charles Featherstone and Ian Smith. The date and time listed in the data file are UTC when each sample bottle was collected.

DIC:
60 locations, 89 samples each 500-ml, 8 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:
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Sample_ID#: 90101, etc.; Station, cast number and Niskin bottle number
PI: Dr. Rik Wanninkhof
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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	01/23/2023	2024.96	2030.78	5.82	12	8
AOML 5	01/25/2023	2024.96	2027.98	3.02	26	8
AOML 5	02/06/2023	2024.96	2028.58	3.63	29	9
AOML 6	02/06/2023	2024.96	2027.42	2.46	23	11

Analysis date: 01/23/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 12.0 counts/min
CRM # 619 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 5: offset 5.82 µmol/kg (2030.78 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 12 min.

Analysis date: 01/25/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 26.0 counts/min
CRM # 507 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 5: offset 3.02 µmol/kg (2027.98 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 02/06/2023
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 29.2 counts/min
CRM # 489 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 5: offset 3.62 µmol/kg (2028.58 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 10 min.

Analysis date: 02/06/2023
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 23.0 counts/min
CRM # 571 was used and with an assigned value of (includes both DIC and salinity):
Batch 195, c: 2024.96 µmol/kg, S: 33.485
CRM values measured: AOML 6: offset 2.46 µmol/kg (2027.42 µmol/kg).
Average run time, minimum run time, maximum run time: 11, 8 and 13 min.

Reproducibility: (# samples and average difference): 8 duplicate samples were collected with an average difference of 2.22 (0.2.8-7.96) and average STDEV of 1.57 (0.2-5.63).

Sample ID	DIC (µmol/kg)	Average	STDEV	Difference
560112	2614.49			
560112	2616.85	2615.67	1.67	2.36
450112	2067.08			
450112	2066.49	2066.78	0.42	0.59
UK_OFF0000	2034.86			
UK_OFF0000	2032.24	2033.55	1.85	2.62
BG10112	2054.86			
BG10112	2055.64	2055.25	0.55	0.78
TB10112	2096.02			
TB10112	2103.97	2099.99	5.63	7.96
KW10112	2078.19			
KW10112	2079.14	2078.66	0.67	0.94
160112	2122.71			
160112	2122.99	2122.85	0.20	0.28
Average			1.57	2.22

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.

One of the duplicates for AM10112 was determined to be compromised that is supported by the intercomparing with the other carbon measurements. That bottle was not reported.
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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.

Station ID: CAL50101 was lost due to equipment malfunction.

pH:

Analysis date: 01/23/2023, 01/25/2023 and 02/06/2023
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 (^{0}C)
700000	21	33.639	20.01
680112	22	34.96	20.022
650112	23	31.481	20.021
600112	24	32.176	20.031
580112	25	34.865	20.028
57.30112	26	35.011	20.025
57.20112	27	34.824	20.026
57.10112	28	33.111	20.031
570112	29	31.534	20.025
560112	30	29.289	20.037
560112	31	29.289	20.033
550112	32	28.478	20.028
540112	33	25.734	20.039
510112	34	33.016	20.031
490112	35	32.782	20.039
450112	36	34.904	20.04
450112	37	34.904	20.04
410112	38	34.706	20.036
310112	39	35.483	20.033
330112	40	35.026	20.041
CAL50101	81	35.687	20.032
CAL50112	82	35.671	19.963
CAL40101	83	35.519	19.967

CAL40112	84	35.244	19.969
CAL30101	85	35.202	19.963
CAL30112	86	34.546	19.955
CAL20112	87	34.213	19.962
CAL10112	88	33.962	19.969
RP10112	89	34.346	19.981
RP20112	90	34.632	19.983
RP30112	91	34.231	19.975
RP40101	92	35.72	19.975
RP40112	93	34.658	19.978
GP50101	94	36.023	19.969
GP50112	95	36.026	19.965
BG40101	96	35.923	19.979
BG40112	97	35.046	19.976
BG30101	98	35.692	19.967
BG30112	99	35.206	19.964
BG20112	100	34.709	19.956
100112	101	35.34	20.045
70112	102	35.27	20.04
UK_IN0000	103	34.616	20.026
UK_MID0000	104	35.836	20.038
UK_OFF0000	105	35.895	20.032
UK_OFF0000	106	35.895	20.032
MR0101	107	35.941	19.97
MR0112	108	35.942	19.962
20112	109	35.797	19.963
BG10112	173	33.502	19.868
BG10112	174	33.502	19.871
V10112	175	35.157	19.871
V50101	176	36.235	19.865
V50112	177	36.202	19.868
V90101	178	36.079	19.873
V90112	179	36.085	19.878
AMI90101	180	36.276	19.879
AMI90112	181	36.102	19.873
AMI50101	182	36.354	19.866
AMI50112	183	36.174	19.869
AMI10112	184	34.693	19.873
AMI10112	185	34.693	19.868
TB10112	186	34.532	19.88
TB10112	187	34.532	19.882

TB40101	188	36.295	19.889
TB40112	189	36.3	19.879
TB100101	190	36.372	19.87
TB100112	191	36.153	19.885
CW30112	192	35.104	19.878
CW10112	461	34.58	19.97
L10101	462	35.491	19.972
L10112	463	34.897	19.966
L30101	464	36.063	19.974
L30112	465	36.058	19.966
L50112	466	36.181	19.972
300101	467	35.846	19.977
300112	468	35.851	19.982
KW40101	469	35.583	19.981
KW40112	470	35.584	19.98
KW20101	471	35.337	19.985
KW20112	472	35.345	19.977
KW10112	473	35.054	19.974
KW10112	474	35.054	19.972
WS0112	475	35.954	19.971
WS0101	476	35.957	19.97
21/LK0101	477	35.989	19.965
21/LK0112	478	35.93	19.962
160112	479	36.359	19.96
160112	480	36.359	19.955

Reproducibility: pH @ 20^0C (# samples and average difference): 8 duplicate samples were collected with an average difference of 0.0011 (0.00017– 0.00101) and an average STDEV of 0.0008 (0.00012 – 0.00201).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	560112	30	7.9610			
HP Agilent 8453	560112	31	7.9581	7.9596	0.00201	0.00284
HP Agilent 8453	450112	36	8.097			
HP Agilent 8453	450112	37	8.098	8.0977	0.00036	0.00051
HP Agilent 8453	UK_OFF0000	105	8.150			
HP Agilent 8453	UK_OFF0000	106	8.151	8.1503	0.00071	0.00101
HP Agilent 8453	BG10112	173	8.062			
HP Agilent 8453	BG10112	174	8.063	8.0623	0.00070	0.00099
HP Agilent 8453	KW10112	473	8.0555			
HP Agilent 8453	KW10112	474	8.0557	8.0556	0.00012	0.00017
HP Agilent 8453	160112	479	8.1075			
HP Agilent 8453	160112	480	8.1085	8.1080	0.00069	0.00097
Average					0.0008	0.0011

Reproducibility: pH @ 25^0C (# samples and average difference): 8 duplicate samples were collected with an average difference of 0.0011 (0.0017– 0.0028) and an average STDEV of 0.0008 (0.00012 – 0.0020).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	560112	30	7.887			
HP Agilent 8453	560112	31	7.884	7.8856	0.00198	0.00280
HP Agilent 8453	450112	36	8.022			
HP Agilent 8453	450112	37	8.022	8.0220	0.00036	0.00050
HP Agilent 8453	UK_OFF0000	105	8.074			
HP Agilent 8453	UK_OFF0000	106	8.075	8.0741	0.00071	0.00100
HP Agilent 8453	BG10112	173	7.987			
HP Agilent 8453	BG10112	174	7.988	7.9870	0.00069	0.00098

HP Agilent 8453	KW10112	473	7.980			
HP Agilent 8453	KW10112	474	7.981	7.9805	0.00012	0.00017
HP Agilent 8453	160112	479	8.032			
HP Agilent 8453	160112	480	8.033	8.0323	0.00068	0.00096
Average					0.0008	0.0011

Remarks

One of the duplicates for AM10112 was determined to be compromised that is supported by the intercomparing with the other carbon measurements. That bottle was not reported.

One of the duplicates on station TB1 was found to be very inconsistent with compared carbonate parameters and was not reported

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 20^0C at Full Scale (pH 0-14). The pH was reported at 20^0C and 25^0C.

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: 01/24/2023, 01/26/2023 and 02/07/2023
Titration system used: Open cell
Batch 195, CRM #619 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #571 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #489 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #558 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.
Batch 195, CRM #507 Salinity = 33.485, cert. TA = 2213.51 µmol/kg.

On 01/24/2023 CRM #619 was analyzed before and after sample analysis on System 1.
On 01/26/2023 CRM #571 was analyzed before and after sample analysis on System 1.
On 02/07/2023 CRM #489 was analyzed before and after sample analysis on System 1.
On 01/24/2023 CRM #558 was analyzed before and after sample analysis on System 2.
On 01/26/2023 CRM #507 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	01/24/2023	10:10:56	619	2213.18	0.33
1	01/24/2023	16:12:25	619	2214.07	0.56
1	1/26/2023	09:15:43	571	2210.79	2.72
1	1/26/2023	17:09:54	571	2212.22	1.29
1	2/7/2023	09:04:48	489	2209.66	3.85
1	2/7/2023	19:45:44	489	2213.74	0.23
2	1/24/2023	12:13:27	558	2035.68	5.87
2	1/24/2023	16:04:01	558	2038.46	6.98
2	1/26/2023	10:26:22	507	2033.91	1.12
2	1/26/2023	16:59:12	507	2032.67	0.79

Reproducibility: (# samples and average difference): 8 duplicate samples were collected with an average difference of 3.79(0.19 – 10.36) and an average STDEV of 2.68 (0.13 – 7.33).

Station	Sample ID	TA (umol/kg)	Average	STDEV	Difference
56	560112	2835.3			
56	560112	2835.5	2835.4	.13	.19
45	450112	2353.1			
45	450112	2350.9	2352.0	1.56	2.20
UK_OFF	UK_OFF0000	2354.7			
UK_OFF	UK_OFF0000	2349.0	2351.8	4.04	5.71
BG1	BG10112	2314.97			
BG1	BG10112	2311.17	2313.1	2.69	3.80
Average				1.75	2.48

Remarks

One of the duplicates for AM10112 was determined to be compromised that is supported by the intercomparing with the other carbon measurements. That bottle was not reported.

One of the duplicates on station TB1 was found to be questionable compared to other carbonate parameters and was not reported in the duplicate.

One of the duplicates on station 16 was found to be questionable compared to other carbonate parameters and was not reported in the duplicate.

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

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:

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).

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 -80^0C 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.