Cruise: WS21032
Ship: R/V Walton Smith
Expo Code: 33WA20210201
Funding Project Title: Near-shore Carbonate Sampling
Funding Project ID: Near-shore-OA
Dates: February 1st – February 7th, 2021
Chief Scientist: Ian Smith
Equipment: CTD and Flow-Through
Total number of stations: 52
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:
52 locations, 73 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:
52 locations, 73 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:
52 locations, 73 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

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	02/08/2021	2063.31	2068.46	5.15	15.0	9
AOML5	02/09/2021	2063.31	2064.13	0.82	15.0	8
AOML 6	02/08/2021	2063.31	2067.14	3.83	14.3	8
AOML 6	02/09/2021	2063.31	20266.74	3.43	12.0	8

Analysis date: 02/08/2021
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 15.0 counts/min
CRM # 321 was used and with an assigned value of (includes both DIC and salinity):
Batch 169, c: 2063.31 µmol/kg, S: 33.518
CRM values measured: AOML 5: offset 5.15 µmol/kg (2068.46 µmol/kg).
Average run time, minimum run time, maximum run time: 9, 8 and 9 min.

Analysis date: 02/09/2021
Coulometer used: DICE–CM5017O-AOML 5
Blanks: 15.0 counts/min
CRM # 312 was used and with an assigned value of (includes both DIC and salinity):
Batch 169, c: 2063.31 µmol/kg, S: 33.518
CRM values measured: AOML 5: offset 0.82 µmol/kg (2064.13 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 13 min.

Analysis date: 02/08/2021
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 14.3 counts/min
CRM # 955 was used and with an assigned value of (includes both DIC and salinity):
Batch 169, c: 2063.31 µmol/kg, S: 33.518
CRM values measured: AOML 6: offset 3.83 µmol/kg (2067.14 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 10 min.

Analysis date: 02/09/2021
Coulometer used: DICE–CM5017O-AOML 6
Blanks: 12.0 counts/min
CRM # 938 was used and with an assigned value of (includes both DIC and salinity):
Batch 169, c: 2063.31 µmol/kg, S: 33.518
CRM values measured: AOML 6: offset 3.43 µmol/kg (2066.74 µmol/kg).
Average run time, minimum run time, maximum run time: 8, 7 and 20 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.00 (0.72-1.31) and average STDEV of 0.71 (0.51-0.93).

Sample ID	DIC (µmol/kg)	Average	Difference	STDEV
UKOFF0000	2054.68			
UKOFF0000	2055.54	2055.11	0.86	0.61

540112	2536.50			
540112	2537.22	2536.86	0.72	0.51
CAL10112	2249.12			
CAL10112	2250.43	2249.77	1.31	0.93
RP30112	2123.95			
RP30112	2124.94	2124.45	0.98	0.69
BG20112	2139.97			
BG20112	2139.24	2139.60	0.72	0.51
V90101	2090.78			
V90101	2089.50	2090.14	1.28	0.90
TB100112	2095.21			
TB100112	2096.05	2095.63	0.84	0.59
Average			1.00	0.71

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 5017-O from UIC. Inc.

pH:

Analysis date: 02/08/2021 and 02/09/2021
A CRM was analyzed before sample analysis.
02/08/2021, Batch 169, CRM #23, pH = 7.811072
02/09/2021, Batch 169, CRM #636, pH = 7.810571

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

Sample ID	Sample BTL #	Salinity	Analysis T (^{0}C)
CRM169_23	23	33.518	19.978

CRM169_636	636	33.518	19.986
UKIN0000	1	36.283	20.024
UKMID0000	2	36.154	20.016
UKOFF0000	3	36.109	20.030
UKOFF0000	4	36.109	20.032
700000	5	31.713	20.025
680112	6	33.390	20.036
650112	7	29.136	20.033
640112	8	29.136	20.036
600112	9	32.955	20.036
580112	10	34.837	20.033
5730112	11	34.375	20.034
5720112	12	33.732	20.043
5710112	13	34.054	20.029
570112	14	33.427	20.027
560112	15	33.157	20.029
550112	16	31.922	20.031
540112	17	30.989	20.029
540112	18	30.989	20.031
490112	19	33.968	20.021
470112	20	33.971	20.042
450112	21	33.987	20.031
410112	22	33.799	20.024
310112	23	34.664	20.029
330112	24	33.997	20.024
CAL50101	25	34.926	20.023
CAL50112	26	34.927	20.031
CAL40101	27	34.632	20.029
CAL40112	28	34.366	20.032
CAL30101	29	34.185	20.021
CAL30112	30	34.186	20.027
CAL20112	31	33.977	20.026
CAL10112	32	32.093	20.037
CAL10112	33	32.093	20.023
RP10112	34	33.981	20.039
RP20112	35	34.183	20.032
RP30112	36	34.694	20.017
RP30112	37	34.694	20.030
RP40101	38	35.375	20.029
RP40112	39	35.376	20.028
GP50101	40	35.874	20.037

GP50112	421	35.876	19.978
BG40101	422	35.377	19.989
BG40112	423	35.377	19.991
BG30101	424	34.842	19.991
BG30112	425	34.842	19.985
BG20112	426	34.262	19.997
BG20112	427	34.262	19.996
V10112	428	34.182	20.003
V20101	429	34.277	20.006
V20112	430	33.648	19.994
V30101	431	35.028	19.982
V30112	432	34.362	19.994
V40101	433	35.353	20.000
V40105	434	35.223	19.993
V40112	435	34.823	20.004
V70101	436	36.000	20.001
V70112	437	35.965	20.016
V90101	438	36.174	20.006
V90101	439	36.174	19.999
V90112	440	36.198	20.005
AMI90101	441	36.125	19.991
AMI90112	442	36.132	20.003
AMI50101	443	36.142	20.009
AMI50112	444	36.143	20.012
AMI10112	445	33.559	20.009
TB10112	446	32.951	20.003
TB40101	447	35.984	20.013
TB40112	448	35.983	20.009
TB100101	449	35.984	20.014
TB100112	450	35.944	20.017
TB100112	451	35.944	20.013
CAL60101	452	35.657	20.010
CAL60112	453	35.701	20.014
300101	454	35.496	20.013
300112	455	35.572	20.019
KW40101	456	35.586	20.016
KW40112	457	35.529	20.023
KW20101	458	35.052	20.019
KW20112	459	35.093	20.023
KW10112	460	35.079	20.016

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.00281 (0.0000-0.0092) and an average STDEV of 0.00199 (0.0000-0.0129).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	UKOFF0000	3	8.131365			
HP Agilent 8453	UKOFF0000	4	8.131479	8.13142	0.0001	0.0001
HP Agilent 8453	540112	16	7.863115			
HP Agilent 8453	540112	17	7.862034	7.86257	0.0008	0.0011
HP Agilent 8453	CAL10112	32	7.975280			
HP Agilent 8453	CAL10112	33	7.975538	7.97541	0.0002	0.0003
HP Agilent 8453	RP30112	36	8.022707			
HP Agilent 8453	RP30112	37	8.026654	8.02468	0.0028	0.0039
HP Agilent 8453	BG20112	426	8.002324			
HP Agilent 8453	BG20112	427	8.002321	8.00232	0.0000	0.0000
HP Agilent 8453	V90101	438	8.111065			
HP Agilent 8453	V90101	439	8.112373	8.11172	0.0009	0.0013
HP Agilent 8453	TB100112	450	8.104261			
HP Agilent 8453	TB100112	451	8.091316	8.09779	0.0092	0.0129
Average					0.00199	0.00281

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

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: 02/10/2021 and 02/11/2021
Titration system used: Open cell
Batch 169, CRM #312 Salinity = 33.518, cert. TA = 2207.03µmol/kg.
Batch 169, CRM #693 Salinity = 33.518, cert. TA = 2207.03µmol/kg.
Batch 169, CRM #636 Salinity = 33.518, cert. TA = 2207.03µmol/kg.
Batch 169, CRM #1005 Salinity = 33.518, cert. TA = 2207.03µmol/kg.

On 02/10/2021 CRM #312 was analyzed before and after sample analysis on System 1.
On 02/11/2021 CRM #693 was analyzed before and after sample analysis on System 1.
On 02/10/2021 CRM #636 was analyzed before and after sample analysis on System 2.
On 02/11/2021 CRM #1005 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	02/10/2021	09:56:07	312	2210.77	3.74
1	02/10/2021	18:37:27	312	2212.12	5.09
1	02/11/2021	10:03:45	693	2209.84	2.81
1	02/11/2021	17:43:35	693	2208.87	1.84
2	02/10/2021	10:53:18	636	2207.11	0.08
2	02/10/2021	18:44:57	636	2200.68	6.35
2	02/11/2021	10:16:08	1005	2205.66	1.37
2	02/11/2020	17:37:43	1005	2200.69	6.34

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 4.22 (1.01-6.80) and an average STDEV of 2.98 (0.71-4.81).

Station #	Sample ID	TA (µmol/kg)	Average	Difference	STDEV
UK-OFF	UKOFF0000	2376.76			
UK-OFF	UKOFF0000	2377.76	2377.26	1.01	0.71
54	540112	2733.13			
54	540112	2726.33	2729.73	6.80	4.81

CAL 1	CAL10112	2463.29			
CAL 1	CAL10112	2469.96	2466.63	6.67	4.72
RP 3	RP30112	2373.48			
RP 3	RP30112	2368.62	2371.05	4.86	3.44
BG 2	BG20112	2376.00			
BG 2	BG20112	2370.67	2373.34	5.33	3.77
V 9	V90101	2391.92			
V 9	V90101	2394.42	2393.17	2.50	1.77
TB 10	TB100112	2395.65			
TB 10	TB100112	2393.30	2394.48	2.35	1.66
Average				4.22	2.98

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: 02/16/2021
PI: Dr. Jia-Zhong Zhang
Analyzed by: Ian Smith

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).

Chlorophyll and Phaeophytin:
Analysis Date: 02/18/2021
PI: Dr. Christopher Kelble
Analyzed by: Ian Smith

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.