

Cruise: WS22141

Ship: R/V Walton Smith

Expo Code: 33WA20220521

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

Funding Project ID: 21403

Dates: May 21st – May 27th 2022

Chief Scientist: Ian Smith

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

Total number of stations: 55

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

DIC:

55 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

pH:

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

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

PI: Dr. Rik Wanninkhof

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TAlk:

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

PI: Dr. Rik Wanninkhof

Analyzed by: Patrick Mears

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	06/16/2022	1952.65	1959.65	7.00	12	7
AOML 5	06/29/2022	1952.65	1956.26	3.52	12	8
AOML 6	06/16/2022	1952.65	1956.64	3.99	12	10
AOML 6	06/29/2022	1952.65	1957.13	4.48	12	12

Analysis date: 06/16/2022

Coulometer used: DICE-CM5017O-AOML 5

Blanks: 12.0 counts/min

CRM # 262 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65 $\mu\text{mol/kg}$, S: 33.782

CRM values measured: AOML 5: offset 7.00 $\mu\text{mol/kg}$ (1956.65 $\mu\text{mol/kg}$).

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

Analysis date: 06/29/2022

Coulometer used: DICE-CM5017O-AOML 5

Blanks: 12.0 counts/min

CRM # 321 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65 $\mu\text{mol/kg}$, S: 33.782

CRM values measured: AOML 5: offset 1.96 $\mu\text{mol/kg}$ (2027.13 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 8, 7 and 9 min.

Analysis date: 06/16/2022

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 197 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65 $\mu\text{mol/kg}$, S: 33.782

CRM values measured: AOML 6: offset 3.82 $\mu\text{mol/kg}$ (2028.99 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 10, 9 and 13 min.

Analysis date: 06/29/2022

Coulometer used: DICE-CM5017O-AOML 6

Blanks: 12.0 counts/min

CRM # 683 was used and with an assigned value of (includes both DIC and salinity):

Batch 178, c: 1952.65 $\mu\text{mol/kg}$, S: 33.782

CRM values measured: AOML 6: offset 4.84 $\mu\text{mol/kg}$ (2030.01 $\mu\text{mol/kg}$).

Average run time, minimum run time, maximum run time: 12, 9 and 14 min.

Reproducibility: (# samples and average difference): 7 duplicate samples were collected with an average difference of 1.33 (0.03-2.74) and average STDEV of 0.94 (0.02-1.94).

Sample ID	DIC		Average	STDEV	Difference
		($\mu\text{mol/kg}$)			
CAL20112	2130.3				
CAL20112	2128.9		2129.64	0.97	1.38
CAL10112	2142.4				
CAL10112	2145.1		2143.73	1.94	2.74
BG20112	2085.1				
BG20112	2083.2		2084.16	1.35	1.90
BG10112	2067.8				
BG10112	2066.5		2067.14	0.88	1.25
410112	2195.1				
410112	2195.1		2195.08	0.02	0.03
57.20112	2081.2				
57.20112	2080.8		2080.99	0.33	0.46
600112	2132.1				
600112	2133.7		2132.92	1.10	1.56
Average				0.94	1.33

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 50170 from UIC. Inc.

pH:

Analysis date: 06/16/2022 and 06/29/2022

No CRMs were analyzed before sample analysis.

Spectrophotometer used: HP Agilent 8453

Temperature and salinity of pH samples analyzed.

<u>Sample ID</u>	<u>Sample BTL #</u>	<u>Salinity</u>	<u>Analysis T (°C)</u>
20112	1	36.190	19.958
MR0101	2	36.296	19.951
MR0112	3	36.360	19.967
UK_OFF0000	4	36.334	19.965
UK_MID0000	5	36.347	19.96
UK_IN0000	6	36.767	19.955
70112	7	37.078	19.978
100112	8	37.949	19.978
160112	9	37.847	19.981
21/LK0101	10	36.342	19.966
21/LK0112	11	36.514	19.969
WS0101	12	36.738	19.964
WS0112	13	36.779	19.971
KW10112	14	37.144	19.967
KW20101	16	37.019	19.959
KW40101	17	36.856	19.965
KW40112	18	36.862	19.961
300101	19	36.725	19.965
300112	20	36.736	19.967
310112	21	36.151	19.967
330112	22	36.125	20.027
CAL50101	23	36.051	19.917
CAL50112	24	36.060	19.915
CAL40101	25	35.884	19.941
CAL40112	26	35.885	19.932
CAL30101	27	35.462	19.92
CAL30112	28	35.453	19.926
CAL20112	29	35.428	19.925
CAL20112	30	35.428	19.972

CAL10112	31	35.148	19.928
CAL10112	32	35.148	19.924
RP10112	33	35.199	19.927
RP20112	34	35.593	19.929
RP30112	35	35.631	19.927
RP40101	36	35.920	19.922
RP40112	37	35.933	19.933
GP50101	38	36.215	19.934
GP50112	39	36.288	19.923
BG40101	40	35.992	19.922
BG40112	81	36.043	19.975
BG30101	82	35.711	19.91
BG30112	83	35.709	19.928
BG20112	84	35.498	19.922
BG20112	85	35.498	19.933
BG10112	86	35.254	19.923
BG10112	87	35.254	19.921
V10112	88	35.825	19.93
V50101	89	36.143	19.921
V50112	90	36.144	19.928
V90101	91	36.499	19.933
V90112	92	36.568	19.926
AMI90101	93	36.415	19.927
AMI90112	94	36.549	19.92
AMI10112	95	35.499	19.931
AMI50101	96	36.228	19.925
AMI50112	97	36.444	19.927
TB10112	98	34.971	19.926
TB40101	99	35.924	19.926
TB40112	100	35.922	19.925
KW20112	112	37.016	19.967
TB100101	173	36.322	19.961
TB100112	174	36.470	19.959
410112	175	36.310	19.963
410112	176	36.310	19.959
450112	177	36.535	19.964
490112	178	37.296	19.978
510112	179	36.957	19.969
57.10112	180	37.327	19.973
570112	181	37.223	19.973
560112	182	37.144	19.973

550112	183	37.321	19.986
540112	184	37.267	19.984
57.20112	185	36.331	19.965
57.20112	186	36.331	19.959
57.30112	187	36.180	19.977
580112	188	36.455	19.971
600112	189	37.157	19.964
600112	190	37.157	19.978
650112	191	39.233	19.979
680112	192	39.301	19.976

Reproducibility: pH @ 20⁰C (# samples and average difference): 7 duplicate samples were collected with an average difference of 0.00211 (0.0003 – 0.0090) and an average STDEV of 0.0015 (0.0002 – 0.0064).

Instrument	Sample ID	Bottle #	pH @20deg C	Average	STDEV	Difference
HP Agilent 8453	CAL201012	29	8.1072			
HP Agilent 8453	CAL201012	30	8.1075	8.1074	0.0002	0.0003
HP Agilent 8453	CAL101012	31	8.0679			
HP Agilent 8453	CAL101012	32	8.0701	8.0069	0.0016	0.0022
HP Agilent 8453	BG201012	84	8.1210			
HP Agilent 8453	BG201012	85	8.1221	8.1216	0.0008	0.0011
HP Agilent 8453	BG101012	86	8.1222			
HP Agilent 8453	BG101012	87	8.1219	8.1221	0.0002	0.0003
HP Agilent 8453	4101012	175	8.1269			
HP Agilent 8453	4101012	176	8.1275	8.1272	0.0004	0.0006
HP Agilent 8453	57.201012	185	8.2201			
HP Agilent 8453	57.201012	186	8.2111	8.2156	0.0064	0.0090
HP Agilent 8453	6001012	189	8.1212			
HP Agilent 8453	6001012	190	8.1200	8.1206	0.0008	0.0012
Average					0.0015	0.0021

Reproducibility: pH @ 25⁰C (# samples and average difference): 7 duplicate samples

were collected with an average difference of 0.0015 (0.0003 – 0.0089) and an average STDEV of 0.0021 (0.0002 – 0.0063).

Instrument	Sample ID	Bottle #	pH @25deg C	Average	STDEV	Difference
HP Agilent 8453	CAL20112	29	8.0315			
HP Agilent 8453	CAL20112	30	8.0318	8.0317	0.0002	0.0003
HP Agilent 8453	CAL10112	31	7.9926			
HP Agilent 8453	CAL10112	32	7.9948	7.9937	0.0016	0.0022
HP Agilent 8453	BG20112	84	8.0453			
HP Agilent 8453	BG20112	85	8.0463	8.0458	0.0007	0.0011
HP Agilent 8453	BG10112	86	8.0465			
HP Agilent 8453	BG10112	87	8.0462	8.0463	0.0002	0.0003
HP Agilent 8453	410112	175	8.0510			
HP Agilent 8453	410112	176	8.0516	8.0513	0.0004	0.0006
HP Agilent 8453	57.20112	185	8.1435			
HP Agilent 8453	57.20112	186	8.1346	8.1390	0.0063	0.0089
HP Agilent 8453	600112	189	8.0454			
HP Agilent 8453	600112	190	8.0442	8.0448	0.0008	0.0012
Average					0.0015	0.0021

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: 06/17/2022 and 06/30/2022

Titration system used: Open cell

Batch 178, CRM #262 Salinity = 33.782, cert. TA = 2216.53 $\mu\text{mol/kg}$.

Batch 178, CRM #683 Salinity = 33.782, cert. TA = 2216.53 $\mu\text{mol/kg}$.

Batch 178, CRM #381 Salinity = 33.782, cert. TA = 2216.53 $\mu\text{mol/kg}$.

Batch 178, CRM #321 Salinity = 33.782, cert. TA = 2216.53 $\mu\text{mol/kg}$.

Batch 178, CRM #197 Salinity = 33.782, cert. TA = 2216.53 $\mu\text{mol/kg}$.

On 03/22/2022 CRM #198 was analyzed before and after sample analysis on System 1.

On 03/24/2022 CRM #382 was analyzed before and after sample analysis on System 1.

On 03/22/2022 CRM #518 was analyzed before and after sample analysis on System 2.

On 03/24/2022 CRM #436 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	06/17/2022	09:48:49	262	2218.69	2.16
1	06/17/2022	17:09:06	262	2216.31	0.22
1	06/30/2022	09:05:49	683	2221.23	4.70
1	06/30/2022	16:55:20	381	2211.13	5.40
2	06/17/2022	10:02:15	197	2223.06	6.53
2	06/17/2022	17:19:55	197	2223.08	6.55
2	06/30/2022	08:48:47	321	2219.28	2.75
2	06/30/2022	16:36:06	381	2222.78	6.25

Reproducibility: (# samples and average difference): 7 duplicate samples were collected. Only 5 duplicates are reported due to one of the TA measurements of the pair being significantly different compared to the calculated TA values using other carbonate measurements. The average difference of 2.33 (0.43 – 4.38) and an average STDEV of 1.72 (0.30 – 3.10).

Station	Sample ID	TA		STDEV	Difference
		(umol/kg)	Average		
CAL1	CAL10112	2431.3			
CAL1	CAL10112	2435.7	2433.5	3.10	4.38
BG2	BG20112	2393.5			
BG2	BG20112	2394.3	2393.9	0.54	0.77
BG1	BG10112	2371.9			
BG1	BG10112	2369.4	2370.6	1.75	2.48
41	410112	2543.0			
41	410112	2539.4	2541.2	2.55	3.60
60	600112	2467.3			
60	600112	2467.7	2467.5	0.30	0.43
Average				1.7	2.33

Remarks

On 6/30/2023 both Systems 1 and 2 ran CRMs from bottle 381 because there was not enough CRM left in the initial CRM bottle to run a duplicate at the end of the sample runs. An average of both CRM measurements from the beginning and the end of the sample runs were used to correct the sample measurements.

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.

One of the duplicates on Station IDs 57.20112 and CAL20112 were determined to be bad samples based on parameter comparisons and calculations based on measurements. They are not included in the data.

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: 06/02/2022

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: 07/12/2022

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.