Cruise: EX1507 Ship: Explorer of the Seas Expo Code: 33KF20150212 Dates: February 12<sup>th</sup> – 19<sup>st</sup>, 2015 Chief Scientist: Kevin Sullivan Equipment: TSG-Flow thru system Total number of stations: 20 Location: Port Canaveral, FL to Willemstad, Curacao

# Sample Collection

The discrete samples were collected from the TSG-flow thru system onboard the Royal Caribbean ship Explorer of the Seas by Kevin Sullivan. The date and time listed in the data file are UTC when each sample bottle was collected.

# DIC:

20 locations, 20 samples each 500-ml, 4 duplicate samples. Sample\_ID#: 301, etc.; Sample bottle number PI: Dr. Rik Wanninkhof Analyzed by: Charles Featherstone

# pH:

20 locations, 20 samples each 500-ml, 4 duplicate samples. Sample\_ID#: 301, etc.; Sample bottle number PI: Dr. Rik Wanninkhof Analyzed by: Charles Featherstone

# TAlk:

20 locations, 20 samples each 500-ml, 4 duplicate samples.
Sample\_ID#: 301, etc.; Sample bottle number
PI: Dr. Rik Wanninkhof
Analyzed by: Dr. Leticia Barbero, Dr. Denis Pierrot and Charles Featherstone

### <u>Sample Analysis</u> DIC:

| Instrument<br>ID | Date       | Certified<br>CRM<br>(µmol/kg) | CRM Value<br>(µmol/kg) | CRM Offset<br>(µmol/kg) | Blank<br>(Counts) | Avg.<br>Sample<br>Analysis<br>Time |
|------------------|------------|-------------------------------|------------------------|-------------------------|-------------------|------------------------------------|
| AOML 3           | 03/05/2015 | 2016.65                       | 2021.75                | 5.10                    | 12.0              | 8                                  |

Analysis date: 03/05/2015 Coulometer used: DICE–CM5015- AOML 3 Blanks: 12.0 counts/min CRM # 0965 was used and with an assigned value of (includes both DIC and salinity): Batch 129, c: 2016.65 µmol/kg, S: 33.361 CRM values measured: AOML 3: offset 5.10 µmol/kg (2021.75 µmol/kg).

Average run time, minimum run time, maximum run time: 8, 8 and 10 min.

| <br>Instrument<br>ID | Sample<br>ID | Bottle<br># | Corrected DIC<br>(µmol/kg) | Average | Difference | STDEV |
|----------------------|--------------|-------------|----------------------------|---------|------------|-------|
| AOML3                | 304          | 304         | 2020.06                    |         |            |       |
| AOML3                | 305          | 305         | 2025.79                    | 2022.93 | 5.73       | 4.05  |
|                      |              |             |                            |         |            |       |
| AOML3                | 308          | 308         | 2002.80                    |         |            |       |
| AOML3                | 309          | 309         | 2014.18                    | 2008.49 | 11.37      | 8.04  |
|                      |              |             |                            |         |            |       |
| AOML3                | 316          | 316         | 2001.34                    |         |            |       |
| AOML3                | 317          | 317         | 2001.19                    | 2001.26 | 0.15       | 0.11  |
|                      |              |             |                            |         |            |       |
| AOML3                | 319          | 319         | 2039.95                    |         |            |       |
| AOML3                | 320          | 320         | 2035.40                    | 2037.68 | 4.55       | 3.22  |
|                      |              |             |                            |         |            |       |
| Average              |              |             |                            |         | 5.45       | 3.86  |

**Reproducibility:** (# samples and average difference): 4 sets of duplicate samples, average difference 5.45 µmol/kg (0.15-11.37), average STDEV of 3.86 (0.11-8.04).

CRM, salinity and HgCl2 correction applied: Salinity correction was applied using TSG salinity.

# Remarks

The volume correction was applied due to added HgCl<sub>2</sub> (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. End blank (AOML 3 = 12.0).

The samples were analyzed using the DICE (AOML 3) and a new coulometer from UIC, Inc. CM5015 with CM5011 emulation software.

Duplicates were sampled 1 to 1.5 minutes apart from the ships TSG flow thru system.

# pH:

Analysis date: 03/05/2015 Spectrophotometer used: HP Agilent 8453

| Instrument      | Sample_ID | Bottle # | pH @20deeg C | Average | STDEV  | Difference |
|-----------------|-----------|----------|--------------|---------|--------|------------|
| HP Agilent 8453 | 3040000   | 304      | 8.1410       |         |        |            |
| HP Agilent 8453 | 3050000   | 305      | 8.1482       | 8.1446  | 0.0051 | 0.0072     |
|                 |           |          |              |         |        |            |
| HP Agilent 8453 | 3080000   | 308      | 8.1475       |         |        |            |
| HP Agilent 8453 | 3090000   | 309      | 8.1500       | 8.1487  | 0.0017 | 0.0024     |
|                 |           |          |              |         |        |            |
| HP Agilent 8453 | 3160000   | 316      | 8.1452       |         |        |            |
| HP Agilent 8453 | 3170000   | 317      | 8.1355       | 8.1404  | 0.0069 | 0.0097     |
|                 |           |          |              |         |        |            |
| HP Agilent 8453 | 3190000   | 319      | 8.1394       |         |        |            |
| HP Agilent 8453 | 3200000   | 320      | 8.1353       | 8.1374  | 0.0029 | 0.0042     |
|                 |           |          |              |         |        |            |
|                 |           | Average  |              |         | 0.0042 | 0.0059     |
|                 |           | -        |              |         |        |            |

**Reproducibility:** (# samples and average difference): 4 sets of duplicate samples, average difference 0.0059 (0.0024-0.0097), average STDEV of 0.0042 (0.0017-0.0069).

### <u>Remarks</u>

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<sup>0</sup>C at Full Scale (pH 0-14).

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 syringe before DIC analysis to determine the pH.

Duplicates were sampled 1 to 1.5 minutes apart from the ships TSG flow thru system.

### TAlk:

The results posted are analyses from the same sample bottles used for DIC and pH. Analysis dates: 03/10/2015Titration system used: Open cell CRM batch: 129, S = 33.361, certified TA = 2237.32 µmol/kg

2 CRM samples were run on each cell, before and after the seawater samples. The TA for the water samples was corrected using the averaged ratios between the certified and measured values of the 2 CRMs run on each cell. The following table shows the CRM measurements for each cell.

| Cell<br>System | Date      | Time     | Bottle # | ТА        | $ \Delta CRM $ |
|----------------|-----------|----------|----------|-----------|----------------|
| 1              | 3/10/2015 | 09:23:23 | 533      | 2221.96   |                |
| 1              | 3/10/2015 | 15:52:53 | 601      | 2223.04   | 1.08           |
| 2              | 3/10/2015 | 09:59:22 | 533      | 2214.91   |                |
| 2              | 3/10/2015 | 16:26:57 | 601      | 2214.36   | 0.55           |
|                |           |          |          | Average   | 0.82           |
|                |           |          |          | Std. Dev. | 0.37           |

**Reproducibility:** 4 sets of duplicate samples were run in the same cell, with an average absolute difference of 5.74  $\mu$ mol/kg (0.6 – 11.91), and a Standard Deviation of 5.84. The duplicates were sampled 1 to 1.5 minutes apart from the ships TSG flow thru system.

| Bottle<br># | System | Date      | Time     | S     | ТА        | Difference | Comments |
|-------------|--------|-----------|----------|-------|-----------|------------|----------|
| 304         | 1      | 3/10/2015 | 10:50:25 | 36.03 | 2360.55   | 9.54       |          |
| 305         | 1      | 3/10/2015 | 11:39:50 | 36.04 | 2351.01   |            |          |
| 308         | 1      | 3/10/2015 | 12:39:54 | 35.57 | 2333.49   | 11.91      |          |
| 309         | 1      | 3/10/2015 | 12:58:58 | 35.59 | 2345.40   |            |          |
| 316         | 1      | 3/10/2015 | 14:26:55 | 35.49 | 2330.18   | 0.6        |          |
| 317         | 1      | 3/10/2015 | 14:50:45 | 35.49 | 2330.78   |            |          |
| 319         | 1      | 3/10/2015 | 15:09:26 | 36.03 | 2359.54   | 0.92       |          |
| 320         | 1      | 3/10/2015 | 15:28:59 | 36.04 | 2358.62   | 0.72       |          |
|             |        |           |          |       |           |            |          |
|             |        |           |          |       | Average   | 5.74       |          |
|             |        |           |          |       | Std. Dev. | 5.84       |          |

### <u>Remarks</u>

The two systems behaved well during the analyses.

Duplicates were sampled 1 to 1.5 minutes apart from the ships TSG flow thru system and reproducibility was affected by this.

# <u>Comments</u>

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 Sample ID is the sample station, cast number and Niskin bottle number for the discrete samples.

#### UPDATE:

Between March and June of 2021, all of the data for the discrete samples was put into a uniform format. The supporting information was checked for accuracy, especially the expocode, date, time, and positions.

Additionally, pH results were recalculated to 20 and 25 degrees Celsius.