Carbonate chemistry, Svalbard 2009 experiment

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1   DIC measurements

DIC was measured by M.-D. Pizay and J.-P. Gattuso on the AIRICA. Batch 95 from Dickson was used (S=33.3, DIC = 2017.04 μmol kg^{-1}, TA = 2214.75 μmol kg^{-1}).

DIC measurements were performed using 1200 μl samples. For calibration, 1100, 1200 and 1300 μl samples of the CRM were measured, a regression line drawn and the area for 1200 μl calculated using the regression parameters. The correlation coefficients were usually > 0.99 (Fig. 1).

1.1   Standard deviation of the measurements

Four to about 10 replicate measurements were performed on each sample. Outliers were removed until standard deviation (s.d.) of the area was below 24 but this process was stopped in order to have at least 3 replicate measurements left. About 55% of the samples had a s.d. of less than 3 μmol kg^{-1}, 65% of less than 4 μmol kg^{-1} and 83% of less than 5 μmol kg^{-1} (2). It is suspected that most of the variability is generated by bubbles appearing in the sample line. This is despite the fact that the samples were kept in a water bath at a temperature lower than the room (22 vs 21°C. Advice on how to get rid of that would be welcome.

1.2   Accuracy and reproducibility

Accuracy and reproducibility was checked on batch 95 (Figure 3). The offset is -2.3 μmol kg^{-1} and almost all measurements are well within the $\pm$ 2 x sd.

1.3   Comparison of measured DIC with DIC estimated from pH and TA

DIC measured with the AIRICA is compared with the DIC estimated from pHT and total alkalinity. The relationship is quite good (Fig. 4). It must be noted that, on most days,

the times of pH measurement and of DIC sampling did not coincide. Since the carbonate chemistry of the header tanks changed a lot on short (1 h) time scales, most variability was generated by the lack of synchronicity. This is well illustrated by the data collected on 13 May (Fig. 4 and Fig. 5). pH was measured and seawater sampled for DIC at the same time and the correlation is excellent ($y = 40.66 + 0.9804x; r^2 = 0.9892, n = 15$). The intercept is not significantly different from 0 and the slope is not significantly different from 1.

2   pH measurements

pH in the header tanks was measured on the total scale using a pH meter (Metrohm, 826 pH mobile) with a glass electrode (Metrohm, electrode plus) calibrated every second day on the total scale using Tris/HCl and 2-aminopyridine/HCl buffer solutions with a salinity of 35.0 [1]. pH (in mV) and temperature were recorded for both buffers at seven different temperatures between 0 and 5°C. A non linear regression was applied to obtain an estimation of the calibration values for all the temperatures (0 to 4°C) used during the experiments.

3   Total alkalinity measurements

Total alkalinity in the header tanks was measured by Steeve Comeau and Frédéric Gazeau using a Metrohm Titrando titrator following the procedure described by [1] Accuracy and reproducibility was checked on batch 95 (Figure 6). The offset is +1.7 μmol kg^{-1} and all measurements but one are within the ± 2 x sd.

4   Carbonate chemistry

The carbonate chemistry was calculated, with the R package *seacarb* [2], using total alkalinity and either pH$_T$ or DIC.

5   Workflow for calculations and figures

The workflow is horrendously complicated and should be made simpler next trip.

1. Fill pH_svalbard_date

2. DIC

    - fill dic_svalbard_date.xls
    - calculate regression
    - copy slope and intercept in the corresponding columns
    - paste the data range with a yellow background color into svalbard_dic.dat

- run svalbard_dic9.R

- paste the resulting DIC values in svalbard_dic.csv in pH_svalbard_date.xls

3. copy pH_svalbard_date.xls and paste in svalbard_carbonate_chemistry_date.dat

4. run svalbard_carbonate_chemistry8.R

5. copy svalbard_carbonate_chemistry.csv in svalbard_carbonate_chemistry_date.xls

6. Upload sur Gmail: "File>Upload new version"

6 Monitoring of the carbonate system in the header tanks

See figures 7 and 8.

References

[1] A. G. Dickson, C. L. Sabine, and J. R. Christian. Guide to best practices for ocean co2 measurements. *PICES Special Publication*, 3:1–191, 2007.

[2] H Lavigne, A. Proye, and J-P Gattuso. seacarb 2.0, an r package to calculate parameters of the seawater carbonate system. 2008.

[3] Pierre Legendre. *lmodel2: Model II Regression*, 2008. R package version 1.6-3.

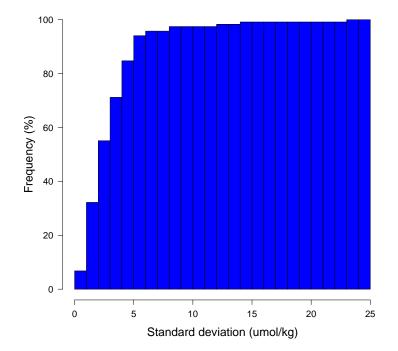Figure 1: Regression line of area versus time with CRM 95 (13 May 2009).

Figure 2: Cumulative frequency distribution of the standard deviation of all DIC measurements carried out during the campaign.
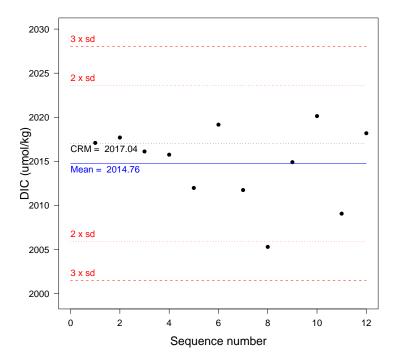
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Figure 3: DIC property control chart. 12 samples were measured on batch 95. The calibration was carried out using the first 4 measurements and applied to all 12 measurements.
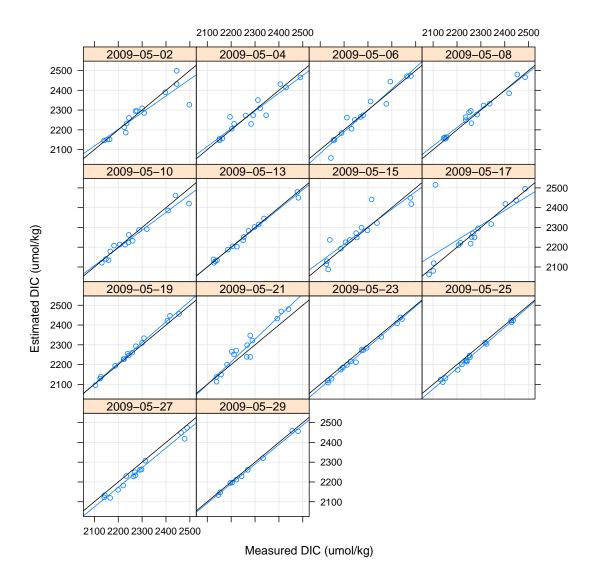
Figure 4: DIC estimated from pH and total alkalinity as a function of DIC measured with the AIRICA. The model I regression lines are shown in blue while the 1:1 line is shown in black. Note that model I regression should not be used when both variables are subject to measurement error. See text and figure 5 for the major axis model II regression on 13 May.
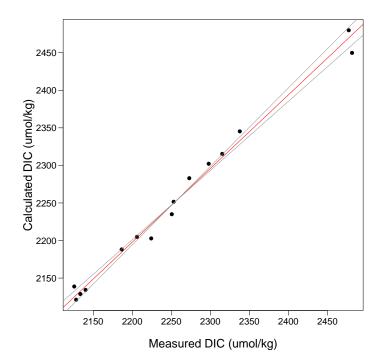
Figure 5: DIC estimated from pH and total alkalinity as a function of DIC measured with the AIRICA. Major axis model II regression [3] was used. The equation is given in the text.
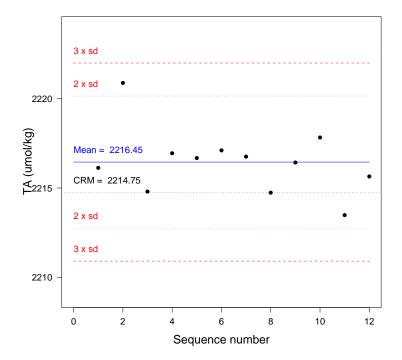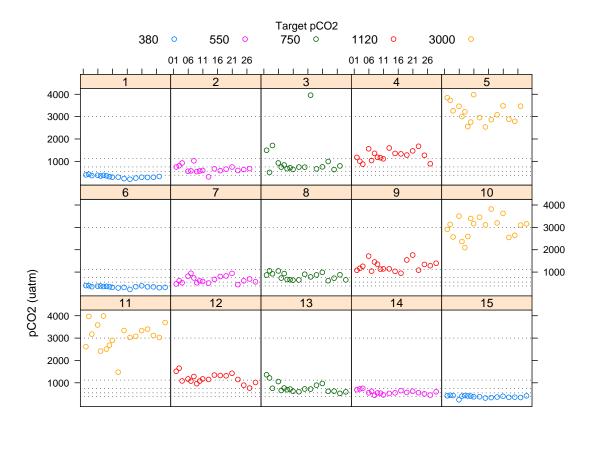
Figure 6: TA property control chart. 12 samples were measured on batch 95.

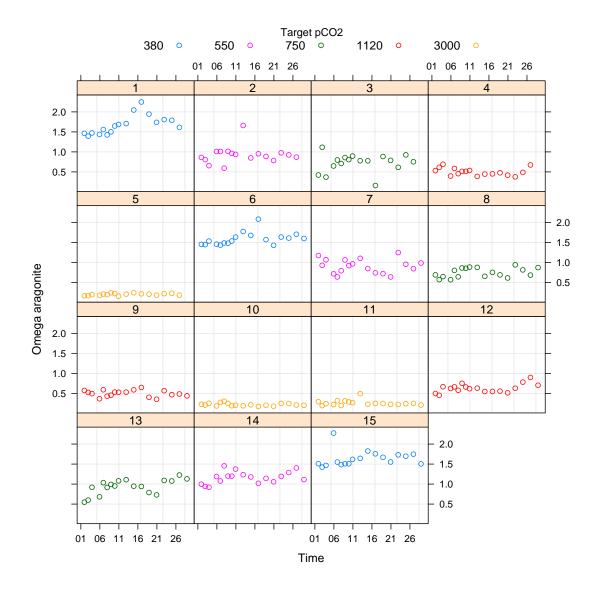Figure 7: pCO2 in the header tanks estimated from pH and total alkalinity measurements.

Figure 8: $\Omega_{aragonite}$ in the header tanks estimated from pH and total alkalinity measurements.