GA10 carbonate chemistry

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1. Sampling and analysis

1.1. Sample collection

During RRS *Discovery* cruise D357 [*Henderson*, 2010] and RRS *James Cook* cruise JC068 [*Henderson*, 2012], seawater samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) were transferred from the CTD rosette bottles to 250 ml borosilicate glass bottles (Schott Duran) via silicone tubing following best practices [*Dickson et al.*, 2007]. These glass bottles were thoroughly rinsed and allowed to overflow with excess sample before sealing shut with ground glass stoppers, which were held in place with elastic bands. The bottles were then stored in the dark until analysis.

1.2. Measurements

Measurements were carried out at sea mostly within 24 hours of sampling using a VINDTA 3C instrument (Marianda, Germany). This instrument extracts all DIC from a subsample by lowering the pH with excess 10 % phosphoric acid and by using a nitrogen carrier gas to carry the evolved CO_2 for coulometric titration. The TA is measured in a separate subsample by potentiometric titration with hydrochloric acid. A modified Gran plot approach was used to calculate TA from the titration data [*Humphreys*, 2015a]. Measurements of certified reference material batches 104 (for D357) and 114 (for JC068) obtained from A.G. Dickson (Scripps Institution of Oceanography, USA) [*Dickson et al.*, 2003] were carried out during each analysis session and used for calibration.

1.3. Precision

Across both cruises, 30 samples were collected and measured in duplicate, each pair from the same 20-litre rosette sample. The one-sigma precisions for these sampling duplicates were: 2.9 μmol kg^{-1} for DIC (n = 30), and 1.9 μmol kg^{-1} for TA (n = 30).

2. Combining the datasets

Cruise D357 sampled only the eastern part of the GA10 transect – it was cut short for logistical reasons [*Henderson*, 2010] – while JC068 covered its full extent [*Henderson*, 2012]. However, during cruise JC068, sampling in the region where the two cruises overlapped was mostly limited to the upper part of the water column (above 400 m), where interannual variability is highest. To generate the most coherent combined GA10 dataset we therefore used all of the measurements from JC068, but only included results from D357 that were from deeper than 400 m. This combined GA10 dataset is available from the British Oceanographic Data Centre [*Humphreys et al.*, 2016].

3. Cross-over analysis

3.1. Method

The accuracy of the different measurements was assessed by comparing DIC and TA measured during the GA10 cruises with similar results at equivalent σ_4 from cruises in the GLODAPv2 data synthesis [*Olsen et al.*, 2016]. For these assessments, we used the XOVER toolbox [*Humphreys*, 2015b], which follows a procedure similar to that of Lauvset and Tanhua [2015]. Explicitly, the following three steps were carried out separately for each GA10 sampling station: (1) all measurements in GLODAPv2 within a 50 km horizontal radius of the GA10 station were selected; (2) a piecewise cubic Hermite interpolating polynomial (PCHIP) [*Fritsch and Carlson*, 1980; *Kahaner et al.*, 1988] was implemented by MATLAB to interpolate values for the variables of interest measured on GA10 to match the selected GLODAPv2 results, using σ_4 as the interpolant; (3) the interpolated GA10 values were subtracted from their matching GLODAPv2 measurements, to give the residuals. Once these steps had been carried out for each GA10 station, the mean of all residuals of samples from depths greater than 1500 m

across all GA10 stations were calculated separately for each GLODAPv2 cruise, reported for each variable X as $R(X)$. A one-sample t-test was performed on all of the $R(X)$ values for each variable in order to test the null hypothesis that the mean $R(X)$ was equal to zero. Secular changes in the variables of interest were identified by ordinary least-squares regression of their $R(X)$ values against the cruise mean sampling dates.

3.2. Results

The one-sample t-tests were used to check if there was a systematic offset between the GA10 measurements and the external data from GLODAPv2. The null hypothesis was that the mean of the cruise residuals $R(X)$ for each variable X was equal to zero. At the 10 % significance level, the t-tests did not reject the null hypothesis for R(TA), so there was no evidence that the GA10 measurements of this variable are incompatible with the external results. However, the null hypothesis was rejected for R(DIC). To investigate further, the cruise sampling dates were also taken into account. Ordinary least-squares regressions between the residuals and the cruise dates revealed secular trends in DIC, but not in TA (Figure 1). For DIC, the regression lines intersected the $R(X)$ axis (i.e. the residual was zero) within a year of the date range in which the GA10 cruises were carried out. The R(DIC) regression revealed an increase in DIC at a rate of 0.56 μmol kg^{-1} yr^{-1} (r^2 = 0.89). The directions and magnitudes of this trend is consistent with well-documented observations that have been made on a global scale of recent multi-decadal DIC accumulation [*Sabine and Tanhua*, 2010] in the interior ocean. Consequently, the GA10 measurements for DIC are also considered to be concordant with GLODAPv2.

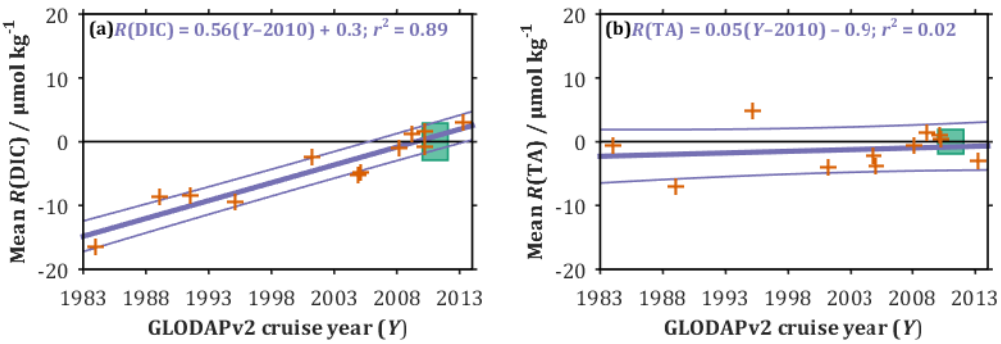

Figure 1. Secular changes in mean cruise residuals between GLODAPv2 cruises and GA10 for (a) dissolved inorganic carbon (DIC), (b) total alkalinity (TA). Mean residual for each GLODAPv2 cruise is indicated by an orange +. Thick violet lines illustrate ordinary least-squares regression equation at the top of each panel, and thin violet lines indicate ± 50 % uncertainty. Width of green boxes show the range of dates for GA10 sampling and height shows ± one-sigma precision for each variable measured during the GA10 cruises. If the thick violet line passes through the green box, as happens for both DIC and TA, then this indicates that the GA10 measurements are consistent with GLODAPv2.

4. References

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