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Measurements of the stable carbon isotope composition of dissolved inorganic carbon in the Northeastern Atlantic and Nordic Seas during summer 2012

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57

Abstract

The stable carbon isotope composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) in seawater was measured in samples collected during two cruises in the Northeastern Atlantic and Nordic Seas from June to August 2012. One cruise was part of the UK Ocean Acidification research programme, and the other was a repeat hydrographic transect of the Extended Ellett Line. In combination with measurements made of various other variables on these and other cruises, these data can be used to constrain the anthropogenic component of DIC in the interior ocean, and also assist in determining the influence of biological carbon uptake on surface ocean carbonate chemistry. The measurements have been processed, quality-controlled and submitted to an in-preparation global compilation of seawater $\delta^{13}\text{C}_{\text{DIC}}$ data, and are available from the British Oceanographic Data Centre. The observed $\delta^{13}\text{C}_{\text{DIC}}$ values fall in a range from -0.58 to $+2.37$ ‰, relative to the Vienna Pee Dee Belemnite standard. From duplicate samples collected during both cruises, the precision for the 552 results is 0.07 ‰, which is similar to other published studies of this kind. Data doi:10.5285/09760a3a-c2b5-250b-e053-6c86abc037c0 (Northeastern Atlantic), doi:10.5285/09511dd0-51db-0e21-e053-6c86abc09b95 (Nordic Seas).

1 Introduction

The ocean has taken up between a third and a half of anthropogenic carbon dioxide (CO₂) emitted since the late 18th century (Khatiwala et al., 2009; Sabine et al., 2004). It continues to absorb about a quarter of contemporary annual emissions (Le Quéré et al., 2009), thereby substantially reducing the atmospheric accumulation of CO₂. The consequences of this oceanic uptake include a pH reduction (ocean acidification) which is expected to persist for centuries beyond the atmospheric CO₂ transient (Caldeira and Wickett, 2003), and which will have consequences for marine ecosystems and biogeochemistry that we are only recently beginning to understand (Doney et al., 2009).

58

To predict the future response of the ocean carbon sink to continued changes to the atmospheric CO₂ partial pressure ($p\text{CO}_2^{\text{atm}}$), it is essential first to understand the existing spatial distribution of anthropogenic dissolved inorganic carbon (DIC), and a variety of methods have been employed to achieve this (Sabine and Tanhua, 2010), including: back-calculation from DIC, alkalinity and oxygen measurements (Brewer, 1978; Chen and Millero, 1979; Gruber et al., 1996); correlation with distributions of other anthropogenic transient tracers such as CFCs (Hall et al., 2002); and multi-linear regressions between observational data from pairs of cruises separated in time (Tanhua et al., 2007). Multi-decadal measurements have shown that increases in the $p\text{CO}_2^{\text{atm}}$ and ocean DIC have been accompanied by reductions in their carbon-13 content relative to carbon-12 ($\delta^{13}\text{C}$, Eqs. 1 and 2), a phenomenon known as the Suess effect (Keeling, 1979). This occurs because anthropogenic CO₂ is isotopically lighter (has a lower $\delta^{13}\text{C}$ signature) than pre-industrial and present-day atmospheric CO₂, and it provides one way to investigate the spatial distribution of anthropogenic DIC and quantify its inventory (Quay et al., 1992, 2003, 2007; Sonnerup et al., 1999, 2007). Additionally, because the $\delta^{13}\text{C}$ of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) takes approximately 10 times longer to equilibrate with the atmosphere than DIC, their relative rate of change in the interior ocean can constrain the length of time a given water mass last spent at the ocean surface (McNeil et al., 2001; Olsen et al., 2006). Finally, $\delta^{13}\text{C}_{\text{DIC}}$ measurements are important for verification of predictions made by ocean carbon cycle models (Sonnerup and Quay, 2012).

We present measurements of seawater $\delta^{13}\text{C}_{\text{DIC}}$ from two cruises during summer 2012. The first cruise (RRS *James Clark Ross*, JR271), was carried out by the Sea Surface Consortium, part of the UK Ocean Acidification research programme (UKOA). These $\delta^{13}\text{C}_{\text{DIC}}$ measurements will contribute towards quantifying the impact of ocean acidification upon the ocean carbon cycle and the biogeochemical processes which affect it, a high-level objective for this Northeastern Atlantic/Nordic Seas cruise and the UKOA. The second cruise (RRS *Discovery*, D379) was a repeat occupation of the Extended Ellett Line (EEL) hydrographic transect in the Northeastern Atlantic. These

are the first $\delta^{13}\text{C}_{\text{DIC}}$ measurements made during an EEL cruise, establishing a baseline for future work on the transect.

2 Sample collection

2.1 Cruise details

Samples for $\delta^{13}\text{C}_{\text{DIC}}$ measurements were collected during two cruises. (1) RRS *James Clark Ross* cruise JR271, which took place in the period between 1 June and 2 July 2012 in the Northeastern Atlantic and Nordic Seas (Leakey, 2012). Most stations sampled for JR271 were shallower than 500 m, determined by the overall sampling strategy for that cruise. The underway surface water samples collected during JR271 were from a transect across the Fram Strait at approximately 79° N, the northernmost section of the cruise. (2) RRS *Discovery* cruise D379, which took place in the period between 31 July and 17 August 2012, in the Northeastern Atlantic (Griffiths, 2012). The EEL transect covered by D379 runs from Scotland to Iceland via the Rockall Trough and plateau, and the northernmost section of the route (at 20° W) overlaps the end of the A16 WOCE transect. The samples collected cover the full depth range. For both cruises, the sample locations are illustrated by Fig. 1, and information about the number and types of samples collected is given in Table 1.

2.2 Collection and storage methods

Prior to sample collection, the containers were thoroughly rinsed with deionised water (MilliQ water, Millipore, $> 18.2 \text{ m}\Omega \text{ cm}^{-1}$). Samples were collected from the source (either niskin bottle or underway seawater supply) via silicone tubing, following established best-practice protocols (Dickson et al., 2007; McNichol et al., 2010). The containers were thoroughly rinsed with excess sample directly before filling until overflowing with seawater, taking care not to generate or trap any air bubbles. Two different sample

containers were used: (1) 100 mL glass bottles with ground glass stoppers, lubricated with Apiezon[®] L grease and held shut with electrical tape; (2) 50 mL glass vials with plastic screw-cap lids and PTFE/silicone septa. 0.02 % of the sample container volume of saturated mercuric chloride solution was added to sterilise each sample before sealing. A 1 mL air headspace was also introduced to the bottles, but the vials were sealed completely full of seawater. The samples were stored in the dark until analysis.

3 Sample analysis

The $\delta^{13}\text{C}_{\text{DIC}}$ samples were analysed at the Scottish Universities Environmental Research Centre Isotope Community Support Facility (SUERC-ICSF) in East Kilbride, UK between June and August 2013.

The abundance of ^{13}C relative to ^{12}C in a given substance X is given by:

$$R_X = \frac{[^{13}\text{C}]_X}{[^{12}\text{C}]_X} \quad (1)$$

where $[^{13}\text{C}]_X$ and $[^{12}\text{C}]_X$ are the concentrations of ^{13}C and ^{12}C respectively in X . For each sample, this value is then normalised to a reference standard using the following equation:

$$\delta^{13}\text{C} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000\text{‰} \quad (2)$$

Samples were analysed in a batch process. For each batch, $\delta^{13}\text{C}$ was measured in 88 Exetainer[®] glass vials, each of 12 mL volume. At least 18 vials per batch were set aside for calibration standards ("standard vials"), while the rest were used for seawater samples ("sample vials").

61

Most of the standards were analysed before any samples, at the start of each batch ("initial standards"), except for a pair near the middle and at the end ("mid-point standards" and "end-point standards" respectively). Three SUERC-ICSF in-house standards (powdered carbonate/bicarbonate solids called MAB, NA and CA; see Table 2) were used to calibrate the $\delta^{13}\text{C}_{\text{DIC}}$ results to the Vienna–Pee Dee Belemnite (V–PDB) international standard (Coplen, 1995). These in-house standards have previously been calibrated against the NBS 19 international standard. The initial standards consisted of a range of masses of all 3 of the in-house standards. The mid- and end-point standards, used for drift correction, were of similar mass and the same type (MAB for batches 1 and 2, and NA thereafter).

A total of 103 seawater samples were subsampled twice and analysed consecutively ("analysis duplicates"). This was carried out for all samples in the first 2 batches, and every 10th sample thereafter.

The analysis procedure for each batch was necessarily slightly different for the standards and samples because of their different states (solid and liquid respectively).

The standard and sample vials were soaked and rinsed with deionised water, then dried overnight at 65 °C. The calibration materials were weighed into the standard vials, whilst 80 μL of concentrated phosphoric acid (mixed with phosphorus pentoxide to result in minimum 100 % saturation) was added to each sample vial, to convert all of the dissolved carbonate and bicarbonate in the seawater sample (added later) into CO_2 . All vials were then closed using plastic screw-cap lids with PTFE/silicone septa to make an air-tight seal. These lids were not removed until the entire analysis process was complete. All addition or removal of fluids from the vials after this point was via injection of a needle through the septa.

The air in each vial was replaced to remove CO_2 by flushing with helium for 15 min ("overgassing"). This was an automated process carried out by a CTC Analytics PAL system. After overgassing, 1 mL of the phosphoric acid/phosphorus pentoxide diluted with deionised water to 10 % concentration was added to each standard vial. For each sample, a syringe was rinsed 3 times with the sample and then used to transfer 1 mL of

62

that sample into the vial. All of the vials were then left for at least 24 h for the standard or sample to fully react with the acid and equilibrate with the gas headspace.

Finally, the gas headspace in each vial was automatically sampled by the PAL System, and the $\delta^{13}\text{C}$ of the CO_2 measured 10 times by a Thermo Scientific Delta V mass spectrometer attached to a Thermo Scientific Gasbench 2. The set of 10 measurements for each sample or standard are henceforth referred to as “technical replicates”.

4 Measurement processing

4.1 Batch-by-batch processing

The raw $\delta^{13}\text{C}$ results were processed using MATLAB[®] software in five steps: (1) erroneous measurement removal, (2) averaging, (3) peak area correction, (4) calibration to V-PDB, and (5) drift correction. Except where specified, these steps were applied to each analysis batch independently, using only data from that batch.

4.1.1 Erroneous measurement removal

To begin, erroneous $\delta^{13}\text{C}$ measurements were removed from the sets of technical replicates. These typically occurred when the CO_2 concentration in a replicate was too high or low, resulting in the peak area falling outside of the calibration range. Therefore, only measurements with a peak area between 10 and 145 were retained, and if fewer than 6 of the original 10 technical replicates for a given sample fell in the acceptable peak area range, the entire sample was discarded.

4.1.2 Averaging

After erroneous measurements were removed, the mean $\delta^{13}\text{C}$ and peak area was calculated from each sample's technical replicates. These mean values were used for the remainder of the data processing.

63

4.1.3 Peak area correction

Plots of peak area against raw $\delta^{13}\text{C}$ reveal relationships which are different for seawater and each of the 3 calibration standards. Peak area is controlled by CO_2 concentration, so a range of peak areas can be generated by using a range of masses of calibration standards, or volumes of seawater, in different analyses, and these results can be used to quantify and correct for the relationships between peak area and raw $\delta^{13}\text{C}$. All corrections were made to a peak area of 35, which is approximately equal to the mean peak area for all seawater samples across all analysis batches.

For the calibration standards, the corrections were derived using the initial standards. For each batch, a linear least-squares regression between peak area and raw $\delta^{13}\text{C}$ was derived for each standard. Regressions were discarded if the range of input peak areas either (i) did not include the value 35 or (ii) was smaller than 30. The mean gradient for each of the three standards (excluding discarded regressions) was then calculated across all batches and used to make the peak area correction for each standard (Fig. 3).

For the seawater samples, 6 subsamples of a large homogeneous seawater sample were taken in volumes from 0.50 to 1.50 mL (in 0.25 mL increments). These were measured consecutively during analysis batch #6, and a linear least-squares regression of $\delta^{13}\text{C}$ against peak area was used to make the linearity correction for all seawater samples from all batches (Fig. 4).

4.1.4 Calibration to V-PDB

The mean of the peak-area-corrected $\delta^{13}\text{C}$ for each of the 3 calibration standards was calculated (L), using only the measurements of the initial standards. A non-linear fit (Eq. 3) between L and the corresponding certified values relative to V-PDB (C , Table 2) was used to determine constants x , y and z for each batch, and then calibrate the samples to the V-PDB international standard. The fit used an equation of the form:

$$L^2 + C^2 + x \cdot L + y \cdot C = 0. \quad (3)$$

4.1.5 Drift correction

An interpolation between three points was used to correct for instrument drift during each batch. The index was the analysis position, with the mean analysis positions for the initial, mid-point and end-point standards as sample points for the interpolation.

- 5 The initial point was assigned a value (drift) of 0, and mid-point and end-point values were calculated by subtracting the mean calibrated $\delta^{13}\text{C}$ for each of the mid-point and end-point standard pairs from their certified values (Table 2). Piecewise cubic hermite interpolating polynomial fits (Fritsch and Carlson, 1980) between analysis position and drift were generated and used to correct all results other than the initial standards.

10 4.2 Quality control

- After calibration, the mean $\delta^{13}\text{C}_{\text{DIC}}$ and its SD was calculated for all seawater samples in all batches. Four of the 608 measurements had extremely low $\delta^{13}\text{C}_{\text{DIC}}$ values, more than 6 SDs away from the mean. These measurements were discarded; they are assumed to represent sample containers where the air-tight seal failed and so the DIC is contaminated with atmospheric CO_2 , which has a much lower $\delta^{13}\text{C}$ than typical ocean DIC (Lynch-Stieglitz et al., 1995).

- 15 The $\delta^{13}\text{C}_{\text{DIC}}$ measurements were finally combined with their cruise metadata, using the mean values for pairs of analysis and sample duplicates, and the differences between the two samples in each duplicate pair calculated for statistical evaluation. 20 Figures 6 and 7 illustrate the observed $\delta^{13}\text{C}_{\text{DIC}}$ distributions.

4.3 Data availability

- The final, calibrated $\delta^{13}\text{C}_{\text{DIC}}$ results have been archived with the British Oceanographic Data Centre and are publicly accessible, free of charge (Humphreys et al., 2014a, b). Measurements of additional hydrographic variables for cruise D379 are similarly available from the Carbon Dioxide Information Analysis Center (Hartman et al., 2014). The 25

$\delta^{13}\text{C}_{\text{DIC}}$ results have also been submitted to an ongoing global compilation of seawater $\delta^{13}\text{C}_{\text{DIC}}$ data (Becker et al., 2015) as part of which they will undergo a secondary quality-control procedure.

5 Discussion and statistics

5 5.1 Erroneous measurement removal

- The process of removing erroneous measurements from the raw data eliminated approximately 1 % of the seawater sample technical replicates, but reduced the mean and maximum SD of these sets of replicates by one and three orders of magnitude respectively. Limiting the range of acceptable peak areas was responsible for almost 10 all of the reduction in the mean SD and significantly reduced the maximum SD. The second step of discarding samples with fewer than 6 technical replicates in this acceptable peak area range made little difference to the mean SD, but resulted in a further significant reduction to the maximum SD (Table 3).

5.2 Calibration to V-PDB

- 15 Initially, a linear fit was used to calibrate the raw $\delta^{13}\text{C}$ measurements to the V-PDB standard. However, application of this calibration to the same standards that it was generated from resulted in overestimations of the MAB and CA standards, and underestimations for NA, relative to the certified values. The over/underestimations were consistent in polarity across all batches, with mean values of +0.08, -0.10 and +0.03 % for MAB, NA and CA respectively. This was resolved by using a non-linear calibration fit. A circular fit (Eq. 3) was used, rather than an ordinary polynomial, because it 20 maintains constant curvature in the calibration space, which has the same units of per mille (‰) on both axes. With the non-linear fit, for all standards across all 11 batches, the mean \pm SD of the difference between calibrated and certified $\delta^{13}\text{C}$ was 0.00 ± 0.06

(MAB, 59 analyses), 0.00 ± 0.11 (NA, 73 analyses) and 0.00 ± 0.08 ‰ (CA, 47 analyses) (Fig. 5).

5.3 Precision from duplicates

Comparison with published estimates of precision for $\delta^{13}\text{C}_{\text{DIC}}$ measurements is complicated by the various different definitions used in the literature. In this study, the mean absolute difference in calibrated $\delta^{13}\text{C}_{\text{DIC}}$ for all analytical duplicate pairs was 0.053‰. This is very close to published values which we believe to be equivalently defined. For example, Olsen et al. (2006) quote a long-term precision for $\delta^{13}\text{C}$, based on replicates, of 0.05‰.

To evaluate the true measurement precision, including error introduced by the sampling process, it is necessary to use the sample duplicates rather than the analytical duplicates (Table 4). The mean duplicate pair difference for samples in the same type of container was 0.080‰. However, where the duplicate samples were collected in different containers (one in a bottle, one in a vial), the mean absolute duplicate pair difference took the higher value of 0.168‰. This suggests that the small differences in the sampling method for the different containers introduced a small but measurable increase in the error. To test if there was a systematic offset in $\delta^{13}\text{C}_{\text{DIC}}$ measured in the different container types, we subtracted the vial value from the bottle value for these duplicate pairs with non-matching containers, and performed a one-sample t test for the null hypothesis that the resulting distribution had a mean value of 0. It was not possible to reject the null hypothesis at the 95 % certainty level, so we did not find a consistent offset between the container types.

The expected SD of a large number of measurements of the same sample (i.e. precision) can be estimated from the mean duplicate pair absolute difference by dividing by 1.128 (Thompson and Howarth, 1973). For this study, for the duplicates from both cruises which were in the same type of container, the precision is 0.070‰. As for the analytical precision, this compares well with equivalent published values. For example: Olsen et al. (2006) found an SD of 0.07‰ for 16 samples taken in seawater with

67

“very similar physical and chemical water mass characteristics”; McNichol et al. (2010) record a “replication” of ± 0.03 ‰ from measurements of duplicate seawater samples from the Niskin bottle; and Griffith et al. (2012) calculated a “pooled SD” for 8 duplicate $\delta^{13}\text{C}_{\text{DIC}}$ samples of 0.23‰.

Author contributions. M. P. Humphreys, E. P. Achterberg and A. M. Griffiths determined sampling strategy and collected the samples. M. P. Humphreys, A. McDonald and A. J. Boyce carried out the measurements and data processing. M. P. Humphreys prepared the manuscript with contributions from all co-authors.

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Table 1. Quantities and types of samples collected during cruises JR271 and D379, and types of sample containers used. D379 duplicates where one sample was collected in each type of container are counted in the “Unique samples – Bottles” cell (asterisked). The rows labelled “Both” show the total number of samples collected during both cruises.

Cruise		CTD stations		Underway	Total
		Bottles	Vials	Bottles	
JR271	Unique samples	210	0	17	227
	Incl. duplicates	221	0	17	238
D379	Unique samples	62*	263	0	325
	Incl. duplicates	66	284	0	35
Both	Unique samples	272	263	17	552
	Incl. duplicates	287	284	17	588

Table 2. The SUERC-ICSF in-house calibration standards.

Name	Chemical composition	Certified $\delta^{13}\text{C}$ V-PDB/‰
MAB	CaCO_3	+2.48
NA	NaHCO_3	-4.67
CA	CaCO_3	-24.23

Table 3. Summary of the erroneous measurement removal process for all of the seawater samples. Numbers in each row are for all data after application of the measurement removal step indicated in the first column. Tech. rep. SD = SD of uncalibrated $\delta^{13}\text{C}_{\text{DIC}}$, calculated for each sample's set of 10 technical replicates.

Measurement removal step	Number of measurements	Number of sample sets	Mean tech. rep. SD/‰	Max. tech. rep. SD/‰
All raw data	7410	741	0.240	66.60
10 < peak area < 145	7349	740	0.029	0.616
Valid tech. reps ≥ 6	7329	734	0.028	0.058

Table 4. Mean absolute differences between sampling duplicates. The “sample container” column indicates whether the duplicates were collected in the same type of container as each other, or different containers (i.e. one in a vial, one in a bottle).

Cruise	Sample container	Number of pairs	Mean absolute difference/%
D379	Same	16	0.109
JR271	Same	11	0.080
Both	Same	27	0.097
D379	Different	9	0.168

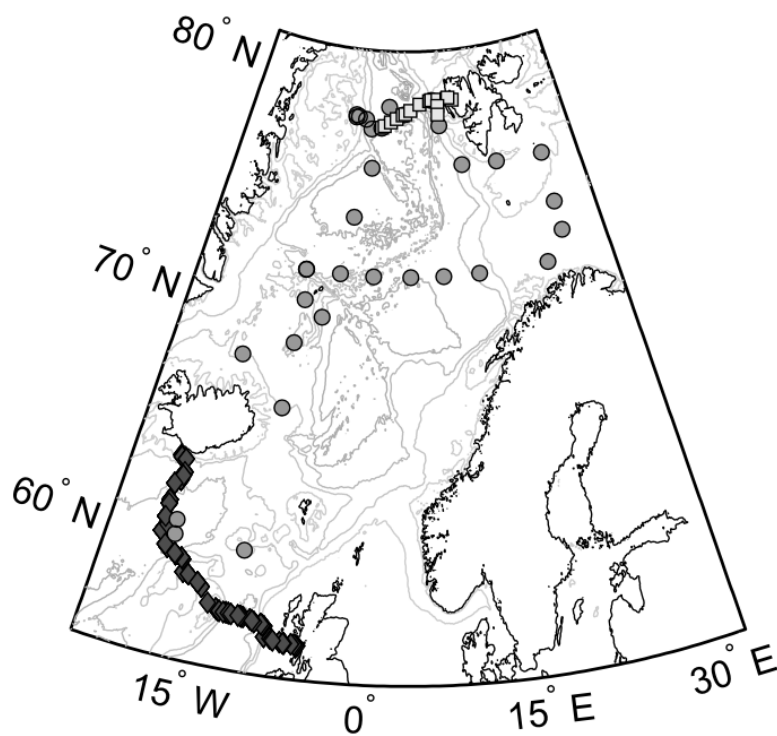


Figure 1. Samples locations for cruises D379 (dark grey diamonds) and JR271 (CTD stations are medium grey circles, underway samples are light grey squares).

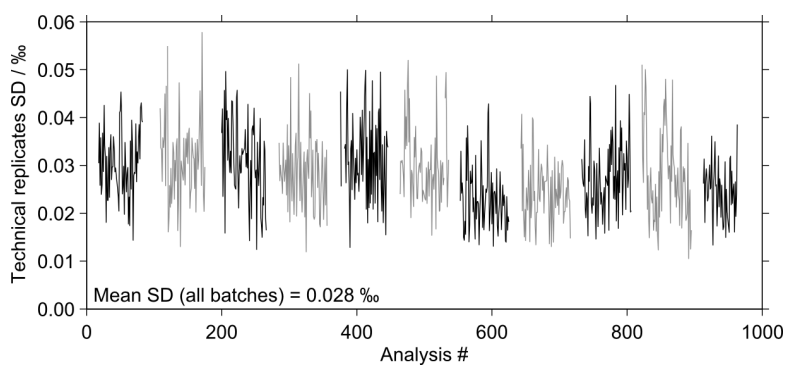


Figure 2. SD of technical replicates for each seawater sample, after erroneous peak removal. Alternating black and grey sections indicate separate analysis batches.

77

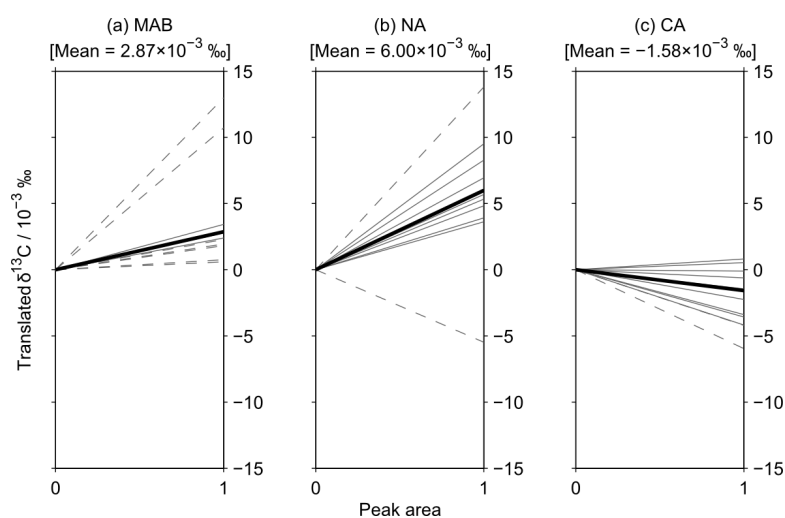


Figure 3. Peak area vs. $\delta^{13}\text{C}$ relationships used for the peak area correction of the calibration standards. The grey lines are the linear least-squares best fit for each analysis batch, but translated to have a y intercept of 0 (so that the value of the line at peak area = 1 is equal to the gradient). The dashed lines indicate batches excluded from calculation of the mean gradient for each standard (thick black line; see text for exclusion criteria).

78

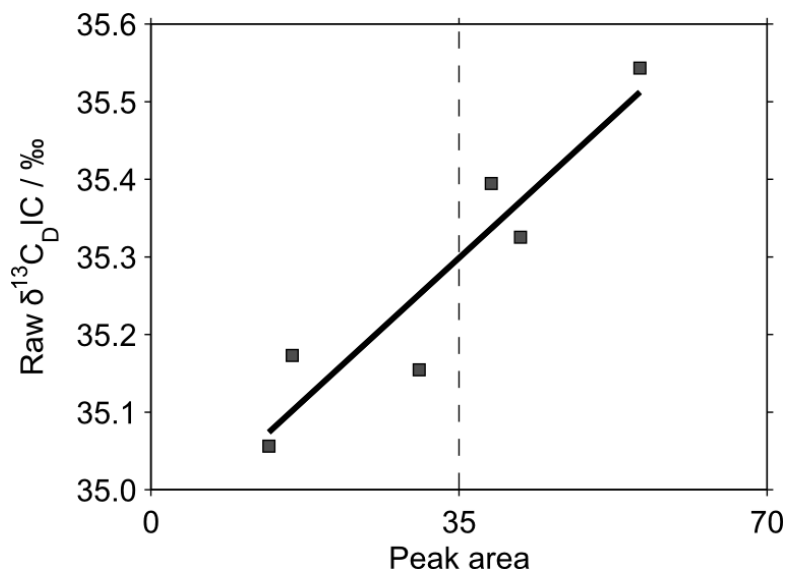


Figure 4. Peak area vs. $\delta^{13}\text{C}$ relationship for homogeneous seawater sampled at a range of volumes from 0.5 to 1.5 mL (grey squares). The black best-fit line shows the relationship used to correct all seawater samples for peak area, and the vertical dashed line at (peak area) = 35 indicates the peak area to which corrections have been made.

79

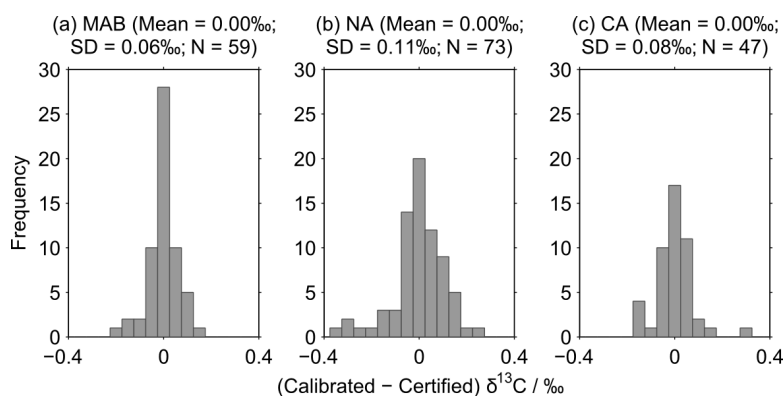


Figure 5. Distributions of the difference between calibrated and certified $\delta^{13}\text{C}$ for all calibration standards in all batches. N = number of analyses.

80

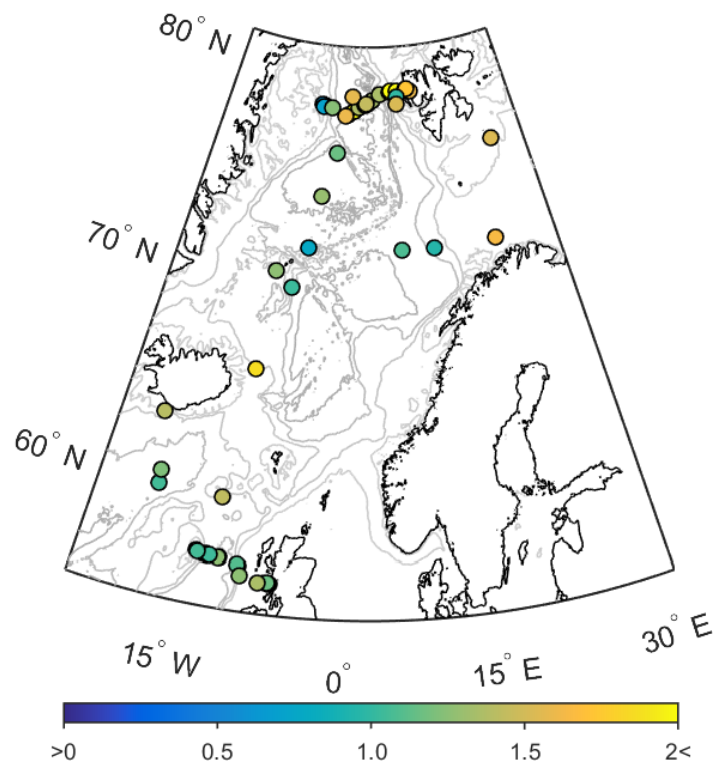


Figure 6. Measured $\delta^{13}\text{C}_{\text{DIC}}/\text{‰}$ for all samples from both cruises collected at a depth shallower than 10 m. $\delta^{13}\text{C}_{\text{DIC}}$ values in this figure are in the range from +0.22 to +2.37 ‰; the colour scale is identical to Fig. 7.

81

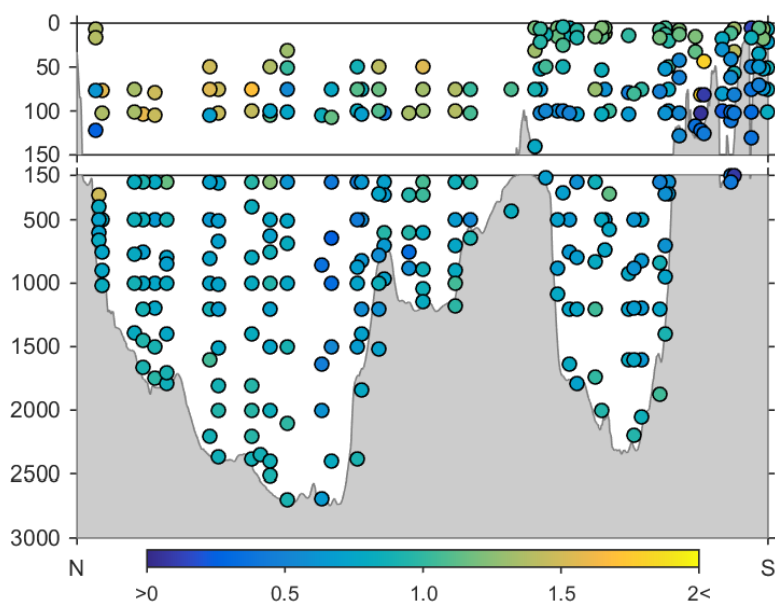


Figure 7. Measured $\delta^{13}\text{C}_{\text{DIC}}/\text{‰}$ for all samples from cruise D379. $\delta^{13}\text{C}_{\text{DIC}}$ values in this figure are in the range from +0.08 to +1.82 ‰; the colour scale is identical to Fig. 6. Section runs from Iceland to Scotland from left to right, see Fig. 1 for precise route. Bathymetry is approximate.

82