Supplemental methods for **"Dynamic deep Atlantic storage of glacial CO_2 revealed from combined boron $[CO_3^{2-}]$ and pH proxies"**

1. Hydrographic Data

Hydrographic data for the sites (used for carbonate system calculations) were gathered from the GLODAP dataset (Key et al., 2004), and are presented in Table 1:

Table 1

Site	Lat (°)	Lon (°)	Depth (m)	Temp (°C)	Sal (psu)	Carbonate ion (µmol/kg)	pH
ODP 980	55.5 N	14.7 W	2170	4	35	119.9	8.00
IODP 1313	41.0 N	32.6 W	3426	3	35	123.0	7.97
IODP 1308	49.9 N	24.2 W	3871	3	35	116.8	7.96
ODP 999	12.4 N	78.4 W	2839 (1800 effective)	4	35	108.0	7.88

2. Analytical techniques

Sediment samples from core material were washed with deionised water and sieved to >63μm, to separate fine and coarse fractions. Individual foraminifera (*Cibicides wuellerstorfi*) were hand separated from the 212-500 μm size fraction. Although the boron concentration of benthic foraminiferal calcite is relatively high (~25ppm) compared to planktic foraminifera (<10 ppm), relatively low overall benthic abundances (~300 μg *C. wuellerstorfi*/g sediment) resulted in difficulty in carrying out reliable dual $\delta^{11}B$ and B/Ca analyses from the same sample material (in contrast to some other, lower resolution studies; e.g. Rae et al. (2011); Yu et al. (2008). B/Ca data were therefore gathered in isolation for around 40-70 sample intervals per core (~1 per 2-4 kyrs) and around 30 tests of *C. wuellerstorfi* were separated from ~20 (1 per 7 kyrs) sediment samples for separate $\delta^{11}B$ measurements. Both sample sets were cleaned and dissolved in a boron-free laboratory suite at the University of Southampton. Following established protocols (Rae et al., 2011) clays were physically removed from the lightly crushed benthic foraminifera by repeated rinses with 18.2 MΩ cm MQ water. Oxidative cleaning to remove organic material was then undertaken using a buffered 1% H_2O_2 solution. Finally a weak acid (0.0005 M nitric acid) leach step was undertaken after sample transfer to Teflon vials prior to dissolution in ~0.075 M nitric acid. These analytical methods follow those of

Foster (2008); Henehan et al. (2013); Rae et al. (2011) and are only significantly modified to allow for reduced sample loss during cleaning, for instance care was taken to crack foraminifera individually and no sample transfer step was undertaken for Me/Ca (Metal - calcium) analysis. Mg/Ca ratios from the same analyses are also presented as temperature is included in the calculation for pH from $\delta^{11}B$, although the effect is relatively small (0.1 mmol/mol ~ 0.3 °C ~ 0.036 pH units), and thus we use the hydrographic temperature for all calculations (from Table 1). As all work is carried out on shallowly buried well preserved tests, the level of physical cleaning (Barker et al., 2003) could be reduced to minimise sample loss, though strict criteria are used to rule out clay contaminated results (samples with Al/Ca >100µmol/mol removed). For those samples analysed for $\delta^{11}B$ only, an aliquot of ~10% was removed from the cleaned and dissolved sample for elemental analysis for this purpose. Clay contamination can be a problem for boron isotope analysis due to the relatively high concentration of boron in clays (B^{3+} can substitute for Al^{3+}) and the low $\delta^{11}B$ of clay derived boron (Deyhle and Kopf, 2004; Oi et al., 1989).

3. Determination of boron isotopic composition

Boron was separated from the calcite matrix using boron-specific anionic exchange resin Amberlite IRA 743 (Kiss, 1988) in a 20 µl purpose made column (Foster, 2008; Foster et al., 2013). Prior to separation the dissolved foraminifera samples were buffered using an acetic acid and Na-acetate mixture to ensure the correct pH for boron retention. Columns were carefully calibrated and were checked during the processing of each sample to ensure complete sample elution (in each case >>99% of B eluted). Samples were measured for boron isotope composition on Thermo Scientific Neptune MC-ICPMS at the University of Southampton, following previous protocols (Foster, 2008). External reproducibility of the MC-ICPMS $\delta^{11}B$ method (at 95% confidence, 2SD) is based upon repeat measurements of an in house standard and is a function of sample concentration (Foster et al., 2013; Henehan et al., 2013; Rae et al., 2011), this typically ranges from 0.6‰ to 0.2‰ (for 10-30 tests, see equation below).

Equation 1.

$$2\sigma = 1.87 \cdot e^{-20.6[^{11}B]} + 0.22 \cdot e^{-0.43[^{11}B]}$$

Where $[^{11}B]$ is the intensity of ^{11}B signal in volts (see Henehan et al. (2013) for full details).

2.1 Element ratios

For the $\delta^{11}B$ samples a suite of Me/Ca ratios were measured but due to small samples sizes (≤0.5 mmol/litre Ca) only Al/Ca ratios were used in order to assess cleaning efficacy (see above). For the B/Ca-samples B/Ca and other Me/Ca ratios (Li, B, Na, Mg, Al, Mn, Sr, Cd, Ba, Nd, and U/Ca) were determined on solutions with [Ca] of 0.5 to 4 mmol/l using a Thermo Element 2XR ICP-MS at the University of Southampton. Analytical precision at 95% confidence is determined by the reproducibility of several in house standards and is <5% for all elements and <4% for B/Ca ratios (~7 μmol/mol). All samples are matrixed match to a gravimetrically determined standard, to eliminate concentration effects on the ratios produced (e.g. Henehan et al. (2015)).

2.2 Carbonate system reconstructions and calculations

B/Ca was converted to $[CO_3^{2-}]$ using the species specific core top calibration of Yu and Elderfield (2007), see below.

Equation 2.

$$[CO_3^{2-}]_{SITE} = \Delta[CO_3^{2-}] + [CO_3^{2-}]_{sat}$$

Where: $\Delta[CO_3^{2-}] = \frac{B/Ca-177.1}{1.14}$ (Yu and Elderfield, 2007)

Modern $[CO_3^{2-}]_{sat}$ ($[CO_3^{2-}]/\Omega$),where Ω is the calcite saturation state is calculated for each site and is quality checked against data measured from the core top that were not part of the original calibration.

pH is calculated from boron isotopes using the following equation (Hemming and Hanson, 1992);

Equation 3.

$$pH = pK_B - log\left(-\frac{\delta^{11}B_{SW} - \delta^{11}B_{CaCO_3}}{\delta^{11}B_{SW} - \alpha_B \cdot \delta^{11}B_{CaCO_3} - 1000 \cdot (\alpha_B - 1)}\right)$$

where, following (Rae et al., 2011), only the charged $B(OH)_4^-$ species of oceanic boron is incorporated into the benthic foraminiferal calcite ($\delta^{11}B_{CaCO3}$). $\delta^{11}B_{sw}$ is the boron isotopic composition of seawater that is well constrained over the period of this study due to its long residence time, and we have used a value of 39.61‰ (Foster et al., 2010; Lemarchand et al., 2000) α_B is taken as 1.0272 ± 0.0006 (Klochko et al., 2006) and pK_B is the -$\log_{10}$ of the dissociation constant of boric acid in seawater that is a function of salinity, temperature and pressure (Dickson, 1990; Zeebe, 2005). Due to a number of issues surrounding the reliability of epifaunal benthic foraminiferal Mg/Ca ratio as a recorder of bottom water temperature, we use modern deep-water temperature and salinity and pressure calculated from the water depth (also modern) throughout each record. An uncertainty of 3°C and 3 psu (for temperature and salinity respectively), significantly more than is thought likely is propagated into the error envelopes through changes to the pK_B (shown at 95% confidence). Of course, the change in salinity over the glacial is large and globally systematic, but for both temperature and salinity, there is no necessity for local systematic change over the glacial cycle, especially in face of changing watermasses. Fortunately the effect of these parameters on pK_B and hence pH is very (~0.005 psu^{-1} and ~0.012 $^{\circ}\text{C}^{-1}$), thus our uncertainty comprehensively covers the range of possibilities. All oceanographic parameters are included in the calibration uncertainty for B/Ca (Yu and Elderfield, 2007).

2.3 LOESS best fit lines.

The local regression (LOESS) lines fitted in Figure 6 were calculated in the R statistical software, using a smoothing function which takes account of all depths but with decreasing weighting according to the cube of their distance in the depth domain. We find that this function accurately captures the main features of depth structure and in the modern ocean the observational dataset, while not matching noise occurring from local changes to one or two sites in our sample set. It should be noted that the fewer points making up the loess function, the less accurate it is likely to be in describing the oceanic data, and this becomes more apparent in the early parts of the glacial.

2.4 pH and [CO_3^{2-}] cross-plot

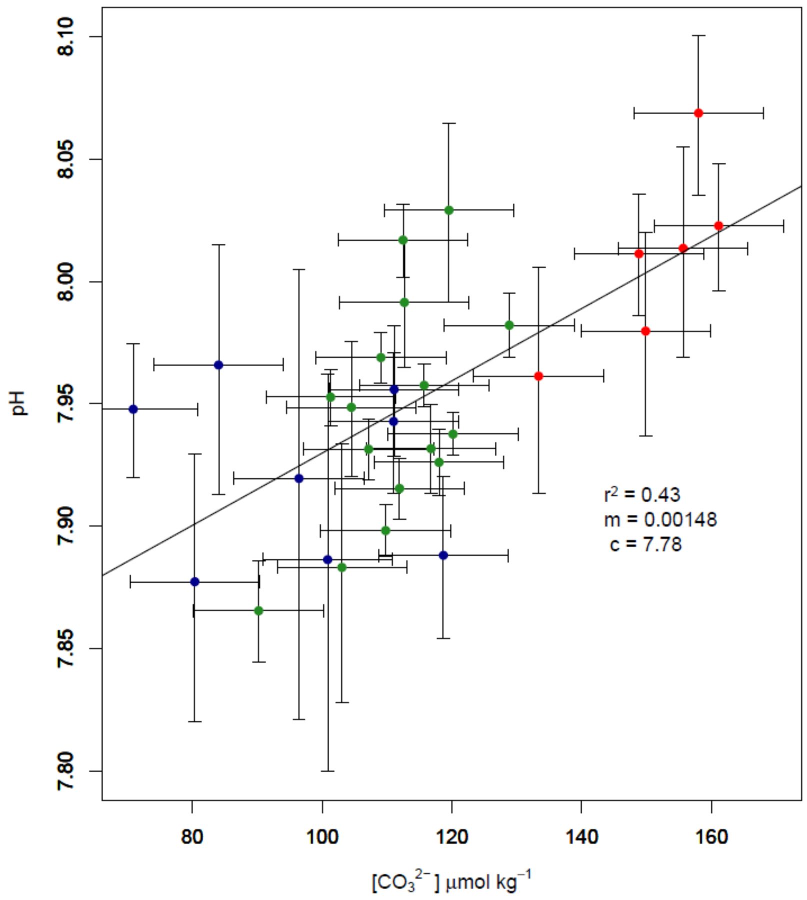

Figure S1. A plot showing cross-plotted $\delta^{11}B$ derived pH and B/Ca derived [CO_3^{2-}] on the same sample material. Blue data show IODP U1308, green show IODP U1313 and red show ODP 980. The r^2 is 0.43.

Supplemental References

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