Paleoceanography

Supporting Information for

Data constraints on Glacial Atlantic Water Mass Geometry and Properties

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Introduction

This supplementary information includes figures of oceanographic properties not included in the main text, stratigraphic information for the gravity and piston cores used in this study, core-top benthic foraminiferal B/Ca data, addition figures deriving from the glacial inversion, and table with locations of cores used in this study. All unpublished data associated with this contribution are included in Supplementary data files, in Excel.

As noted in the main text, all new stable isotope measurements were made at the Woods Hole Oceanographic Institution on a Finnigan MAT253 mass spectrometer equipped with an
integrated automated carbonate device using standard procedures (Ostermann & Curry, 2000). Data were converted to VPDB using NBS-19 standards analyzed in each run. Measurement precision, as determined by NBS-19, was ±0.05‰ for δ¹³C and ±0.08‰ for δ¹⁸O.

Elemental ratios (Cd/Ca, B/Ca, among others) were measured on 5-15 pooled tests of the benthic foraminifera. Foraminifera were cleaned following the full trace metal protocol (Boyle & Keigwin, 1985; Rosenthal et al. 1995). Demerara Rise core-top data and glacial measurements on C. pachyderma from core 46CDH were collected at Woods Hole Oceanographic Institution, and glacial levels of several Blake Outer Ridge cores were determined at the University of Colorado, respectively, both on a Thermo-Finnigan Element2 sector field single collector ICP-MS following the method of Rosenthal et al. (1999) and subsequent modifications (Huang et al. 2008; Lear et al., 2002; Marchitto, 2006). Glacial measurements on Uvigerina from core 46CDH and on the glacial section of other Demerara Rise cores were generated at Academia Sinica on a Thermo-Scientific Element XR sector field single collector ICP-MS, using the same methods. At the time of these measurements, the long-term precision (2RSD) for all elemental ratios was better than 3% (2.4 % for Cd/Ca; 3% B/Ca) at WHOI, ~3.6% for Cd/Ca U. Colorado, and 2.5% at Academia Sinica, based on matrix-matched consistency standards.

As noted in text, Cd/Ca of seawater collected on Demerara Rise hydrocasts was also measured at WHOI. Briefly, filtered seawater samples were acidified at sea with ultrapure 11N HCl (BASELINE®, SEASTAR) to pH < 2, and were sub-sampled (20 mL) into acid-clean 30 mL polypropylene bottles (Nalgene®) in a clean room environment. The 20 mL aliquots were adjusted to pH = 6.0 ± 0.2 by adding ultrapure 11M ammonia solution (BASELINE®, SEASTAR) for the Cd purification using Chelex-100 resin (Bio-Rad, 200-400 mesh, bed volume: 0.25 mL). After cleaning once with 5 mL 2N HNO₃ and 15 mL deionized water (DIW), the columns were conditioned with 5 mL 1M ammonia acetate (NH₄CH₃CO₂). After sample loading, 14 mL 1M NH₄CH₃CO₂, followed by 0.5 mL DIW, were added to remove matrix elements. Cd was then collected by adding 2 mL DIW and 3 mL 2N HNO₃. The chemical yield for Cd was better than 97 ± 2% (RSD, n = 12) through processing the synthetic seawater standard (doped with 0.020 μg/L of Cd). A series of reference seawater standards were measured to further validate our methodology. The measured Cd concentrations of NASS-5 (0.196 ± 0.004 nM, 2SD, n = 6), CASS-5 S (0.240 ± 0.005 nM, 2SD, n = 6), and SAFe-D2 (6.99 ± 0.35 nM, 2SD, n = 6) are in excellent agreement with the published results (Milne et al., 2010, and references therein). Ca concentrations were calculated based on the salinity data.
**Figure S1.** General location of KNR140- and KNR197-3 cores used in this study. Zoom of Demerara Rise cores in shown in Figure S2. Figure made in Ocean Data View (Schlitzer, 2015).

**Figure S2.** Location of KNR197-3 piston and gravity cores on the Demerara Rise used in this study. Figure made in Ocean Data View (Schlitzer, 2015).
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**Figure S16.** Modern $\Delta [\text{CO}_3^{2-}]$ at the Demerara Rise (solid line) estimated as in Figure 2, main text, compared to B/Ca of *Uvigerina* in multicore-tops (orange) and LGM-age sediment (blue). Although core-top *Uvigerina* is poorly correlated to $\Delta [\text{CO}_3^{2-}]$ lower values occur within the $\Delta [\text{CO}_3^{2-}]$ minimum than above or below it. Higher glacial B/Ca values, including at one site within the modern $\Delta [\text{CO}_3^{2-}]$ minimum are consistent with the *C. pachyderma* B/Ca data suggesting higher $\Delta [\text{CO}_3^{2-}]$ during the LGM (main text, Figure 2)
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**Figure S18.** Ratio of remineralized phosphate to total phosphate along the western Atlantic GEOSECS transect top Glacial reconstruction bottom the glacial-modern difference. Modern reconstruction is shown in Fig. S10.
Table 1
Captions for Datasets S1 –

Dataset S1. Labelled Dataset S1 in Excel File, uploaded separately. Includes elemental data from core-tops from KNR197-3 multicores and cadmium seawater measurements. These data are needed to replicate figures 1 and 2, main text. Fields include

1. Core name
2. Latitude
3. Longitude
4. Core depth
5. Species
6. Cd/Ca
7. Distribution coefficient used to estimate paleo CdW (dotted line in Figure 1)
8. CdW estimated using D in column 7
9. Cadmium of seawater interpolated from measurements made from water collected on hydrocast (Dataset S2)
10. Cd distribution coefficient estimated from Columns 6 and 9
11. B/Ca
12. Mn/Ca
13. Al/Ca
14. Fe/Ca
15. Carbonate saturation estimated from CO2SYS as described in text.

Dataset S2. Labelled Dataset S2 in Excel File, uploaded separately. Includes elemental data from core-tops from KNR197-3 multicores and cadmium seawater measurements. These data are needed to replicate figure 1, main text. Fields include

1. Sample ID
2. CTD latitude
3. CTD longitude
4. Seafloor depth at CTD station
5. Water sample depth
6. Sample salinity
7. Sample Cd
8. Uncertainty on Cd measurement

Dataset S3. Labelled Dataset S3 in Excel File, uploaded separately. Includes carbon and oxygen isotope data from core-tops from KNR197-3 multicores. All measurements are on individual specimen > 212 microns. Fields include:

1. Core name
2. Latitude
3. Longitude
4. Core depth
5. Species
6. $\delta^{13}C$ value (VPDB)
7. anomalous $\delta^{13}C$ measurements omitted from Figure 4 and average and standard error
8. $\delta^{13}C$ mean
9. $\delta^{13}C$ standard error
10. $\delta^{18}O$ value (VPDB)
11. anomalous $\delta^{18}O$ measurements omitted average and standard error in columns 12 and 13.
12. $\delta^{18}O$ mean
13. $\delta^{18}O$ standard error

Datasets S4 – S11. Benthic Isotope and radiocarbon data for KNR197-3 cores 23GGC, 47CDH, 46CDH, 9GGC, 53GGC, 45GGC, 36GGC, and 60GGC, respectively, in Excel File uploaded separately. Fields include:

1. Assigned age (sometimes blank)
2. Depth (cm)
3. $\delta^{13}C$ ‰ VPDB
4. $\delta^{18}O$ ‰ VPDB
5. Species
6. Left Blank to separate from radiocarbon columns
7. Labcode for radiocarbon measurement
8. Depth (cm)
9. Species
10. Raw radiocarbon age
11. Reported error
12. $\delta^{13}C$ ‰ (sometimes blank, 1 ‰ assumed)
13. Calibration curve
14. Sigma range
15. Number of ranges
16. Upper age bound (Before Present)
17. Lower age bound (Before Present)
18. Relative probability
19. Median Probability
20. Notes if rejected from age model in Column 1

Dataset S12. Excel File, uploaded separately. KNR197-3 Glacial Cd/Ca and B/Ca data. Fields include:

1) Core ID
2) Latitude
3) Longitude
4) Core depth (m)
5) Distribution coefficient used
6) Depth of glacial sample(s) used for C. pachyderma and C. wuellerstofi
7) Cib. Species
8) Cibicidoides Cd/Ca
9) Cibicidoides CdW estimate
10) Depth of glacial sample(s) used for Uvigerina
11) Uvigerina Cd/Ca
12) Uvigerina CdW estimate
13) Cibicidoides B/Ca
14) Uvigerina B/Ca

Dataset S13. In Excel File, uploaded separately. KNR140-2 Glacial Elemental Cd/Ca and B/Ca data. Fields include:
1) Core ID
2) Latitude
3) Longitude
4) Core depth (m)
5) Depth of glacial sample(s) used
6) Species
7) Cd/Ca
8) Mn/Ca
9) CdW estimate using distribution coefficients discussed in text

Dataset S14. In Excel File, uploaded separately. Glacial CdW estimates, using distribution coefficients described in text. Although original references are cited, new distribution coefficients are applied to the CdW estimates in compilation in Marchitto & Broecker (2006). Where their estimates cited a mix of estimates on calcitic and aragonitic species, the CdW estimates were not included in this compilation (four data points).
Fields include:
1) Core ID
2) Latitude
3) Longitude
4) Core depth (m)
5) New CdW estimate
6) Reference

Dataset S15. In Excel File, uploaded separately. Glacial $\delta^{13}$C and $\delta^{18}$O estimates, using distribution coefficients described in text. Although original references are cited where possible, much of the data was previously compiled in Curry et al. (1988) and Marchitto & Broecker (2006). Fields include:
1) Core ID
2) Latitude
3) Longitude
4) Core depth (m)
5) $\delta^{13}$C
6) $\delta^{18}$O (99 indicates that $\delta^{18}$O was not compiled for this study)
7) Reference