SUPPLEMENTARY INFORMATION

Materials and Methods

Deep Sea Drilling Project (DSDP) Site 607 (41° 00.068'N, 32° 57.44'W) is situated at a depth of 3427 m on the upper western flank of the Mid-Atlantic Ridge (Fig. DR 7). Situated today in the core of North Atlantic Deepwater, this site was instrumental in the early studies examining Plio-Pleistocene ocean circulation (e.g., Raymo et al., 1990). Cores were sampled at a resolution of 5 to 15 cm to obtain a time step of between 2 and 5 kyr spanning the entire MPT (~0.4-1.1 Ma). We use the age model of Lawrence et al. (2013), which is based on the oxygen isotope stratigraphy of Lisiecki and Raymo (2005). We measured new benthic foraminiferal stable isotopes in order to pair the values with trace metals analyses. To fill a stratigraphic gap, we used five sample residues from Site 607A to complete the trace metal records between 0.77 and 0.80 Ma (Lawrence, personal communication, 2015). For these five samples we used interpolated $\delta^{18}O$ and $\delta^{13}C$ values from Raymo et al. (1990). About 10 cm^3 of bulk sediment were oven-dried at 60°C, washed through a 63 μm sieve, dried and dry-sieved into sub-fractions (63–125, 125–250, 250–500, >500 μm). In each fraction 800 grains (if present) were counted and various biogenic, clastic and authigenic components (among them radiolaria) differentiated to yield percentage composition of the sand fraction. Stable isotope analyses were conducted primarily on 1–3 *Cibicidoides wuellerstorfi* and *C. mundulus* picked from the >255 μm fraction. *Cibicidoides* spp. are commonly integrated to reconstruct water mass properties (e.g., Mackensen and Bickert, 1999). In an effort to reduce the length of gaps in the upper section of the record, we also used *Oridorsalis umbonatus* (n=16), applying the published correction factors of +1.22 per mil for $\delta^{13}C$ and -0.78 per mil for $\delta^{18}O$ (Poirier and Billups, 2014). As discussed by Poirier and Billups (2014), this species has been used to augment stable isotope stratigraphies for the purpose of tracing water masses (Katz et al., 2003, Poli et al., 2000; Ferretti et al., 2005; Billups et al., 2011). All samples were further oven-dried for at least 24 hours prior to isotopic analysis. Analyses were performed at the University of Delaware using a GVI IsoPrime equipped with a Multiprep peripheral for the automated reaction of individual samples with phosphoric acid (at 90°C). The values are reported versus Vienna PeeDee Belemnite using an in-house standard (Carrara Marble) and National Bureau of Standards-19. The $\delta^{18}O$ record was adjusted for laboratory offsets by subtracting 0.4 per mil (Poirier and Billups, 2014). The analytical precision of the instrument is about 0.08 per mil for $\delta^{18}O$ and 0.06 per mil for $\delta^{13}C$ in the size range of 20-150 μg.

For trace metal analyses, three species of benthic foraminifera (*Cibicidoides wuellerstorfi, Uvigerina sp.,* and *Oridorsalis umbonatus*) were picked from the 250-355 μm size fraction. Between 1 and 33 individuals were picked per sample, depending on abundance. There was no trend between the number of individuals analysed and measured values (DR Fig. 8). The samples were cleaned following the protocol of Boyle and Keigwin, (1985/86), which includes a reductive step. Between the clay removal and reductive steps the samples were examined under a binocular microscope, and non-carbonate particles were removed using a fine paintbrush (Barker et al., 2003). The redox sensitive uranium proxy measures the degree of authigenic coating on the exterior of the foraminiferal tests (Boiteau et al., 2012). Therefore, 40 individuals of the planktonic foraminifera *G. bulloides* (250-355μm size fraction) were prepared using a modified cleaning technique, which included the clay removal stage, but omitted both the oxidative and reductive cleaning stages. This resulted in significantly higher signal to noise in the U/Ca record compared to the full foraminiferal cleaning technique, which was used on the benthic samples (DR Fig. 2D). Samples were analysed for Cd/Ca, Mn/Ca, B/Ca, Al/Ca, Fe/Ca and U/Ca using matrix-matched standards on a Thermo Element XR ICP-MS at Cardiff University (long-term precision determined by analysing independent standards over the course of 2 years is better than 3% on all of these ratios (r.s.d.)).

Interpretation of $\delta^{13}C$ record

DSDP Site 607 $\delta^{13}C$ record reflects a combination of many different factors, including global changes in whole ocean $\delta^{13}C$, the concentration of nutrients / respired organic carbon, and air-sea gas exchange. Following accepted paleoceanographic practice (e.g., Raymo et al., 1997) we remove the effects of changes in whole ocean $\delta^{13}C$ by subtracting the Pacific $\delta^{13}C$ record, although this has the potential to introduce some inaccuracies due to miscorrelation on the sub-orbital-scale. We take this approach in Fig. 2, DR Fig. 4, and in calculating the air-sea exchange signal. We accomplished this by subtracting the Pacific Site 849 benthic $\delta^{13}C$ record from the Atlantic Site 607 $\delta^{13}C$ record (both records having been synchronized via the Lisiecki and Raymo (2005) $\delta^{18}O$ stack). We refer to this as the 'corrected 607 $\delta^{13}C$ record'. The trends observed in the 849 $\delta^{13}C$ record are offset from but similar to those at North Atlantic Site 552 (Raymo et al., 1997). Site 552 is situated at 2301 m water depth at 56°N, compared with Site 607's position at 3427 m water depth at 41°N. It therefore seems likely that Site 552 was more consistently bathed by a northern source water mass, and that the similar trends in the Site 849 and Site 552 records represent changes in whole ocean $\delta^{13}C$, rather than the changing water mass mixing signal observed at Site 607 (Raymo et al., 1997). The changes in whole ocean $\delta^{13}C$ are likely dominated by changes in the terrestrial biosphere (Raymo et al., 1997), although they may contain an air-sea exchange component themselves.

Interpretation of Cd/Ca record

Previous work implies a lack of consistent benthic foraminiferal interspecies offsets for Cd/Ca (Boyle, 1988; Boyle, 1992), although within a global compilation, the 1:1 relationship between species breaks down at a handful of sites (Boyle, 1992). There are no apparent interspecies offsets for Cd/Ca in our records (DR Fig. 1A), consistent with previous work (Fig. DR 9). We analysed co-existing *Uvigerina* and *C. wuellerstorfi* in 35 samples, the mean *Uvigerina-C. wuellerstorfi* offset was -0.008 μmol/mol (2 s.e. = 0.006 μmol/mol). We analysed co-existing *Uvigerina* and *O. umbonatus* in 41 samples, the mean *Uvigerina-O. umbonatus* offset was -0.010 μmol/mol (2 s.e. = 0.03 μmol/mol). We analysed co-existing *O. umbonatus* and *C. wuellerstorfi* in 39 samples, the mean *O. umbonatus-C. wuellerstorfi* offset was 0.0003 μmol/mol (2 s.e. = 0.007 μmol/mol). This suggests there are very small, or no, consistent interspecies offset in Cd/Ca in our records. We therefore compile the Cd/Ca data into one record without using interspecies offsets. We use the deep-water cadmium partition coefficient (D_{Cd}) of 2.9 to calculate seawater [Cd] (Boyle, 1988), assuming seawater [Ca] is 0.01 mol/kg (Equation 1).

$$D_{Cd} = (Cd/Ca)_{foram} / Cd/Ca_{water} \qquad \text{(Equation 1)}$$

We then use the Atlantic Cd/Ca-PO_4 relationship (α=2.5) to calculate seawater [PO_4] (Equation 2) (Elderfield and Rickaby, 2000) (Fig. 1C).

$$Cd_{sw} = Cd_T / \{\alpha_{Cd/P} (P_T/P_{sw} - 1) + 1 \} \qquad \text{(Equation 2)}$$

Where Cd_{sw} is calculated using equation 1, Cd_T is 1.2 nmol/kg, $\alpha_{Cd/P}$ is 2.5, P_T is 3.3 μmol/kg and P_{sw} is seawater [PO_4] (Elderfield and Rickaby, 2000).

Replicate analyses of samples containing between 4 and 20 individual benthic foraminifera produced a pooled standard deviation of 0.007 μmol/mol (Bryan and Marchitto, 2010). Assuming this variability is similar to our samples, this would correspond to an uncertainty of ± 0.17 μmol/kg [PO_4] for our mean Cd/Ca value (±2 s.d.). We therefore display a ± 0.17 μmol/kg uncertainty window in Figure 1C. The implied assumption of constant oceanic Cd/Ca should not significantly affect the trends in our record, because although the residence time of Cd in seawater is around 10^5 years, the Cd inventory appears relatively constant through time (Delaney and Boyle, 1987). In the absence of air-sea exchange effects, a 1 μmol/kg increase in [PO_4] would be expected to be associated with a 1.1‰ decrease in $\delta^{13}C$ (Broecker and Maier-Reimer, 1992). We therefore use the [PO_4] record (Fig. 1C) to calculate the 'Cd/Ca-predicted $\delta^{13}C$' using equation (3) (DR Fig. 4):

$$\delta^{13}C_{predicted} = \delta^{13}C_{mean}-(([PO_4]-[PO_4]_{mean})*1.1) \qquad \text{(Equation 3)}$$

Where $\delta^{13}C_{mean}$ is the mean of our corrected *Cibicidoides* sp. $\delta^{13}C$ record (0.64 ‰) and $[PO_4]_{mean}$ is the mean of our [PO_4] record (1.6 μmol/kg).

Interpretation of B/Ca record

To generate a bottom water record of carbonate saturation state ($\Delta CO_3^{=}$), we use the B/Ca record of the epifaunal foraminifera *C. wuellerstorfi* (DR Fig. 1B), as this species will not be affected by porewater buffering processes (Elderfield et al., 2010). We use the modern empirical calibration determined on this species (Yu and Elderfield, 2007) to calculate changes in $\Delta CO_3^{=}$ (Fig. 1D) (equation 4). The implied assumption of constant oceanic B/Ca should not significantly affect the trends in our record, because the residence times of B and Ca in seawater are ~10^7 and 10^6 years respectively (Broecker and Peng, 1982).

$$B/Ca_{C.wuellerstorfi} = 1.14 \times \Delta CO_3^{2-} + 177.1 \quad \text{(Equation 4)}$$

We use the bottom water [ΔCO_3^{2-}] record (Fig. 1D) and the $\delta^{13}C$-[ΔCO_3^{2-}] Redfield relationship calculated in Yu et al., (2008) to calculate the 'B/Ca-predicted $\delta^{13}C$' (equation 5) (DR Fig. 4):

$$\delta^{13}C_{predicted} = \delta^{13}C_{mean}+(([\Delta CO_3^{2-}]-[\Delta CO_3^{2-}]_{mean})*1/43)$$

(Equation 5)

Where $\delta^{13}C_{mean}$ is the mean of our corrected *Cibicidoides* sp. $\delta^{13}C$ record (0.64 ‰) and $[\Delta CO_3^{2-}]_{mean}$ is the mean of our [ΔCO_3^{2-}] record (24 μmol/kg).

Interpretation of U/Ca records

Our foraminiferal U/Ca record reflects the amount of authigenic coatings on foraminiferal tests, which in turn reflects redox conditions in the sediment pore waters (Jaccard et al., 2009). Several factors can impact pore water redox conditions, including organic matter flux, sedimentation rate and bottom water [O_2]. Our U/Ca record correlates well with the alkenone mass accumulation record at the same site (Lawrence et al., 2013) (DR Fig. 2A). The mass accumulation rate of organic matter in the sediment column could be interpreted as a 'production' or 'preservation' feature (with preservation being favored when the site is bathed by a poorly ventilated water mass). However, the abundance of alkenones in the sediment column at Site 607 has been argued to reflect productivity changes in the overlying waters, (Lawrence et al., 2013). The similarity between our U/Ca record, the alkenone mass accumulation rate record and the abundance of radiolaria (DR Fig. 2) therefore suggests that the U/Ca record is most likely dominated by a local productivity signal. If these changes in productivity caused significant shifts in the concentration of remineralised organic matter at the seafloor, they could impact benthic foraminiferal Cd/Ca records. However, maxima in U/Ca (and hence productivity) are not associated with maxima in Cd/Ca (DR Fig. 2C). While we acknowledge that both the U/Ca and Cd/Ca records are impacted by multiple processes, we therefore make the assumption that the Cd/Ca record is not dominated by local changes in productivity, and hence we interpret this record in terms of nutrient concentration of the bottom water mass.

Foraminiferal Mn/Ca as an indicator of contamination on Cd/Ca

Foraminiferal tests can become coated with oxide phases rich in both Mn and Cd, so elevated Mn/Ca ratios have been used to exclude potentially contaminated Cd/Ca data (Boyle, 1983). However, all the benthic foraminiferal samples analysed here were subjected to the full cleaning technique, which includes a reductive step to remove oxide coatings (Boyle and Keigwin, 1985/86). The three benthic foraminiferal species analysed here have clear interspecies offsets for Mn/Ca, but not for Cd/Ca (DR Fig. 5). Furthermore, there is no correlation between benthic foraminiferal Mn/Ca and Cd/Ca (DR Fig. 6). It is therefore difficult to envision how the Mn/Ca records could reflect the degree of oxide coatings. Instead we propose that the measured Mn reflects Mn incorporated into the foraminiferal calcite during the precipitation process. While this is likely related to sediment redox conditions it does not appear to reflect a contaminant rich in Cd.

Supplementary References

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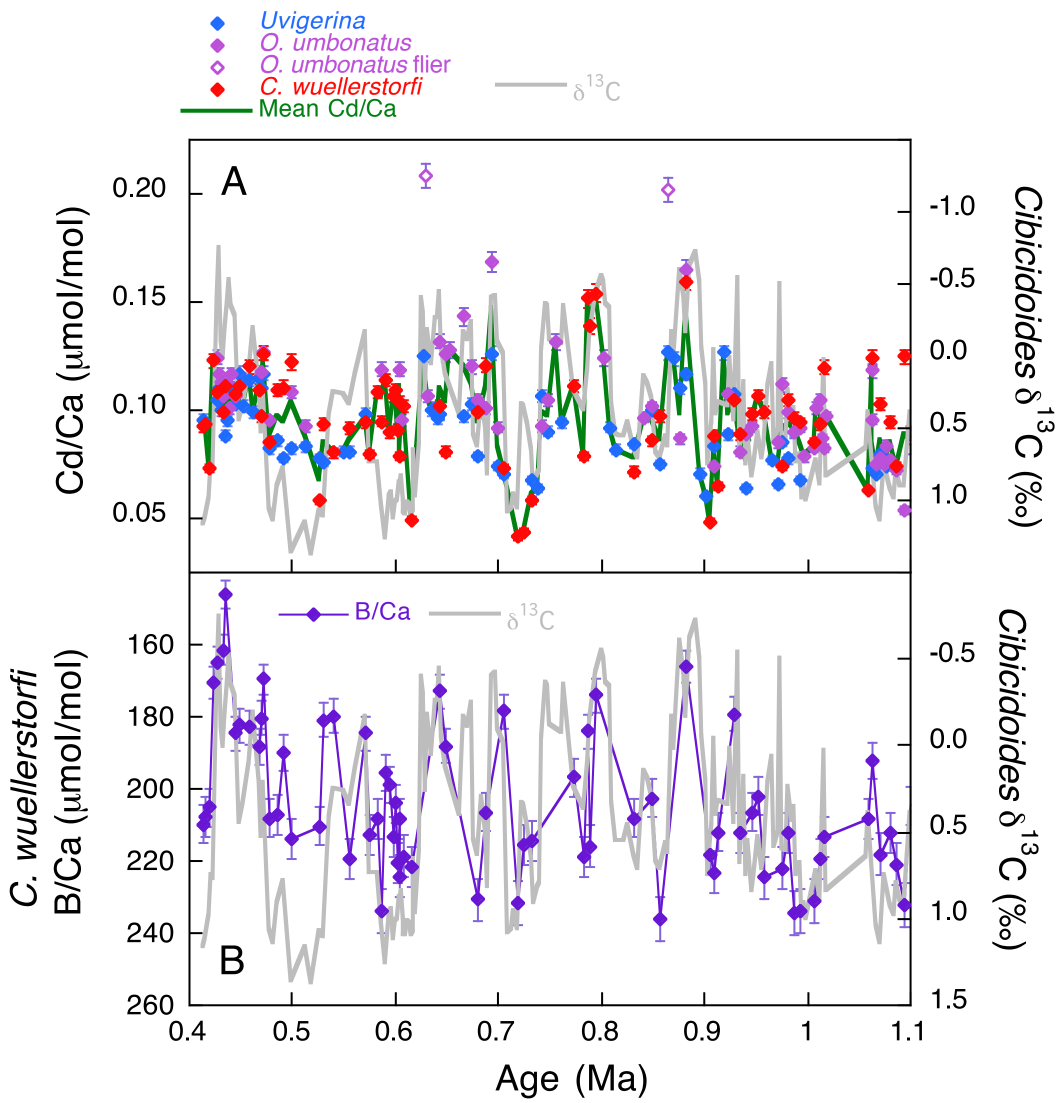
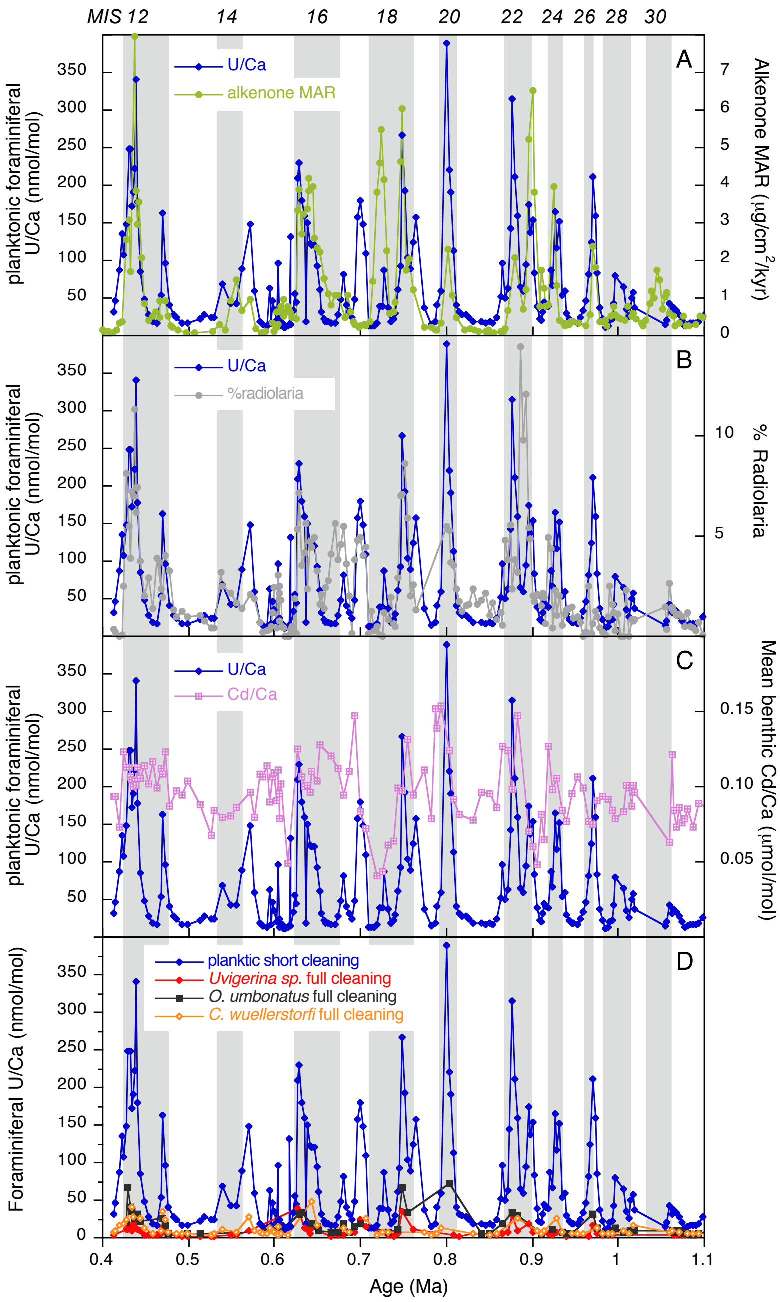
Data Repository Figure 1

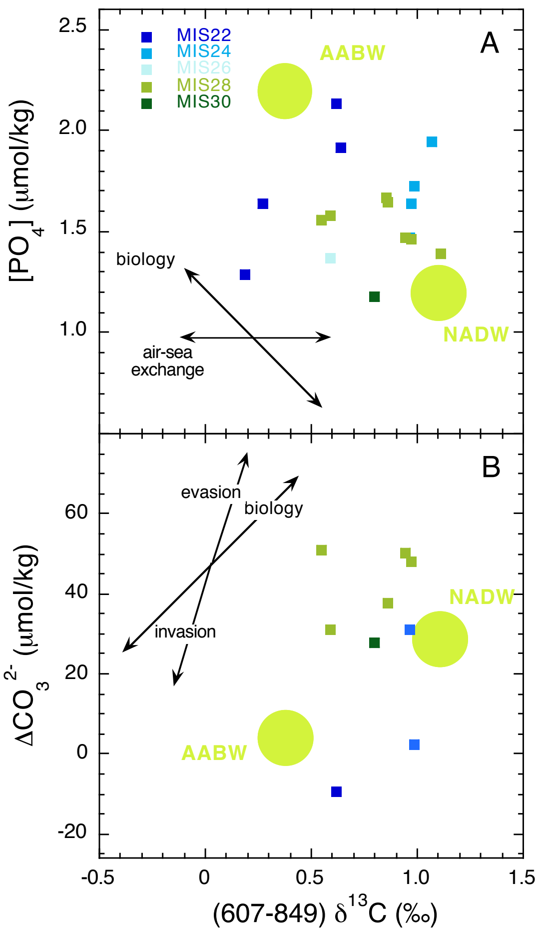
(A) *Cibicidoides* sp. $\delta^{13}C$ (gray line) and benthic foraminiferal Cd/Ca from three species. The green line depicts the mean Cd/Ca of each sample. Error bars show analytical precision for Cd/Ca (r.s.d. = 2.7%) (B) *Cibicidoides* sp. $\delta^{13}C$ (gray line) and *C. wuellerstorfi* B/Ca (purple diamonds). Error bars show analytical precision for B/Ca (r.s.d. = 2.6%).



Data Repository Figure 2 (A) DSDP Site 607 *G. bulloides* U/Ca (this study) and alkenone mass accumulation rates (Lawrence et al., 2013). (B) *G. bulloides* U/Ca and % abundance of radiolaria in the >63μm sediment size fraction. (C) *G. bulloides* U/Ca and mean Cd/Ca of the 3 benthic foraminiferal species analysed. (D) Foraminiferal U/Ca. The *G. bulloides* samples were subjected to the clay removal step only, the benthic species were subjected to the full cleaning, including the oxidizing and reducing steps. Gray bars highlight the timing of marine isotope stages (MIS) after Lisiecki and Raymo (2005).

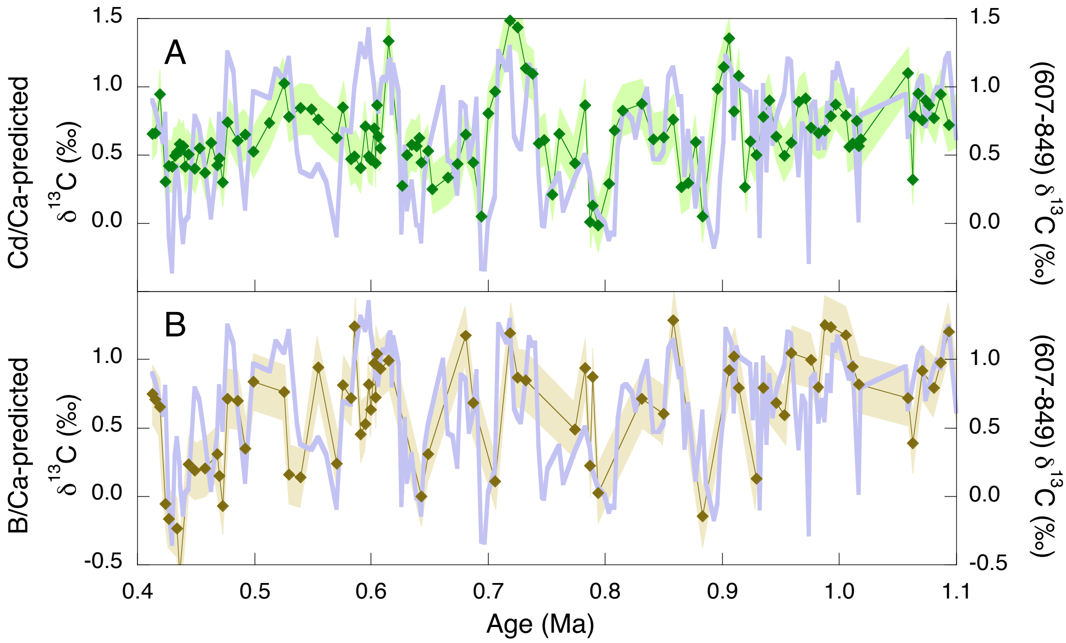


Data Repository Figure 3 Corrected $\delta^{13}C$ (Deep Sea Drilling Project Site 607 $\delta^{13}C$ minus ODP Site 849 $\delta^{13}C$) versus (A) reconstructed bottom water [PO_4] and (B) reconstructed carbonate saturation state (ΔCO_3^{2-}) for glacial intervals only between MIS 30 and 22 based on the timings provided in Lisiecki and Raymo (2005). The "biology" arrow in A shows expected trendlines caused by changes in concentration of respired organic matter, based on modern Redfield ratios and carbon isotopic composition of organic matter (Lynch-Stieglitz et al., 1995). Horizontal arrow indicates that changes in air-sea CO_2 exchange will not impact [PO_4]. The slopes of the corresponding arrows in panel B are from Yu et al., (2008). The green circles represent the composition of modern Antarctic Bottom Water (AABW) and North Atlantic Deep Water (NADW).



Data Repository Figure 4

Predicted δ¹³C calculated assuming the record is controlled solely by biological effects, based on (A) the Cd/Ca record and (B) the B/Ca record, compared with the corrected δ¹³C record (Site 607 δ¹³C minus Pacific Site 849 δ¹³C). Pale green envelope represents the uncertainty associated with the [PO_4] reconstruction (see DR for details), Pale brown envelope represents the uncertainty associated with the ΔCO_3^{2-} reconstruction (see DR for details). Major discrepancies between the two records in panel A point to air-sea gas exchange effects (see text for detail).



287 **Data Repository Figure 5**

288 (A) Benthic foraminiferal Mn/Ca and (B) benthic foraminiferal Cd/Ca records
289 from DSDP Site 607. Blue diamonds are *Uvigerina sp.,* gray circles are *Oridorsalis*
290 *umbonatus* and purple squares are *Cibicidoides wuellerstorfi*. The two fliers in
291 panel B are not used to calculate seawater [PO_4] in Figure 1.

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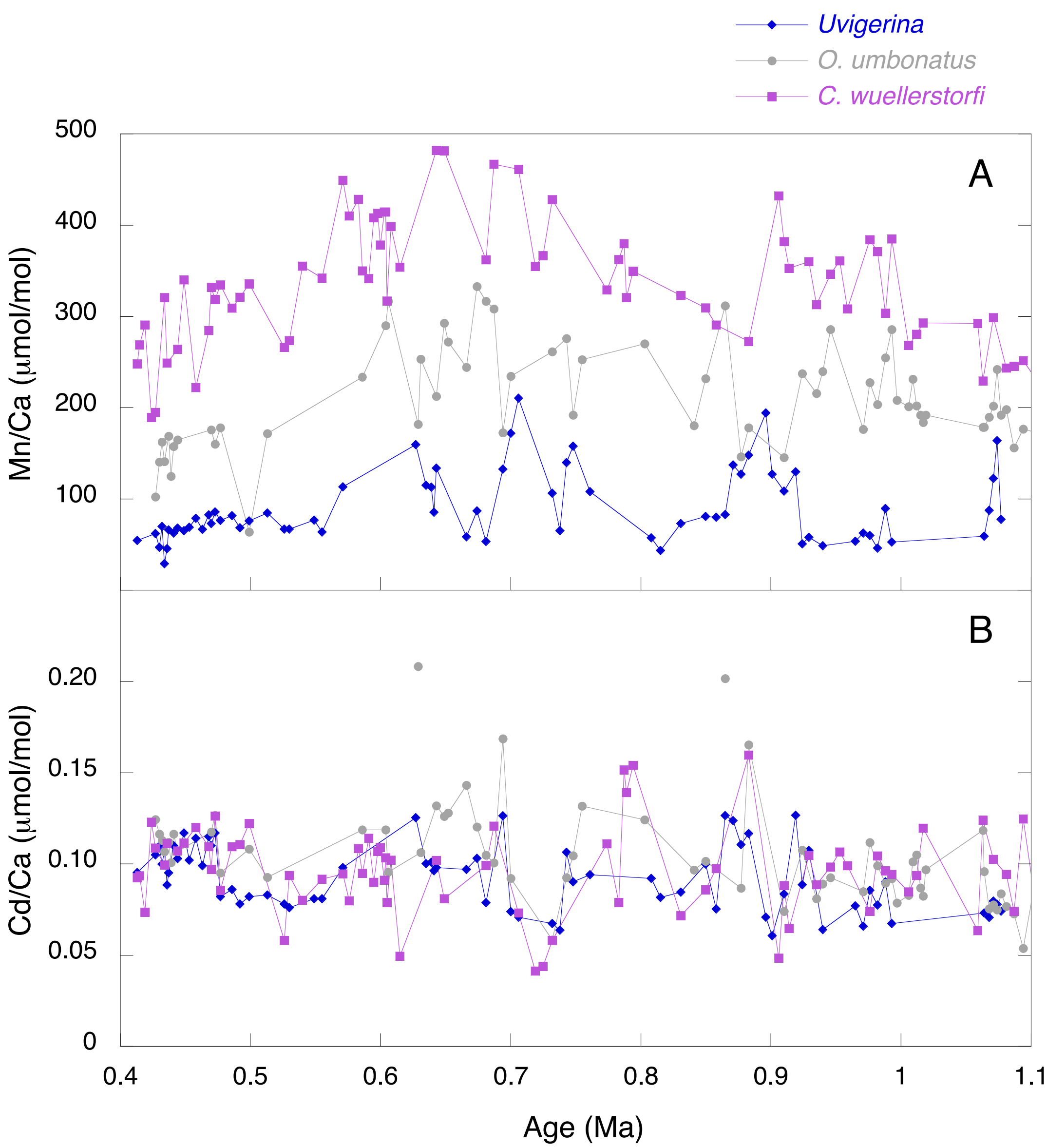

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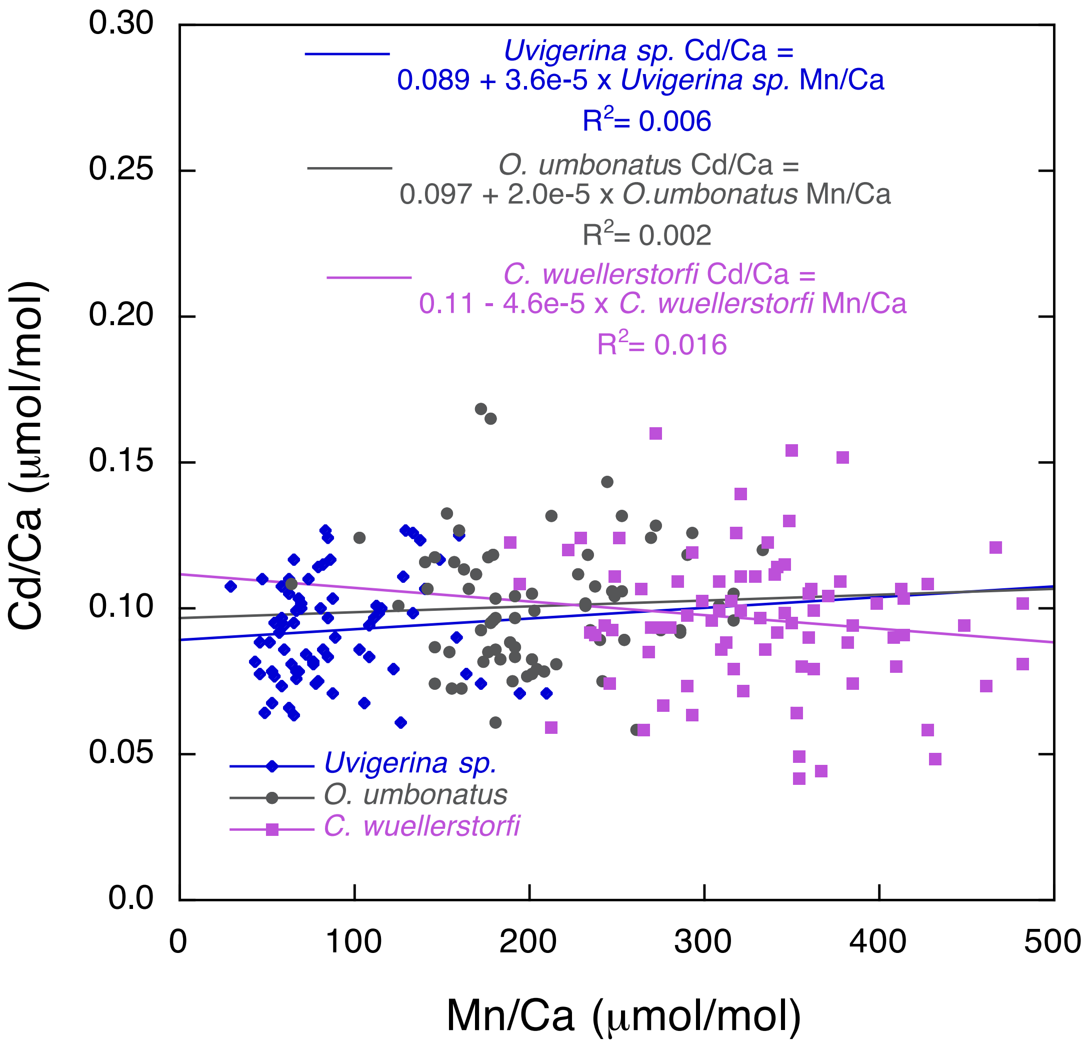
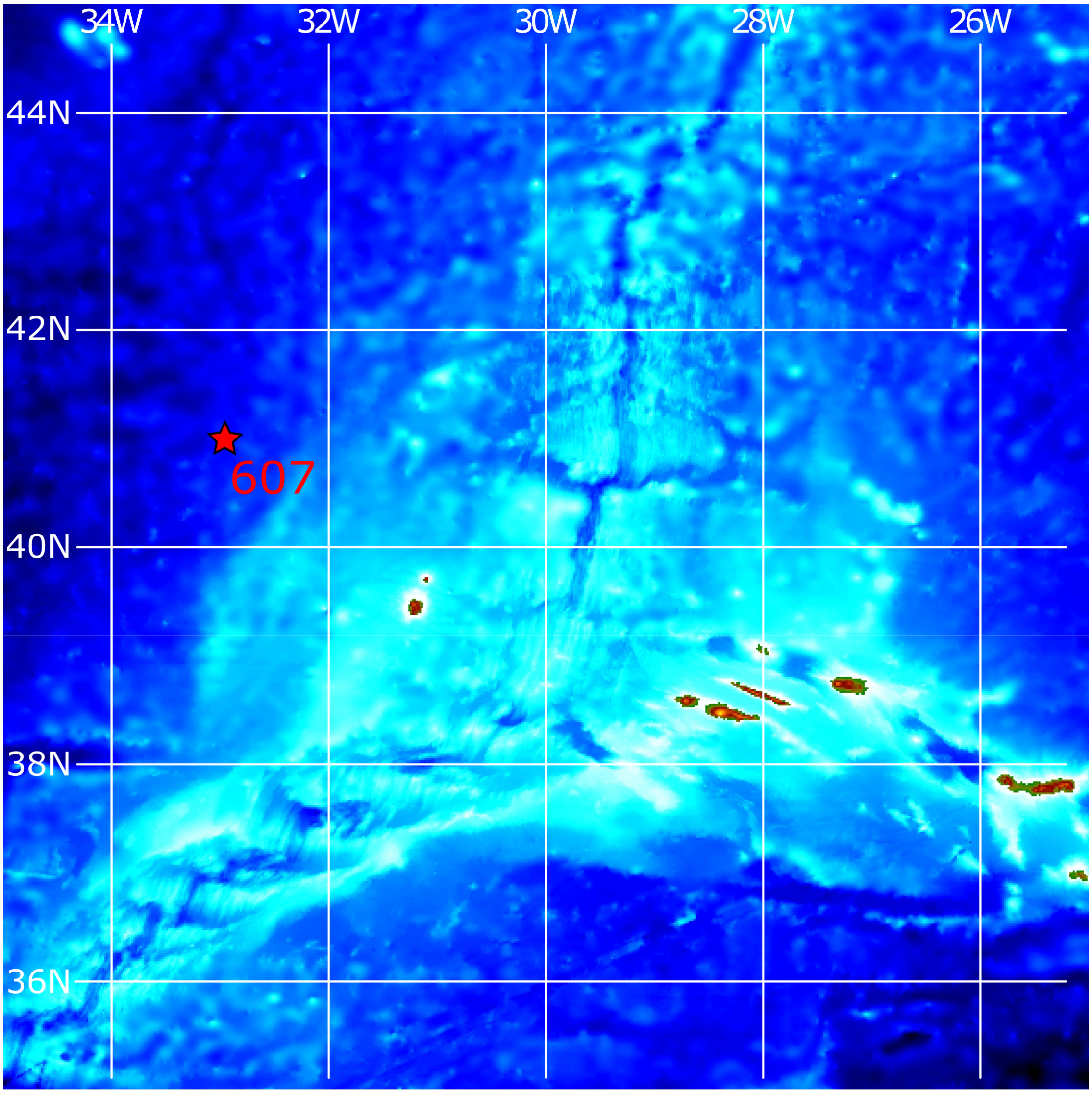
Data Repository Figure 6

DSDP Site 607 Benthic foraminiferal Mn/Ca vs Cd/Ca for *Uvigerina sp.* (blue diamonds), *O. umbonatus* (gray circles) and *C. wuellerstorfi* (purple squares).



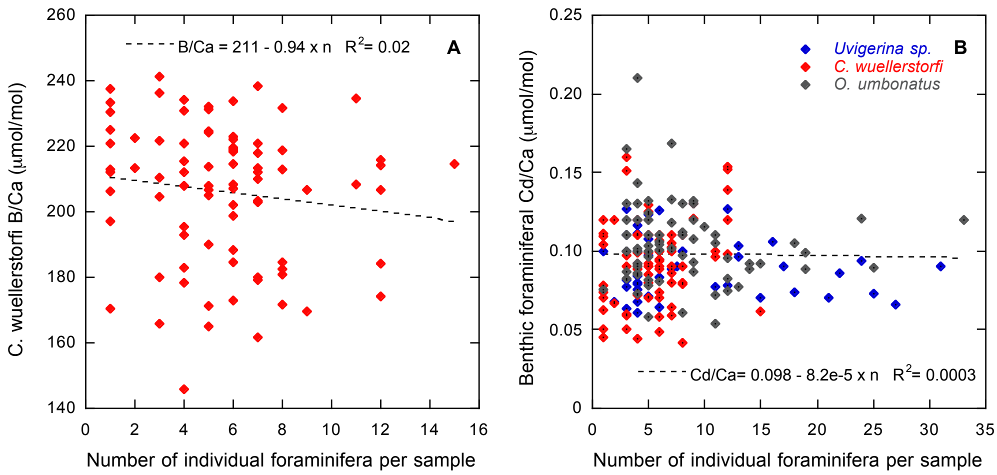
Data Repository Figure 7

Location Map of DSDP Site 607, underlying bathymetry is from the British Oceanographic Data Centre.



Data Repository Figure 8

(A) *C. wuellerstorfi* B/Ca vs number of individual specimens per analysis, (B), Benthic foraminiferal Cd/Ca vs number of individual specimens per analysis, *Uvigerina sp.* (blue), *C. wuellerstorfi* (red) and *O. umbonatus* (gray).



Data Repository Figure 9

C. wuellerstorfi and *O. umbonatus* Cd/Ca versus *Uvigerina* Cd/Ca. Closed squares from Boyle (1988) and Boyle (1992), open circles, this study.