More efficient North Atlantic carbon pump during the Last Glacial Maximum

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During the Last Glacial Maximum (LGM; ~20,000 years ago), the global ocean sequestered a large amount of carbon lost from the atmosphere and terrestrial biosphere. Suppressed CO2 outgassing from the Southern Ocean is the prevailing explanation for this carbon sequestration. By contrast, the North Atlantic Ocean—a major conduit for atmospheric CO2 transport to the ocean interior via the overturning circulation—has received much less attention. Here we demonstrate that North Atlantic carbon pump efficiency during the LGM was almost doubled relative to the Holocene. This is based on a novel proxy approach to estimate air–sea CO2 exchange signals using combined carbonate ion and nutrient reconstructions for multiple sediment cores from the North Atlantic. Our data indicate that in tandem with Southern Ocean processes, enhanced North Atlantic CO2 absorption contributed to lowering ice-age atmospheric CO2.
he North Atlantic Ocean (> ~35°N, including the Nordic Seas and Arctic Ocean) is a major atmospheric CO₂ sink, which has been mitigating anthropogenic atmospheric CO₂ increases. Preindustrial North Atlantic surface water partial pressure of CO₂ (pCO₂) was up to ~100 µatm lower than the contemporary atmospheric pCO₂ of ~280 µatm, which caused substantial atmospheric CO₂ invasion. Despite its modest area, the North Atlantic Ocean accounts for at least ~30% of the global ocean CO₂ uptake today and during preindustrial times. Over longer timescales, large-scale oceanic carbon sequestration also occurred during Plio-Pleistocene glaciations. This is commonly attributed to reduced glacial Southern Ocean CO₂ outgassing, while even the sign of past North Atlantic CO₂ uptake efficiency changes remains unconstrained. Here, we present a novel proxy approach to trace atmospheric CO₂ invasion in the North Atlantic and thereby evaluate its role in carbon sequestration in ice-age oceans. We find that the last glacial North Atlantic carbon absorption became more efficient, highlighting a critical role of the North Atlantic Ocean in regulating glacial–interglacial atmospheric CO₂ changes.

Results

Air–sea CO₂ exchange tracers. Any effect of ocean processes on atmospheric pCO₂ must occur via air–sea CO₂ exchange. In the North Atlantic, high-nutrient utilization decreases surface-water dissolved inorganic carbon (DIC) and causes surface-water pCO₂ to be lower than atmospheric pCO₂ (Supplementary Fig. 1). This leads to net air-to-sea CO₂ transfer, creating an air–sea exchange signature of DIC (DICas). DICas signals can be distinguished by accounting for within-ocean DIC redistributions that are heavily mediated by biology (Fig. 1). Biological cycling of organic matter depletes DIC and nutrients such as phosphate (PO₄) in surface waters and enriches them at depth. Seawater mixing also affects DIC and PO₄ concentrations in the ocean. Nevertheless, PO₄ variations are ultimately determined by biological processes: without biology, PO₄ should be the same everywhere in the ocean regardless of ocean circulation (ignoring the small effect from salinity change). Because marine biology incorporates and releases PO₄ and DIC in a relatively fixed proportion following Redfield stoichiometry, and because PO₄ is not affected by air-sea exchange, PO₄ can be used to estimate biology-driven within-ocean DIC redistributions (Fig. 1). Any within-ocean DIC redistribution associated with CaCO₃ cycling can be accounted for using alkalinity (ALK) and nitrate.

Following the established method to account for within-ocean DIC redistributions by soft-tissue and CaCO₃ cycling, we calculate preindustrial Atlantic DICas using the GLODAP dataset (Fig. 2a). See Methods for details to calculate DICas. More positive DICas values indicate a greater degree of atmospheric CO₂ invasion. At basin-scale, the preindustrial DICas of North Atlantic deep water (NADW) is ~50–80 µmol/kg higher than for Antarctic bottom water (AABW) and Antarctic intermediate water (AAIW). This difference reflects North Atlantic CO₂ uptake and Southern Ocean release. North Atlantic CO₂ absorption is driven by (i) an efficient solubility pump due to strong cooling of northward-flowing Gulf Stream waters and (ii) a strong biological pump associated with high nutrient utilization. This NA DW thus represents an efficient pathway for atmospheric CO₂ sequestration. Through global deep ocean circulation, CO₂ absorbed in the North Atlantic is transported throughout the world ocean, with profound implications for the global carbon cycle.

No proxy exists to reconstruct past seawater DIC and ALK at acceptable precision for direct application, so we employ a linked carbonate system parameter for palaeoceanographic studies. Everything else being equal, atmospheric CO₂ invasion would decrease seawater carbonate ion concentration ([CO₃²⁻]), because CO₂ reacts with carbonate ion to form bicarbonate. We thus develop a new tracer, [CO₃²⁻]as, which essentially reflects seawater [CO₂] contrasts for the same biological (i.e., PO₄) and physical (i.e., temperature–salinity–pressure; T–S–P) conditions (Fig. 2b; see Methods for calculation details). To extract air–sea exchange signals, it is necessary to compare [CO₃²⁻] at the same PO₄–T–S–P conditions because we must first remove influences on [CO₂] from (i) within-ocean DIC and ALK redistributions by biology and (ii) T–S–P variations via their effects on CO₂ system dissociation constants. In the preindustrial Atlantic, the strong negative correlation between [CO₃²⁻]as and DIC as (Fig. 2, Supplementary Fig. 2) indicates that [CO₃²⁻]as variations are affected only by DICas, and thus are ultimately linked to air–sea CO₂ exchange.

The Gulf Stream is a major NADW source, thus, comparing the [CO₃²⁻]as gradient between the Gulf Stream and NADW can provide a measure of CO₂ sequestration intensity during transformation of Gulf Stream waters into NADW. Because Gulf Stream waters are more or less in equilibrium with atmospheric pCO₂ from ~10°N to 35°N, the Gulf Stream–NADW [CO₂]as gradient mainly reflects North Atlantic (> ~35°N) air–sea CO₂

Fig. 1 Concepts to distinguish DICas. For simplicity, only CO₂ invasion associated with organic matter cycling is considered. In the ocean box, vertical solid and dashed lines (a–d) represent mean PO₄ (blue) and DIC (red) in an abiotic ocean (a). Biology redistributes DIC and PO₄ following Redfield stoichiometry (curves; b). This decreases surface-ocean DIC and pCO₂, and hence causes air-to-sea CO₂ transfer (c). Through mixing and ocean circulation, CO₂ invasion raises water-column DIC, i.e., shifting dashed curve (equals the red-solid curve in b) to red-solid curve (c). The shaded region in c represents air-sea exchange DICas signatures. After removing carbon redistribution by biology based on PO₄-related curvature of the profiles (b), DICas can be revealed by the shaded region in d.
exchange (Supplementary Fig. 3). Physical oceanographers have shown that the path of Gulf Stream waters, rather than being a direct conveyor to the polar North Atlantic, is instead a "corkscrew", where Gulf Stream waters are recirculated south in the subtropical gyre and subduct after being made more dense by air–sea heat loss (e.g., refs. 18, 19). However, our interest lies in net CO₂ uptake by the North Atlantic region, and variations in spatial pathways from Gulf Stream to NADW formation sites18,19 should not significantly complicate our conclusion. The greater the [CO₃²⁻] as gradient between Gulf Stream and NADW (instead of their absolute [CO₃²⁻] as values), the more efficient air–sea CO₂ absorption by the North Atlantic. Linked to large-scale overturning circulation, Gulf Stream–NADW [CO₃²⁻] as gradient changes regulate long-term CO₂ sequestration into the deep ocean.

**Downcore reconstructions.** Next, we reconstruct past Gulf Stream–NADW [CO₃²⁻] as gradients to investigate North Atlantic carbon pump efficiency during the LGM (18–27 ka). Previous work suggests that most of North Atlantic subtropical gyre water circulates through the Caribbean Sea before being transported to the subpolar North Atlantic via the Gulf Stream20. We, therefore, use Caribbean Sea ODP Site 999 (12.8°N, 78.7°W) to constrain past Gulf Stream physicochemical conditions (Fig. 3, Supplementary Figs. 4 and 5). The feasibility of using ODP Site 999 to reflect the first-order Gulf Stream carbonate chemistry changes between the Holocene and LGM is supported by observations that (i) Caribbean surface waters have similar [CO₃²⁻] as values to hydrographic sites located within Gulf Stream during the preindustrial (Supplementary Fig. 3), and (ii) cores from the broader western subtropical Atlantic show comparable Holocene and LGM [CO₃²⁻] as signatures as those from ODP 999 (Supplementary Fig. 6). Surface-water T and S are estimated from *Globigerinoides ruber* Mg/Ca and sea level fluctuations, respectively21,22. Previously published *G. ruber* δ¹³B (ref. 21) is used to calculate surface-water pH, while ALK is estimated from S using the modern relationship between S and ALK21,22. Along with T, S, and ALK estimates, pH is then used to calculate surface-water [CO₃²⁻] and DIC. Given the constraint from pH, seawater ALK and DIC must vary systematically within the ocean carbonate system (Supplementary Fig. 5). This allows precise estimation of [CO₃²⁻], because even large ALK uncertainties (100 μmol/kg; ± 2σ, used throughout) only have a minor effect on [CO₃²⁻] (~14 μmol/kg). Given its oligotrophic setting, past surface-water PO₄ at ODP 999 is assumed to be zero2,21,22.

Three cores are used to reconstruct deep-water conditions of northern-sourced waters (Fig. 3). BOFS 17 K (58°N, 16.5°W, 0–50 m) and BOFS 11 K (10°N, 44°W, 2–25 m) are located near the western boundary of the subtropical gyre, at the entrance to the Labrador Sea. BOFS 14 K (29°N, 45°W, 10–500 m) is positioned north of the Gulf Stream at the beginning of its path to the NADW formation region20,21. BOFS 11 K is used to estimate the carbonate chemistry of the Labrador Sea water mass and to assess its contribution to the NADW formation. The feasibility of using ODP Site 999 to reflect the first-order Gulf Stream carbonate chemistry changes between the Holocene and LGM is supported by observations that (i) Caribbean surface waters have similar [CO₃²⁻] as values to hydrographic sites located within Gulf Stream during the preindustrial (Supplementary Fig. 3), and (ii) cores from the broader western subtropical Atlantic show comparable Holocene and LGM [CO₃²⁻] as signatures as those from ODP 999 (Supplementary Fig. 6).
A pragmatic recipe to estimate $[\text{CO}_3^{2-}]_{\text{as}}$ change. Surface-water $[\text{CO}_3^{2-}]$ at ODP 999 is ~150 $\mu$mol/kg higher than deep-water values at BOFS cores (Fig. 3), but this $[\text{CO}_3^{2-}]$ contrast includes influences from physical (via dissociation constants) and biological (via within-ocean DIC and ALK redistributions) changes in addition to any air–sea $\text{CO}_2$ changes between surface and deep waters. Below, we present a pragmatic recipe to estimate $[\text{CO}_3^{2-}]_{\text{as}}$ gradients between water masses. We take advantage of well-defined sensitivities of $[\text{CO}_3^{2-}]$ to T–S–P (Fig. 4) to calculate normalized seawater $[\text{CO}_3^{2-}]$ ([CO$_3^{2-}$]$_{\text{Norm}}$) at conditions of $T = 3^\circ\text{C}$, $S = 35\%$, and $P = 2500$ dbar (Methods). Any variation in T–S–P would affect seawater $[\text{CO}_3^{2-}]$ via (i) changing CO$_2$ system dissociation constants, and (ii) altering the solubility pump and thereby air–sea exchange component CO$_2$ concentrations in seawater. Calculation of [CO$_3^{2-}$]$_{\text{Norm}}$ only corrects for influences from (i), without affecting any air–sea CO$_2$ signal.

After normalization to constant T–S–P conditions and assuming no net air–sea exchange, biological activity drives changes in both $[\text{CO}_3^{2-}]_{\text{Norm}}$ and PO$_4$ along the biological trend (green curves in Fig. 5; Methods). Note that along a certain biological trend, seawater $[\text{CO}_3^{2-}]_{\text{Norm}}$ and PO$_4$ are only affected by within-ocean DIC and ALK redistributions (Fig. 1b). A net air–sea CO$_2$ exchange would cause changes in $[\text{CO}_3^{2-}]_{\text{Norm}}$ and PO$_4$ across biological curves. At the same PO$_4$, $[\text{CO}_3^{2-}]_{\text{Norm}}$ contrasts reflect $[\text{CO}_3^{2-}]_{\text{as}}$ gradients due to air–sea CO$_2$ exchange between water masses.

A plot of $[\text{CO}_3^{2-}]_{\text{Norm}}$ vs. PO$_4$ greatly facilitates investigation of air–sea CO$_2$ exchange from combined [CO$_3^{2-}$]$_{\text{as}}$ and PO$_4$ measurements/reconstructions. Compared to the biological trend, preindustrial North Atlantic surface waters have a steeper trend (Fig. 5a), which reflects CO$_2$ absorption during northward transport. Deep-water data lie on a shallower trend, consistent with mixing between low-[CO$_3^{2-}$]$_{\text{as}}$ (high DIC$_{\text{aw}}$) NADW and high-[CO$_3^{2-}$]$_{\text{as}}$ (low DIC$_{\text{aw}}$) AABW in the deep Atlantic (Fig. 2).

For our downcore reconstructions, benthic Cd/Ca suggests that deep-waters at the BOFS sites had PO$_4$ values of ~1.2 and ~0.8 $\mu$mol/kg during the Holocene and LGM, respectively (Fig. 5b; Supplementary Fig. 8). Assuming no air–sea CO$_2$ exchange, $[\text{CO}_3^{2-}]_{\text{Norm}}$ of ODP 999 surface waters at elevated PO$_4$ due to biological processes can be estimated straightforwardly using the H→H’ and G→G’ trajectories in Fig. 5b for the Holocene and LGM, respectively. For the Holocene, ODP 999 $[\text{CO}_3^{2-}]_{\text{Norm}}$ is ~56 ± 8 $\mu$mol/kg higher than $[\text{CO}_3^{2-}]_{\text{Norm}}$ of BOFS cores at PO$_4$ = 1.2 $\mu$mol/kg. For the LGM, ODP 999 $[\text{CO}_3^{2-}]_{\text{Norm}}$ is ~114 ± 9 $\mu$mol/kg higher than $[\text{CO}_3^{2-}]_{\text{Norm}}$ of BOFS cores at PO$_4$ = 0.8 $\mu$mol/kg. This suggests a Holocene-to-LGM increase of ~58 ± 12 $\mu$mol/kg in the ODP 999—BOFS $[\text{CO}_3^{2-}]_{\text{as}}$ gradient.

We also present a second approach to calculate $[\text{CO}_3^{2-}]_{\text{as}}$ gradients, which involves frequent use of the CO2sys program 28 and intermediate-step ALK and DIC parameters (Supplementary Note 1; Supplementary Figs. 9 and 10). The approach gives
similar results as the above pragmatic recipe, because both methods are essentially based on the same principle, which is to compare $[\text{CO}_3^{2-}]$ of water masses at the same physical and biological conditions.

**Enhanced CO$_2$ uptake in the glacial North Atlantic.** What caused the greater ODP 999–BOFS $[\text{CO}_3^{2-}]_{\text{as}}$ gradient during the LGM? We consider influences from biogenic matter composition variations, surface-water ALK and PO$_4$ changes, ocean circulation changes, and North Atlantic air–sea exchange. In Fig. 5, we have used a soft-tissue Redfield C/PO$_4$ of 127 and a rain ratio ($R = C_{\text{organic}}/C_{\text{CaCO}_3}$) of 4 (refs. 3,10,29,30) to predict the biological trend. Raising LGM C/PO$_4$ to 140 (the high end value in today’s North Atlantic30) and $R$ to 8 (doubling of the modern value) could lower the LGM $[\text{CO}_3^{2-}]_{\text{as}}$ gradient by $\sim$16 μmol/kg (Supplementary Fig. 15), still leaving $\sim$42 μmol/kg $[\text{CO}_3^{2-}]_{\text{as}}$ gradient increase to be explained by other processes. Evidence for such large biological changes is lacking. Importantly, any increase in C/PO$_4$ and $R$ would implicitly sequester more atmospheric CO$_2$ via an enhanced soft-tissue pump and weakened carbonate pump15. Inclusion of a whole ocean ALK inventory change6 or any increased glacial surface-water PO$_4$ at ODP 999

**Fig. 4** Carbonate system sensitivities to various changes. 

**a** Salinity effect. 

**b** Temperature effect. 

**c** Pressure effect. 

**d** Biological effect. 

**e** Air–sea CO$_2$ exchange effect. Calculations are based on GLODAP$^2$ ($n = 55,399$; blue) and a LGM output from LOVECLIM$^{58}$ ($n = 71,768$; gray). For **a–d**, calculations assume no net air–sea CO$_2$ change. Best fits of data are shown by red curves. See Methods for calculation details.
would raise the LGM \( [\text{CO}_3^{2-}]_{\text{as}} \) gradient (Supplementary Figs. 16 and 17).

Regarding ocean circulation changes, most AAIW upwellings in the tropics and less than \( \sim 25\% \) of today’s NADW is fed directly by AAIW without surfacing at low latitudes\(^{17}\). Northward AAIW transport is thought to have been reduced substantially in the glacial Atlantic\(^{23,31-33}\) in the face of vigorous GNAIW production\(^34\). Assuming a constant total carbon uptake by the North Atlantic, a complete shutdown of AAIW contribution would only raise the ODP 999–BOFS \( [\text{CO}_3^{2-}]_{\text{as}} \) gradient by \( \sim 30\% \), which is much smaller than the \( \sim 100\% \) increase from the Holocene (\( \sim 56 \mu\text{mol/kg} \)) to LGM (\( \sim 114 \mu\text{mol/kg} \)) (Fig. 5b). Any increased mixing of glacial AABW at BOFS sites would reduce the ODP 999–BOFS \( [\text{CO}_3^{2-}]_{\text{as}} \) gradient during the LGM. Given the proximity of our deep-water sites to the core of GNAIW and Nordic Sea overflow waters\(^{23,24,31,35,38}\), the larger LGM \( [\text{CO}_3^{2-}]_{\text{as}} \) gradient between ODP 999 and BOFS cores likely reflects a greater DIC\(_{\text{as}}\) increase from Gulf Stream to GNAIW. North Atlantic CO\(_2\) invasion was responsible for the preindustrial Gulf Stream-NADW \( [\text{CO}_3^{2-}]_{\text{as}} \) gradient (Fig. 2). Therefore, we ascribe the increased ODP 999–BOFS \( [\text{CO}_3^{2-}]_{\text{as}} \) gradient during the LGM to more efficient atmospheric CO\(_2\) uptake via air–sea exchange and subsequent transport to at least \( \sim 2\text{ km depth} \) (BOFS 11 K core depth) in the glacial North Atlantic.

**Quantification of North Atlantic CO\(_2\) uptake.** With reconstructed ODP 999–BOFS \( [\text{CO}_3^{2-}]_{\text{as}} \) gradients, we further quantify North Atlantic air–sea CO\(_2\) absorption changes between the Holocene and LGM. \( [\text{CO}_3^{2-}]_{\text{as}}/\text{DIC}_{\text{as}} \) sensitivities can be precisely estimated (Fig. 4e), making \( [\text{CO}_3^{2-}]_{\text{as}} \) gradients a useful proxy to calculate DIC\(_{\text{as}}\) changes. The \( 58 \pm 12 \mu\text{mol/kg} \) Holocene-to-LGM \( [\text{CO}_3^{2-}]_{\text{as}} \) increase (Fig. 5b) indicates a DIC\(_{\text{as}}\) increase of \( 91 \pm 20 \mu\text{mol/kg} \) due to enhanced North Atlantic air–sea CO\(_2\) absorption (Methods). Compared to the preindustrial Gulf Stream-NADW DIC\(_{\text{as}}\) gradient of \( \sim 90 \mu\text{mol/kg} \) (Fig. 2, Supplementary Fig. 3), this suggests a doubling of CO\(_2\) uptake efficiency in the LGM North Atlantic.

Beside DIC\(_{\text{as}}\) gradient changes, which indicate air–sea CO\(_2\) uptake efficiency, knowledge of northern-sourced-water volumes in the global deep ocean is required to determine total North Atlantic carbon sequestration. Figure 6 shows the total extra carbon absorbed by the LGM North Atlantic for a range of northern-sourced-water volumes (Methods). Sedimentary Pa/Th, radiocarbon, neodymium isotopes, and paired benthic Cd/Ca–\( ^{81}\text{C} \) suggest\(^{32,34,35,37} \) vigorous glacial northern-sourced intermediate water production and subsequent transport to the remaining world ocean. Based on previous estimates\(^{35,36,38,39} \), we tentatively assume that NADW- and GNAIW-derived waters occupy \( \sim 50\% \) and \( \sim 30\% \), respectively, of the global deep ocean volume (\( 1 \times 10^{18} \text{ m}^3 \) for \( >1 \text{ km} \)). In this case, our \( \sim 91 \mu\text{mol/kg} \) Holocene-to-LGM DIC\(_{\text{as}}\) increase yields \( \sim 100 \text{ Petagrams} \) of CO\(_2\) sequestration by the LGM North Atlantic (Fig. 6; Methods). To maintain similar total carbon uptake between the Holocene and LGM, GNAIW would need to be less than \( \sim 50\% \) of NADW in volume, which we consider unlikely given evidence for intensive GNAIW export to the global ocean\(^{23,32,34,35,37} \). We acknowledge uncertainties associated with our calculations, and encourage future work to better constrain volumes and carbonate chemistry changes of various water masses in the past.

**Discussion**

Previous work\(^{40-42} \) has tried to constrain air–sea CO\(_2\) exchange by reconstructing surface conditions. This requires reconstructions of the air–sea pCO\(_2\) difference (influenced by T, S, and nutrient
utilization), the gas transfer velocity (a power function of wind speed), solubility of CO₂ in seawater (mainly affected by T), and the area and contact time of surface waters available for air–sea exchange. Sea ice cover might possibly expanded, reducing glacial North Atlantic CO₂ absorption. A larger LGM meridional surface temperature gradient would enhance the North Atlantic solubility pump. Existing planktonic δ¹³C and Cd/Ca data suggests conflicting results regarding the glacial North Atlantic nutrient conditions, perhaps due to complications associated with surface-water proxies and spatial/seasonal nutrient variations in the North Atlantic. A decreased preformed nutrient in the glacial North Atlantic might be inferred from a lower GNAIW PO₄ (Fig. 3), but faster ventilation and/or reduced glacial AAIW could also cause a nutrient decline in GNAIW. Little is known about past wind intensity and air–sea contact time changes. Consequently, potential North Atlantic glacial CO₂ invasion remains poorly understood. Bypassing the necessity to reconstruct surface-water conditions for which some proxies are still lacking (e.g., wind), our new approach, to our knowledge, offers the first proxy-based quantitative estimate of air–sea CO₂ uptake efficiency in the glacial North Atlantic.

In contrast to previous calculations which concern combined biological (i.e., within-ocean DIC redistribution) and air–sea exchange carbon changes (Fig. 1c), our total North Atlantic carbon cycle. Therefore, by overcoming this opposing “volume effect”, the improved glacial North Atlantic efficiency increased DIC values of northern-sourced deep waters (termed the “endmember effect”) and thereby contributed substantially to air–sea DIC sequestration in the LGM deep ocean.

Atmospheric pCO₂ is controlled by both CO₂ gains (e.g., via Southern Ocean outgassing) and losses (e.g., via North Atlantic absorption). Growing evidence indicates that processes outside the Southern Ocean may have affected past atmospheric CO₂ variations. Our proxy-based results indicate that the North Atlantic CO₂ pump efficiency during the LGM was almost doubled relative to the Holocene. This increased efficiency and associated “endmember effect” effectively outcompeted the opposing “volume effect” due to any shrinkage of northern-sourced deep waters in the world ocean. In addition to the well-recognized role of reduced outgassing in the Southern Ocean, we therefore suggest that variations in the uptake and sequestration of atmospheric CO₂ via the North Atlantic were important contributors to the glacial-interglacial carbon cycle.

Methods

CO₂ system calculations. For both the preindustrial ocean and down-core CO₂ system calculations, seawater carbonate system variables were calculated using the CO2sys.xls program with dissociation constants K₁ and K₂ according to Mehrbach et al. and KₓCO₂ according to Dickson. Seawater total boron concentration was calculated from the boron-salinity relationship of Lee et al. The GLODAP dataset, the anthropogenic CO₂ contribution was subtracted from the measured DIC to obtain preindustrial DIC values.

Preindustrial Atlantic DIC and and [CO₂⁻]ₐ_{norm}. The GLODAP dataset is used to calculate preindustrial ocean CO₂ system variables. Following the established method of Broecker and Peng, we account for DIC anomalies created by (1) freshwater addition or removal based on S, (2) soft-tissue carbonation and respiration based on PO₄, and (3) CaCO₃ formation and dissolution based on ALK and nitrate (NO₃). See Fig. 1 for the simplified concept. We adopt the term DIC_{norm} to represent net air–sea exchange component DIC signatures from:

\[
\text{DIC}_{\text{norm}} = \text{DIC} - (\text{PO₄} - \text{PO₄}^{\text{res}}) \times C/\text{PO₄} \\
\quad \quad \quad - \frac{1}{2} \times (\text{ALK} - \text{ALK}^{\text{res}} + \text{NO₃} - \text{NO₃}^{\text{res}}) - \text{DIC}_{\text{const}}
\]

where the subscript “s” represents values normalized to S of 35 (e.g., DIC_{s} = DIC × S/35); the superscript “res” denotes mean ocean values at S = 35 (PO₄^{res} = 2.2 µmol/kg, ALK^{res} = 2383 µmol/kg, DIC^{res} = 2267 µmol/kg, and NO₃^{res} = 31 µmol/kg); C/PO₄ represents the soft-tissue stoichiometric Redfield ratio; and the arbitrary DIC_{const} (= 2285 µmol/kg) is designed to bring zero DIC to close to the NADW–AABW boundary (Fig. 2). The term (PO₄ – PO₄^{res}) × C/PO₄ corrects for DIC changes due to photosynthesis and soft-tissue degradation, and the term \( \frac{1}{2} \times (\text{ALK} - \text{ALK}^{\text{res}} + \text{NO₃} - \text{NO₃}^{\text{res}}) \) accounts for DIC changes caused by CaCO₃ formation and dissolution. To be consistent with previous work, we used C/PO₄ = 127 to calculate DIC_{norm} and [CO₃^{2−}]_{norm} in Fig. 2. Using other C/PO₄ values does not significantly affect spatial DIC and [CO₃^{2−}]_{norm} (Fig. 3a, b). Neither are their patterns affected by using other PO₄-ALK-NO₃ values to replace global mean values in Eq. (1) (Supplementary Figs. 11 and 12). Ideally, DIC_{const} would be the mean DIC value of an abiotic ocean (Fig. 1), but this value cannot be simply determined from modern observations. Because our interest lies in spatial DIC contrasts instead of absolute values, the choice of DIC_{const} has no effect on our interpretation.

To obtain [CO₂⁻]_{fl}, we first calculate [CO₂⁻]_{as,T=4} using (DIC_{as} + DIC_{const}). ALK^{as}, and PO₄^{as} (Fig. 2). Using other C/PO₄ values does not significantly affect spatial DIC and [CO₂⁻]_{norm} values. We then change S to 35% and other chemical concentrations proportionally. For example, ALK and DIC will change as follows:

\[
\text{ALK}_{35} = \text{ALK} / S, \quad \text{DIC}_{35} = \text{DIC} / S.
\]

We use S = 35%, ALK_{35}, DIC_{35}, PO₄_{35}, and [SiO₃]_{35} along with hydrographic T and P to calculate [CO₂⁻]_{fl} for Tik (4–5°C). The [CO₂⁻]_{fl} to S sensitivity (Sen_S) is calculated by:

\[
\text{Sen}_S = \left( \frac{\left[ \text{CO}_2^{\text{fl}} \right]}{\left[ \text{CO}_2^{\text{norm}} \right]} \right)_{S = 35}/S.
\]

To estimate temperature effects, we calculate [CO₂⁻]_{fl,3°C−T;3°C} using S = 35%, ALK_{35}, DIC_{35}, PO₄_{35}, and [SiO₃]_{35} at 3°C, and hydrographic P. The sensitivity of [CO₂⁻]_{fl} to temperature (Sen_T) is defined by:

\[
\text{Sen}_T = \left( \frac{\left[ \text{CO}_2^{\text{fl}} \right]}{\left[ \text{CO}_2^{\text{norm}} \right]} \right)_{T = 3°C}/(3 − T).
\]

Regarding pressure effects, we calculate [CO₂⁻]_{fl}_{P;2500} using S = 35%, ALK_{35}, DIC_{35}, PO₄_{35}, [SiO₃]_{35}, and 3°C; and P = 2500 dbar. The sensitivity of [CO₂⁻]_{fl} to pressure (Sen_P) is defined by:

\[
\text{Sen}_P = \left( \frac{\left[ \text{CO}_2^{\text{fl}} \right]}{\left[ \text{CO}_2^{\text{norm}} \right]} \right)_{P = 2500}/(P_{2500} − P)/100.
\]

To estimate the influence on [CO₂⁻]_{fl} from within-ocean ALK–DIC redistributions by biological processes, we assume a 0.1 µmol/kg increase in PO₄ (i.e., ΔPO₄ = 0.1 µmol/kg) due to biological respiration (photosynthesis has an opposite effect). The resultant ALK (ALK_{35−respiration}) and DIC (DIC_{35−respiration}) can then be calculated from:

\[
\text{ALK}_{35−\text{respiration}} = \text{ALK}_{35} + \Delta \text{PO}_4 \times C/\text{PO}_4
\]

\[
\Delta \text{DIC} = \text{DIC}_{35} + \Delta \text{PO}_4 \times C/\text{PO}_4 \times C/\text{PO}_4 /
\]

\[
\text{ΔDIC}_{35−\text{respiration}} = \text{DIC}_{35−\text{respiration}} - \text{DIC}_{35}.
\]

Resultant [CO₂⁻]_{norm} = [CO₂⁻]_{norm−\text{respiration}} values are calculated using

\[
\text{ALK}_{35−\text{respiration}} \text{ and } \text{PO}_4 {35−\text{respiration}} \text{ at constant physical conditions of } T = 3°C, S = 35, \text{ and } P = 2500 \text{ dbar}.
\]
[CO$_3^{2-}$]$_{\text{Norm}}$ to PO$_4$ is defined by:

$$\text{[CO}_3^{2-}\text{]}_{\text{Norm}} = \frac{\text{[CO}_3^{2-}\text{]}_{\text{Norm-np}} \cdot \text{PO}_4}{\text{PO}_4}. \quad (9)$$

We consider four Redfield stoichiometric scenarios: C/PO$_4$ = 127, R = 4 (the reference concentration; Fig. 4d); C/PO$_4$ = 140, R = 4; C/PO$_4$ = 127, R = 8; and C/PO$_4$ = 140, R = 8 (Supplementary Fig. 15). In all cases, strong exponential correlations exist between CO$_3^{2-}$PO$_4$ sensitivity and [CO$_3^{2-}$]$_{\text{Norm}}$ (Fig. 4d). The correlations may reflect the buffering effect of the seawater CO$_3$ system: for seawater with high DIC (low [CO$_3^{2-}$] and high buffering capability), [CO$_3^{2-}$]$_{\text{Norm}}$ would be relatively less sensitive to biological DIC and ALK disturbances. All of the above sensitivity calculations assume no net air–sea CO$_3$ change.

To calculate air–sea exchange sensitivities, we assume a 10 μmol/kg increase in DIC$_{\text{a}}$ due to atmospheric CO$_3$ invasion (i.e., ΔDIC$_{\text{a}}$ = 10 μmol/kg). We calculate [CO$_3^{2-}$]$_{\text{Norm}}$ using $S = \text{35.9‰}$, ALK$_{\text{a}}$ = DIC$_{\text{a}}$ + ΔDIC$_{\text{a}}$, and $\text{[CO}_3^{2-}\text{]}_{\text{Norm}}$ = 56 μmol/kg, [CO$_3^{2-}$]$_{\text{Norm}}$ was 114 μmol/kg (Fig. 5), terms 0.61 and 0.58, respectively, represent the absolute LGM and Holocene [CO$_3^{2-}$]$_{\text{DIC}}$ sensitivities (Fig. 4e) used to transfer [CO$_3^{2-}$]$_{\text{Norm}}$ into ODP999-BOF DIC$_{\text{a}}$ contrasts (LGM: 186 μmol/kg, Holocene: 95 μmol/kg), and the number 12 converts C from molles into weight.

Based on previous estimates, NADW is thought to be ≈50‰ (ref. 38), whereas δGNAIW remained roughly similar to δNADW or shrank (refs. 35,36). These estimates are debated and have large uncertainties, and we thus calculate $\Delta_{\text{LGM–Holocene}}$ for a range of δGNAIW and δNADW values (Fig. 6). Any influence from AAIW is ignored because of its similar [CO$_3^{2-}$]$_{\text{DIC}}$ signals to Gulf Stream during the Holocene (Supplementary Fig. 3) and much reduced northward advection during the LGM (refs. 31,35). We tentatively treat $\Delta_{\text{LGM–Holocene}}$ of −100 PγC using δNADW = 50‰ and δGNAIW = 30‰ as our best estimate. Assuming no Holocene–LGM DIC$_{\text{a}}$ gradient change (i.e., the same CO$_3$ uptake efficiency and everything else equal), $\Delta_{\text{LGM–Holocene}}$ would be $\sim$240 PγC at δNADW = 50‰ and δGNAIW = 30‰.

Cores, age models, samples, and analytical methods. We used ODP Site 999 for Gulf Stream surface-water reconstructions (Fig. 2). The age model is from Schmidt et al.59. Planktonic foraminiferal Globigerinoides ruber (sensu stricto, variable white) δ18O, Mg/Ca, and δ13B data are from refs. 31,22,36. Briefly, about 25 and 35 shells from the 250–350 μm size fraction were used for δ18O and Mg/Ca analyses, respectively. Samples for δ13B analyses were sonicated in methanol for 5–10 s, roasted under vacuum at 375°C for 30 min, and analyzed on a Finnigan Optima IRMS with a precision of <0.06‰. Shells for Mg/Ca were cleaned following the reductive cleaning procedure66 and measured on an inductively-coupled plasma (MC)–ICP–MS following ref. 21. The analytical error in δ13B is about ±0.25‰. Due to the relatively large sample size requirement, shell availability, and lengthy chemical treatments for δ13B, we present low-resolution δ13B for C. mundulus from ODP 17K and for C. wuellerstorff from BOFS 11K. Note that consistent [CO$_3^{2-}$]$_{\text{a}}$ results from B/Ca and δ13B strengthen the reliability of our reconstructions (Fig. 3).

We consider four Redfield stoichiometric scenarios: C/PO$_4$ = 127, R = 4 (the reference concentration; Fig. 4d); C/PO$_4$ = 140, R = 4; C/PO$_4$ = 127, R = 8; and C/PO$_4$ = 140, R = 8 (Supplementary Fig. 15). In all cases, strong exponential correlations exist between CO$_3^{2-}$PO$_4$ sensitivity and [CO$_3^{2-}$]$_{\text{Norm}}$ (Fig. 4d). The correlations may reflect the buffering effect of the seawater CO$_3$ system: for seawater with high DIC (low [CO$_3^{2-}$] and high buffering capability), [CO$_3^{2-}$]$_{\text{Norm}}$ would be relatively less sensitive to biological DIC and ALK disturbances. All of the above sensitivity calculations assume no net air–sea CO$_3$ change.

To calculate air–sea exchange sensitivities, we assume a 10 μmol/kg increase in DIC$_{\text{a}}$ due to atmospheric CO$_3$ invasion (i.e., ΔDIC$_{\text{a}}$ = 10 μmol/kg). We calculate [CO$_3^{2-}$]$_{\text{Norm}}$ using $S = \text{35.9‰}$, ALK$_{\text{a}}$ = DIC$_{\text{a}}$ + ΔDIC$_{\text{a}}$, and $\text{[CO}_3^{2-}\text{]}_{\text{Norm}}$ = 56 μmol/kg, [CO$_3^{2-}$]$_{\text{Norm}}$ was 114 μmol/kg (Fig. 5), terms 0.61 and 0.58, respectively, represent the absolute LGM and Holocene [CO$_3^{2-}$]$_{\text{DIC}}$ sensitivities (Fig. 4e) used to transfer [CO$_3^{2-}$]$_{\text{Norm}}$ into ODP999-BOF DIC$_{\text{a}}$ contrasts (LGM: 186 μmol/kg, Holocene: 95 μmol/kg), and the number 12 converts C from molles into weight.

Based on previous estimates, NADW is thought to be ≈50‰ (ref. 38), whereas δGNAIW remained roughly similar to δNADW or shrank (refs. 35,36). These estimates are debated and have large uncertainties, and we thus calculate $\Delta_{\text{LGM–Holocene}}$ for a range of δGNAIW and δNADW values (Fig. 6). Any influence from AAIW is ignored because of its similar [CO$_3^{2-}$]$_{\text{DIC}}$ signals to Gulf Stream during the Holocene (Supplementary Fig. 3) and much reduced northward advection during the LGM (refs. 31,35). We tentatively treat $\Delta_{\text{LGM–Holocene}}$ of −100 PγC using δNADW = 50‰ and δGNAIW = 30‰ as our best estimate. Assuming no Holocene–LGM DIC$_{\text{a}}$ gradient change (i.e., the same CO$_3$ uptake efficiency and everything else equal), $\Delta_{\text{LGM–Holocene}}$ would be $\sim$240 PγC at δNADW = 50‰ and δGNAIW = 30‰.
Subtropical western North Atlantic surface [CO$_2$]$_1$. Because most of North Atlantic subtropical gyre waters circulate through the Caribbean Sea before being transported to the subpolar North Atlantic via the Gulf Stream, ODP 999 from Caribbean Sea is used to constrain past Gulf Stream carbonate chemistry$^{39}$. To further test the feasibility of using ODP 999 to represent the first-order Gulf Stream [CO$_2$]$_1$ changes during the Holocene and LGM, we have estimated surface-water [CO$_2$]$_1$ for four sites across the wider subtropical Western Atlantic region (33°-33°35’N, longitude: 61°-81°W). Among these sites, KN24.0-51GGC (33°N, 76°W) is located within the Gulf Stream$^{40}$. Because subtropical surface waters cycle multiple times through the upper ocean gyre circulation, it is possible that surface waters have been in equilibrium with past atmospheric PCO$_2$ (refs. [32,33]). Therefore, we assume surface-water PCO$_2$ of 270 and 194 ppm for the holocene and LGM, respectively. We assign ±1.5 ppm error to surface-water PCO$_2$ to account for any potential air-sea CO$_2$ disequilibrium. For these sites, we use surface temperature and salinity reconstructions from previous publications$^{41-43}$. ALK is calculated based on the same approach for ODP 999. The reconstructed in situ [CO$_2$]$_1$ values show some differences between cores, due to local T-S conditions. Since we are interested in air-sea CO$_2$ exchange signals, we convert reconstructed in situ [CO$_2$]$_1$ into [CO$_3$]$^{2-}$ using Eq. (11). As can be seen from Supplementary Fig. 6 and Supplementary Data 2, these cores show similar [CO$_3$]$^{2-}$ values estimated from the GLODAP dataset$^{45}$, where [CO$_3$]$^{2-}$ is the preindustrial (PI) deep-water [CO$_3$]$^{2-}$ value estimated from the GLODAP dataset$^{45}$. All CaCO$_3$-containing taxa (Fig. 4) is used to obtain a proxy-based estimates, we use ODP 999 data for calculations in the main text.

Benthic B/Ca and δ¹⁸O to deep-water [CO$_2$]$_1$. Most deep-water [CO$_2$]$_1$ values are reconstructed using benthic Ca (refs. [47-49]) from [CO$_3$]$^{2-}$/benthic Ca = [CO$_3$]$^{2-}$ [CO$_3$]$^{2-}$/Ca + AlkB/Amgcalcite-consumption/k, where [CO$_3$]$^{2-}$ is the preindustrial (PI) deep-water [CO$_3$]$^{2-}$ value estimated from the GLODAP dataset$^{45}$. All CaCO$_3$-containing region (latitude: 1.5–2°C, and ϕ = −1°) is used to normalize δ¹⁸O to a constant condition (i.e., no error with respect to δ¹⁸Oglobal_sealevel was estimated from Fig. 2). Using δ¹⁸Oglobal_sealevel offsets we define B/Ca and δ¹⁸O to deep-water [CO$_2$]$_1$ reconstructions for the Holocene and LGM.

Benthic C/Ca to deep-water PO$_4$$_{3-}$. We follow the established approach$^{36,46,50-52}$ to convert benthic (C. wuellerstorff, C. mundulus, and Uvigerina spp) foraminiferal C/Ca into deep-water Ca concentrations. Partition coefficients (D$_{Ca}$) are used to calculate deep-water Ca from: C/Ca (nmol/kg) = [Ca/Ca]$_{core-top}$/D$_{Ca}$. Bertram et al.$^{50}$ used empirical D$_{Ca}$ values of 2.3, 2.2, and 2.7 for BOFS 17, 14, and 11, respectively. However, these D$_{Ca}$ values would result in Holocene C/Ca of 0.3–0.4 nmol/kg, higher than the observed value of ~0.25 nmol/kg from modern graphic measurements (Supplementary Fig. 7). This offset may suggest higher D$_{Ca}$ values for the North Atlantic Ocean, which has been acknowledged recently$^{51}$. We thus adjust D$_{Ca}$ (25% increase) so that the calculated Holocene deep-water Ca concentrations match modern measurements. This adjustment is supported by consistent Cd reconstructions from this study and previous reconstructions based on Ca/Cd measurements for H. elegans. Compared to Cibicides, D$_{Cd}$ into H. elegans is higher$^{52}$. As can be seen from Supplementary Fig. 8 for cores with similar benthic δ¹⁸C from similar water depths (i.e., bathed in similar water masses), our Cd reconstructions match favorably with those based on H. elegans measurements$^{52}$. Deep-water Ca is converted into PO$_4$$_{3-}$ using the relationship based on the latest North Atlantic Ocean measurements (Supplementary Fig. 7). Using older published Ca-P relationships$^{53,54}$ only marginally affects our PO$_4$$_{3-}$ estimates.

Uncertainties associated with Cd and PO$_4$$_{3-}$ reconstructions are estimated as follows. Error for Cd is estimated using 2σ$_{Cd}$$^3$ = ($2σ_{Cd,up}$$^3$ + $2σ_{Cd,down}$$^3$)$^{1/2}$, where 2σ$_{Cd,up}$ and 2σ$_{Cd,down}$ (5%) are errors for Cd$_{up}$ and Cd$_{down}$, respectively. Due to poorly defined uncertainty for D$_{Cd}$ from the literature, we assume an error of 50%, and then compare final error reports with literature estimates to assess the appropriateness of our calculations. SeaAmp PO$_4$$_{3-}$ is calculated from Cd$_{core}$ using: PO$_4$$_{3-}$ = Cd$_{core}$ × (2σ$_{Cd}$)$^{1/2}$ (2σ$_{Po}$)$^{1/2}$ (2σ$_{D_{Ca}}$)$^{1/2}$ (2σ$_{D_{po}}$)$^{1/2}$ (2σ$_{Ca}$)$^{1/2}$, where $σ_{Po}$ and $σ_{Ca}$, respectively, represent 95% confidence errors associated with a and b (Supplementary Fig. 7b). The PO$_4$$_{3-}$ uncertainty was calculated from:

\[
2σ_{PO4} = \sqrt{(2σ_{Po,b} - 2σ_{Po,a})^2 + (2σ_{Ca,b} - 2σ_{Ca,a})^2 + (2σ_{D_{Cd},b} - 2σ_{D_{Cd},a})^2 + (2σ_{D_{Po},b} - 2σ_{D_{Po},a})^2 + (2σ_{D_{Ca},b} - 2σ_{D_{Ca},a})^2},
\]

where $σ_{Po}$, $σ_{Ca}$, $σ_{D_{Cd}}$, and $σ_{D_{Ca}}$ are errors for PO$_4$$_{3-}$, Cd$_{core}$, Cd$_{up}$, and Cd$_{down}$, respectively. Finally, these uncertainties (already included in error calculations) are compared with previously published uncertainties (~0.08 nmol/kg for Cd and ~0.17 nmol/kg for PO$_4$$_{3-}$). The error estimates are based on relatively weak sensitivities of [CO$_3$]$^{2-}$ and Ca$_{core}$ variations with respect to deep-water [CO$_2$]$_1$ reconstructions for the Holocene and LGM. Our reconstructions (Fig. 3) are consistent with high benthic δ¹³C and low benthic Cd/Ca at numerous glacial North Atlantic mid-depths$^{55,56,60,61}$.

Deep-water temperature and salinity estimates. Deep-water temperature ($T_{deep}$) is estimated from the ice volume corrected benthic δ¹³C (δ¹³C$_{B/18O}$) and the δ¹³C$_{OIVC}$ relationship of Marchitto et al.$^{62}$ from $T_{deep} = 2.5 - (δ¹³C_{B/18O} - 2.8)/0.224$, where δ¹³C$_{B/18O} = δ¹³C_{benthic} - δ¹³C_{global_sealevel}$ was estimated from sea level curves$^{63,64}$ with a global δ¹³C$_{OIVC}$-sea level scaling of 0.0085‰/m (ref. 59). Deep-water salinity ($S_{deep}$) is calculated by: $S_{deep} = S_{core-top} + 1.11 × δ¹³C_{global_sealevel}$, which was calculated from Supplementary Fig. 7b. The PO$_4$$_{3-}$ uncertainty was calculated from: $2σ_{PO4} = \sqrt{(2σ_{Po,b} - 2σ_{Po,a})^2 + (2σ_{Ca,b} - 2σ_{Ca,a})^2 + (2σ_{D_{Cd},b} - 2σ_{D_{Cd},a})^2 + (2σ_{D_{Po},b} - 2σ_{D_{Po},a})^2 + (2σ_{D_{Ca},b} - 2σ_{D_{Ca},a})^2}$, where $σ_{Po}$, $σ_{Ca}$, $σ_{D_{Cd}}$, and $σ_{D_{Ca}}$ are errors for PO$_4$$_{3-}$, Cd$_{core}$, Cd$_{up}$, and Cd$_{down}$, respectively, User±50 dbar in P, respectively. Therefore, these uncertainties (already included in error calculations) are relatively less important compared to the reconstruction error from ±100 µmol/kg for deep-water [CO$_2$]$_1$. Data availability

The data reported in the paper are presented in Supplementary Data.

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Author contributions
J.Y. conceived the idea and wrote the paper. L.M. assisted with the model data used. Z.J./F.Z. picked the foram shells. E.J.R./Y.D. assisted with the statistics. G.L.F./J.Y. measured the foram shells. F.Z. picked the foram shells. E.J.R./Y.D. assisted with the statistics. G.L.F./J.Y. measured the boron isotopes. All authors (L.M., Z.J., D.T., G.F., E.R., N.M., J.M., Y.D., H.R., F.H., F.Z., P.C. and A.R.) contributed to improving the paper.

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