Episodic release of CO₂ from the high-latitude North Atlantic Ocean during the last 135 kyr

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Antarctic ice cores document glacial-interglacial and millennial-scale variability in atmospheric pCO₂ over the past 800 kyr. The ocean, as the largest active carbon reservoir on this timescale, is thought to have played a dominant role in these pCO₂ fluctuations, but it remains unclear how and where in the ocean CO₂ was stored during glaciations and released during (de)glacial millennial-scale climate events. The evolution of surface ocean pCO₂ in key locations can therefore provide important clues for understanding the ocean’s role in Pleistocene carbon cycling. Here we present a 135-kyr record of shallow subsurface pCO₂ and nutrient levels from the Norwegian Sea, an area of intense CO₂ uptake from the atmosphere today. Our results suggest that the Norwegian Sea probably acted as a CO₂ source towards the end of Heinrich stadials HS1, HS4 and HS11, and may have contributed to the increase in atmospheric pCO₂ at these times.
The ongoing rise in atmospheric pCO$_2$ and associated observations of reduced Arctic winter sea-ice coverage are projected to suppress the high-latitude North Atlantic ocean circulation over the coming decades, in turn affecting regional climate and the large-scale atmospheric circulation$^{1,2}$. Regional reconstructions of past changes in surface ocean pCO$_2$ and temperature are important for understanding how climate, ocean circulation and the carbon cycle are linked. Greenland and Antarctic ice core records document a millennial-scale bipolar seesaw in air temperature changes during late Pleistocene glaciations and deglaciations$^3$. Warm interstadial conditions over Greenland coincided with periods of gradual cooling over Antarctica, whereas cold stadial periods in Greenland coincided with warming over Antarctica$^4$. In Greenland ice cores, these millennial-scale events have been termed Dansgaard–Oeschger events and are characterized by abrupt warming during the transitions to interstadials$^4$. In contrast, Antarctic ice core reports only gradual climate changes$^5$. The longest stadials include Heinrich events, and are called Heinrich Stadials (HS) (ref. 5).

These interhemispheric climate patterns may be explained by variations in the Atlantic Meridional Overturning Circulation and associated changes in the northward heat export$^6$. Atmospheric pCO$_2$ was ~80–100 ppm lower during glacial periods compared with interglacial periods$^7$. During the last deglaciation (~20–10 ka), atmospheric pCO$_2$ increased in two pronounced steps, by ~50 ppm during H1 (~18–14.5 ka) and by another ~30 ppm during the Younger Dryas (~13–11.5 ka) (ref. 8). The last glacial period was furthermore characterized by millennial-scale variability in atmospheric pCO$_2$, with an increase of roughly 25 ppm beginning during most of the Heinrich stadials, and peaking at or less than a thousand years after the onset of the interstadials$^7$. Thereafter, pCO$_2$ decreased gradually in phase with cooling in Antarctica$^8$.

The high-latitude North Atlantic, north of 50°N, is one of the most efficient CO$_2$ uptake areas in the modern ocean, because of cold sea surface temperatures, deep-water formation, strong primary productivity and high-wind speeds$^{10–12}$. Therefore, it is an important region to study glacial-interglacial and millennial-scale variations in air-sea CO$_2$ exchange. This study aims to quantify the evolution of shallow subsurface ocean carbonate chemistry in the Norwegian Sea over the past 135 kyr, using the foraminiferal δ$^{13}$C and δ$^{18}$O excursions on our results, we calculated pCO$_2$-depth profiles for the upper 250 m of the water column in the Norwegian Sea based on modern hydrographic data (total dissolved inorganic carbon, total alkalinity, temperature, salinity, phosphate and silicate) covering the late spring to early autumn (Fig. 2b). The resulting modern pCO$_2$-profile (Fig. 2b) shows that the average pCO$_2$ of the surface ocean (0–25 m water depth) is 30–50 ppm lower than atmospheric pCO$_2$, but at the calcification depth of N. pachyderma (~ ≥ 50 m water depth) average aqueous pCO$_2$ is approximately equal to atmospheric pCO$_2$. We thus calculated the difference in pCO$_2$ between the surface ocean and the atmosphere (ΔpCO$_2$sea-air) by subtracting 40 ppm from ΔpCO$_2$cal-air, assuming that the pCO$_2$ gradient between the surface ocean and calcification depth of N. pachyderma remained constant through time (see ‘Discussion’).

To characterize the changes in availability and utilization of nutrients, we measured Cd/Ca and δ$^{13}$C in N. pachyderma. The Cd/Ca recorded by symbiont-barren planktic foraminifera such as N. pachyderma is sensitive to Cd concentrations in seawater$^{22}$, an element that shows strong similarity to the seawater distribution of the nutrient phosphate$^{23}$. Thus, foraminiferal Cd/Ca can be used to reconstruct the levels of phosphate in seawater, and provides clues for the abundance and utilization of phosphate through time$^{24}$, albeit with a potential side control of temperature on the Cd incorporation into planktic foraminiferal shells$^{25}$. In addition, planktic foraminiferal δ$^{13}$C responds to changes in nutrient cycling, air-sea gas exchange, exchange between global carbon reservoirs$^{26}$ and carbonate chemistry$^{27}$.

Seawater pH and pCO$_2$. The studied sediment core JM-FI-19PC spans the last 135 kyr (refs 14–16) and has been correlated closely to the age model of the Greenland ice core NGRIP (ref. 28) (see Methods and Supplementary Fig. 1). The δ$^{18}$O record displays ~1.5‰ higher glacial values compared with interglacials and the core top samples. In addition, negative δ$^{13}$C excursions of up to ~1.5‰ occurred during H1 and HS4 (Fig. 3a). Correspondingly, glacial pH was elevated by ~0.16 units in the shallow subsurface compared with the Holocene, similar to results from earlier studies of tropical regions$^{29,30}$, but the record is punctuated by brief episodes of acidification during some Heinrich stadials (Fig. 3b). The reconstructed shallow subsurface pCO$_2$ shows lowest values of ~200 μatm during the Last Glacial Maximum (LGM) (~24–19 ka), whereas it increased to 320 μatm during HS1 at ~16.5 ka, and then gradually dropped to ~230 μatm over the Bolling-Allerød interstadials (14.7–12.7 ka)

Results

Geochmical proxies of ocean pCO$_2$ and nutrient changes. Because the speciation and isotopic composition of dissolved boron in seawater depends on seawater pH, and borate ion is the dominant species incorporated into planktic foraminiferal shells, their recorded δ$^{11}$B serves as a pH-proxy$^{17}$, and paleo-pH can be quantified if temperature and salinity can be constrained independently (see Methods for details). When pH is paired with a second parameter of the carbon system, aqueous pCO$_2$ can be estimated. Here we applied foraminiferal δ$^{13}$O and Mg/Ca measurements to estimate foraminiferal calcification temperature and salinity, and then used the modern local relationship between salinity and total alkalinity to estimate coeval changes in total alkalinity (see Methods for details). Finally, we calculated the difference between our reconstructed shallow subsurface pCO$_2$ and atmospheric pCO$_2$ from ice core measurements$^{15}$.

The ΔpCO$_2$sea-air is a measure for the tendency of a water mass to absorb/release CO$_2$ from/to the atmosphere$^{10}$. However, because N. pachyderma lives below the sea surface, this difference represents the difference between atmospheric pCO$_2$ (‘air’) and the seawater pCO$_2$ (pCO$_2$cal) at the calcification depth and growth season of N. pachyderma (ΔpCO$_2$cal-air). Neogloboquadrina pachyderma is thought to inhabit a wide and variable range of calcification depths in the Nordic Seas from 40 to 250 m water depth$^{19}$. It migrates vertically in the water column$^{19}$ and is most abundant during late spring to early autumn$^{20}$. To assess the influence of the seasonal occurrence and calcification depth of N. pachyderma on the results, we calculated pCO$_2$-depth profiles for the upper 250 m of the water column in the Norwegian Sea based on modern hydrographic data (total dissolved inorganic carbon, total alkalinity, temperature, salinity, phosphate and silicate) covering the late spring to early autumn (Fig. 2b). The resulting modern pCO$_2$-profile (Fig. 2b) shows that the average pCO$_2$ of the surface ocean (0–25 m water depth) is 30–50 ppm lower than atmospheric pCO$_2$, but at the calcification depth of N. pachyderma (~ ≥ 50 m water depth) average aqueous pCO$_2$ is approximately equal to atmospheric pCO$_2$. We thus calculated the difference in pCO$_2$ between the surface ocean and the atmosphere (ΔpCO$_2$sea-air) by subtracting 40 ppm from ΔpCO$_2$cal-air, assuming that the pCO$_2$ gradient between the surface ocean and calcification depth of N. pachyderma remained constant through time (see ‘Discussion’).

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The highest Cd/Ca values are recorded on this interval in our record. The shallow subsurface stadials, because of the high sedimentation rate and good age and boron analyses in some Heinrich stadials, we chose to focus on measurements, and inadequate sample sizes for high-resolution a prominent increase in the trends are similar to previous studies, for example, similar Cd/Ca and dCO2 variability as changes in nutrient levels. However, it is notable that our Cd/Ca results show absolute values that are an order of magnitude lower than previous studies from the modern ocean, where the core site region is characterized by terrestrial carbon 31, and elevated [CO3^2-] at the higher pH characteristic for the LGM. Elevated pH (and/or [CO3^2-]) has been observed to lower the δ13C recorded by planktic foraminifera relative to seawater δ13COW, but the sensitivity is species-specific and N. pachyderma has not yet been examined in this regard27. Compared with the Holocene, the lower δ13C values are likely due to a smaller air-sea gas exchange in response to the higher temperatures during the Eemian relative to the Holocene32 (0.1‰ decrease in δ13C per 1°C increase; ref. 34) (see Discussion below).

Discussion

The most striking observation from these data is the large increase in ΔpCO2_cal-air by +80 to +100 μatm during the final stages of HS1, HS4 and HS11. In the modern Norwegian Sea, the average pCO2 at the calcification depth of N. pachyderma is ~40 μatm lower than in the surface ocean, where the CO2 exchange with the atmosphere actually occurs (Fig. 2b). If the paleo-pCO2 gradient between the calcification depth of N. pachyderma and the surface ocean was similar to the modern ocean (~40 μatm), the re-calculated ΔpCO2Sea-air values of +40 to +60 μatm during HS1, HS4 and HS11 (Fig. 3f) suggest that the Norwegian Sea, and perhaps the Nordic Seas in general, acted as a CO2 source during these intervals. This is very different from the modern ocean, where the core site region is characterized by intense CO2 uptake from the atmosphere (Figs 1 and 2b).

In contrast, the negative ΔpCO2Sea-air (~ +40 μatm) during the LGM and BA interstadial could be interpreted as enhanced CO2 uptake, similar to the Holocene (Fig. 3f). However, the lower...
aqueous pCO₂ values during the mid Eemian relative to the Holocene are more likely explained by a decrease in the CO₂ solubility because of increased sea surface temperatures. Mg/Ca temperature estimates in core JM11-FI-19PC indicate a 2°C warming at the calcification depth of *N. pachyderma*¹⁵, but faunal assemblages, which may reflect temperatures in the mixed layer, where CO₂ is exchanged, suggest an even greater warming up to ~4°C compared with the present³³.

In the discussion above, we assumed that the pCO₂ gradient between the calcification depth of *N. pachyderma* and the surface ocean (~40 μatm) remained constant through time. We cannot provide evidence for past changes in this gradient; however, the modern spatial variability of this pCO₂ gradient in the Nordic Seas combined with inferred past changes in ocean circulation can provide some insights. Importantly, previous studies from the Nordic Seas based on planktic foraminiferal assemblages³⁵ and sea-ice proxies (IP₂₅ and phytoplankton-based sterols) (ref. 16) suggest that the polar front moved towards our study area during cold stadial periods. A modern pCO₂-depth profile from the polar frontal zone in the Greenland Sea²¹ (Fig. 2c) shows that the pCO₂ gradient between the surface ocean and the calcification depth of *N. pachyderma* (~20 μatm on average) (as well as the upper water column pCO₂ in general) is smaller at the polar front than in the Norwegian Sea (Fig. 2b,c). This pattern argues against the possibility that a larger than modern pCO₂ gradient existed between the surface ocean and the calcification depth of *N. pachyderma* during Heinrich stadials. Our recalculated ΔpCO₂sea-air (Fig. 3f) may therefore actually represent a minimum estimate of the ΔpCO₂sea-air during these time intervals.

It is notable that earlier findings by Yu et al.³² using evidence...
from B/Ca and a low-resolution $\delta^{11}\text{B}_{\text{N. pachyderma}}$ record from the Iceland Basin, suggested that the high-latitude North Atlantic region remained a CO$_2$ sink throughout the last deglaciation. This result contrasts with our $\delta^{11}\text{B}$ record despite the fact that our B/Ca record looks very similar to the B/Ca record of Yu et al.\textsuperscript{32} (Supplementary Fig. 3). However, because Pleistocene planktic B/Ca records typically display large variability that rarely relates to oceanic pH variations\textsuperscript{36}, we suggest that the $\delta^{11}\text{B}$ proxy is a more reliable pH proxy. The $\delta^{11}\text{B}$ proxy has been validated against ice core CO$_2$ data and consistent variations in $\delta^{11}\text{B}$ have been reconstructed between different core sites, where CO$_2$ is in equilibrium with the atmosphere\textsuperscript{29,30}. Furthermore, the earlier $\delta^{14}\text{B}$ study\textsuperscript{32} does not extend beyond HS1 and may therefore fail to capture the full glacial/interglacial variability (Supplementary Fig. 3). Nevertheless, because we reconstruct air-sea disequilibrium conditions, which may be spatially variable, the discrepancy between these two $\delta^{11}\text{B}$ records across HS1 (Supplementary Fig. 3) warrants additional research to further explore the spatial extent of the high-latitude North Atlantic pCO$_2$ source during Heinrich Stadials.

The increase in $\Delta$pCO$_{\text{sea-air}}$ during HS1, HS4 and HS11 in the Norwegian Sea could be the result of the following scenarios: (1) mixing with or surfacing of older water masses with accumulated CO$_2$, (2) changes in primary productivity and nutrient concentrations, (3) increased rate of sea ice formation, (4) enriched CO$_2$ content of the inflowing Atlantic water (that is, changes in the pCO$_2$ of the source water at lower latitudes) and/or (5) slowdown of deep-water formation. Concerning scenario (1), shallow subsurface radiocarbon reconstructions from the high-latitude North Atlantic\textsuperscript{37–39} display a prominent decrease in reservoir ages (that is, better ventilated 'young' water) at 16.5 ka, when our record shows an increase in pCO$_2$. This comparison eliminates mixing with an aged, CO$_2$-rich water mass as an explanation for our $\Delta$pCO$_{\text{sea-air}}$ record. For scenario (2), the increased $\Delta$pCO$_{\text{sea-air}}$ during HS1, HS4 and HS11 coincides with low $\delta^{13}\text{C}$ and high Cd/Ca values.

Figure 3 | Seawater carbonate chemistry and nutrient reconstructions in sediment core JM-FI-19PC from the Norwegian Sea. (a) $\delta^{11}\text{B}$ measured in $\text{N. pachyderma}$ with analytical uncertainty. (b) seawater-pH inferred from $\delta^{11}\text{B}$. (c) estimated seawater pCO$_2$ at the calcification depth and growth season of $\text{N. pachyderma}$. The envelope reflects the uncertainty boundaries based on the propagated error of the individual uncertainties in the parameters used to calculate pCO$_2$. (d) Atmospheric pCO$_2$ from Antarctic ice cores\textsuperscript{18}. (e) the difference between reconstructed shallow subsurface pCO$_2$ at our site and atmospheric pCO$_2$ ($\Delta$pCO$_{\text{calc-atm}}$). (f) $\Delta$pCO$_{\text{sea-air}}$ calculated as $\Delta$pCO$_{\text{calc-atm}}$ minus the modern pCO$_2$ gradient between the calcification depth of $\text{N. pachyderma}$ (40–200 m water depth) and surface ocean (0–30 m water depth). The green circle indicates present day average $\Delta$pCO$_{\text{sea-air}}$ in the Norwegian Sea\textsuperscript{21}. (g) Cd/Ca measured in $\text{N. pachyderma}$. (h) $\delta^{13}\text{C}$ measured in $\text{N. pachyderma}$.
so we interpret our observations as a decrease in nutrient utilization and primary production at the sea surface. A decrease in primary productivity would reduce nutrients and CO$_2$ utilization (that is, high Cd/Ca and high pCO$_2$), and $\delta^{13}$CDIC would not be elevated by preferential photosynthetic removal of $^{12}$C (that is, low foraminiferal $\delta^{13}$C). A decrease in the concentration of phytoplankton-induced sterols during HS4 and to some extent during HS1 (ref. 16) support the scenario of diminished primary productivity (Fig. 4). The increase in seawater pCO$_2$ and nutrients might also be caused by enhanced transfer of terrestrial carbon during Heinrich events and subsequent release via respiration. Hoff et al.\textsuperscript{16} recorded a relative decrease in $\delta^{13}$Corg during HS1 and HS4 (Fig. 4d), which may reflect a combination of both decreased primary productivity (that is, decrease in the relative proportion of marine organic matter) and increased proportion of terrigenous organic matter\textsuperscript{40}.

Figure 4 | Proxy records of sediment core JM-FI-19PC plotted with North Greenland Ice Core Project $\delta^{18}$O values. (a) $\Delta$pCO$_{\text{sea-air}}$. (b) Cd/Ca measured in N. pachyderma. (c) $\delta^{13}$C measured in N. pachyderma. (d) $\delta^{13}$C measured in organic matter ($\delta^{13}$C$_{\text{org}}$) (ref. 16). (e) concentration of brassicasterol\textsuperscript{16}. (f) concentration of dinosterol\textsuperscript{16}. (g) C$_{25}$ isoprenoid lipid (IP$_{25}$) (ref. 16). High concentration of IP$_{25}$ suggests presence of seasonal sea ice, whereas absence of IP$_{25}$ suggests either permanent sea-ice cover (when the concentration of sterols is low) or open ocean conditions (when the concentration of sterols is high) (see Hoff et al.\textsuperscript{16} for details). Note the break in the y-axes of plots e–g. (h) shallow subsurface (black) and bottom water (grey) temperature\textsuperscript{14,15}. Bottom water temperatures are based on Mg/Ca in the benthic foraminiferal species Melonis barleeanus (triangles) and Cassidulina neoteretis (squares). Shallow subsurface temperatures are based on Mg/Ca in N. pachyderma. (i) North Greenland Ice Core Project (NGRIP) ice core $\delta^{18}$O values\textsuperscript{28,67}. Red stars on the x-axis indicate tephra layers that are common to sediment core JM11-FI-19PC and Greenland ice cores (Supplementary Fig. 1).
Regarding scenario (3), studies from the modern East Greenland current region show that total dissolved inorganic carbon is rejected more efficiently than total alkalinity during sea-ice formation, causing the brines beneath the ice to be enriched in CO₂ compared with normal seawater. Furthermore, modern observations from the coastal Arctic zone show substantial seasonal variations in surface ocean pCO₂ because of formation and melting of sea ice; with positive ΔpCO₂sea-air during spring and negative ΔpCO₂sea-air during the summer attributed to complex biogeochemical processes. Because of the increased extent of sea ice during Heinrich stadials at our site (Fig. 4e–g), the effect of sea ice growth/decline may have exerted a longer-term and larger-scale influence on the surface ocean pCO₂ in the Arctic Ocean and Nordic Seas. For scenario (4), reconstructions from the Nordic Seas of stadial ocean circulation patterns indicate a subsurface incursion of warm Atlantic water into the Nordic Seas below a well-developed halocline. Thus, we cannot rule out that some of the pCO₂ increase has occurred in the source water somewhere at lower latitudes. In addition, the increase in the surface subsurface temperature (Fig. 4h) may have enhanced the degradation of organic matter. Last, for scenario (5), a slow-down or cessation of deep-water formation in the Nordic Sea (Fig. 3a) has probably promoted the pCO₂ increase in the shallow subsurface depth via slowing down of the carbon transfer from the sea surface to the ocean interior.

As illustrated above, several processes may have contributed to the pCO₂ increase during HS1, HS4 and HS11 including decreased primary productivity, increased input of terrestrial organic matter, high rate of sea ice formation and suppression of deep water formation. Conversely, during the interstadials studied herein (interstadial 8 and the BA interstadial) increased productivity, decreased input of terrestrial organic carbon, melting of sea ice (Fig. 4) and enhanced deep water formation, resulted in the consumption and/or dilution of the CO₂ content. Heinrich stadials 3 and 6 are at least partially resolved in this study, but do not show similar changes in seawater carbonate chemistry as HS1, HS4 and HS11. It is notable, however, that nutrients, export productivity and sea-ice proxies suggest similar changes for all resolved Heinrich stadials (Fig. 4). We have measured δ¹⁸O only for the early part of HS3 (for example, no measurements at the Cd/Ca peak), which shows a tendency towards decreasing values similar to other Heinrich stadal (Fig. 3a). During HS6, our δ¹³C record displays an increase (that is, decrease in aqeous CO₂) based on one data point (Fig. 3a). One additional difference that characterizes HS6 is the increase in δ¹³Corg, which suggests a relative decrease in the input of terrestrial organic matter during this event compared with other Heinrich stadials (Fig. 4). Nevertheless, higher resolution δ¹³C records are required to assess the carbonate chemistry evolution across HS3 and HS6.

How was the oceanic CO₂ released to the atmosphere during HS1, HS4 and HS11 in the Norwegian Sea? The presence of thick perennial or near-perennial sea ice cover during these times may have acted as a barrier for oceanic CO₂ outgassing. Earlier studies have suggested that a gradual build-up of a heat reservoir occurred during stadial periods because of subsurface inflow of warm Atlantic water to the Nordic Seas (Fig. 3a). Surfaceing of this warm water, evidenced by a large decrease in bottom water temperature (Fig. 4h), occurred during the rapid transition to interstadial periods. We therefore suggest that the CO₂ was released to the atmosphere, along with the advection of subsurface heat, at the terminations of the Heinrich stadials. The increases in surface pCO₂ in the Nordic Seas may thus have contributed to the rapid increase in atmospheric pCO₂ (~10 μatm) that occurred at the terminations of some Heinrich stadials.

In summary, we show significant changes in the marine carbon system in the Norwegian Sea associated with well-known regional climatic anomalies during the last 135 kyr. Our data indicate that the Norwegian Sea, and possibly the broader Nordic Seas, was an area for intense CO₂ uptake from the atmosphere during the LGM and the interstadials investigated in this study (that is, interstadials 8 and Bolling-Allerød), similar to modern conditions, whereas it may have acted as a CO₂ source during the ends of HS1, HS4 and HS11. Our shallow subsurface pCO₂ record presents the first indication that changes in primary productivity and ocean circulation in the Nordic Seas may have played a role in the late Pleistocene variations in atmospheric pCO₂.

Methods

Age model. The logging, sampling and dating of the sediment core (JM-FI-19PC) are described in Esat et al. The sediment core JM-FI-19PC is located adjacent to the Greenland Sea. Each sample was collected in a subsurface layer at 0.1 cm depth with a North Pacific Golden eagle core barrel. The samples were dried and weighed to determine the amount of acid required for dissolution. Immediately before loading, samples were dissolved in ultrapure 2N HCl and then centrifuged to separate out any insoluble mineral grains. One ml of boron-free seawater followed by an aliquot of sample solution (containing 1–1.5 ng B per aliquot) were loaded onto outgassed Rhenium filaments (zoned refined), then slowly evaporated at an ion current of 0.5A and finally mounted into the mass spectrometer. Depending on sample size, five to ten replicates were loaded per sample. Boron isotopes were measured as B₂O₃ ions on masses 43 and 42 using a Thermo Triton thermal ionization mass spectrometer at the Lamont-Doherty Earth Observatory (LDEO) of Columbia University. Each sample was heated up slowly to 1,000 ± 20 °C and then 320 boron isotope ratios were acquired over ~40 min. Boron isotope ratios are reported relative to the boron isotopic composition of SRM 951 boric acid standard, where δ¹¹B (‰) = [(43/42sample/43/42standard) − 1] × 1000. Analyses that fractionated >1‰ over the data acquisition time were discarded. The analysis of multiple replicates allows minimizing analytical uncertainty, which is reported as δ±2s.d./‰, where n is the number of sample aliquots analysed. The analytical uncertainty in δ¹¹B of each sample was then compared with the long-term reproducibility of an in-house vaterite standard (±0.34‰ for n = 3 to ±0.19‰ for n = 10) and the larger of the two uncertainties was adopted (Supplementary Table 1). Two samples were further cleaned using the oxidative-reductive cleaning procedure from Pena et al. and yielded indistinguishable δ¹¹B values (Supplementary Table 1).

Trace and minor element analytical procedures followed cleaning after Martin and Lea and included clay removal, reductive, oxidative, alkaline elution (with DIP solution) and weak acid leaching steps with slight modifications. Only pristine material for each sample was used (Supplementary Table 2). These modifications included rinsing samples with NH₄OH (ref. 49) instead of using 0.01 N NaOH (ref. 48) as a first step to remove the DTPA solution, followed by rinsing the samples three times with cold (room temperature) MilliQ water, 5-min immersion in hot (~80 °C) MilliQ water and then rinsing with cold MilliQ water. After dissolution, the samples were heated up to 2% HNO₃ and finally analysed by ICPQ Inductively-Coupled Plasma Mass Spectrometry at LDEO. Based on repeated measurements of in-house standard solutions, the long-term precision is < 1.4, 1.9 and 2.1% for Mg/Ca, B/Ca and Cd/Ca, respectively. Five samples were split after clay removal, reduction and oxidation steps; one half was cleaned by the full cleaning procedure, while the alkaline chelation step was omitted for the other half. This approach was applied to test the influence of the chelation step on Cd/Ca and B/Ca. The results with and without the alkaline chelation show an average difference of 0.0003 μmol mol⁻¹ and 5 μmol mol⁻¹ for Cd/Ca and B/Ca, respectively (Supplementary Table 2). The Mg/Ca values from the two cleaning methods are comparable, but two samples showed a significant decrease in Mg/Ca, Fe/Ca, Mn/Al and Ca/Al values when the alkaline chelation step was applied (Supplementary Table 2). This might be due to a more efficient removal of contaminants that are rich in Mg, but not in Cd or B. All our Mn/Al values from the full cleaning method are < 105 μmol mol⁻¹, indicating that our results are unlikely affected by diagenetic coatings. Only minor/trace element results from the full cleaning method were used in this study. All cleaning and loading steps for boron isotope and minor/trace element analyses used.
were done in boron-free filtered laminar flow benches and all used boron-free Milli-Q water.

Stable isotope analyses. Pristine specimens of the benthic foraminifera Melonis barleeanus (~30 specimens, size fraction 150–315 μm) and the planktic foraminifera N. pachyderma (~50 specimens, size fraction 150–250 μm) were picked for stable isotope analyses. The stable oxygen and carbon isotope analyses were performed using a Finnigan MAT 251 mass spectrometer with an automated carbonate preparation system by MATUR. Unknowns, external standards, and calibrated species were used for internal standards of Bremen. The standard error for the oxygen and carbon isotope analyses are ±0.07‰ and ±0.05‰, respectively. Values are reported relative to the Vienna Pee Dee Belemnite (VPDB), calibrated by using the National Bureau of Standards (NBS) 18, 19 and 20. The oxygen isotope data were previously presented14–15, while the carbon isotope results are presented here for the first time (Supplementary Data 1).

Salinity and temperature reconstructions. We used the calcification temperature and δ18OSW values from Ezat et al.15 based on parallel δ18O and Mg/Ca measurements in N. pachyderma (Supplementary Data 1). Previous studies suggested that carbonate chemistry may exert a significant secondary effect on Mg/Ca in N. pachyderma22. The possible influence of secondary factors on temperature reconstructions are discussed in detail in Ezat et al.15 In brief, the main effect of the secondary factors appears to be the elevated pH and carbonate ion concentration during the LGM; a correction for this effect may lower the temperatures by 0–2°C. However, the exact effect remains uncertain15. Here we used the temperature and δ18OSW reconstructions with no correction for non-temperature-related effects on Mg/Ca (see supporting information below). In the absence of a direct proxy for salinity, we estimated the salinity from our reconstructed δ18OSW. There is a quasi-linear regional relationship between salinity and δ18OSW in the modern ocean, as both parameters co-vary because of addition/removal of freshwater31. However, temporal changes in the δ18OSW composition of freshwater sources and/or their relative contribution to a specific region, as well as changes in ocean circulation complicates using a local modern δ18OSW-salinity relationship to infer past changes in salinity. We therefore estimate salinity using the δ18OSW-salinity mixing line from the Norwegian Sea32 for the Holocene and the Eemian, when the hydrological cycle and ocean circulation were likely similar to modern conditions for the deglacial and last glacial periods, we use the δ18OSW-salinity mixing line2 based on data from the Kangerdlugssuag Fjord, East Greenland, where the dominant source of freshwater is glacial meltwater from tidewater glaciers with δ18OSW values ranging from ~30 to ~20‰. These conditions are probably more representative of the sources of glacial meltwater during deglacial and glacial times.55. Our salinity estimates during the deglacial and last glacial periods would have been ~1.5‰ lower if we had used the modern δ18OSW-salinity mixing line from the Norwegian Sea. Although this salinity difference may appear large, it has little consequence for our pH and pCO2 reconstructions and our conclusions (see ‘Sensitivities tests’ below).

pH and pCO2 estimations. The boron isotopic composition of biogenic carbonate is sensitive to seawater pH (Ref. 17), because the relative abundance and isotopic composition of the two dominant dissolved boron species in seawater, boric acid [B(OH)3] and borate [B(OH)4−] changes with pH (Ref. 54), and borate is the species predominantly incorporated into marine carbonates. Culture experiments with planktic foraminifera provide empirical support for using their boron isotopic composition as a proxy for seawater pH but specific δ11B offsets are also observed, which are widely ascribed to ‘vital effects’57. Linear regressions of δ11B(CaCO3) versus δ11B(borate) relationships allow to infer δ11B(borate) from δ11B(CaCO3) (ref. 30) as follows:

\[ \delta^{11}B_{\text{borate}} = \left( \frac{\delta^{11}B_{\text{CaCO3}} - \delta^{11}B_{\text{CaCO3}}^{\text{modern}}}{\delta^{11}B_{\text{CaCO3}}^{\text{modern}}} \right) \times c + m \]

where ‘c’ is the intercept and ‘m’ is the slope of the regression. pH can then be estimated from foraminiferal δ11B-based δ11B(borate) using the following equation:

\[ pH = -\log_2\left( 1 + \frac{-1}{\delta^{11}B_{\text{borate}} - \delta^{11}B_{\text{CaCO3}}^{\text{modern}} - m\delta^{11}B_{\text{CaCO3}}^{\text{modern}} - 1} \right) \]

where pK is the equilibrium constant for the dissociation of boric acid for a given temperature and salinity55, δ11B(CaCO3) is the δ11B of seawater (moder δ11B(CaCO3) = 39.67‰; ref. 59), and δ11B(borate) is the fractionation factor for aqueous boron isotopes in the exchange between boric acid and borate. Klöckho et al.54 determined the boron isotope fractionation factor in seawater \( \delta^{11}B_{\text{borate}} \) = 1.0272 ± 0.0006. Because δ11B in the symbiont-barren N. pachyderma has so far only been calibrated from core top sediments, with large uncertainties and over a very limited natural pH range38; the pH sensitivity of this species is uncertain. However, we can use evidence from other calibrated symbiont-barren planktonic foraminifera species to further constrain the pH sensitivity of this species. Martínez-Botí et al.60 suggested a pH sensitivity for the symbiont-barren planktonic foraminifera G. bulloides similar to values predicted from aqueous boron isotope fractionation (that is, slope m in eq. (1) = 1.075). We therefore used a slope value of 1.075 in equation (1) to calculate the calculated pH for N. pachyderma by calibrating our core top foraminiferal δ11B to a calculated pre-industrial pH (that is, δ11B(borate)). Pre-industrial pH was estimated from modern hydrographic carbonate data (total Dissolved Inorganic Carbon ‘DIC’, total alkalinity, phosphate, silicate, temperature, salinity; ref. 21) from the southern Norwegian Sea (Fig. 2a, Supplementary Fig. 4), and subtracting 50 μmol kg−1 from DIC (ref. 61) to correct for the anthropogenic CO2 effect. We used the hydrographic data collected during June 2002 and from the 22nd of September to 2nd of October 2003 (that is, within the assumed calcification season of N. pachyderma; refs 19,20) and our assumed calculated depth (that is, 40–120 m). This approach allows us to determine δ11B(borate) from δ11B(CaCO3) (equation 1), which can then be used to calculate pH based on equation 2.

Although the slope determined for G. bulloides55 is similar to the coretop calibration of N. pachyderma55; neither calibration encompasses a wide pH range, and the uncertainty in the slopes is therefore large. In culture experiments with (symbiont-bearing) planktonic foraminifera cover a much wider pH-range but display a lesser pH sensitivity (slope in equation (1) = ~ 0.7) than predicted from aqueous boron isotope fractionation55. However, this difference in slope has little consequence for our pH and pCO2 reconstructions.

If two of the six carbonate parameters (total Dissolved Inorganic Carbon (DIC), total alkalinity, carbonate ion concentration, bicarbonate ion concentration, pH and CO2), are known in addition to temperature, pressure and salinity, the other parameters can be calculated22. We used the modern local salinity-total alkalinity relationship (Alkalinity = 69.127 × Salinity − 116.42, R2 = 0.76, ref. 21) to estimate total alkalinity. Because weathering processes are slow and alkalinity is relatively high in the ocean, alkalinity can be considered a quasi-conservative tracer on these time scales, and we do not consider potential past changes in the salinity-total alkalinity relationship. Nonetheless, if we use the modern alkalinity-salinity relationship from the polar region as a possible analogue for our area during the last glacial, this would decrease the error in total alkalinity (because of the uncertainty in salinity) by up to 65 μmol kg−1 (Supplementary Fig. 5). Aquatic pCO2 is then calculated using CO2sys.xls (ref. 63), with the equilibrium constants K1 and K2 from Millero et al.64, KB is from Dickson59 and the seawater boron concentration from Lee et al.55

Sensitivity tests of pCO2 reconstructions. Supplementary Fig. 6 shows that pH and pCO2 reconstructions based on very different temperature, salinity and total alkalinity scenarios are very similar and do not significantly affect the large pCO2 differences during HS1, HS4 and HS11. A sensitivity test using slopes of m = 1.074 (ref. 60) and m = 0.7 (refs 30,55,56) shows little difference between the two estimates (see section ‘Sensitivities tests’ below).

The uncertainty in the calcification depth of N. pachyderma has significant effect on the amplitude of our deep core pCO2 variations (Supplementary Fig. 7).

In addition, to assess the uncertainty in our pH and pCO2 estimations because of the uncertainty in the δ18O in the B(CaCO3) versus δ18O sensitivity in N. pachyderma, we recalculated the δ11B(borate) using slope value of m = 0.7 instead of m = 1.074 in equation (1) as suggested for some symbiont-bearing planktic foraminifera species39,55,56, and re-adjusted the intercept ‘c’ accordingly (≈ −4.2‰). This test shows that the uncertainty in species-specific pH-sensitivity has no effect on our pH and pCO2 reconstructions for the Heinrich stadial events, while the main difference is in the increase in the glacial/interglacial pCO2 by ~30 μatm, when a slope value of m = 0.7 is used (Supplementary Fig. 8). This brings δ18OCO2at-lim for the LGM to values of ~30 μatm (and δ18Osea-lim = ~70 μatm), strengthening our conclusion about enhanced oceanic CO2 uptake in our area during the LGM. Finally, because our δ18OCO2at-lim record can be biased because of errors in the age model especially for the Heinrich stadials (times with increasing atmospheric pCO2), we performed a sensitivity study, in which 500 and 1,000 years were both added and subtracted from our age model (Supplementary Fig. 9). This arbitrary sensitivity study shows that such errors in the age model do not significantly affect the large increases in δ18OCO2at-lim during HS1, HS4 and HS11 (Supplementary Fig. 9).
For the assessment of uncertainty in our temperature estimates, one should ideally consider uncertainties associated with empirical calibrations and other non-temperature factors that affect Mg/Ca in *N. pachyderma*. Because the sensitivity of Mg/Ca in *N. pachyderma* to factors other than temperature (for example, carbonate chemistry) is not known, we only include an error of ± 0.7 °C, based on the calibration and analytical uncertainties of Mg/Ca (see ref. 15). This uncertainty translates to ± 7 μatm average CO₂ on average. Ezat et al. discussed that the correction for elevated carbonate ion concentration during the LGM on Mg/Ca may lower the LGM temperature by 0–2 °C; however, the exact effect is very uncertain. A decrease in LGM temperatures would decrease our reconstructed pCO₂ values (∼10 μatm decrease per 1 °C decrease), strengthening our conclusion that our study region was an intense area for CO₂ uptake at that time.

**Data availability.** The data generated and analysed during the current study are available along the online version of this article at the publisher’s web-site.

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**Author contributions**

M.M.E. sampled the core, performed the boron isotope analyses, cleaned the foraminiferal samples for the minor/trace analyses and wrote the first draft of the paper. T.L.R. conceived the study and contributed substantially to all aspects. B.H. supervised the boron isotope analyses, cleaning of foraminiferal samples and all carbonate chemistry calculations. All authors interpreted the results and contributed to the final manuscript.

**Additional information**

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

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