**Boron isotope evidence for oceanic CO₂ leakage during the last
deglaciation**

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27 Atmospheric CO₂ fluctuations over glacial-interglacial cycles remain a major
28 challenge to our understanding of the carbon cycle and the climate system.
29 Leading hypotheses put forward to explain glacial-interglacial atmospheric CO₂
30 variations invoke changes in deep ocean carbon storage^{1,2}, likely modulated by
31 processes in the Southern Ocean where much of the deep ocean is ventilated³. A
32 central aspect of these Southern Ocean-centric models is that, during
33 deglaciations, an isolated glacial deep ocean carbon reservoir is re-connected
34 with the atmosphere, driving the atmospheric CO₂ rise observed in ice core
35 records⁴⁻⁶. However, direct documentation of changes in surface ocean carbon
36 content and the associated transfer of carbon to the atmosphere during
37 deglaciations has been hindered by the lack of proxy reconstructions that
38 unambiguously reflect the oceanic carbonate system. ¹⁴C tracks changes in ocean
39 ventilation⁶, but not in its carbon content, whereas proxies that record increased
40 deglacial upwelling^{4,7} do not constrain the proportion of upwelled carbon that is
41 degassed versus that taken up by the biological pump. Here we apply the boron
42 isotope-pH proxy in planktic foraminifera to two sediment cores from the
43 Subantarctic Atlantic and the Eastern Equatorial Pacific as a more direct tracer
44 of oceanic CO₂ outgassing. We show that surface waters at both locations, which
45 partly derive from deep water upwelled in the Southern Ocean^{8,9}, became a
46 significant source of carbon to the atmosphere during the last deglaciation, when
47 atmospheric CO₂ was increasing. This oceanic CO₂ outgassing supports the view
48 that the ventilation of a deep ocean carbon reservoir in the Southern Ocean
49 played a key role in the deglacial CO₂ rise, although our results allow for the
50 possibility that processes operating in other regions may also have been
51 important for the glacial-interglacial ocean-atmosphere exchange of carbon.

The modern Southern Ocean (SO) is a region of vigorous upwelling of carbon- and nutrient-rich waters³. Much of the upwelled CO₂ is outgassed to the atmosphere, due to incomplete nutrient utilisation in the SO surface³. These waters are then re-subducted as intermediate waters and feed the thermocline of the low-latitude oceans, such as the Eastern Equatorial Pacific (EEP)¹⁰, which is, currently, one of the main oceanic sources of CO₂ to the atmosphere¹¹ (Figure 1). Many of the mechanisms proposed to reduce atmospheric CO₂ during glacial periods focus on a reduction of SO CO₂ leakage, via increased ocean stratification¹² and/or a more efficient biological pump (likely boosted by iron fertilisation)¹³. During deglaciation, this situation is reversed, and previously isolated deep-ocean carbon is thought to be upwelled and re-exposed to the atmosphere⁴.

Deglacial upwelling of aged, nutrient-rich waters in the SO, and their subsequent advection to the EEP, has been suggested on the basis of several proxies^{4,6,7}, including biogenic opal fluxes, $\delta^{13}\text{C}$, and $\Delta^{14}\text{C}$. Although these reconstructions provide valuable insights into ocean nutrient dynamics, circulation, and ventilation history, none of them directly tracks ocean-atmosphere CO₂ exchange. For instance, if biological productivity efficiently utilised upwelled nutrients and carbon, as possibly indicated by the deglacial increase in SO and EEP opal fluxes^{4,14}, then CO₂ leakage to the atmosphere may have been dampened or even negated completely. Similarly, the appearance of low $\delta^{13}\text{C}$ signatures in the upper ocean at a wide number of locations globally during the deglaciation^{7,15}, usually taken as evidence for the re-ventilation of nutrient-enriched (low- $\delta^{13}\text{C}$) waters, could be modulated by changing air-sea CO₂ fractionation¹⁵. Finally, perhaps the most compelling evidence to date for the importance of the re-communication of a deep ocean carbon reservoir with the

atmosphere via the SO comes from the collapse in $\Delta^{14}\text{C}$ gradients in deep waters around Antarctica due to the deglacial break-down of stratification in that region⁶. However, whilst this correlates well with the atmospheric $\Delta^{14}\text{C}$ record and the first rise in atmospheric partial pressure of CO_2 ($p\text{CO}_2^{\text{atm}}$) during Heinrich Stadial 1, there is little response during the second rise of $p\text{CO}_2^{\text{atm}}$ centred on the Younger Dryas.

There is therefore an urgent requirement for direct evidence of deglacial CO_2 variations in the surface waters of key areas of the global ocean, such as the SO and EEP, thereby testing the hypothesis that oceanic CO_2 outgassing was central to the glacial-interglacial $p\text{CO}_2^{\text{atm}}$ rise^{4,7}. We addressed this issue by analysing the boron isotopic composition ($\delta^{11}\text{B}$) of planktic foraminifera, a proxy^{16,17} for oceanic pH that provides a direct link to seawater CO_2 content. [Figure 2](#) compares records of atmospheric CO_2 concentration⁵ with new planktic foraminiferal $\delta^{11}\text{B}$ and Mg/Ca-derived temperature for the Subantarctic Atlantic (site PS2498-1; 44.15°S, 14.23°W, 3,783 m water depth) and the EEP (site ODP1238; 1.87°S, 82.78°W, 2,203 m water depth) ([Figure 1](#)). Surface waters at PS2498-1 are currently influenced by water upwelled in the Antarctic Zone and advected northward via Ekman pumping⁸, while ODP1238 is mostly influenced by the Equatorial Undercurrent¹⁸, a subsurface current originating in the Western Equatorial Pacific and fed by water masses of Southern Ocean (~70%) and North Pacific (~30%) origin¹⁹. Previous literature has suggested an effective connection between the Subantarctic and the EEP via intermediate waters¹⁸, through a process often referred to as “oceanic tunnelling”⁹ (see [Methods](#)).

The $\delta^{11}\text{B}$ record for the surface-dwelling foraminifer *Globigerina bulloides* in the Subantarctic core PS2498-1 displays an early deglacial to Holocene change of ~1.3‰

(~0.13 pH units; [Figure 2a,b](#)). Unfortunately, the very low abundance of *G. bulloides* prior to ~16 ka precluded $\delta^{11}\text{B}$ analyses for the Last Glacial Maximum (LGM), which limited our evaluation of the full glacial-interglacial $\delta^{11}\text{B}$ (and pH) shift at this site. PS2498-1 $\delta^{11}\text{B}$ record does not exhibit a gradual change through the deglaciation into the Holocene, but features two distinct decreases (lower pH). At the EEP (ODP1238), there is a brief negative excursion in the $\delta^{11}\text{B}$ of the surface-dweller *Globigerinoides sacculifer* at 19 ka, and the ensuing deglacial change is larger (~2 ‰ $\approx$ 0.2 pH units) and more gradual than that recorded by *G. bulloides* at PS2498-1 ([Figure 2f,g](#); [Extended Data Figure 1](#)).

To highlight the main patterns of variability in the $\delta^{11}\text{B}$ -derived time series and to probabilistically account for all the uncertainties associated with our reconstructions, we used a Monte Carlo approach that employs a non-parametric regression (LOESS function; [Figure 2b,c,g,h](#); see [Methods](#)). A comparison of the PS2498-1 and ODP1238 pH records against the pH expected if surface waters remained in equilibrium with the atmosphere ([green lines in Figure 2b,g](#)), reveals “excess” surface ocean acidification in both these areas during deglaciation and early Holocene. To gain further insight into deglacial ocean-atmosphere CO_2 exchange, we use the $\delta^{11}\text{B}$ -pH data, along with estimates of temperature, salinity, and alkalinity, to calculate the partial pressure of CO_2 in seawater²⁰ ($p\text{CO}_2^{\text{sw}}$; see [Methods](#)). Note that the temperature, salinity, and alkalinity exert only a minor control on $p\text{CO}_2^{\text{sw}}$ (at most $\pm 13 \mu\text{atm}$, $\pm 15 \mu\text{atm}$, and $\pm 12 \mu\text{atm}$, respectively), which is driven mainly by the $\delta^{11}\text{B}$ -derived pH, given the strong correlation of pH and $[\text{CO}_2]$ within the ocean carbonate system²⁰. The $p\text{CO}_2^{\text{sw}}$ profiles are compared to $p\text{CO}_2^{\text{atm}}$ from ice core records to yield $\Delta p\text{CO}_2$ ($\Delta p\text{CO}_2 = p\text{CO}_2^{\text{sw}} - p\text{CO}_2^{\text{atm}}$) and, notably, our late Holocene

$\Delta p\text{CO}_2$ estimates agree within uncertainties with modern water column data from nearby locations¹¹, supporting the accuracy of our $\delta^{11}\text{B}$ -pH calibrations (Figure 2c-h).

Our EEP $\Delta p\text{CO}_2$ record reveals that this region became a significant CO_2 source to the atmosphere during deglaciation and early Holocene, reaching at ~13 ka a peak of $+90 \pm 16 \mu\text{atm}$ (2σ), which exceeds by ~45 μatm average modern values at this location¹¹ (Figure 2h). Comparison with earlier studies in the Western and Central Pacific²¹⁻²³ that reported deglacial $\Delta p\text{CO}_2$ values of +100 to $\geq +185 \mu\text{atm}$ shows the widespread nature of the CO_2 outgassing in the equatorial Pacific (Extended Data Figure 2). The $\Delta p\text{CO}_2$ data from the Subantarctic Atlantic Ocean also indicate that this region acted as a source of CO_2 to the atmosphere from ~16 to ~7.5 ka, but in the form of two prominent multi-millennial events, with a maximum of $+50 \pm 18 \mu\text{atm}$ (i.e., ~65 μatm higher than present-day average values¹¹) at ~15 ka (Figure 2c).

The occurrence of upper ocean acidification in the Subantarctic Atlantic and EEP during the deglaciation coincided, within uncertainties, with excursions toward higher opal fluxes at nearby sites^{4,14} (Figure 3a,b,f,g). This observation provides compelling evidence for the hypothesized link between resumption of Antarctic upwelling⁴ and attendant Ekman transport^{8,10} of deep waters enriched in nutrients and $[\text{CO}_2]$, and oceanic $\Delta p\text{CO}_2$ rise in the wider SO. It further suggests that advection to the EEP, via oceanic tunnelling, of these CO_2 -rich waters may (at least partly) explain the deglacial $\Delta p\text{CO}_2$ maximum documented in ODP1238. This interpretation is corroborated by the broad synchronicity of the acidification phases with excursions toward depleted surface ocean $\delta^{13}\text{C}$ at our core locations (Figure 3c,h), with the deglacial rise in the

concentration of atmospheric CO₂ (Figure 3e,l), and with the negative shift⁵ of its $\delta^{13}\text{C}$ (Figure 3e,k).

However, the differences in the patterns of pH, $\Delta p\text{CO}_2$, $\delta^{13}\text{C}$, and opal at the two locations (Figures 2, 3; Extended Data Figure 1), suggest that the EEP record does not merely represent a downstream expression of the deglacial CO₂ outgassing in the SO, and that additional processes and/or CO₂ sources need to be considered to fully explain its structure. SO-sourced intermediate waters incorporate remineralized carbon during transit to the EEP, which may modify their geochemical characteristics²⁴. Additionally, as source waters of the EUC also include North Pacific-origin waters (~30%)¹⁹, these may provide a potential supplementary source²⁵ of CO₂. During the early Holocene, both our $\Delta p\text{CO}_2$ records also indicate continued oceanic CO₂ outgassing, yet $p\text{CO}_2^{\text{atm}}$ shows little change. This suggests that ocean outgassing at this time was balanced by CO₂ uptake, possibly due to forest re-growth and peat buildup as the continental ice sheets retreated from the Northern continents^{2,26}, in line with the near contemporaneous rise⁵ in atmospheric $\delta^{13}\text{C}$ (Figure 3e,k).

Although millennial changes in the mean position of SO frontal systems²⁷, and in the upwelling strength in the EEP due to shifts of the Intertropical Convergence Zone²⁸, have the potential to change $\Delta p\text{CO}_2$ at our sites, such changes seem unlikely to exert a dominant influence on our records. If the high $\Delta p\text{CO}_2$ spikes we document were driven by a northward shift of the regional oceanic fronts (PS2498-1) or increased upwelling (ODP1238), they should be accompanied by surface cooling, whereas both sites feature a warming trend during these intervals (Figure 2 and Methods). It is also

unlikely that the signals are driven by migration in foraminiferal depth habitat. In the Subantarctic, pH vertical gradients are small, while in the EEP migration to deeper and more-acidic waters is inconsistent with the warming signal in Mg/Ca (Figure 2) and with the structural similarity of *G. sacculifer* $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records with those for the strict surface-dweller *Globigerinoides ruber* (see Methods; Extended Data Figure 3).

Local changes in the efficiency of the biological pump, stimulated by Fe-fertilisation, also have the potential³ to influence surface water $p\text{CO}_2$. The evidence that the EEP was a weaker CO_2 source (or even a sink) during the LGM may be ascribed to a dust-derived relaxation of Fe-limitation and attendant strengthening of the biological pump^{29,30}. It is also possible that the gradual decrease in the Fe supply to the EEP and Subantarctic regions during the deglaciation^{13,29} could explain part of the high deglacial $\Delta p\text{CO}_2$ at these sites. However, the marked differences between the structure of the dust flux records and our $\Delta p\text{CO}_2$ reconstructions argue against this hypothesis (Extended Data Figure 4).

It therefore seems most plausible that the $\Delta p\text{CO}_2$ pulses that we report here using planktic foraminifera $\delta^{11}\text{B}$ reflect oceanic CO_2 outgassing during the last deglaciation. A common origin for the $\Delta p\text{CO}_2$ anomalies reported here likely involved the renewed upwelling of aged⁶ deep water enriched in nutrients⁴ and carbon in the Southern Ocean, which subsequently “leaked” to the atmosphere contributing to the deglacial $p\text{CO}_2^{\text{atm}}$ rise and the atmospheric $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ decreases^{5,31}. However, our analysis also indicates that other carbon sources, possibly located in the wider Pacific Ocean²⁵,

may need to be invoked to fully explain glacial-interglacial ocean-atmosphere CO₂ exchange.

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Figure legends

Figure 1. Location of cores PS2498-1 and ODP1238. Site locations are overlain on a map of mean annual $\Delta p\text{CO}_2$ (ref. 11).

Figure 2. $\delta^{11}\text{B}$, pH, and $\Delta p\text{CO}_2$ records from the Subantarctic Atlantic (left) and Eastern Equatorial Pacific (right) during the last deglaciation. (a) *Globigerina bulloides* $\delta^{11}\text{B}$ with analytical uncertainties (1σ , dark grey envelope; 2σ , light grey envelope); (b) $\delta^{11}\text{B}$ -based pH (blue) reconstruction for PS-2498-1 and calculated seawater pH in equilibrium with atmospheric $p\text{CO}_2$ ($p\text{CO}_2^{\text{atm}}$) (green curve) at the

331 same site; **(c)** $\delta^{11}\text{B}$ -derived $\Delta p\text{CO}_2$ ($p\text{CO}_2^{\text{sw}} - p\text{CO}_2^{\text{atm}}$). Black circle denotes present-
 332 day annual average $\Delta p\text{CO}_2$ near PS2498-1 with 2σ uncertainties¹¹; **(d)** *G. bulloides*
 333 Mg/Ca-based sea surface temperature (SST); **(e)** and **(j)** $p\text{CO}_2^{\text{atm}}$ from Antarctic ice
 334 cores⁵; **(f)** *Globigerinoides sacculifer* $\delta^{11}\text{B}$ with analytical uncertainties (1σ , dark grey
 335 shading; 2σ , light grey shading); **(g)** $\delta^{11}\text{B}$ -based pH (red) for ODP1238 and calculated
 336 seawater pH in equilibrium with $p\text{CO}_2^{\text{atm}}$ (ref. 5) (green curve). **(h)** $\delta^{11}\text{B}$ -based $\Delta p\text{CO}_2$.
 337 Black circle denotes present-day mean annual $\Delta p\text{CO}_2$ near ODP1238 with 2σ
 338 uncertainties¹¹. **(i)** *G. sacculifer* Mg/Ca-based SST. The Late Holocene data in **(f)**, **(g)**,
 339 and **(h)** have been averaged (individual measurements are shown as empty red circles)
 340 (see [Methods](#)). Envelopes in **(b)**, **(c)**, **(g)**, and **(h)** are 68% and 95% uncertainty
 341 bounds (light blue/red shading and dotted lines, respectively) based on a LOESS
 342 regression of the $\delta^{11}\text{B}$ -derived records using a Monte Carlo approach; thick line
 343 denotes the maximum probability fit to the data. YD: Younger Dryas; BA: Bølling-
 344 Allerød; ACR: Antarctic Cold Reversal; HS1: Heinrich Stadial 1; LGM: Last Glacial
 345 Maximum. Filled triangles at the bottom indicate calibrated ^{14}C ages (see [Methods](#)).

Figure 3. $\Delta p\text{CO}_2$ and $\delta^{13}\text{C}$ records from the Subantarctic Atlantic (left) and the Eastern Equatorial Pacific (right) during the last deglaciation compared to opal fluxes, $p\text{CO}_2^{\text{atm}}$, and $\delta^{13}\text{C}_{\text{atmosphere}}$. (a) surface ocean $\Delta p\text{CO}_2$ reconstruction for PS2498-1; (b) opal fluxes for TN057-13-4PC (Antarctic Zone)⁴; (c) PS2498-1 *Globigerina bulloides* $\delta^{13}\text{C}$ (blue dots) with a LOESS non-parametric regression of the data (span = 0.4) (solid line; see Methods); (d) and (j) atmospheric CO_2 concentrations from Antarctic ice cores⁵; (e) and (k) atmospheric $\delta^{13}\text{C}$ record from Antarctic ice cores⁵; (f) surface ocean $\Delta p\text{CO}_2$ reconstruction in ODP1238; (g) opal fluxes for V19-30 (EEP)¹⁴; (h) and (i) ODP1238 *Globigerinoides sacculifer* and *Neogloboquadrina dutertrei* $\delta^{13}\text{C}$ (pink and electric blue dots, respectively) with a LOESS non-parametric regression of the data (solid lines; span = 0.7 and 0.33, respectively). YD: Younger Dryas; BA: Bølling-Allerød; ACR: Antarctic Cold Reversal; HS1: Heinrich Stadial 1; LGM: Last Glacial Maximum.

METHODS

Material and methods. Core PS2498-1 was retrieved by the R/V *Polarstern* from the eastern flank of the mid-Atlantic Ridge (44.15°S, 14.23°W, 3783 m water depth), in the Subantarctic Atlantic Ocean^{32,33} (Figure 1). Between 400-650 individuals of *Globigerina bulloides* were picked from the 300-355 µm size fraction (10 µg/shell with B/Ca 35 µmol/mol) from this site. Ocean Drilling Program (ODP) Site 1238 (1.87°S, 82.78°W, 2203 m water depth) was drilled during Leg 202 by the R/V *Joides Resolution* from the southern flank of Carnegie Ridge, offshore Ecuador in the Eastern Equatorial Pacific³⁴ (EEP) (Figure 1). From ODP1238 we picked 15-90 individuals of *Globigerinoides sacculifer* of mixed morphotypes (see below) from the 425-500 µm size fraction (40 µg/shell with B/Ca ~ 100 µmol/mol) for $\delta^{11}\text{B}$ and trace elements, and 10-20 individuals from the 355-425 µm size fraction for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. 20 individuals of *Globigerinoides ruber* sensu stricto from the 250-355 µm size fraction were picked for $\delta^{18}\text{O}/\delta^{13}\text{C}$, and 30 individuals of *Neogloboquadrina dutertrei* from the 355-500 µm size fraction for trace elements and $\delta^{18}\text{O}/\delta^{13}\text{C}$. Foraminiferal samples were crushed between cleaned glass microscope slides prior to cleaning and analyses.

Age models. For core PS2498-1, we converted existing³² accelerator mass spectrometry (AMS) ^{14}C data to calendar ages using the Calib 7.0 program^{35,36} with the Marine13 dataset³¹. Local reservoir corrections of $\Delta R=300$ yr (ref. 37) and $\Delta R=900$ yr were used for the last 16 kyr and between 16 and 26 ka, respectively (Extended Data Figure 5a), following recent studies^{6,38} (cf. ref. 39). Different ΔR may affect the chronology by up to 0.9 kyr for the LGM and early deglacial sections,

although these potential changes in age model do not impact our conclusions unduly
(Extended Data Figure 5b).

The age model for ODP1238 is based on 10 new AMS ^{14}C dates (Extended Data Figure 6a). Monospecific samples of *Neogloboquadrina dutertrei* (~300 individuals, ~12 mg) were analysed at the Lawrence Livermore National Laboratory Centre for Accelerator Mass Spectrometry. ^{14}C ages were calibrated using the Calib 7.0 program^{35,36} with the Marine13 dataset³¹. In line with previous studies^{40,41} in the EEP, an average ΔR of 72 ± 35 yr was applied to all ^{14}C data (<http://calib.qub.ac.uk/marine>). To derive an age model for ODP1238, the relationship between sediment depth and calibrated ages was fit with a third order polynomial regression (Extended Data Figure 6b). A potential complication in constructing ^{14}C -based age models in the EEP is the possible presence of old waters during some intervals of the last deglaciation^{42,43}. The gradual increase of age with depth at ODP1238, with no sign of age reversals (cf. refs 42,43) however suggests that our age model is unlikely influenced by extremely old ^{14}C , or that the influence, if present, was small. Moreover, there is good agreement between the benthic and planktic $\delta^{18}\text{O}$ in ODP1238 and that of other EEP cores^{7,40,41,44} (Extended Data Figure 7). While this does not represent a definitive validation, as all these sites could potentially be influenced by the same aged water mass, it documents the coherence of our age model with the published literature for this region.

Foraminiferal signal carriers. *Globigerina bulloides* is ubiquitous in the South Atlantic⁴⁵ and its abundance appears generally associated with the phytoplankton productivity maxima during austral summer⁴⁶. In the proximity of PS2498-1, *G.*

bulloides dwells in the upper ~60 m of the water column, with a distinct maximum between 0 and 25 m (ref. 46).

A number of proxy systems based on *Globigerinoides sacculifer* in the EEP have been demonstrated to reflect mean annual environmental conditions⁴⁷⁻⁴⁹. In the Panama Basin the depth distribution of *G. sacculifer* is morphotype-dependant⁵⁰: *G. sacculifer* without sacc-like final chamber dwells predominantly in the surface mixed layer, while *G. sacculifer* with sacc-like final chamber dwells in the thermocline⁵⁰ (25-37 m). Another study⁵¹ showed that close to the coastal upwelling region of the EEP (where ODP1238 is located) both morphotypes of *G. sacculifer* have similar depth ranges (0-30 m), which also overlap with that of the surface-dweller *G. ruber* (0-25 m). *G. sacculifer* is also known to add gametogenic calcite at thermocline depths, which can account for up to 30% of the final test weight⁵². Although these and other⁵³ studies may imply an influence of a thermocline signal on the *G. sacculifer* mixed morphotype-based reconstructions, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data from ODP1238 (Extended Data Figure 3) indicate a similar depth habitat for *G. sacculifer* and the surface-dweller *G. ruber*^{50,51} (which does not add gametogenic calcite⁵⁴) throughout the last 25 kyr.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses. Prior to stable isotope determination, foraminiferal samples were rinsed with methanol, ultrasonicated, and then oven-dried at 40°C. Analyses for *G. bulloides* (PS2498-1, complementing ref. 55), *G. sacculifer* (ODP1238), and *N. dutertrei* (ODP1238) were performed at the Universitat Autònoma de Barcelona, using a Thermofinnigan MAT253 mass spectrometer coupled to a Kiel IV device for CO₂ sample gas preparation. External reproducibility (1 σ) of carbonate standards was

436 better than $\pm 0.05\text{‰}$ ($\delta^{18}\text{O}$) and $\pm 0.03\text{‰}$ ($\delta^{13}\text{C}$). ODP1238 *G. ruber* $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data
437 were measured at MARUM-Center for Marine Environmental Sciences, University of
438 Bremen, using a Thermo Finnigan MAT 252 mass spectrometer coupled to a Bremen-
439 type automatic carbonate preparation device. Precision (1σ) was better than 0.07‰
440 ($\delta^{18}\text{O}$) and 0.05‰ ($\delta^{13}\text{C}$), based on replicates of an internal limestone standard.

441
442 **Trace element and $\delta^{11}\text{B}$ analyses.** Foraminiferal samples were oxidatively
443 cleaned⁵⁶⁻⁵⁸, dissolved in ~ 0.15 M Teflon-distilled HNO_3 , and centrifuged. An aliquot
444 (~ 20 μl ; $\sim 7\%$ of the total sample) was taken for trace element analyses, which were
445 performed on a Thermo Scientific Element 2 single collector ICPMS at the University
446 of Southampton (ref. 17). Mg/Ca ratios were converted to calcification temperatures
447 using the calibration of ref. 59 for *G. sacculifer* (ODP1238) and ref. 60 for *G.*
448 *bulloides* (PS2498-1). Analytical reproducibility for Mg/Ca was $\pm 2.7\%$ (2σ), and the
449 efficiency of the foraminiferal cleaning^{17,58} was verified using Al/Ca ratios (all
450 samples < 100 $\mu\text{mol/mol}$, and typically < 60 $\mu\text{mol/mol}$). *N. dutertrei* (355-500 μm)
451 Mg/Ca record was produced at the University of Bristol and at the University of
452 Southampton using the same standard set to ensure comparability. Samples were
453 reductively cleaned^{57,61} and measured on a Thermo Scientific Element 2 single
454 collector ICPMS following ref. 17. Calcification temperatures were derived from ref.
455 59.

456
457 Boron was separated from the remaining sample using Amberlite IRA-743 boron-
458 specific anion exchange resin¹⁷. $\delta^{11}\text{B}$ was measured on a Thermo Scientific Neptune
459 multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) at the
460 University of Southampton (see ref. 17,58,62). External reproducibility of $\delta^{11}\text{B}$

analyses is calculated following the approach of Rae *et al.*⁵⁸, and is described by the relationship:

$$2\sigma = 1.87 \cdot \exp^{-20.6[^{11}B]} + 0.22 \cdot \exp^{-0.43[^{11}B]} \quad (1)$$

where [¹¹B] is the intensity of ¹¹B signal in volts (see ref. 62 for further details).

Due to the low abundance of *G. sacculifer* during the Holocene in ODP1238, the associated 2σ uncertainties (calculated using Eq. 1) were relatively large (0.56-0.84‰). These four samples are averaged with a 2σ uncertainty calculated as the mean of the individual uncertainties (from Eq. 1) divided by the square root of n-1 (n=4).

The boron isotope-pH proxy. The boron isotope-pH proxy has been extensively described in previous studies^{16,17,58}. Briefly, boron in seawater exists mainly as two different species, boric acid (B(OH)₃) and borate ion (B(OH)₄⁻), and their relative abundance is pH dependent. There are two isotopes of boron, ¹¹B (~80%) and ¹⁰B (~20%), with a ratio normally expressed in delta notation as:

$$\delta^{11}B(\text{‰}) = \left[\left(\frac{^{11}B/^{10}B_{\text{sample}}}{^{11}B/^{10}B_{\text{NIST951}}} \right) - 1 \right] \times 1000 \quad (2)$$

where ¹¹B/¹⁰B_{NIST951} is the isotopic ratio of NIST SRM 951 boric acid standard⁶³ (¹¹B/¹⁰B=4.04367).

There is a pronounced isotopic fractionation between the two boron species, with boric acid being enriched⁶⁴ in ^{11}B by 27.2‰. As the concentration of each species is pH dependent, their isotopic composition also has to change with pH in order to maintain a constant seawater $\delta^{11}\text{B}$. Calibration studies^{58,65,66} have shown that the borate species is predominantly incorporated into foraminiferal CaCO_3 , and therefore ocean pH can be calculated from the $\delta^{11}\text{B}$ of borate as follows:

$$pH = pK_B^* - \log \left(- \frac{\delta^{11}B_{\text{sw}} - \delta^{11}B_{\text{borate}}}{\delta^{11}B_{\text{sw}} - \left({}^{11-10}K_B \cdot \delta^{11}B_{\text{borate}} \right) - 1000 \cdot \left({}^{11-10}K_B - 1 \right)} \right) \quad (3)$$

where pK_B^* is the dissociation constant for boric acid at in situ temperature, salinity and pressure⁶⁷, $\delta^{11}B_{\text{sw}}$ is the isotopic composition of seawater⁶⁸ (39.61‰), $\delta^{11}B_{\text{borate}}$ is the isotopic composition of borate ion, and ${}^{11-10}K_B$ is the isotopic fractionation between the two aqueous species of boron in seawater⁶⁴ (1.0272 ± 0.0006).

Calibration of $\delta^{11}\text{B}$ -pH proxy in *G. bulloides*. We combined core-top and sediment trap data to calibrate the $\delta^{11}\text{B}$ -pH proxy in *G. bulloides* over a broad range ($\sim 2\%$) of $\delta^{11}B_{\text{borate}}$ (ref. 69). Core-top samples were taken from core archives at the University of Tübingen (Germany) and NIWA (New Zealand) ([Extended Data Figure 8](#)). ^{14}C -dating⁷⁰ (samples from NIWA) and the presence of Rose Bengal-stained living benthic foraminifera (samples from University of Tübingen) confirmed recent ages for the samples used. pH was estimated for core-top sites using surface water oceanographic data^{11,37,71} (following ref. 62), and regional Total Alkalinity (TA)-salinity-temperature relationships⁷². Pre-industrial partial pressure of CO_2 in seawater ($p\text{CO}_2^{\text{sw}}$) at each core-top site was estimated by applying monthly ocean-atmosphere

$\Delta p\text{CO}_2$ interpolated from surrounding sites¹¹ (and corrected for the post-industrial changes in flux⁷³) to a pre-industrial atmospheric $p\text{CO}_2$ value from ice-core data. Monthly estimates of pH were then calculated with CO2sys-Matlab⁷⁴, using the constants of refs 67,75,76, and temperature and salinity data¹¹. Monthly-resolved in situ $\delta^{11}\text{B}_{\text{borate}}$ could then be calculated from pH, temperature, and salinity. For each sample site, the average of twelve monthly estimates of $\delta^{11}\text{B}_{\text{borate}}$ was taken as mean annual in situ $\delta^{11}\text{B}_{\text{borate}}$, and two standard deviations of the monthly variability taken as 2σ uncertainty (representing intra-annual variation in $\delta^{11}\text{B}_{\text{borate}}$ at each site). These core-top samples are complemented by sediment trap samples from the Cariaco Basin CAR22(Z), collected in January 2007. pH, temperature, and salinity data for the sediment trap site are interpolated from data from December 2006 and February 2007 (www.imars.usf.edu/CAR). These new calibration data are presented and plotted in [Extended Data Figure 8](#). Equation 4, with associated 2σ uncertainties, can be then used to calculate the appropriate $\delta^{11}\text{B}_{\text{borate}}$ from *G. bulloides* $\delta^{11}\text{B}$ ($\delta^{11}\text{B}_{\text{calcite}}$). Size fraction was not found to produce any effect on $\delta^{11}\text{B}$ (ref. 69); in this study we used the 300-355 μm size fraction.

$$\delta^{11}\text{B}_{\text{borate}} = (\delta^{11}\text{B}_{\text{calcite}} + 3.440 \pm 4.584) / 1.074 \pm 0.252 \quad (4)$$

$\delta^{11}\text{B}$ -pH proxy in *G. sacculifer*. Conversion of $\delta^{11}\text{B}$ of *G. sacculifer* to pH follows the approach described in ref. 77. Despite analytical biases between MC-ICPMS and N-TIMS analysis⁵⁸, it can be assumed that the pH sensitivity of *G. sacculifer* $\delta^{11}\text{B}$ described by culture calibration⁷⁸ (N-TIMS) is applicable to MC-ICPMS data^{58,79}. The $\delta^{11}\text{B}$ -pH calibration used here therefore incorporates both culture data (ref. 78), which

we recalculated following ref. 62, and existing core-top data¹⁷ ([Extended Data Figure 8](#)). To account for the analytical bias between MC-ICPMS and N-TIMS, we corrected the data set of ref. 78 by applying an offset of -3.32‰. This is derived from the comparison between core-top *G. sacculifer* measurements by MC-ICPMS¹⁷ and N-TIMS⁸⁰ from adjacent sites⁸⁰. The following equation (with 2σ uncertainties) can be then used to calculate the appropriate δ¹¹B_{borate} from *G. sacculifer* δ¹¹B (δ¹¹B_{calcite}):

$$\delta^{11}\text{B}_{\text{borate}} = (\delta^{11}\text{B}_{\text{calcite}} - 3.600 \pm 0.722) / 0.834 \pm 0.036 \quad (5)$$

Carbonate system calculations: pH, $p\text{CO}_2^{\text{sw}}$, and $\Delta p\text{CO}_2$. To calculate pH from δ¹¹B_{borate} ([Eq. 3](#)), temperature and salinity estimates are required. Temperatures are derived from foraminiferal Mg/Ca (see above) and salinity is calculated taking into account the freshwater loss from the ocean due to the glacial growth of continental ice sheets⁸¹. A Monte Carlo approach was used to generate 10,000 realisations of pH by randomly sampling the relevant input parameters within their given uncertainty bounds (2σ): δ¹¹B ± analytical uncertainty ([Eq. 1](#)) and ± calibration uncertainty ([Eq. 4](#) and [5](#)), temperature ± 1°C, and salinity ± 1 psu. To fully propagate the calibration uncertainty 10,000 realisations of each of the calibration data points were first made by randomly varying each point within its X- and Y-uncertainty and fitting a separate regression line for each set of δ¹¹B_{borate} and δ¹¹B_{calcite}. This approach therefore accounts for the co-variation in slope and intercept uncertainty on the average δ¹¹B_{borate}- δ¹¹B_{calcite} calibration line shown in [Extended Data Figure 8](#) (note that this co-variation arises because a fit to the data with a high slope has a low intercept and vice versa). For each of the 10,000 realisation of the down core δ¹¹B records from the Monte Carlo approach one of these calibrations was randomly chosen and applied to

the whole time series (no calibration was chosen more than once). For each data point in the ensuing pH time series the maximum probability of the distribution of the 10,000 pH estimates is determined and the uncertainty is given by the 2.5th, 16th, 84th, and 97.5th percentiles.

To calculate $p\text{CO}_2^{\text{sw}}$, another variable of the ocean carbonate system besides pH is required²⁰. Here, we use TA. Both pH and $p\text{CO}_2^{\text{sw}}$ are governed by the ratio of Dissolved Inorganic Carbon (DIC) to TA in seawater, so pH changes are proportional to changes in $p\text{CO}_2^{\text{sw}}$ (refs 20,82). Although our knowledge of TA is largely uncertain⁸³, modelling studies by Toggweiler (ref. 84) and Hain *et al.* (ref. 85), provide useful constraints on Glacial-Interglacial (G-IG) TA change. The G-IG TA change is +120 $\mu\text{mol/kg}$ in the “Seven-box model” of ref. 84 and +140 $\mu\text{mol/kg}$ in ref. 85. There is no available information, however, on the secular evolution of TA during the deglaciation.

$p\text{CO}_2^{\text{sw}}$ was calculated using the equations of ref. 20 and the “seacarb” package⁸⁶ of R. The relevant input parameters were taken from the 10,000 pH-Monte Carlo simulations above with the addition of TA, that randomly varied for each data point in the simulation from “modern -25 $\mu\text{mol/kg}$ ” to “modern +125 $\mu\text{mol/kg}$ ” with a “flat” probability (i.e., an equal probability of TA being any value between these extremes at any point of the record). This approach avoids ascribing weight to any particular TA value and fully explores the likely range given the available, model-based, constraints.

It is important to note that $p\text{CO}_2^{\text{sw}}$ estimates are mostly determined by the

reconstructed pH and that TA has little influence. For example, assuming that TA in both ODP1238 and PS2498-1 records is constant at either “modern+125 $\mu\text{mol/kg}$ ” or “modern -25 $\mu\text{mol/kg}$ ” only modifies reconstructed $p\text{CO}_2^{\text{sw}}$ by a maximum of ~ 22 μatm (Extended Data Figure 9). Similarly, temperature and salinity have little control on our pH and $p\text{CO}_2^{\text{sw}}$ calculations, which are overwhelmingly determined by $\delta^{11}\text{B}$ and its associated uncertainties. The uncertainties associated with these parameters for PS2498-1 (ODP1238) are, at most: ± 19 (± 9) μatm for calibration uncertainty, ± 10 (± 12) μatm for TA, ± 8 (± 15) μatm for salinity, and ± 9 (± 13) μatm for temperature (Extended Data Figure 9).

To calculate “equilibrium pH”, i.e., surface seawater pH expected at each core location if waters had remained in equilibrium with the contemporaneous atmosphere during the last 25 kyr (Figure 2b,g), we used interpolated ice-core $p\text{CO}_2$ data^{5,87,88} and the calculated temperature, salinity, and TA for each of our samples (see above). Calculations were made using the “seacarb” package⁸⁶ of R with the constants of refs 67,75,76.

$\Delta p\text{CO}_2$ is defined here as the partial pressure of CO_2 in seawater minus the partial pressure of CO_2 in the atmosphere:

$$\Delta p\text{CO}_2 = p\text{CO}_2^{\text{sw}} - p\text{CO}_2^{\text{atm}} \quad (7)$$

Our reconstructed $\Delta p\text{CO}_2$ for the most recent samples in PS2498-1 and ODP1238 are -3 (± 16) and +27 (± 17) μatm , respectively, which agree within uncertainties with modern mean annual $\Delta p\text{CO}_2$ from nearby locations (-15 (± 8) and +45 (± 8) μatm ¹¹,

respectively). As $\Delta p\text{CO}_2$ is a comparison between our $p\text{CO}_2$ records and the Antarctic ice-core $p\text{CO}_2$ record⁵, the resulting $\Delta p\text{CO}_2$ can be affected by the chronology used, especially in periods of rapid $p\text{CO}_2^{\text{atm}}$ increase. To account for this factor, the uncertainty in $\Delta p\text{CO}_2$ due to our age models has been approximated by propagating a ± 0.5 kyr uncertainty in our records using a Monte Carlo approach. The resulting uncertainty in calculated $\Delta p\text{CO}_2$ is, at most, ± 12 μatm for PS2498-1 and ± 7 μatm for ODP1238 ([Extended Data Figure 9](#)).

To derive CO_2 flux between the ocean and the atmosphere, $\Delta p\text{CO}_2$ and air-sea gas transfer rate (normally parameterized as a function of wind speed¹¹) need to be considered. However, a visual comparison between our [Figure 1](#) and [Figure 13](#) in ref 11 illustrates that areas of high $\Delta p\text{CO}_2$ tend to correspond to areas of sea-air CO_2 flux. Consequently, and in agreement with previous literature, in our interpretations we assume that a positive $\Delta p\text{CO}_2$ implies CO_2 outgassing from the ocean to the atmosphere.

Smoothing of the records and Monte Carlo simulations. The $\delta^{11}\text{B}$ -derived and $\delta^{13}\text{C}$ records presented in this study have been smoothed by fitting a non-parametric regression (LOESS function). Smoothing was performed in R with the degree of smoothing (the “span” term) optimised using both “general cross-validation” and “leave-one-out cross-validation” methods⁸⁹. These approaches identified nearly identical optimal degrees of smoothing for the $\delta^{11}\text{B}$ -derived records (span = 0.25 for PS2498-1 and 0.23 for ODP1238), and the most likely smoothed fit to the data was obtained using a probabilistic approach. To achieve this a LOESS function was fitted to each of the 10,000 realisations (for pH, $p\text{CO}_2^{\text{sw}}$, and $\Delta p\text{CO}_2$) generated using the

Monte Carlo approach described above and for each time step the distribution of smoothed lines was examined and the maximum probability and the 2.5th, 16th, 84th, and 97.5th percentiles were determined⁹⁰. This approach fully accounts for the uncertainty in all of the input parameters and provides an uncertainty on the most likely smoothed fit to the data. Uncertainty envelopes in the $\Delta p\text{CO}_2$ records also include the uncertainty associated with our age models.

Hydrographic control on seawater pH in the Subantarctic Atlantic. Millennial-scale reorganizations of the interhemispheric climate^{91,92} were accompanied by meridional shifts of the oceanic fronts of the Antarctic Circumpolar Current²⁷ (ACC). PS2498-1 sits between the Subtropical (STF) and the Subantarctic (SAF) fronts⁹³, the migrations of which may have influenced surface ocean hydrography and carbonate system parameters at this location. The main negative shifts in the PS2498-1 *G. bulloides* $\delta^{11}\text{B}$ record (and pH) generally occurred during warming episodes, as revealed by the co-registered *G. bulloides* Mg/Ca (Figure 2d). This would agree with the contemporaneous southward shifts of the STF at a nearby location²⁷ that are interpreted as the response of the South Atlantic interhemispheric climate changes (e.g., Heinrich Stadial 1, Younger Dryas). Today, surface ocean pH *decreases* southward across the ACC⁹⁴, implying that a southward shift of the STF would have plausibly caused an pH *increase* (as opposed to the observed *decrease*). Hence, the pH variability in the PS2498-1 does not reflect reorganizations of the regional oceanic fronts, because these, at most, would have worked to counteract and/or dampen the reconstructed acidification events.

Intertropical Convergence Zone (ITCZ) migrations in the EEP. The mean latitudinal position of the ITCZ likely migrated southwards during Northern Hemisphere (NH) cold phases^{28,95-97}. ITCZ southward shifts during boreal winter currently coincide with decreased upwelling in the EEP (and vice versa). The timing of the main shifts towards low $\delta^{11}\text{B}/\text{pH}$ (high $\Delta p\text{CO}_2$) in the ODP1238 matched NH cooling events and attendant ITCZ southward displacements²⁸. However, they cannot be explained by variations in EEP upwelling rates because reduced upwelling would cause *lower* $\Delta p\text{CO}_2$, as opposed to the observed *higher* $\Delta p\text{CO}_2$. In addition, the appearance of low-pH waters in the ODP1238 deglacial record are associated with considerably increased temperatures, both in surface and, especially, in thermocline waters⁹⁸ (Figure 2i, Extended Data Figure 10), which cannot be fully explained by deglacial warming. In fact, these positive temperature excursions at ODP1238 exceeded Holocene temperatures, indicating that the ITCZ shifts cannot explain the observed carbonate chemistry and temperature changes documented in our EEP records.

Oceanic tunneling. It refers to the transfer of intermediate waters (Antarctic Intermediate Waters/Subantarctic Mode Waters), and of the geochemical and thermal signals that they transport, from the SO to the Equatorial Pacific^{9,41}. These intermediate waters entrain upwelled deep waters during their formation in the high latitude SO, and therefore during the last deglaciation their chemical characteristics would have been influenced by changes in upwelling around Antarctica. After formation, they spread northward (being modified along their path²⁴) and feed the Pacific Equatorial Undercurrent (EUC), an eastward-flowing subsurface current that transports thermocline waters from the western Pacific along the equator^{99,100} and

upwells in the EEP¹⁸. Therefore, this intermediate water route provides an efficient connection¹⁰¹ between the Southern Ocean and the EEP^{4,7,41}.

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883 **Extended Data Figures Legends**

884

885 **Extended Data Figure 1.** Comparison of PS2498-1 (blue) and ODP1238 (red)
886 records. **a**, $\delta^{11}\text{B}$. **b**, pH, **c**, $\Delta p\text{CO}_2$.

887

888 **Extended Data Figure 2.** $\delta^{11}\text{B}$ -derived $\Delta p\text{CO}_2$ compilation for the Equatorial Pacific
889 during the last deglaciation and Holocene. Foraminifera-based record from the
890 Western Equatorial Pacific²¹ (grey), *Porites* coral-based record from the Central
891 Equatorial Pacific^{22,23} (as published in ref. 22, green), and foraminifera-based record
892 from the EEP (this study, red). The records of refs 21 and 22 have been smoothed by
893 fitting a LOESS function with a degree of smoothing (span) of 0.2 and 0.4,
894 respectively (see [Methods](#)), to allow a better comparison with the ODP1238 record
895 (see main text). ODP1238 is located in the EEP, and therefore represents a direct
896 record of upwelling of CO_2 -rich waters, while the signal at Central and Western
897 Equatorial sites may have been modified during the westward transit of waters by e.g.,
898 equilibration with the atmosphere and/or nutrient utilization by the biological pump.

899

Extended Data Figure 3. a, Planktic $\delta^{18}\text{O}$ records from OPD1238. Red: *Globigerinoides ruber* sensu stricto (ss) 250-355 μm . Green: *Globigerinoides sacculifer* (mixed morphotypes) 355-425 μm . Black: *Neogloboquadrina dutertrei* 355-500 μm . **b**, Planktic $\delta^{13}\text{C}$ records from OPD1238. To facilitate comparison between species, $\delta^{13}\text{C}$ data has been normalized (ref. 53). Red: *G. ruber* ss 250-355 μm . Green: *G. sacculifer* (mixed morphotypes) 355-425 μm . Black: *N. dutertrei* 355-500 μm .

Extended Data Figure 4. $\Delta p\text{CO}_2$ records from the Subantarctic Atlantic (left) and Eastern Equatorial Pacific (right) during the last deglaciation compared with indicators of dust input. **a**, $\delta^{11}\text{B}$ -derived $\Delta p\text{CO}_2$ in core PS2498-1. **b**, logarithm of the mass accumulation rates (MAR) of iron (Fe) in the Subantarctic site ODP1090 (ref. 13). **c** and **f**, $p\text{CO}_2^{\text{atm}}$ measured on a suite of Antarctic ice cores⁵. **d**, $\delta^{11}\text{B}$ -derived $\Delta p\text{CO}_2$ in core ODP1238. **e**, dust fluxes in the EEP²⁹. Dust fluxes from ref. 29 were demeaned and divided by its own standard deviation and are displayed in standard deviation units.

Extended Data Figure 5. a, chronology of Subantarctic core PS2498-1. ^{14}C -calendar age-depth relationships in core PS2498-1. Grey shading indicates 95% confidence limits of calendar ages. **b**, PS2498-1 *Globigerina bulloides* $\delta^{11}\text{B}$ record plotted using the different chronologies described in [Methods](#) and compared with atmospheric $\text{CO}_2^{5,87,88}$ (green) and with Antarctic opal flux⁴ (orange) records. Red, constant ΔR (=300 yr); green, ΔR =900 yr for intervals older than 16 ka and ΔR =300 yr for younger intervals⁶; magenta, variable ΔR correction³⁸ (ranging between 500 and 900 yr between 13 and 16 ka).

Extended Data Figure 6. a, radiocarbon ages for ODP1238 determined on *Neogloboquadrina dutertrei* tests at LLNL-CAMS. **b**, age model for ODP1238. Orange circles: calendar ages; black line: linear fit; red line: third order polynomial fit (see [Methods](#)).

Extended Data Figure 7. a, benthic $\delta^{18}\text{O}$ stratigraphy for ODP1238 compared to other benthic $\delta^{18}\text{O}$ stratigraphies from EEP cores. Black circles: Unpublished benthic $\delta^{18}\text{O}$ data for ODP1238 generated by J.F. McManus (LDEO, Columbia University). Red line: site TR163-22 (ref. 40). Blue line: sites RC13-140, RC23-22, and RC23-15 (ref. 44). **b**, *Globigerinoides ruber* $\delta^{18}\text{O}$ stratigraphy for ODP1238 compared to other *G. ruber* stratigraphies from EEP cores. Black circles: ODP1238 (see [Methods](#)). Green squares: site TR163-19 (ref. 7). Red line: site TR163-22 (ref. 40). Blue line: site ODP1240 (ref. 41).

Extended Data Figure 8. $\delta^{11}\text{B}$ -pH calibrations for *Globigerina bulloides* and *Globigerinoides sacculifer*. **Green symbols and text:** New calibration for *G. bulloides* (with associated 2σ uncertainties). X-error bars for core-top samples are 2 standard deviations of intra-annual variability in calculated monthly $\delta^{11}\text{B}_{\text{borate}}$, while for sediment trap samples it reflects the range of $\delta^{11}\text{B}_{\text{borate}}$ between Dec-Feb 2007. Y-error bars represent the analytical reproducibility (2σ) as calculated by [Equation 1](#) in [Methods](#). PS2498-1 most recent sample (2.2 ka) (black-filled circle) was not used in the calibration process, and is included to show its agreement with the calibration line. **Red symbols and text:** Calibration for *G. sacculifer* (with associated 2σ uncertainties). The calibration line incorporates both culture⁷⁸ (empty symbols) and

core-top (red-filled symbols) data¹⁷. Culture data analysed by N-TIMS (grey symbols and text)⁷⁸ has been corrected by applying a laboratory offset of -3.32‰ (see [Methods](#)) (grey arrow indicates an original N-TIMS calibration data point that falls outside the plot area). ODP1238 late Holocene average (black-filled square) was not used to produce the calibration equation, and is included to show its agreement with the calibration line. X-error bars for core-top samples are 2 standard deviations of intra-annual variability in calculated monthly $\delta^{11}\text{B}_{\text{borate}}$, while for culture samples they represent quoted uncertainty⁷⁸ in pH. Y-error bars represent quoted uncertainty in $\delta^{11}\text{B}$ measurements^{17,78} (2σ). In order to calculate monthly pH variations at ODP1238 location, the method described in the *G. bulloides* calibration section has been used⁶² (with TA derived using the TA-salinity-temperature relationship for the “Equatorial upwelling Pacific Zone” in ref. 72). Black line denotes a 1:1 relationship, i.e., a pH sensitivity equal to that of borate ion. Heavy/light shaded regions around calibration lines represent 1σ and 2σ uncertainties, respectively.

Extended Data Figure 9. Effect of $\delta^{11}\text{B}$ -pH calibration, TA, and chronological uncertainties on $p\text{CO}_2$ and $\Delta p\text{CO}_2$ records. **a**, PS2498-1 $\delta^{11}\text{B}$ - $p\text{CO}_2$ record calculated with the *G. bulloides* calibration equation (thick blue line), and its associated 2σ uncertainty (blue shaded envelope). **b**, PS2498-1 $\delta^{11}\text{B}$ - $p\text{CO}_2$ record assuming a constant TA of (i) modern values at PS2498-1 location (blue), (ii) modern values -25 $\mu\text{mol/kg}$ (green), and (iii) modern values +125 $\mu\text{mol/kg}$ (red). **c**, PS2498-1 $\Delta p\text{CO}_2$ record calculated using (i) age derived from our age model (blue), (ii) age +0.5 kyr (green), and (iii) age -0.5 kyr (red). **d**, ODP1238 $\delta^{11}\text{B}$ - $p\text{CO}_2$ record calculated with the *G. sacculifer* calibration equation (thick red line), and its associated 2σ uncertainty (shaded red envelope). **e**, ODP1238 $\delta^{11}\text{B}$ - $p\text{CO}_2$ record assuming a

constant TA of (i) modern values at ODP1238 location (blue), (ii) modern values -25 $\mu\text{mol/kg}$ (green), and (iii) modern values +125 $\mu\text{mol/kg}$ (red). **f**, ODP1238 $\Delta p\text{CO}_2$ record calculated using (i) age derived from our age model (blue), (ii) age +0.5 kyr (green), and (iii) age -0.5 kyr (red). Note the different X-Y axes for each panel.

Extended Data Figure 10. *Globigerinoides sacculifer* Mg/Ca-based sea surface temperature (SST) (red) and *Neogloboquadrina dutertrei* Mg/Ca-based thermocline temperature (TT) (green) at ODP1238.