Orbital CO₂ reconstruction using boron isotopes during the late Pleistocene, an assessment of accuracy.

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Abstract.

Boron isotopes in planktonic foraminifera are a widely used proxy to determine anc~~ii~~ent surface seawater pH, and by extension atmospheric CO_2 concentration and climate forcing on geological time scales. Yet, to reconstruct absolute values for pH and CO_2, we require a $\delta^{11}B_{foram-borate}$ to pH calibration and independent determinations of ocean temperature, salinity, a second carbonate parameter, and the boron isotope composition of seawater. Although $\delta^{11}B$-derived records of atmospheric CO_2 have been shown to perform well against ice core-based CO_2 reconstructions, these tests have been performed at only a few locations and with limited temporal resolution. Here we present two highly resolved CO_2 records for the late Pleistocene from ODP Sites 999 and 871. Our $\delta^{11}B$-derived CO_2 record shows a very good agreement with the ice core CO_2 record with an average offset of 13±46 (2σ) ~~4.6 ± 49 (2σ) ppm~~, and a RMSE of 26 ~~25~~ ppm, with minor short-lived overestimations of CO_2 (of up to ~50 ppm) occurring during some glacial onsets. We explore potential drivers of this disagreement and conclude that partial dissolution of foraminifera has a minimal effect on the CO_2 offset. We also observe that the general agreement between $\delta^{11}B$--derived and ice core CO_2 is improved by optimising the $\delta^{11}B_{foram-borate}$ calibration. Despite these minor issues a strong linear relationship between relative change in climate forcing from CO_2 (from ice core data) and pH change (from $\delta^{11}B$) exists over the late Pleistocene, confirming that pH change is a robust proxy of climate forcing over relatively short (<1 million year) intervals. Overall, these findings demonstrate that the boron isotope proxy is a reliable indicator of CO_2 beyond the reach of the ice cores and can help improve determinations of climate sensitivity for ancient time intervals.

1- Introduction.

The boron isotope composition of ancient planktonic foraminifera shells is widely used to reconstruct past concentrations of atmospheric CO_2 to understand the drivers and responses of climate change over orbital and geological time scales. Unlike many environmental proxies where it is difficult to assess the accuracy of the resulting reconstructions (e.g. for sea surface temperature), the boron isotope pH/CO_2 proxy can directly be compared with the ice core CO_2 records, i.e. the West Antarctic ice sheet divide (Ahn et al., 2012), the EPICA (European Project for Ice Coring in Antarctica) dome Concordia ice core record (Siegenthaler et al., 2005; Lü~~üu~~thi et al., 2008; Bereiter et al., 2015), and the Vostock ice core

45 record (Petit et al., 1999). This comparison of CO_2 over the last 800 kyr provides a very powerful test
46 of proxy accuracy. Several past intervals have been studied to test the boron isotope proxy in this way
47 (Sanyal et al., 1995; Foster, 2008; Hönisch and Hemming, 2005; Henehan et al., 2013; Rait~~sz~~sch et al.,
48 2018).

49 Given the success of these comparisons, the boron isotope proxy has been used to investigate the
50 interaction between CO2, the ocean carbon cycle and climate beyond the reach of the ice cores, such as
51 during the Mid-Pleistocene transition (Hönisch et al., 2009; Chalk et al., 2017; Dyez et al., 2018), the
52 Pliocene (Martinez-Boti et al., 2015, de la Vega et al., 2020), the Miocene (Foster et al., 2012; Greenop
53 et al., 2014, Guillermic et al., 2022), the Eocene (Anagnostou et al., 2016, 2020; Harper et al., 2020),
54 Paleocene-Eocene boundary (Penman et al., 2014; Gutjahr et al. 2017) and the Cretaceous-Palaeogene
55 boundary (Henehan et al., 2019). Application of the boron isotope proxy is however complicated by the
56 need for: (i) an empirical species-specific calibration of $\delta^{11}B_{foraminifera}$ to $\delta^{11}B_{borate}$ in the pH expression
57 (Henehan et al., 2013, 2016, hereafter $\delta^{11}B_{foram-borate}$ calibration), sometimes including extinct species
58 for deep-time reconstruction; (ii) $\delta^{11}B$ of seawater ($\delta^{11}B_{sw}$), temperature and salinity in the past to
59 calculate pH from $\delta^{11}B$; and (iii) a second carbonate parameter (typically total alkalinity, ~~total~~ dissolved
60 inorganic carbon, DIC, or calcite saturation state) to convert pH to CO_2. While these variables do not
61 influence the magnitude of uncertainty equally in all time intervals, assessment of the boron-based
62 reconstructions against existing ice-core records is a powerful test of the proxy's accuracy.
63
64 Recently, Hain et al. (2018) suggested that the radiative forcing from CO_2 change (ΔF_{CO2}) is linearly
65 related to pH change (ΔpH) of equilibrated water of the low-latitude surface ocean when the CO_2 change
66 occurs faster than the residence time of carbon with respect to silicate weathering (e.g., ~1 million years
67 (Myr)). That is, glacial/interglacial CO_2 climate forcing could be estimated directly from reconstructed
68 ΔpH. Given that one of the main priorities for accurate reconstructions of past CO_2 levels is to allow
69 determinations of climate sensitivity, defined as the temperature response to a radiative forcing –
70 typically a doubling of CO_2 with associated slow and fast feedbacks (e.g. Rohling et al., 2013, 2018) –
71 this recognition may provide a useful shortcut. Climate forcing is a perturbation of the planet's energy
72 balance averaged over the planet (Hansen et al., 2008) and CO_2 forcing, ΔF_{CO2} expressed in $W.m^{-2}$, at a
73 given time can be written as:

74 $$\Delta F_{CO2} \cong \alpha_{2xCO2} * \frac{\Delta \log_{10} CO_2}{\log_{10} 2} \quad (1)$$

75 where α_{2xCO2} is the sensitivity of the radiative balance per doubling of CO_2, and $\Delta \log_{10}CO_2$ is the CO_2
76 change over time expressed in terms of how many 10-foldings of proportional (not absolute) CO_2
77 change (Hain et al., 2018).
78
79 By considering basic equilibrium reactions of carbon species, $\Delta \log_{10}CO_2$ can be derived and expressed
80 as:
81
82 $$\Delta \log_{10} CO_2 \cong \Delta \log_{10} DIC + \Delta pK_0 + \Delta pK_1 - \Delta pH \quad (2)$$
83
84 Hain et al. (2018) showed that the terms $\Delta \log_{10}DIC$ and $\Delta pK_0 + \Delta pK_1$ are small and that $\Delta logCO_2$ can
85 therefore simply be expressed as :
86
87 $$\Delta \log_{10} CO_2 \cong -\Delta pH \quad (3a)$$
88
89 $$\Delta F_{CO2} \cong -\frac{\log_{10} 2}{\alpha_{2xCO2}} \Delta pH \cong -12.3\Delta pH \quad (3b)$$
90

91 To assess the uncertainty of this approximate -1:1 $\Delta \log_{10}CO_2/\Delta pH$ relationship Hain et al. (2018)
92 considered three different end-member causes to compute the accurate $\Delta \log_{10}CO_2/\Delta pH$ relationship:
93 (1) DIC addition/removal yields a slope of -1.3:1 (relative to the basic formalism), (2) $CaCO_3$
94 addition/removal (e.g. precipitation/dissolution, riverine input) yields a slope of -0.9:1, and (3)

95 warming/cooling yields a slope of -1.1:1. That is, even if ΔpH was known exactly this range of
96 plausible slopes results in estimated $\Delta log_{10}CO_2$ and ΔF_{CO2} that are systematically biased by -10% for
97 change caused purely by $CaCO_3$ variations or +30% for change purely caused by DIC variations
98 relative to the approximate -1:1 $\Delta log_{10}CO_2/\Delta pH$ relationship. -While introducing such structural
99 uncertainty in the estimation of ΔF_{CO2} is a concern, this approach eliminates the need to assume a
100 second carbonate system parameter and the uncertainty incurred thereby. An estimate of $\delta^{11}B_{sw}$ is still
101 needed to reconstruct pH based on the boron isotope proxy system (Foster and Rae, 2016) but
102 estimated pH change (i.e., ΔpH) is much less sensitive to error in assumed $\delta^{11}B_{sw}$ than is absolute pH
103 (Hain et al., 2018). An important caveat to estimating ΔF_{CO2} directly from ΔpH is that the intercept of
104 the $\Delta log_{10}CO_2/\Delta pH$ relationship can change with silicate weathering carbon cycle dynamics thought
105 to be important on a ~~million year~~million-year timescale, such that the approach is applicable for
106 orbital timescale variability and short-term shifts but not for long-term trends in ΔF_{CO2}. Therefore, the
107 orbital timescale ice age cycles of atmospheric CO_2 reconstructed from air occluded in Antarctic ice
108 cores offer a unique opportunity to determine the $\Delta log_{10}CO_2/\Delta pH$ relationship observationally and
109 compare to theory. ~~Furthermore, Hain et al., (2018) raise the possibility that the $\Delta log_{10}CO_2/\Delta pH$~~
110 ~~relationship could be decomposed based on the different end-member slopes to constrain the relative~~
111 ~~importance of the mechanism causing the pH and CO_2 changes.~~ Furthermore, given the principal
112 drivers of the glacial-interglacial CO_2 cycles (e.g. change in water mass, sea-ice cover, the soft tissue
113 pump, the solubility pump, the $CaCO_3$ counter pump and the disequilibrium pump; see Sigman et al.,
114 2010; Hain et al., 2010, 2014 for a full review), will impact the $\Delta log_{10}CO_2/\Delta pH$ relationship in
115 different ways, comparing the slope of the regressed $\Delta F/\Delta pH$ line from data to theoretical
116 endmembers (temperature, DIC, $CaCO_3$) could allow the primary controlling mechanisms during
117 Glacial-Interglacial (G-IG) cycles to be deciphered.

118
119 In light of these recent advances, our aims here are twofold. First, we extend previous ice-core validation
120 studies (Foster, 2008; Henehan et al. 2013; Chalk et al., 2017) and test the extent to which boron
121 isotopes reconstruct CO_2 faithfully when current methods and assumptions are applied. In contrast to
122 most previous studies, we use two deep ocean sites and present $\delta^{11}B$ and CO_2 data at high temporal
123 resolution (1 sample every ~3 to 6 kyr). This enables: (i) a thorough test of the assumptions typically
124 made including the central tenet of atmospheric CO_2 proxies that surface ocean CO_2 remains in
125 equilibrium with the atmosphere over time at any given site, (ii) an evaluation of the overall uncertainty
126 of the proxy; (iii) an evaluation of the influence of variable foraminiferal preservation on the accuracy
127 of the CO_2 reconstructed; and (iv) a refinement of a number of the input assumptions and uncertainties,
128 including the $\delta^{11}B_{borate-foram}$ calibration. Second, we evaluate the approach of Hain et al. (2018) and
129 assess the robustness of pH change to not only provide insights into the magnitude of climate forcing
130 from CO_2 change, but also the ability of this approach to provide insights into the causes of CO_2 change
131 over glacial-interglacial cycles.

132 **2.   Methods.**

133 **2.1   Core location and oceanographic setting.**

134 To accurately reconstruct atmospheric CO_2 with the $\delta^{11}B$-CO_2 proxy, it is essential to measure $\delta^{11}B$ in
135 foraminifera from locations where the CO_2 flux between the ocean and the atmosphere is in near
136 equilibrium. We therefore target regions of the ocean where the water column is stratified and
137 oligotrophic as these regions are most likely to attain this condition (Takahashi et al., 2009). Here,
138 following previous studies (Foster, 2008, Henehan et al., 2013; Chalk et al., 2017), we report and add
139 new-data from ODP Site 999 (Figure 1, 12.75°N, 78.73°W, water depth 2827 m, sedimentation rate 3.7
140 cm/ky) in the Caribbean and supplement this well studied site with samples from ODP Site 871 in the
141 Western Pacific (5.55°N, 172.35°E, water depth 1255m, sedimentation rate ~1 cm/ky). The sediments
142 studied at ODP Site 871 are shallowly buried and the site today features a deep thermocline and is
143 located off the equator, hence they are unlikely to be influenced by significant equatorial upwelling

144 (Dyez and Ravelo, 2013, 2014). These two sites show a minor annual mean disequilibrium of +12 ppm
145 (range ~0 to ~30 ppm, Takahashi et al., 2009) for ODP Site 871, and +21 ppm (Olsen et al., 2004;
146 Foster, 2008) for ODP Site 999. These disequilibria are used to correct our CO_2 data derived from $\delta^{11}B$
147 and are assumed to be constant throughout the entire record presented here (with an uncertainty of $\pm$ 10
148 ppm).

149 Whilst we recognised that both sites have a minor disequilibrium, this is often a necessary
150 compromise as areas of the ocean that are in strict equilibrium with the atmosphere are often located
151 in the middle of oceanic gyres and tend to have deep sediments located under the lysocline, have a
152 low sedimentation rate and/or are outside the preferred geographic habitat of *G. ruber*. Furthermore,
153 we present surface $\delta^{18}O$ and $\delta^{13}C$ (site 871) and temperature (both sites) from *G. ruber* that provide
154 insight into the potential influence of upwelling (see section 4.2.2) at these locations. Recent Earth
155 System Model (IPSL-CM5A-MR) outputs (Gray and Evans, 2019) also show that relative pH
156 difference at our core sites between the last glacial maximum (LGM) and the pre-industrial (PI),
157 compared to the ocean average pH difference are close to 0, giving confidence that changes in local
158 disequilibrium are unlikely to drive large changes in our CO_2 reconstructions (at least during the last
159 glacial period).

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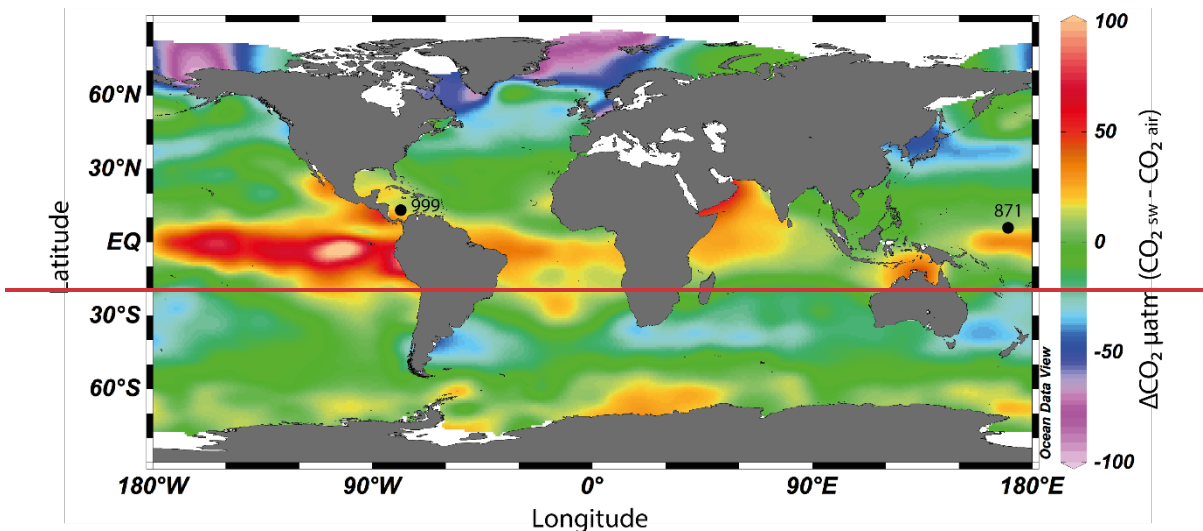
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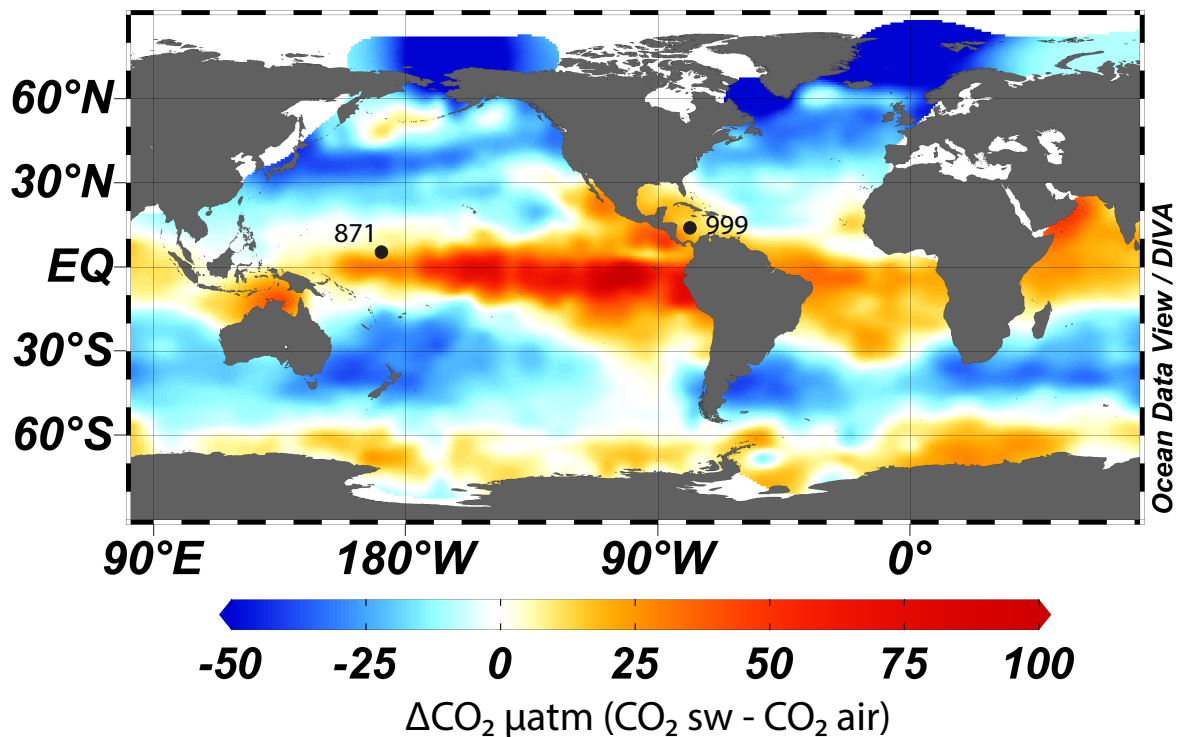
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169 Figure 1. Map of air-sea CO₂ disequilibrium (seawater – air) in ppm and location of ODP sites used in this study.
170 CO₂ data from Takahashi et al. (2009). The map was made with Ocean Data View (Schlitzer, 2022).

2.2   Samples.

2.2.1 Sample selection and preparation.

Samples of deep-sea sediment from our two study sites were taken at 6cm (~3ky) and 10cm (~6ky) resolution at ODP 871 and 999 respectively. Around 1-2 mg of the foraminifer (between 120 and 200 individuals) from ~~to~~ the species *Globigerinoides ruber sensu stricto white* (here after *G. ruber ss*) were hand-picked from the size fraction 300-355 μm for a target of 10 to 20 ng of boron. *G. ruber ss* was chosen here because it is readily identified, is abundant throughout our chosen time interval and a $\delta^{11}B_{foram-borate}$ calibration that accounts for vital effects is available from culture, plankton tows and core-top samples (Henehan et al., 2013). It is also known to live in the upper surface of the ocean with a relatively small depth range (Rebotim et al., 2017) which prevents significant influence of deeper more remineralised CO₂-rich waters on the measured $\delta^{11}B$. The morphotype *G. ruber sensu lato* (hereafter *G. ruber sl*) has slightly different morphology (Aurahs et al, 2001; Carter et al., 2017) and is thought to live in deeper water compared to *G. ruber ss* (Wang, 2000). The morphotype *G. ruber sl* was also hand separated and analysed at lower resolution at ODP 871 to monitor any change over time in morphotype differences in $\delta^{11}B$ that could result from different habitats. For similar reasons, carbon and oxygen isotopes ($\delta^{18}O$ and $\delta^{13}C$) were also measured on *G. ruber ss* and *sl* for comparison on the whole record at ODP 871. For this, around 10 individuals of *G. ruber* per sample were picked, their shells gently broken open and mixed and then a 100 μg aliquot of the homogenised carbonate was measured using a Thermo KIEL IV Carbonate device at the University of Southampton, Waterfront Campus. . While this number of specimens is lower than classically done for $\delta^{18}O$ and $\delta^{13}C$ analysis, it provides power for the identification of species-specific preferential diagenetic alteration, which may have occurred in the sediment and it was sometimes necessary due to the scarcity of some of the *G. ruber* spp morphotypes.

2.2.2 Age constraints.

Samples were taken from 1.5 to 5 metres below sea floor (mbsf) for ODP 871 and from 9 to 21 mbsf for ODP 999. Sample age at Site 871 was initially determined from sample depth using published age models (Dyez and Ravelo, 2013). At Site 999, the age was determined by developing a new ~~benthic~~*Cibicidoides wuellerstorfi* benthic $\delta^{18}O$ record. The initial age model at Site 871 was refined by measuring $\delta^{18}O$ on the benthic species *~~Cibicoides wuellerstorfi~~Uvigerina peregrina* (50 μg of 3-5 mixed, crushed and homogenised specimens) measured on a Thermo KIEL IV Carbonate device at the University of Southampton, Waterfront Campus. These new $\delta^{18}O$ data (Figure 2) were then tuned to the benthic $\delta^{18}O$ LR04 stack (Lisiecki and Raymo, 2005) using Analyseries (Paillard et al., 1996). A correction of +0.47 was applied to the $\delta^{18}O$ *Cibicidoides wuellestorfi* at ODP Site 999 following Marchitto et al. (2014).

2.2.3 Fragment counts.

Foraminifera fragment counts were conducted on ODP Site 871 to monitor variations in carbonate preservation. Samples were sub-sampled using a splitter (in order to maintain homogeneity) and poured onto a picking tray. The fragmentation index (FI) was calculated following the approach of Howard and Prell (1994) and Berger (1970) where percentage fragment is defined as:

$$FI = 100 * \frac{number\ of\ fragments}{number\ of\ fragments + number\ of\ whole\ tests} \quad (4)$$

Counts of whole intact grains and fragments of grains were conducted three times and averaged. The standard deviation (1σ) of the fragmentation index is 1.69. This approach followed that used in an early study at ODP Site 999 (Schmidt et al. 2006) ensuring that the datasets between the two sites are comparable.

2.2.4 Boron separation.

The hand separated foraminifera tests for boron isotope analysis were broken open, detrital clay was removed, and oxidatively cleaned and leached in a weak-acid to obtain a primary carbonate signal using established methods (Barker et al., 2003). Samples were then slowly dissolved in ~ 100 μl 0.5M HNO_3 added to 200 μl of MQ water. Dissolved samples were then centrifuged for 5 minutes to separate any remaining undissolved contaminants (e.g. silicate grains, pyrite crystals) and transferred to screw top 5 ml Teflon pots for subsequent boron separation. An aliquot equivalent to 7% of each sample was kept for elemental analysis and transferred to acid cleaned plastic vials in 130 μl 0.5M HNO_3. Samples were purified for boron using anion exchange column chemistry method prior to isotope analysis as described elsewhere (Foster, 2008). A total procedure blank (TPB) was conducted for each batch of samples and typically ranged from 0-100 pg. ~~50 pg~~ which represents a blank contribution of up to 2.3% (for samples containing ~10-20 ng of boron). Most samples had a TPB below 40 pg and were not corrected. Two batches had a TPB of 70 and 100 pg for which we corrected using a long-term median TPB $\delta^{11}B$ value of -7.27‰ from the University of Southampton. This represents a $\delta^{11}B$ correction of 0.1 to 0.7 ‰.

~~a very small contribution relative to our sample size (0-0.25%), hence no samples required correction in this study.~~

251 ~~2.4~~ **2.3 Analytical techniques**

252 Boron isotope analyses were performed on a ThermoScientific Neptune multi collector inductively
253 coupled plasma mass spectrometer (MC-ICPMS) with 10^{12} Ω~~W~~ amplifier resistors using a standard-
254 sample bracketing routine with NIST 951 boric acid standard (following Foster et al. 2013 and Foster,
255 2008). Elemental analysis was performed on each dissolved sample using a ThermoScientific Element
256 inductively coupled plasma mass spectrometer (ICPMS). All analyses were carried out at the University
257 of Southampton, Waterfront Campus (following Foster, 2008 and Henehan et al., 2015). Element to
258 calcium ratios were measured with ^{43}Ca and ^{48}Ca and measured against in house mixed element
259 standards. Elemental ratios measured included: B/Ca, Mg/Ca, Al/Ca, Mn/Ca, Sr/Ca. Based on the
260 reproducibility of our in-house standards, the uncertainty for most elemental ratios is ~ 5% (at 95%
261 confidence).

262 ~~2.5~~ **2.4 Constraints on δ ^{11}B-derived pH and CO$_2$.**

263 *2.5.1 From $\delta^{11}B$ to pH.*

264 Seawater pH is related to the boron isotopic composition of dissolved borate ion by the following
265 equation:
266

267 $$pH = pK_B - \log\left(-\frac{\delta^{11}B_{sw} - \delta^{11}B_{borate}}{\delta^{11}B_{sw} - a_B * \delta^{11}B_{borate}(a_B - 1)}\right) \ (5)$$

268
269 where the isotopic fractionation factor α_B between B(OH)$_3$ and B(OH)$_4^-$, is 1.0272 as determined by
270 Klochko et al. (2006) and the δ^{11}B of seawater is 39.61 ‰ (Foster et al., 2010) for both sites and kept
271 constant throughout the record due to the long residence time of boron (10-20 Myrs, Lemarchand et al.
272 2002).

273
274
275 The sea surface temperature (SST) values necessary to calculate pK$_B$ in equation (5) were determined
276 at both sites using the Mg/Ca of *G. ruber* (Dyez and Ravelo, 2013) including a depth-dependent
277 dissolution correction for each site (following Dyez and Ravelo, 2013 for Site 871 and Schmidt et al.,
278 2006 for Site 999) and a pH correction using the iterative approach of Gray and Evans (2019) to account
279 for the observed pH effect on Mg/Ca in *G. ruber* producing higher apparent sensitivity of Mg/Ca during
280 glacial cycles (Gray et al., 2018).

281 Mg/Ca was corrected for depth-dependent dissolution at Site 871 using the following equation (Dyez
282 and Ravelo, 2013):

$$\frac{\text{Mg}}{\text{Ca}}(\text{corrected}) = \frac{\text{Mg}}{\text{Ca}}(measured) + 0.26 * depth + 0.52 \text{ } (6a)$$

284   Mg/Ca from Site 999 was corrected following Schmidt et al. (2006):

$$\frac{\text{Mg}}{\text{Ca}}(\text{corrected}) = \frac{\text{Mg}}{\text{Ca}}(measured) + 0.66 \text{ } (6b)$$

287   To evaluate the effect of various Mg/Ca treatment on temperature and calculated CO_2, we performed
288   seven sensitivity tests (Table S1) with Mg/Ca-derived SST using the calibrations of: (1) Gray et al.
289   (2018) temperature-dependent only (global calibration), (2) Gray and Evans (2019) with a pH
290   correction; (3) Gray et al. (2018) temperature-dependent with Mg/Ca corrected for depth-dependent
291   dissolution; (4) Gray and Evans (2019) with Mg/Ca corrected for depth-dependent dissolution and pH
292   correction; (5,6) Anand et al. (2003) with and without a depth correction; and (6) with temperature
293   kept constant (26°C).

294   The differences in SST and resulting CO_2 can be substantial (Figure S1, Table S2): up to 6 degrees
295   and ~50 ppm, respectively, between the Gray et al. (2018) calibration uncorrected for pH and the
296   Anand et al. (2003) calibration corrected for dissolution. We have chosen the Mg/Ca treatments that
297   accounts for pH effect on Mg/Ca and yields the closest agreement between coretop at both sites and
298   modern temperature from Glodap v2 (Lauvset et al., 2022) This treatment is with a pH correction and
299   Mg/Ca corrected for depth dependent dissolution. Choosing this approach is justified considering (1)
300   the strong offset between Anand et al. (2003) multi-species Mg/Ca-Temperature calibration and the
301   more recent *G. ruber* compilation of Gray et al., (2018); (2) the effect of pH correction as shown in
302   Gray et al., (2018) and Gray and Evans (2019); (3) the suggested influence of dissolution on Mg/Ca
303   (Dyez and Ravelo, 2013; Schmidt et al., 2006) and (4) the better agreement between coretop and
304   modern SST at each site when using a pH and depth correction (Figure S1).

309   the relationship of Anand et al. (2003):

$$SST = \frac{\ln\left(\frac{\frac{\text{Mg}}{\text{Ca}}surf}{0.38(\pm 0.02)}\right)}{0.09(\pm 0.003)} \text{ } (6)$$

313   This calibration does not include a depth correction but yields temperatures from core top samples that
314   are consistent with modern SST (Olsen et al., 2016).
315   The salinity (S) that is used in the expression of pK_B is kept constant for both sites (35 PSU) due to the
316   very minor effect of salinity on calculated pH/CO_2 (1 salinity unit changes pH by 0.006).CO_2.

318   To investigate the effect of the recently proposed pH effect on reconstructed Mg/Ca-derived SST and
319   hence reconstructed CO_2, we've explored a scenario wherein we apply a pH correction on Mg/Ca-SST
320   using the iterative approach of Gray and Evans (2019).

321   *2.5.2   From pH to CO_2.*

322   Calculating CO_2 from boron isotope derived pH is dependent on the determination of a second
323   parameter of the carbonate system. Here we use the modern value of total alkalinity (TA) at each site:
324   2279 and 2350 μmol/kg at ODP 871 and ODP 999, respectively (Shipboard Scientific Party, 1993;

Takahashi et al., 2009). Following Chalk et al. (2017), these values were kept constant throughout the whole record. To account for any variations in alkalinity, a generous uniform (~~or flat~~i.e. equal likelihood of values within the range of uncertainty) uncertainty of 175 μmol/kg, ~~distributed equally on either side of the central value,~~ is applied. ~~(i.e. equal likelihood of values within the range of uncertainty).~~ This range in TA encompasses the likely range in this variable on glacial-interglacial (e.g. Toggweiler, 1999; Hain et al., 2010; Cartapanis et al., 2018) or longer timescales (Hönisch et al. 2009), and its adoption means the local TA record ~~local site~~ is not tied to a global sea-level record as ha~~s~~d been practice~~d~~ previously. We avoid drawing this link because the ~+3% (+68μmol/kg) concentration increase of solute alkalinity occurring from sea-level lowering during the last glacial maximum may not have been the dominant driver of ocean alkalinity change (Boyle, 1988a/b; Sigman et al., 1998; Toggweiler, 1999; Hain et al., 2010; Cartapanis et al., 2018). By assuming a uniform distribution for TA we avoid imposing a temporal evolution to this variable because evolution of TA through a glacial cycle is uncertain and is unlikely to be simply a function of sea-level or salinity (e.g. Dyez et al. 2018) due to the effect of carbonate compensation.

The surface water CO_2 is then calculated as (Zeebe and Wolf-Gladrow, 2001):

$$CO_2 = \frac{TA - \frac{K_B * B_T}{K_B + [H^+]} - \frac{K_W}{[H^+]} + [H^+]}{\frac{K_1}{[H^+]} + \frac{2K_1 K_2}{[H^+]^2}} \quad (7)$$

where TA is the total alkalinity, K_B the equilibrium constant of boron species in seawater, B_T the concentration of boron in seawater (432.6 μmol/kg, Lee et al., 2010), $[H^+]$ the concentration of H^+ determined from $pH = - \log [H^+]$, K_W the dissociation constant of water (function of T, S and pressure), K_1 and K_2 the first and second dissociation constants of carbonic acid (function of T, S and pressure, Luecker et al., 2000). The estimate of atmospheric CO_2 includes site-specific offsets relative to reconstructed surface water CO_2 to account for observed local disequilibrium (+21 ppm and +12 ppm at ODP Sites 999 and 871, respectively).

2.6 Uncertainty.

2.6.1   Analytical uncertainty.

The uncertainty on the measured $\delta^{11}B$ is expressed as the external uncertainty which includes instrumental error and chemical separation of the sample (see a detailed discussion in John and Adkins, 2010). This was determined empirically by long-term repeat measurements of JCp-1 subject to the same chemical purification as our foraminiferal samples. As discussed by Rae et al. (2011) this uncertainty is dependent on the intensity of the ^{11}B signal and is expressed here by the following relationship defined during the duration of this study at the University of Southampton (Anagnostou et al., 2019), for ^{11}B intensities <0.54V:

$$2\sigma = 129600 \, e^{-212 \, x \, [^{11}B]} + 0.3385 \, e^{-1.544 \, x \, [^{11}B]} \quad (8).$$

where $[^{11}B]$ is the intensity of ^{11}B signal in volts. The $\delta^{11}B$ uncertainty for ^{11}B intensities > 0.54V is 0.15‰ (at 95% confidence).

2.6.2   pH and CO_2 uncertainty.

The CO_2 uncertainty we report was calculated with a Monte Carlo simulation (10, 000 realisations) in order to fully account for the uncertainty in all variables used in the calculation of pH and CO_2 (σ_{CO_2} $_{\delta11B\text{-derived}}$). The shape of the uncertainty distribution sampled is either normally distributed (for temperature, salinity and $\delta^{11}B$) or uniform (for alkalinity, as discussed above). The maximum

369 probability of all realisations was used as the central value for CO_2 and an error envelope at 1 and 2σ
370 was calculated based on the 68% and 95 % distribution of the realisations.
371

372 *2.6.3   Uncertainty on the CO_2 offset*

373 To constrain the offset between $\delta^{11}B$-derived CO_2 and ice core CO_2, each sediment age is compared to
374 the ice core CO_2 record by interpolation of the record of highest resolution (in this case the $\delta^{11}B$ record
375 onto the ice core compilation). To fully account for age uncertainty when interpolating the sediment
376 age to the well-dated ice core record, a distribution of the ice core data was calculated within the 4σ
377 uncertainty of the $\delta^{11}B$ age and weighed by the respective likelihood based on the age difference
378 between ice core and sediment core.
379
380 The CO_2 offset (or residual) is defined by:
381

$$Offset_{CO2} = CO_{2 \, \delta11B\text{-derived}} - CO_{2 \, ice} \quad (9)$$

382
383
384 The uncertainty on this offset (σ_{offset}) accounts for the uncertainty of the interpolated ice core CO_2
385 ($\sigma_{CO2.interpol}$) and the one of the $\delta^{11}B$-derived CO_2 ($\sigma_{CO2.\delta11B\text{-derived}}$), such as :
386
387

388
$$\sigma_{offset} = \sqrt{\sigma^2_{CO2.interpol} + \sigma^2_{CO2.\delta11B-derived}} \quad (10)$$

389 **2.7 The relationship between $\delta^{11}B$ -derived pH and ΔF_{CO2}.**

390 The linear relationships between the relative CO_2 forcing ΔF_{CO2} and pH are determined with a York
391 regression (York et al., 2004) that accounts for the uncertainty in both the independent and dependent
392 variable (i.e. x and y axes). The ice core CO_2 interpolation used to calculate ΔF_{CO2} and uncertainty is
393 determined as described in section 2.6.3 (Hain et al., 2018).

394 **2.8 Optimising the *G. ruber* $\delta^{11}B$ borate-foraminifera calibration.**

395 An optimised *G. ruber* calibration was obtained by minimising the root mean square error (RMSE) of
396 the average offset between $\delta^{11}B$-derived CO_2 and ice core CO_2. The steps are illustrated in Figure S2 1.
397 In order to optimise the calibration, 10,000 simulations of $\delta^{11}B_{borate}$ and $\delta^{11}B_{foraminifera}$ from the calibration
398 of Henehan et al. (2013) were performed within their normally distributed uncertainty (1σ), from which
399 we defined the same number of linear models each including their slope and intercept. Then, we
400 calculate the equilibrium pH and resultant equilibrium $\delta^{11}B_{borate}$ from ice core CO_2 and the assumed
401 constant TA at each core site. The $\delta^{11}B_{borate}$ from the 10,000 linear models is then calculated and the
402 difference to the ice core-derived $\delta^{11}B_{borate}$ is determined. The linear model calibration that yields the
403 minimum RMSE between these two borate variables defines the new $\delta^{11}B_{borate\text{-foram}}$ calibration. To assess
404 the effect of $\delta^{11}B$ records from different sites we performed this exercise using the combined records
405 (from both sites 999 and 871), 999 only and 871 only (Figure S3) and show that using a record from
406 one particular site or the combination of sites yields similar CO_2 offsets (Table S3) and so here we use
407 the results from the combined sites. Unless indicated otherwise, to preserve a degree of independence,
408 the pH results presented in this study are calculated with the published calibration (Henehan et al.,
409 2013), and the results with the optimised calibration presented in section 4.2.6.

3 Results.

3.1 Temperature and fragment counts.

The SST at ODP Sites 999 and 871 show a cyclicity that agrees with the well-known glacial interglacial cycles of the late Pleistocene (Figure 2). ~~The Mg/Ca SST corrected for pH (Figure S2) shows lower temperatures of about 0.2 to 2.5°C, yet the glacial variation structure is maintained.~~ The SST determined from *G. ruber sl* ~~Mg/Ca uncorrected~~ (red filled circles, Figure 2B) at Site 871, show ~~systematically cooler~~ equal or cooler temperatures (by 1-2 °C) than *G. ruber ss* (black filled circles). The fragmentation index (Figure 2D) at ODP 871 range from 20 to 50 % and follow the well-documented "Pacific style" dissolution cycles (Sexton and Barker, 2012) with well-preserved carbonate (low fragments) during glacials and less well-preserved carbonates (higher fragments) during interglacials. The percentage sand typically anticorrelates with fragmentation counts at both sites, although it is less clear at ODP 999, perhaps due to the shorter record available. Fragmentation counts reach maxima at ODP 999 of 20 % during interglacials and up to 50 % during marine isotope stage MIS 11 which is concomitant with the mid-Brunhes dissolution interval (MBDI, Barker et al., 2006). The fragmentation counts at ODP 871 show no substantive anomaly during the MBDI.
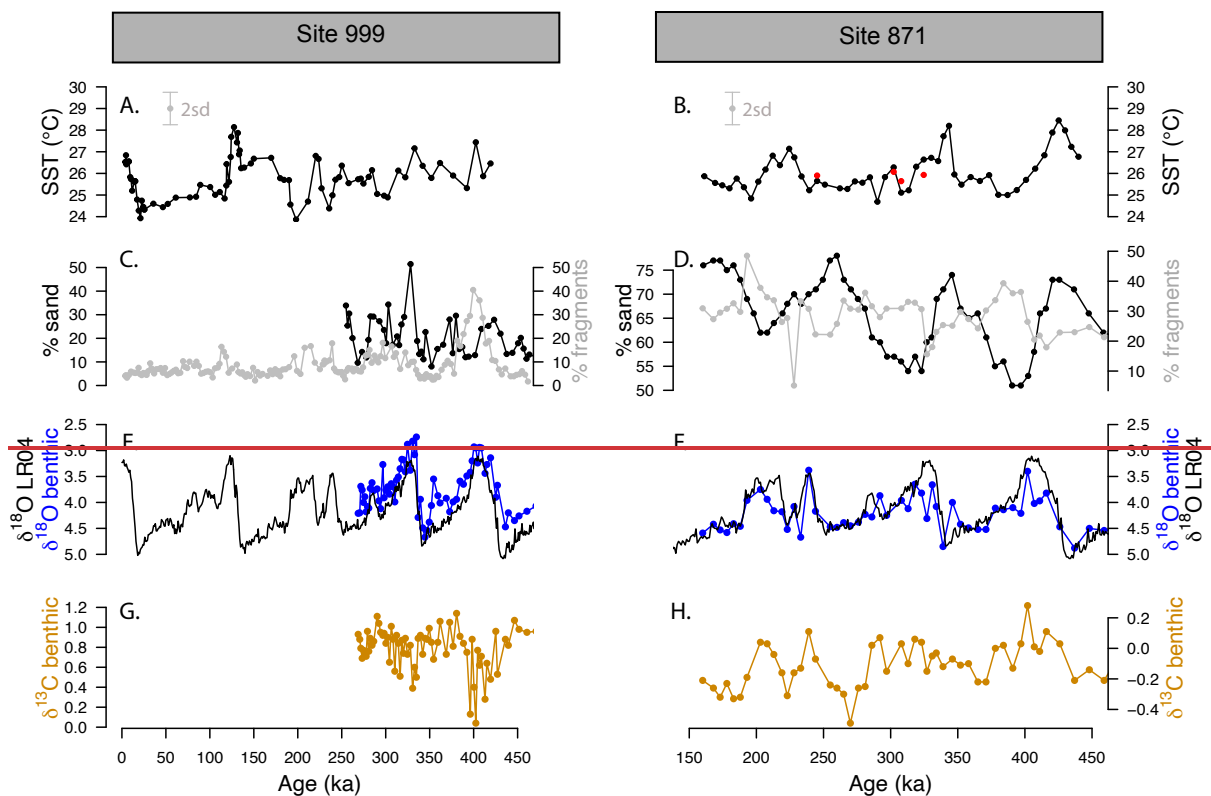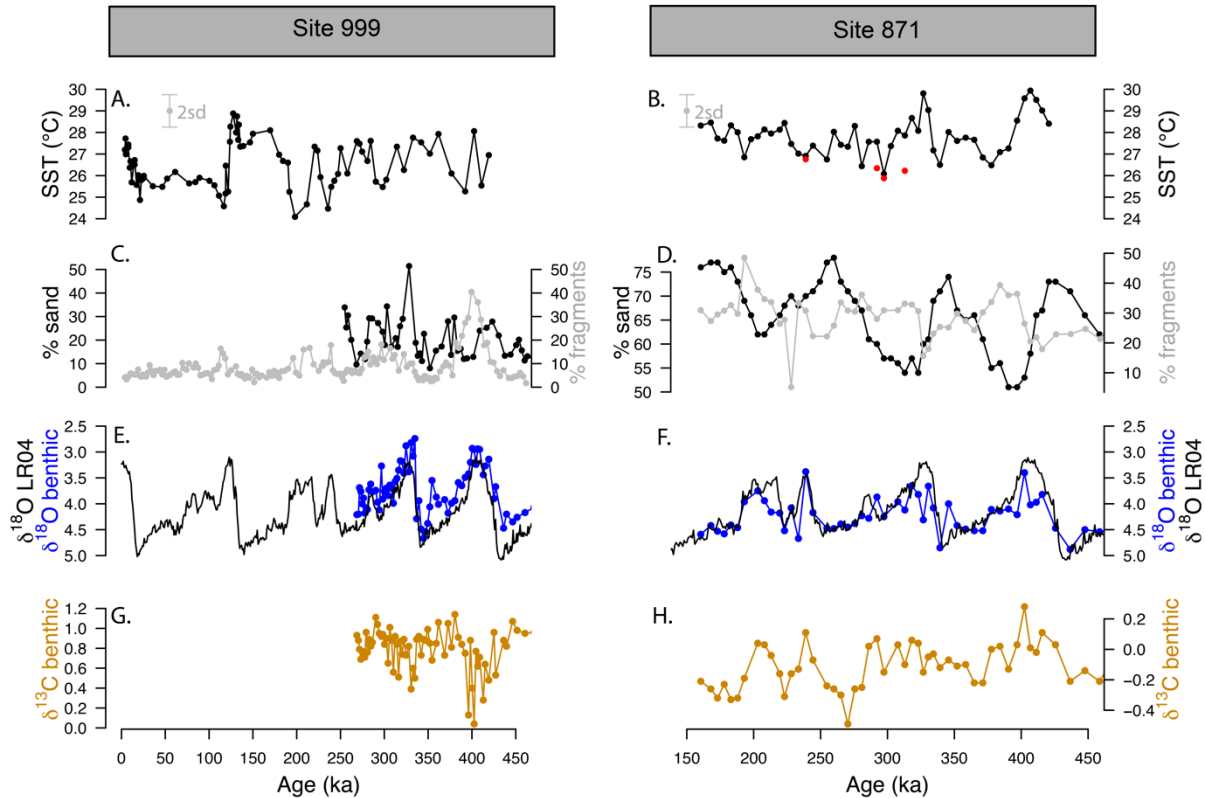
Figure 2. Mg/Ca derived temperature, coarse fraction (sand), fragmentation and benthic δ^{18}O and δ^{13}C at ODP sites 999 and 871. **A, B:** Temperature at ODP 999 (from *G. ruber ss*, black, Schmidt et al., 2006 and this study) and ODP 871 (*G. ruber ss*, black, *G. ruber sl*, red, 2sd indicated by the grey error bar). **C, D:** Fragmentation index (light grey, data from Schmidt et al. (2006) for ODP 999) and sand (black line). **E, F:** Benthic *C. wuellestorfi* (Site 999) and *U. peregrina* (Site 871) δ^{18}O (blue) and LR04 benthic δ^{18}O stack (black). A correction of +0.47̶8̶‰ is applied to ̶o̶u̶r̶ δ^{18}O of *C. wuellestorfi* data in order to adjust for species offset ̶b̶e̶t̶w̶e̶e̶n̶ ̶*C̶.̶ ̶w̶u̶e̶l̶l̶e̶s̶t̶o̶r̶f̶i̶*̶ ̶a̶n̶d̶ ̶L̶R̶0̶4̶. **G, H:** Benthic *C. wuellestorfi* (Site 999) and *U. peregrina* (Site 871) δ^{13}C (orange).

3.2 pH and CO₂ reconstructions.

The δ^{11}B, pH and δ^{11}B-derived absolute CO_2 (Figure 3) from Sites 871 and 999, show clear cyclicity related to glacial-interglacial cycles. The CO_2 values carry an average uncertainty of ±48 ppm and the mean offset from the ice core CO_2 for a combination of the two records is 13±46 ̶-̶4̶.̶6̶ ̶±̶4̶9̶ (2σ) ppm showing that there is a minor overestimation of CO_2 using the boron method yet it agrees on average well within uncertainty. The RMSE of the CO_2 offset for the combined record is 26̶5̶ ppm.

Despite the overall close agreement between δ^{11}B-derived CO_2 and ice core-derived CO_2, each of our δ^{11}B-CO_2 records exhibit some short-lived intervals where the offsets from the ice core record are larger. This is further revealed by the residual CO_2 and the identification of the data above the upper quartile (i.e. the upper 25% of the data, Figure S4 ̶3̶). Those data do not appear to be randomly distributed and instead occur at ~100 ky, ~220-290 ky and ~390 ky at ODP Site 999, in all three cases during the early stages of the glaciation (except for the MIS 8 glacial at 280ky, Figure S4 ̶3̶). The mismatches with the ice core at ODP Site 871 show a similar temporal pattern occurring at ~220 and ~300 and ~ 350-390 ky (i.e. at glacial inceptions).
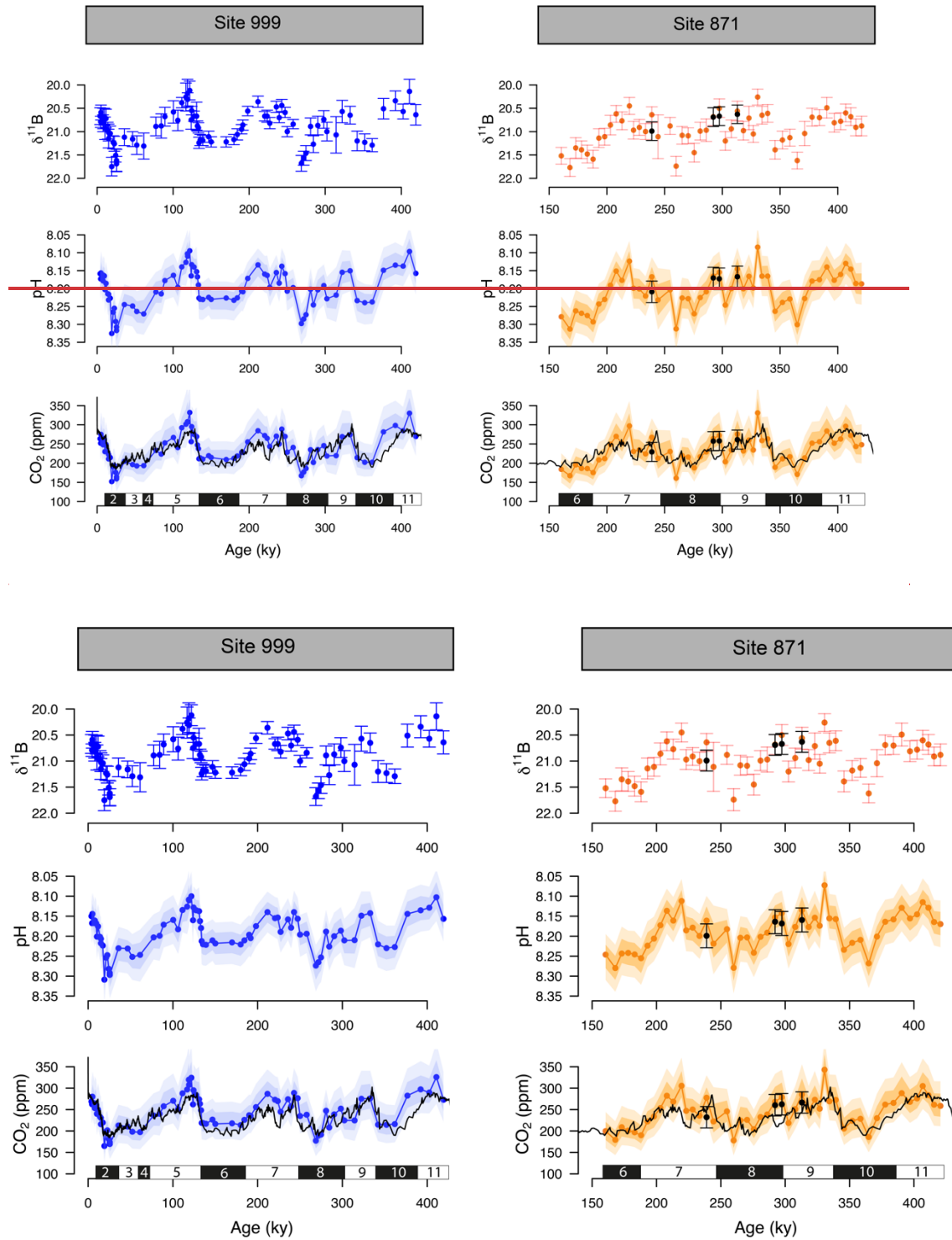
Figure 3. δ^11B, pH and boron-derived CO_2 at site 999 and 871. δ^11B of *G. ruber ss* and *sl* (top row), boron-derived pH (middle row) and CO_2 (bottom row) reconstruction from two core locations: ODP 999 (blue, this study and published data, Foster, 2008; Henehan et al., 2013; Chalk et al., 2017) and ODP 871 (orange, this study). The black line in the CO_2 panels is the composite Antarctic ice core CO_2 record (Bereiter et al., 2015). All δ^11B-derived data points are from *G. ruber ss* except black dots at ODP Site 871 measured on *G. ruber sl*. Numbers at the bottom of the CO_2 records represent marine isotope stages (Bblack boxes for glacials and white boxex for interglacials). Note the age scale is different betweenat Ssites 999 and 871.

3.3 Contrasting $\delta^{11}B$ between morphotypes.

Within error, the few measurements of $\delta^{11}B$ *G. ruber sl* at ODP 871 all agree with $\delta^{11}B$ *G. ruber ss* (Figure 3) albeit the $\delta^{11}B$ of *G. ruber sl* are ~~is~~ higher than *G. ruber ss* for all 4 data pairs available. The CO_2 derived from *G. ruber sl* (Figure 3) is on average 22 ~~15~~ ppm lower than the one derived from *G. ruber ss*; though the much lower resolution (n=4) impedes a thorough comparison at this stage. The $\delta^{18}O$ and $\delta^{13}C$ of both morphotypes were compared for the whole records at ODP 871 (Figure S5 4) and a cross-plot shows a moderate to good agreement between *G. ruber ss* and *sl* (r^2=0.55 and 0.22 for $\delta^{18}O$ and $\delta^{13}C$ respectively, Figure S6 5). This is in contrast to other studies (e.g. Wang et al., 2000; Steinke et al., 2005) that show $\delta^{18}O$ in *G. ruber sl* to be systematically higher.

~~3.4 Dissolution experiments.~~

~~The leaching experiments on *T. sacculifer* and *G. ruber ss* show a different response for the two species (Figure S6). While *G. ruber ss* show no significant variation in measured $\delta^{11}B$ under different treatments, *T. sacculifer* shows no systematic variations in $\delta^{11}B$ for the control and first two treatments (leached in 2 and 4 hours in 0.0001M HNO_3, pH 4) but shows a ~1‰ shift (relative to the control) towards lighter $\delta^{11}B$ after 6 hours at pH 4.~~

~~3.5~~3.4   Relationship between $\delta^{11}B$-pH and CO_2 forcing from the ice core.

A cross plot of $\delta^{11}B$-derived pH CO_2 forcing from the ice core record for each of our marine core study sites is shown in Figure 4 and is compared to the theoretically-derived approximate $\Delta FCO_2/\Delta pH$ relationships as adopted by Hain et al. (2018): -1:1 W/m^2 (dashed black line); $CaCO_3$ addition/removal (-0.9:1 W/m^2 plain yellow line); DIC addition/removal (-1.3:1 W/m^2 dotted-dashed blue); and warming/cooling temperature forcing (-1.1:1 W/m^2, dashed red). Our analysis includes full propagation of uncertainty in pH, in contrast to Hain et al. (2018) who considered only the reported uncertainty of $\delta^{11}B_{borate}$ in their validation exercise. In both cases the uncertainty in ΔF_{CO2} accounts for the error in interpolation arising when comparing age-uncertain $\delta^{11}B$-derived pH with ΔF_{CO2} from the well-dated and high-resolution ice core CO_2 record (see methods 2.7 and 2.6 for details). This treatment of ΔF_{CO2} uncertainty is dominated by the spread of ice core CO_2 data points within the $\delta^{11}B$ age uncertainty. The data are fitted with a York-type regression (thin black line; York et al., 2004) where the grey envelope represents the uncertainty of the linear relationship that best represents the data (i.e., the envelope is not the prediction interval), considering the uncertainty in pH and ΔF_{CO2}. The regressed slope is $\Delta F/\Delta pH$ = - 17.2 ~~15.42~~ ± 10.8 W/m^2 (-1.42:1 relative to basic formalism) and shows a good agreement with the theoretical temperature and DIC driven relationships.

The effect of the uncertainty assigned to pH (fully propagated or using the measurement uncertainty of the boron isotope) on the regressed slope is shown in Figure S7. The slope of the York regression when using the uncertainty from $\delta^{11}B$ only, as in Hain et al. (2018), shows a ~~very~~ close agreement with the basic formalism, with a slope of $\Delta F/\Delta pH$= - 13.7 ~~12.4~~ ± 0.3 W/m^2, (-1.1:1 relative to the basic formalism) but with a unsatisfactory goodness of fit (mean squared weighted deviation, mswd) of 5.36, whereas propagating the full pH uncertainty based on our iterative Monte-Carlo simulations improves goodness of fit to ~0.91 at a $\Delta log_{10}CO_2/\Delta pH$ of -1.42:1 (Figure 4).

506
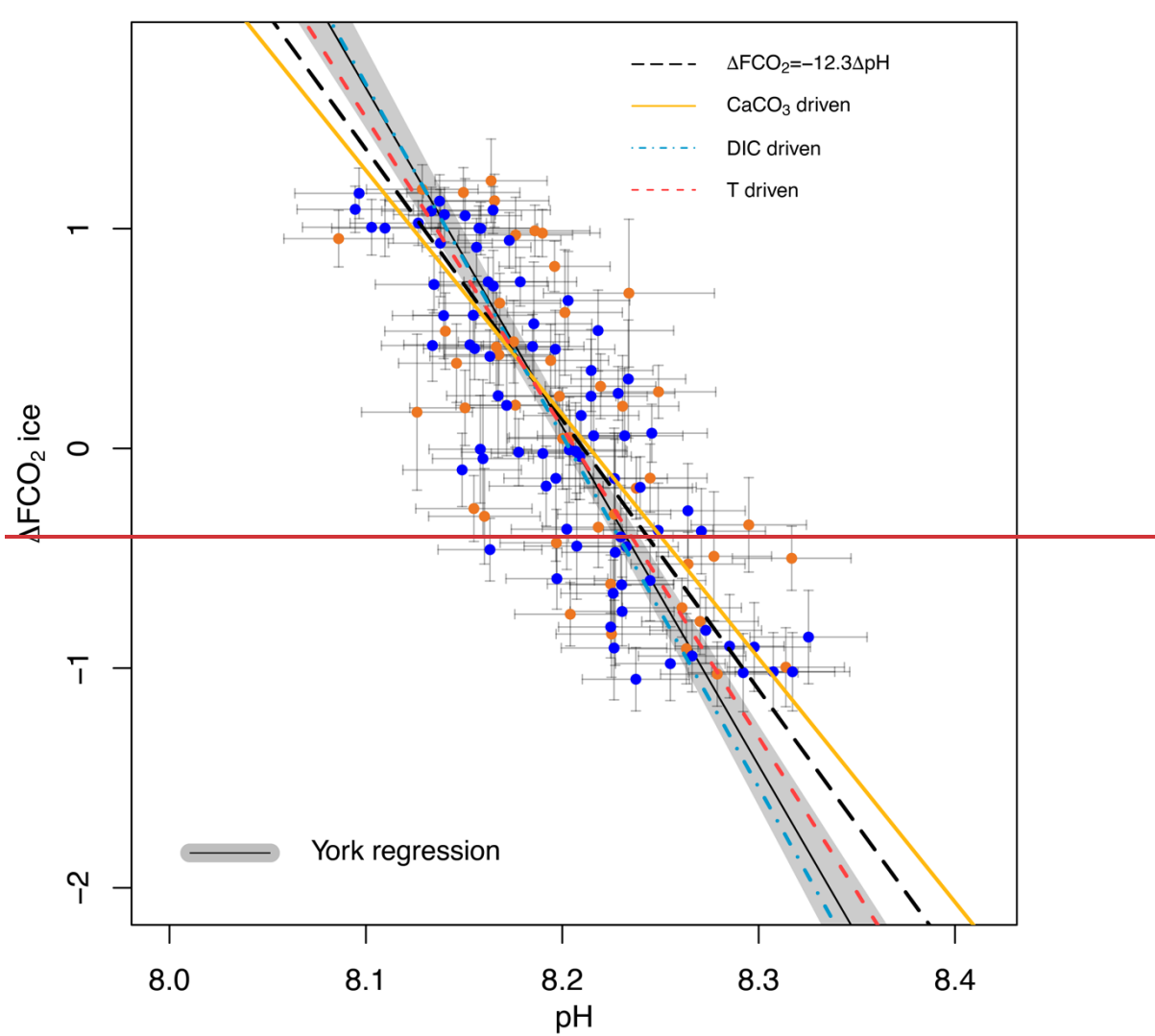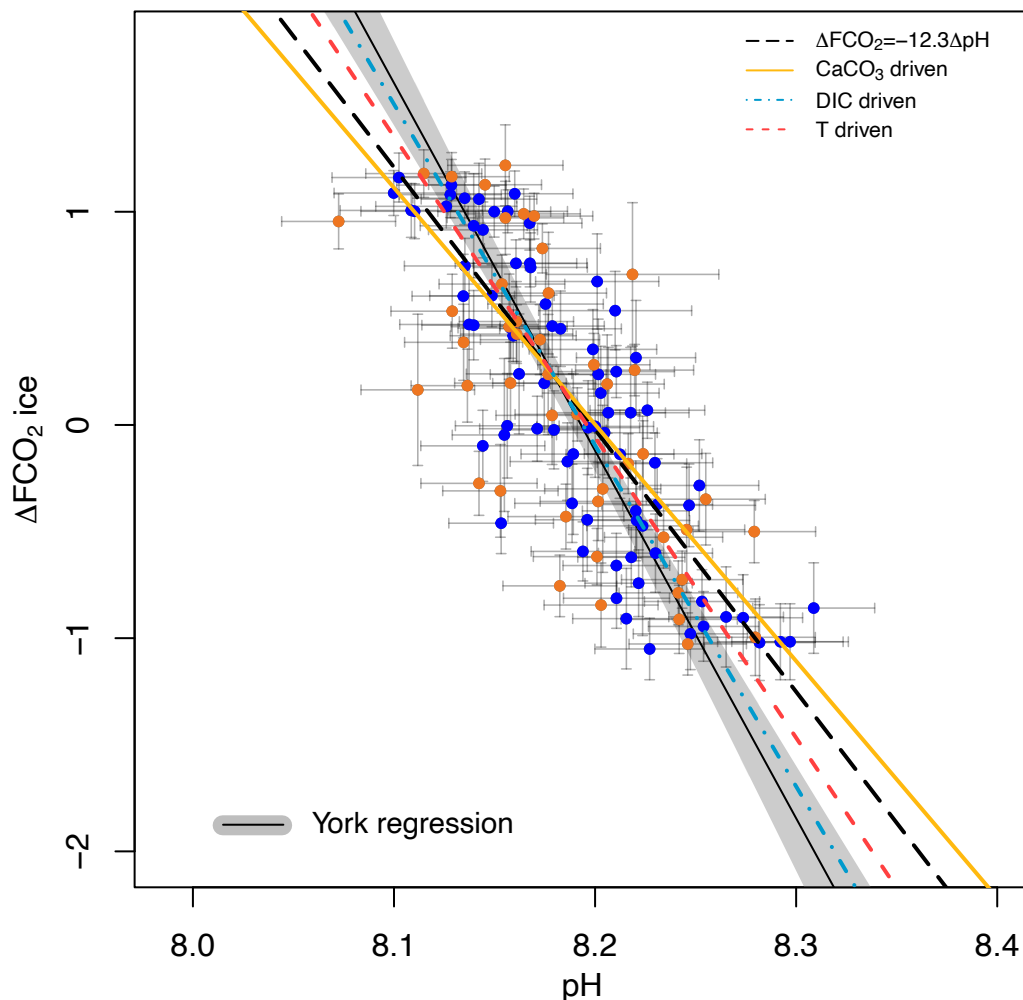
Figure 4. Ice core based ΔFCO_2 (CO_2 forcing) vs. $\delta^{11}B$-based pH for ODP 999 (blue filled circles, this study and published data from Foster, 2008; Henehan et al., 2013; Chalk et al., 2017) and 871 (orange filled circles). The lines show the relationship between ΔFCO_2 and pH for the simplified formalism (see method) $\Delta FCO_2 = -12.3\Delta pH$ (black dashed line), and when driven by changes in DIC only (blue, $\Delta F/\Delta pH = -16$ W/m^2), $CaCO_3$ (yellow, $\Delta F/\Delta pH = -11.1$ W/m^2) and temperature T (red, $\Delta F/\Delta pH = -14.1$ W/m^2). The York regressed line (black line and grey shade) falls close to the DIC-driven line (blue). between the theoretical only pH driven line (black) and CaCO$_3$ line (yellow).

4 **Discussion.**

4.1 Cyclicity in foraminifera preservation.

Percentage fragments and sand fraction ($> 63\mu m$) at both studied core sites are anticorrelated and show a clear cyclicity, with better preservation of carbonates during glacial periods (Figure 2). The anticorrelation is clearer at ODP Site 871 where we have the longest record (Figure 2). Preservation in the Pacific (Farrell and Prell, 1989) show improved (poorer) preservation during glacial (interglacial) and this pattern seems to have originated after the mid Pleistocene transition (MPT) (Sexton and Barker, 2012). The origin of these cycles could be a combination of enhanced ventilation during glacials in the

525 Pacific (Sexton and Barker, 2012), or increased burial due to enhanced global alkalinity following a
526 decrease in burial in the Atlantic (Cartapanis et al., 2018). However glacial periods seem to have been
527 accompanied by a diminution in oxygenation in the deep Pacific (Anderson et al., 2019) that may have
528 also impacted preservation.

530 ~~Sexton and Barker (2012) suggest that this Pacific Ocean pattern of preservation (Farrell and Prell,~~
531 ~~1989) initiated after the mid Pleistocene transition (MPT) around 1 Ma, and that preservation cycles in~~
532 ~~the Pacific prior to MPT showed a more "Atlantic style" of dissolution with better (poorer) preservation~~
533 ~~occurring during interglacials (glacials).~~
534 ~~Several data sets (deep oxygen and carbon isotopes, carbonate ion data, and sortable silt) point towards~~
535 ~~a strengthening of ventilated deep Pacific waters (lower circumpolar deep water LCDW) that lead to~~
536 ~~the better preservation during glacials in the Pacific after the MPT (Sexton and Barker, 2012).~~

538 The observation that the fragmentation records of sites 999 and 871 covary is likely attributable to the
539 different water masses that fill the Caribbean basin relative to the rest of the Atlantic basin. During
540 glacials, the deep Atlantic is filled by nutrient- and carbon-rich corrosive southern sourced waters
541 (Antarctic Bottom Water, ~~AABW~~) with a reduced contribution from the less corrosive, nutrient-poor
542 North Atlantic Deep Water ~~(NADW)~~ (Oppo and Lehman, 1993) causing calcareous sediments in the
543 deep Atlantic Ocean >2500 m to be less well-preserved during glacials than interglacials. The opposite
544 pattern of dissolution is seen in the Caribbean because shoaling of the northern sourced waters during
545 glacials produces a mid-depth well-ventilated water mass that feeds into the Caribbean through its
546 deepest sill (~1900 m, Johns et al., 2002). Thus the deep Caribbean is filled with less corrosive waters
547 during glacials than interglacials improving the preservation of carbonate during glacials in a similar
548 pattern to a Pacific styled dissolution cycle albeit in response to Atlantic circulation changes. During
549 interglacials, the Northern sourced waters are mixed with corrosive southern sourced waters (Antarctic
550 Intermediate Waters and upper circumpolar deep waters) leading to less well-preserved sediments.

4.2 Causes of offset between $\delta^{11}B$ –derived and ice core CO_2.

552 The $\delta^{11}B$-derived CO_2 record from both of our study sites is in very good agreement with the ice core
553 record, with an average offset for combined both cores of 13±46 (2σ) ppm ~~4.6 ±49 (2σ) ppm~~ and
554 corresponding RMSE of ~~24.7~~ 26 ppm. ~~The CO₂ offset calculated with Mg/Ca SST corrected for pH is~~
555 ~~shown in Figure S8 for comparison and the average is -4.8 ±42 (2σ) ppm, showing a reduced offset of~~
556 ~~9 ppm compared to treatment with no pH correction on SST (a difference of -11 ±14 (2σ) and -8 ±12~~
557 ~~(2σ) ppm at ODP site 871 and 999, respectively). This difference is due to the pH correction lowering~~
558 ~~the SST estimates on average without greatly changing the temporal structure of pH and CO₂ offsets.~~
559 ~~In both treatments, the RMSE is smaller than the average CO₂ uncertainty of ±48 ppm (2σ, 95%~~
560 ~~confidence) for each datapoint.~~ However, the minor CO_2 offsets observed in both records do not appear
561 to be random and tend to fall during the first half of each glacial cycle (Figure S4 ~~S2~~). In order to have
562 the highest confidence in CO_2 reconstructions using $\delta^{11}B$, this pattern warrants further investigation
563 (see below). ~~We only discuss the CO₂ records calculated without a pH correction on SST.~~

4.2.1 Comparison between morphotypes of G. ruber

567 If as others suggested (e.g. Wang et al., 2000; Steinke et al., 2005; Numberger et al., 2009) *G. ruber sl*
568 and *G. ruber ss* occupied different depth habitats, then inadvertent sampling of the cryptic *G. ruber sl*
569 morphotype might conceivably produce the biases we observe between $\delta^{11}B$-derived CO_2 and
570 atmospheric CO_2 from the ice cores. However, while our Mg/Ca-derived temperatures for *G. ruber sl*
571 and *G. ruber ss* display variable offsets, they are within uncertainty (Figure 2) and our $\delta^{18}O$ and $\delta^{13}C$
572 data for the two morphotypes at ODP 871 show a good agreement with no consistent differences (Figure
573 S5 ~~S4~~). Thus, while the water column profile of $\delta^{18}O$ and $\delta^{13}C$ can be affected by factors other than

574 temperature, salinity and biological productivity (e.g, carbonate ion effect, Spero et al., 1997), overall,
575 our data suggest that the two morphotypes we analysed shared similar depth habitat preferences. ~

576 Henehan et al. (2013) found that *G. ruber ss* and *sl* record similar $\delta^{11}B$ in core-top sediments, and
577 through necessity, used mixed morphotypes in their culture study. The $\delta^{11}B$-derived pH and CO_2 for *G.*
578 *ruber sl* examined here are consistently higher and lower, than *G. ruber ss* by around +0.02 ~~0.05~~ pH
579 units and -22 ~~15~~ ppm CO_2~~,~~ on average, respectively (Figure 3). This is contrary to expectation if *G.*
580 *ruber sl* lived in deeper more acidic waters as suggested by other studies (Wang et al., 2000; Steinke et
581 al., 2005), but consistent with some data sets that show that the habitat of *G. ruber ss* and *sl* can vary
582 by location and seems to be dependent on local productivity (Numberger et al., 2009). Other data sets
583 from the Atlantic and Indian ocean nevertheless show similar Mg/Ca between both morphotypes (Gray
584 et al., 2018). We acknowledge that the scarcity of *G. ruber sl* in our samples means that our data set for
585 this morphotype is too small to draw firm conclusions and this warrants further investigation at other
586 study sites. Nonetheless, the closeness of the morphotypes in terms of $\delta^{11}B$ and depth habitat throughout
587 our record implies any inadvertent sampling of *G. ruber sl* in the *G. ruber ss* fraction in this study and
588 location would not significantly bias our reconstructions.

589   *4.2.2   Change in upwelling and CO₂ disequilibrium.*

590 ODP sites 871 and 999 are both located today in stratified oligotrophic environments with a deep
591 modern thermocline (base of the thermocline is at ~ 200 and 400 m at ODP 871 and 999, respectively;
592 Olsen et al., 2016). It should be noted, however, that both sites are situated relatively close to regions
593 displaying ΔpCO_2 >40 ppm (Figure 1). However, if local upwelling occurred over the study interval,
594 or if these areas of upwelled water expanded, we would expect these periods to be characterised by
595 relatively low SST, high surface $\delta^{18}O$, and low surface $\delta^{13}C$ due to an increased influence of deep
596 colder and more remineralised waters. The identified anomalous intervals in residual CO_2 at ODP 871
597 (e.g at ~210, ~290 ky, Figure 5) show no particular anomaly in planktonic C and O isotopes (Figure
598 S5 ~~S4~~) or in SST (Figure 2, Figure S8 ~~S9~~), ruling out significant variations in upwelling at that site.
599 The Mg/Ca-derived SST record of nearby Site MD97-2140 (Figure S8) from the Western Pacific
600 warm pool (de Garidel-Thoron et al., 2005) a location outside of the upwelling from the Pacific cold
601 tongue, confirms this view in that the periods of high CO_2 offset at Site 871 are not associated with
602 relatively cold periods at site MD97-2140. Equally, no SST anomaly was identified at ODP 999 to be
603 coincident with the intervals of high residual CO_2 ~~(Figure S9)~~. Foster and Sexton (2014) have also
604 reconstructed CO_2 zonally across the equatorial Atlantic and the Caribbean and showed that while
605 enhanced disequilibrium was detected in the eastern Atlantic, for the last 30 ky at least, Site 999 has
606 remained in equilibrium with the atmosphere. This suggests the CO_2 anomalies revealed in Figure 5
607 are not the result of enhanced local disequilibrium via sub-surface water mixing. Whilst SST is a first
608 order constraint on upwelling, we acknowledge future constrains are needed using paired proxies of
609 local CO_2, temperature and productivity to evaluate changes in local CO_2 fluxes.

610

611   *4.2.3   Partial dissolution.*

612 The CO_2 derived from *G. ruber* $\delta^{11}B$ at ODP 999 and 871 appears to show, at first order at least, positive
613 CO_2 offset during periods of high fragmentation (~100, ~210, ~400ky, red filled circles in Figure 5,
614 defined by the upper 25% quantile of fragments) following a "Pacific style" dissolution cycle (better
615 preservation and lower fragmentation during glacial periods). Periods of high fragmentation at ODP
616 S~~s~~ite 999 and 871 ~~both (incidentally)~~ correspond to a positive CO_2 offset 65 and 75% of the time
617 respectively, and 35 and 25% ~~25%~~ of the time to a negative or no (i.e. ±10 ppm) CO_2 offset, (note that
618 values ±10 ppm ~~close to 0~~ were omitted in the criteria for positive or negative offset~~this calculation~~).
619 We also note that almost all CO_2 offsets uncertainty (2σ) overlap with the 0 line, hence the percentage
620 of CO_2 offset that are above or below the 0 line should be interpreted with caution.
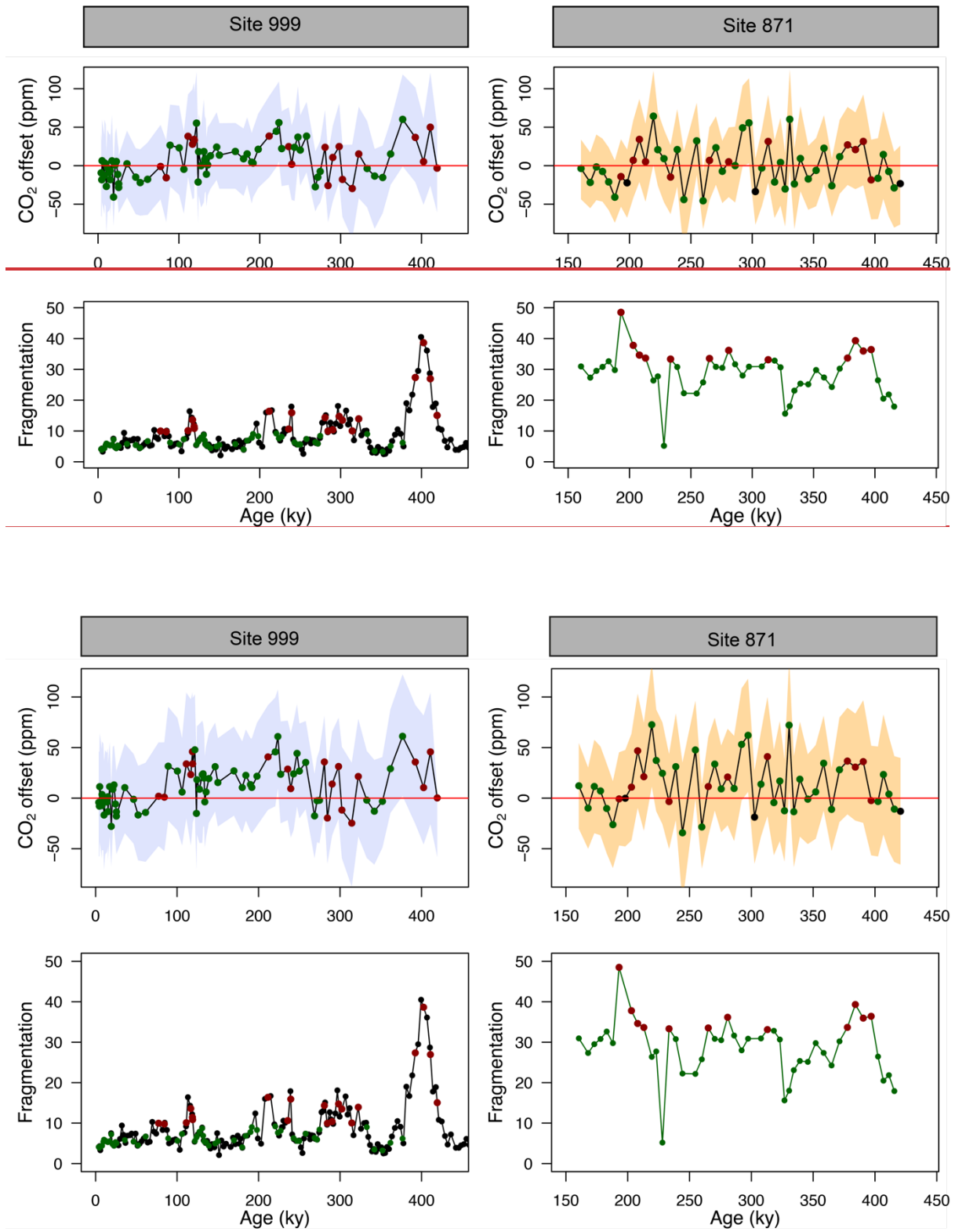
Figure 5. Top panels: CO$_2$ offset (defined as offset = CO$_{2\_\delta11B\text{-derived}}$ − CO$_{2\_ice}$) for ODP Sites 999 (this study and Chalk et al., 2017) and 871. See text for error bars calculations. Bottom panels: fragmentation index at Site 999 (Schmidt et al., 2006) and 871 (this study). Red dots in the lower panels are the fragments above the upper quartile (and corresponding CO$_2$ in the upper panel, red dots). Green dots represent periods of low fragments below the upper quartile (and corresponding CO$_2$ in the upper panel, green dots).

635 In detail however, a cross-plot of fragment counts and CO_2 offset (Supplementary Figure~~S9~~ S10) fitted
636 with a linear regression shows no significant correlation for both core site 999 (r^2=0.06~~0.07~~, p=0.03
637 ~~0.02~~) and 871 (r^2=0.002 ~~0.01~~, p=0.77 ~~0.62~~). Although it should be noted that this simple linear
638 regression presupposes a linear relationship between the variables and does not account for the
639 significant uncertainty in both CO_2 offset and fragmentation index. In particular, the CO_2 offset carries
640 the uncertainty from the interpolated ice core CO_2 (see methods). Fragment counts at ODP 999 also
641 come with the additional uncertainty related to the interpolation of the record of Schmidt et al. (2006),
642 whereas fragments counts and $\delta^{11}B$-derived CO_2 at 871 are measured on the same samples. A cross-
643 correlation function also shows no correlation between CO_2 offset and fragmentation (Figure S10 ~~S11~~).

644 While it seems unlikely the small offsets observed are fully explained by partial dissolution, the positive
645 CO_2 offsets observed during some periods of high fragmentation index (Figure 5), are in line with trends
646 observed in other species like *T. sacculifer* (sacc). For instance field studies observed lower $\delta^{11}B$ in *T.
647 sacculifer* for core-top samples from deeper ocean sites bathed by waters with low calcite saturation
648 state (Hönisch and Hemming, 2004, Seki et al., 2010). Tests of *T. sacculifer* can contain a significant
649 proportion of gametogenic calcite (ranging 30 to 75% of the weight of pregametogenic calcite , Bé,
650 1980; Caron et al 1990) which forms at the end of the life cycle in deeper lower pH cold waters. It has
651 been suggested that $\delta^{11}B$ is lower in gametogenic calcite than in the primary test (Ni et al., 2007)
652 reflecting the digestion and expulsion of symbionts (Bé et al., 1983) before gametogenesis, driving a
653 relative acidification of the micro-environment (no CO_2 uptake by photosynthesis) around the
654 foraminifera (Zeebe et al. 2003; Hönisch et al,. 2003; Henehan et al. 2016), and movement to deeper
655 more acidic waters during that life-stage. It has been shown that this gametogenic calcite is more
656 resistant to dissolution (Hemleben et al., 1989; Wycech et al., 2018) resulting in partial dissolution
657 acting preferentially on ontogenic calcite, and driving $\delta^{11}B$ in the residual test to lower isotopic
658 composition.

659 However, while the decrease in $\delta^{11}B$ in tests of *T. sacculifer* found in corrosive waters is well explained
660 by the lighter isotopic composition of gametogenic calcite, *G. ruber* tests do not contain such
661 gametogenic calcite (Caron et al., 1990). Hence, if the observed occasional decrease in $\delta^{11}B$ (low pH,
662 high CO_2) was caused by partial dissolution, it needs to be explained by other processes. It should also
663 be considered that alternative measures and proxies of dissolution (e.g. benthic B/Ca as an indicator of
664 bottom water carbonate ion concentration) may yield more quantitative constraints on the importance
665 of dissolution in generating our observed CO_2 offsets. Some studies have shown that laboratory
666 dissolved specimens of *T. sacculifer* (Sadekov et al., 2010) and naturally dissolved specimens of *G.
667 ruber* (Iwasaki et al., 2019) undergo targeted partial preferential dissolution of the shell. However,
668 variations in intra-shell $\delta^{11}B$ are currently unknown due to limitations in laser ablation techniques that
669 currently impede a direct evaluation of $\delta^{11}B$ heterogeneity in foraminifera chambers. Future studies are
670 needed to constrain the $\delta^{11}B$ spatial distribution in foraminiferal shells caused by potential variations in
671 $\delta^{11}B$ from dissolution, ontogeny (e.g. Meilland et al., 2021) and/or vital effects (e.g. change in
672 photosymbiotic activity throughout the life cycle, Lombard et al., 2009, Henehan et al., 2013, Takagi
673 et al., 2019). In the absence of these constraints, we conclude that partial dissolution is unlikely to be a
674 significant driver of the $\delta^{11}B$-CO_2 records we present here. Even though it was thought to be a species
675 susceptible to dissolution (Berger, 1970), we confirm that the $\delta^{11}B$ of *G. ruber* appears more resistant
676 to dissolution-driven modification than *T. sacculifer*.

677

678   *4.2.4. Effect of dissolution on Mg/Ca and calculated CO_2.*

679 The direction of change of Mg/Ca with partial dissolution is towards lower ratios in partially dissolved
680 foraminifera (e.g. Brown and Elderfield, 1996; Dekens et al., 2002; Fehrenbacher and Martin, 2014). If
681 the Mg/Ca is impacted during periods of high fragmentation, the lower ratio would result in lower
682 temperatures leading to lower calculated CO_2 values (equation 7). This effect is opposite to the
683 occasional positive deviation of CO_2 observed during intervals of high fragmentation at ODP Site 999.

684   While the weak correlation between fragmentation and CO_2 precludes a firm interpretation of
685   dissolution effect, we conclude that the effect of partial dissolution on Mg/Ca ratio and resulting CO_2
686   (if any) ~~is~~ are negligeable and not responsible for the CO_2 offsets observed during intervals of high
687   fragmentation.

688

689   *4.2.5.   Change in the second carbonate parameter, alkalinity.*

690   Past changes in TA are poorly constrained, although some constraints are starting to emerge for the late
691   Quaternary (e.g. Cartapanis et al., 2018). However, since pH is directly determined by $\delta^{11}B$, pH defines
692   the ratio of alkalinity to DIC (see supplementary information S11 ~~S12~~). Hence, at any given pH, any
693   change in alkalinity must be counteracted by a change in DIC, which has the opposing effect on CO_2.
694   This is demonstrated by the tight relation between pH and CO_2 highlighted by our data (Figure 4). The
695   largest residual CO_2 is ~50 ppm at ODP 999. To produce an effective alkalinity-driven change in CO_2
696   of this magnitude at a given pH requires an alkalinity reduction of about ~300 to 500 μmol/mol
697   (supplementary Figure S12 ~~S13~~). This is far larger than any expected change over a glacial cycle
698   (Cartapanis et al., 2018, Hönisch et al., 2009). We therefore rule out varying TA as the cause of the
699   minor CO_2 offsets observed (Figure 5).

700   *4.2.6   Improving the $\delta^{11}B$ -pH G. ruber calibration*

701   A further potential cause for the minor offsets observed between $\delta^{11}B$-derived and ice core CO_2 could
702   be a small inaccuracy in the calibration between $\delta^{11}B$ of foraminifera and borate for *G. ruber* (Henehan
703   et al., 2013). Having the ice core data to compare with $\delta^{11}B$-derived CO_2 offers an opportunity to explore
704   the effect of altering the input variables of the pH-CO_2 calculation to see if doing so improves the fit to
705   ice-core values. Note that such an exercise is for illustrative purposes only because we seek to retain
706   the independence offered by the $\delta^{11}B$-calibrated data in the context of CO_2 forcing (section 4.3).
707   Nonetheless, in future work we suggest this calibration can be applied in tandem to the empirical
708   relationship of Henehan et al. (2013). The published (Henehan et al., 2013) and obtained optimised
709   calibration (Figure S13 ~~S14~~) are:

710                $$\delta^{11}B_{borate} = \frac{\delta^{11}B_{foram} - 8.87(\pm 1.52)}{0.60(\pm 0.09)}$$ (Henehan et al., 2013)

711   ~~$$\delta^{11}B_{borate} = \frac{\delta^{11}B_{foram} - 6.46}{0.72}$$~~   ~~(optimised calibration)~~

712          $$\delta^{11}B_{borate} = \frac{\delta^{11}B_{foram} - 6.49}{0.71}$$ (optimised calibration)

713

714   The newly calculated CO_2 with the updated calibration shows an improved average CO_2 offset (Figure
715   6) of -4 ± 36 (2σ) ~~-3.43 ± 41 (2σ)~~ ppm (vs 13±46 (2σ) ppm ~~4.6 ± 49 (2σ) ppm~~ with the calibration of
716   Henehan et al., 2013) and an RMSE of 18 ppm ~~20.68 ppm~~ (vs. 26 ~~25~~ ppm with the published
717   calibration).

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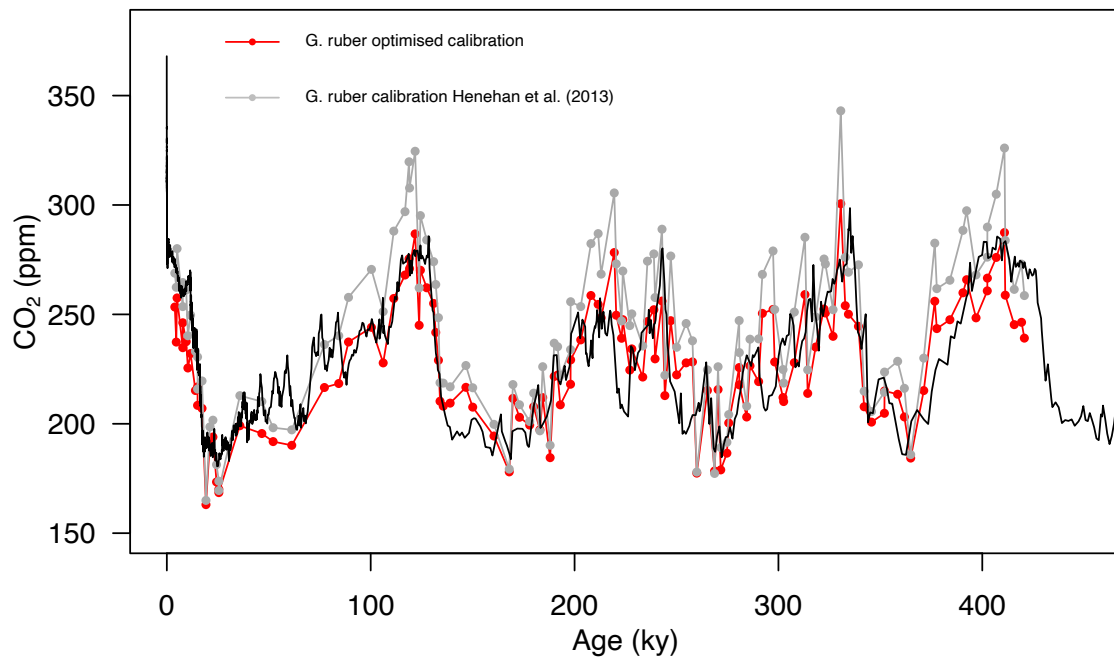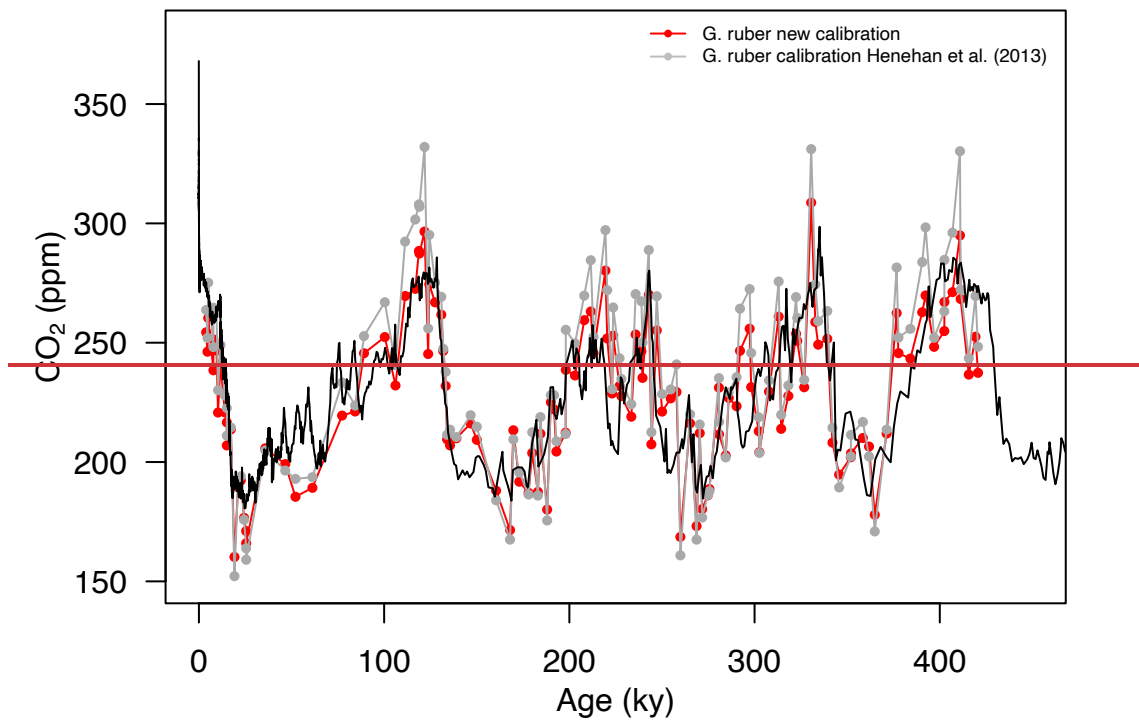
725 Figure 6. ~~–~~Composite $\delta^{11}B$-derived CO_2 from both core sites 999 and 871 using the published $\delta^{11}B_{borate-foram}$
726 calibration (grey points, Henehan et al., 2013) and the optimised ~~improved~~ calibration (red points). The black line
727 is the Antarctic composite ice core CO_2 record (Bereiter et al., 2015).

728 When analysing the CO_2 offset using the optimised *G. ruber* calibration and the fragmentation index
729 at each core location (same approach as Figure 5), we observe that intervals of high fragments
730 (defined as values above the upper quartile) are no longer preferentially associated with positive CO_2
731 offset (Figure S14 ~~15~~). ~~Intervals of high fragments at site 999 have 50% chance of corresponding CO_2~~
732 ~~with positive offsets to the ice core (and 50% with negative offset to the ice core). Intervals of high~~
733 ~~fragments at site 871 have 56% of corresponding CO_2 with a positive offset to the ice core (and 44%~~
734 ~~with a negative offset to the ice core).~~ Intervals of high fragments occur 5% and 33% of the time, at
735 Sites 999 and 871, respectively, during positive CO_2 offsets (and 95 and 67% of the time during
736 negative or no offset to the ice cores).

737 This analysis shows that a small change in the borate *G. ruber* $\delta^{11}B$ calibration is enough to improve
738 the fit to the ice core and diminishes the apparent correlation between high fragmentation and
739 CO_2 offset ~~does not cause any visual correlation between CO_2 offset and fragmentation index~~ (Figure
740 S14 ~~S15~~), and that uncertainty in the $\delta^{11}B_{foram-borate}$ calibration of Henehan et al. (2013) can – at least
741 partly – explain the minor discrepancies we observe between $\delta^{11}B$-derived and ice core CO_2.

4.3 Relative CO_2 forcing and pH.

743 Our new pH data, added to the existing compilation, show a good agreement with the formalism
744 defined by Hain et al. (2018; Figure 4). It should be noted that CO_2 in this case is provided by the ice
745 core directly and is not estimated from the $\delta^{11}B$-derived pH. As discussed above, because these two
746 proxies are independent of one another, the slope of their relationship may be used to interrogate the
747 mechanisms of CO_2 change. Our data fall between the $CaCO_3$ (yellow plain line) and the DIC (dotted-
748 dashed blue line) end-members suggesting that the CO_2 change observed on glacial-interglacial
749 timescales was driven by a mix of mechanisms rather than to a single cause. This is in line with
750 studies that require a number of mechanisms to explain glacial interglacials CO_2 change such as the
751 ~~(~~soft tissue pump, carbonate compensation pump, ~~and~~ solubility ~~thermal~~ pump~~,~~ (e.g. Brovkin et al.,
752 2007, Kohfeld and Ridgwell, 2009, Hain et al., 2010, Chalk et al., 2019, Sigman et al., 2021), and the
753 disequilibrium pump (Eggleston and Galbraith, 2018) . We note that this is a preliminary
754 interpretation because of the sensitivity of our finding to pH uncertainty (section 3.4~~5~~, Figure S7). To
755 overcome this ambiguity in estimating past ΔFCO_2 and to better deconvolve the driving mechanisms
756 of glacial/interglacial CO_2 change, we recommend that future studies collect pH data at higher
757 temporal resolution to examine the change in slope through a glacial cycle and strive to further
758 quantify and reduce uncertainties related to pH determination.

759 The close agreement of the pH and ice core CO_2 data with the theoretical relationships has a number of
760 consequences for the reconstruction of CO_2 change during periods of Earth history beyond the ice core
761 CO_2 and climate records where constrains on $\delta^{11}B_{sw}$ and the second carbonate parameter and
762 temperature are uncertain. The ΔpH formalism still requires an estimation of $\delta^{11}B_{sw}$ and temperature
763 (for the pK_B term, equation 5) however, as discussed in Hain et al. (2018), while absolute reconstruction
764 of pH is significantly influenced by estimates of $\delta^{11}B_{sw}$ and temperature, reconstruction of relative pH
765 change (ΔpH) is inherently much less sensitive to these input variables.

766 Reconstructing ΔFCO_2 from ΔpH is ideally applicable only on relatively short timescales less than 1
767 Myrs, when $\delta^{11}B_{sw}$ ~~–~~is likely to be invariant ~~constant~~ given the multi-million year residence time of
768 boron in the ocean (Lemarchand et al., 2000, Greenop et al., 2017). Furthermore, to reconstruct ΔFCO_2
769 (and thus climate sensitivity to CO_2), the formalism can be applied as long as, in equation 2, ΔpH
770 remains the overwhelming control. This is dependent on the residence time of carbon in the ocean with

771 respect to silicate weathering – approximately one million years (Hain et al., 2018) such that net carbon
772 addition to or removal from the Earth System through volcanic outgassing or silicate weathering is
773 likely to be minor over the million-year timescale. However, during some short events, such as for
774 instance the Palaeocene-Eocene Thermal Maximum, considerable carbon was added to the system in
775 <200 kyr (e.g. Gutjahr et al., 2017) invalidating the formulation described in equation 2 on these
776 intervals. We also emphasize that this formalism is only valid as long as core sites remain in equilibrium
777 with the atmosphere.

778 **4.4 Caveats and future studies.**

779 The aim of this study is to evaluate the capacity of the δ^{11}B-pH proxy in *G. ruber* to accurately
780 reconstruct atmospheric CO_2 in the past. The overall agreement with the high confidence ice core CO_2
781 (e.g. Bereiter et al., 2015) is very promising and gives confidence to δ^{11}B-derived CO_2 reconstructions
782 beyond the ice core record (>800 ky). We have however identified occasional, minor offsets between
783 the two records and explored potential drivers (partial dissolution, δ^{11}B borate-foram calibration, local
784 air-sea disequilibrium). It is likely that the minor disagreement observed (Figure 5) has a combination
785 of drivers and that a single mechanism is not solely responsible for the CO_2 offsets observed. To confirm
786 these trends, we recommend future work to focus on the following:

787 (1) The improved δ^{11}B calibration approach should be tested at more core locations. We note that the
788 improved calibration to the ice core records reported here was achieved using data from two sites. While
789 care is taken in the choice of study site to minimize air-sea CO_2 disequilibrium and sediment dissolution,
790 the newly defined improved δ^{11}B$_{borate-foram}$ calibration should be seen as an exercise that is tailored to the
791 available data in this study, and future high-resolution studies can apply the method used here (section
792 4.2.6 4.5) to further test how the *G. ruber* calibration changes if CO_2 offsets occur in a similar fashion
793 (i.e at a particular time in each glacial cycles). We note the importance of high resolution (at least 3 ky)
794 sampling in future studies because most CO_2 offsets observed are short lived.

795 (2) A multiproxy approach is ideally needed. In particular, reliable indicators of temperature and
796 productivity, to assess change in upwelling and foraminifera ecology. We encourage future studies to
797 expand high resolution boron-derived CO_2 record and ancillary data (C and O isotopes, proxy of
798 carbonate preservation and bottom water corrosiveness, biological productivity) to further constrain the
799 capacity of the boron isotope pH/CO_2 proxy to generate reliable CO_2 records. As more recent IODP
800 expeditions include porewater data, constraints on bottom water conditions and degree of corrosiveness
801 at a given site will become available to evaluate the impact on δ^{11}B signals in foraminifera.

802 (3) Efforts should continue to decrease the analytical uncertainty associated with a δ^{11}B measurement
803 by MC-ICPMS because this still accounts for ~40% of the total uncertainty associated with each δ^{11}B-
804 derived CO_2 estimate.

805 (4) We find little evidence to suggest that partial dissolution of foraminiferal tests (*G. ruber*) is a major
806 driver of uncertainty in δ^{11}B–derived CO_2 estimates but ~~more~~ well constrained ~~thorough~~ dissolution
807 experiments are desirable because of site-to-site differences in foraminifera taphonomy.

809 **5. Conclusion.**

810 We carried out the most thorough test to date of the δ^{11}B–pH (CO_2) proxy by comparing new high-
811 resolution (3 to 6 ky per sample) boron isotope–based pH and CO_2 at two locations with CO_2 from the
812 ice core record. Results suggest that the boron isotope proxy is robust and suited to reconstructing CO_2
813 to a precision of ±46 48 ppm (2σ, RMSE =26 25ppm) over this interval, with little or no systematic
814 bias shown by a mean residual of 13±46 (2σ) ppm 4.6 ± 49 (2σ) ppm. This provides high confidence
815 to the application of the proxy beyond the reach of the ice core records.

816 Despite the overall good agreement, there are some minor short-lived CO_2 offsets that appear to have
817 some temporal structure and we explored a number of possible drivers. A visual correlation between
818 CO_2 offset and fragmentation index at core site 999 is observed (Figure 5) but is not statistically
819 significant. The effect of partial dissolution on $\delta^{11}B$ in *G. ruber* appears to be negligeable in our record,
820 but the possible heterogeneity of $\delta^{11}B$ within shells as well as variable susceptibly to dissolution of the
821 different parts of the foraminifera, encourage~~s~~ further exploration.

822 A~~n~~ revised $\delta^{11}B$ borate–foram calibration was calculated by minimising the offset between $\delta^{11}B-$
823 derived CO_2 and ice core CO_2 using published calibration (Henehan et al., 2013). While the new
824 calibration improves the fit to the ice core records, we caution against its use to estimate CO_2 given that
825 it is no longer independent of the ice core or the assumptions we make here to calculate CO_2 (i.e. that
826 TA is constant).

827 The formalism established by Hain et al. (2018) is robust, showing that relative CO_2 forcing in the past
828 can be determined from pH change alone, even in the face of significant uncertainty in $\delta^{11}B$ of seawater
829 and without the need to determine a second carbonate parameter. This will not only be of great interest
830 to determine CO_2 forcing in ancient geological times where $\delta^{11}B-$ of seawater and a second carbonate
831 parameter are poorly constrained, but the nature of the observed relationship over the last 400 kyr
832 confirms that multiple drivers are likely responsible for glacial-interglacial CO_2 change.

833 **6. Data availability.**
834 All raw data are ~~will be~~ provided as supplementary information.~~ once the manuscript is accepted.~~
835

836 **7. Author contribution.**
837 E.d.l.V generated boron isotope and elemental data and wrote the manuscript. E.d.l.V, T.B.C, M.P.H
838 and G.L.F analysed the data. G.L.F, T.B.C, M.P.H and P.A.W contributed to the editing and
839 reviewing of the manuscript. M.W, R.G and D.C generated oxygen and carbon isotope data and
840 fragmentation index data. R.G and D.C were supervised by T.B.C and G.L.F. C.L assisted with
841 foraminifera picking and boron isotope analysis. E.d.l.V, T.B.C and G.L.F designed the research.
842
843 **8. Competing interest.**
844 The authors declare they have no conflict of interest.
845
846 **9. Acknowledgment.**
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852
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854 **10. References.**
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