1   **Varied contribution of the Southern Ocean to deglacial atmospheric CO$_2$ rise**

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Glacial-interglacial changes in atmospheric CO_2 are generally attributed to changes in seawater carbon chemistry in response to large-scale shifts in the ocean's biogeochemistry and general circulation. The Southern Ocean currently takes-up more CO_2 than any other and it is likely to have played a crucial role in regulating past atmospheric CO_2. However, the physical, biological and chemical variables that control ocean-atmosphere CO_2 exchange during glacial-interglacial cycles are not completely understood. Here we use boron isotopes and carbon isotopes in planktonic foraminifera, and an alkenone-based proxy of temperature, to reconstruct seawater pH and CO_2 partial pressure in sub-Antarctic surface waters south of Tasmania over the past 25,000 years, and investigate the mechanisms regulating seawater CO_2. The new record shows that surface waters in this region were a sink for atmospheric CO_2 during the Last Glacial Maximum. Our reconstruction suggests changes in the strength of the biological pump and the release of deep-ocean CO_2 to surface waters contributed to the last deglacial rise in atmospheric CO_2. These findings demonstrate that variations in upwelling intensity and the distribution of Southern Ocean water masses in this sector played a key role in regulating atmospheric CO_2 during the last glacial-interglacial cycle.

Atmospheric CO_2 concentrations range from minima of ~180 ppmv during glacial intervals to maxima of ~280-300 ppmv during interglacial intervals[1]. The ocean is the largest active carbon reservoir; hence, changes in ocean-atmosphere interactions, ocean circulation and marine biogeochemistry likely played major roles in modulating glacial-interglacial (G-IG) atmospheric CO_2 variability[2-5]. Despite this understanding of the ocean's overall role in modulating atmospheric CO_2, information on the temporal and spatial evolution of ocean source-sink behaviour remains scarce. Determining the factors controlling ocean-atmosphere CO_2 dynamics requires an understanding of the physical and biological processes that affect

49   the state of CO_2 in ocean, and this is of key importance in validating the different

50   mechanisms used in geochemical models to explain G-IG variations in atmospheric CO_2 (e.g.

51   refs. [6-8]). Changes in these processes in the Southern Ocean are hypothesised to have been

52   crucial[8-17]. However, proxy histories of past G-IG changes in surface-ocean pCO$_2$ are limited

53   to one record for the Atlantic sector of the Southern Ocean[13] that only captures part of the G-

54   IG change in atmospheric CO_2. Our study focuses on the Indo-Pacific sector of the Southern

55   Ocean south of Australia and, for the first time, we present a Southern Ocean surface-ocean

56   carbonate chemistry reconstruction that allows the quantification of ocean-atmosphere CO_2

57   exchange accompanying the full G-IG rise in atmospheric CO_2.

58   We analysed $\delta^{18}O$, $\delta^{13}C$, $\delta^{11}B$, and shell weight for the planktonic foraminifer

59   *Globigerina bulloides,* and alkenone unsaturation ratios in sediment core MD972106

60   (45°09'S, 146°17'E, water depth 3310 m; see Methods) and used these proxies to reconstruct

61   surface water pH and CO_2 partial pressure (pCO$_2$) over the last 25 kyr (thousand years) in the

62   Southern Ocean region south of Tasmania. Long-term climatological studies[18] show that the

63   core site is positioned at the southern edge of the Sub-Tropical Front (STF), which marks the

64   northern boundary of the Southern Ocean and separates the Sub-Tropical Zone (STZ) and

65   Sub-Antarctic Zone (SAZ) surface waters (Fig. 1 and Supplementary Fig. 1). As a result, the

66   core site is located just north of the high nutrient, low chlorophyll (HNLC) area of the

67   Southern Ocean[20] and the seafloor there is bathed by Lower Circumpolar Deep Water. Sea-

68   surface temperature (SST) reconstructions for the Late Quaternary indicate that the STF

69   migrated north of its present position during glacial periods and was at its most northerly

70   position at the Last Glacial Maximum (LGM)[21]. Therefore, we infer that surface waters over

71   MD972106 during the LGM had SAZ properties.

72   **The glacial-interglacial proxy record**

73   Down-core variations in *G. bulloides* $\delta^{18}O$ exhibit a G-IG amplitude of ~2 ‰ (Fig. 2a). The

74   G-IG change in global ocean $\delta^{18}O$ is estimated to have been ~1.1 ‰ (ref. [22]), hence the ~2 ‰

75   shift in the *G. bulloides* $\delta^{18}O$ record includes a SST (and carbonate ion effect[23]) component,

76   which we account for here using alkenone derived SSTs. The *G. bulloides* average $\delta^{13}C$

77   values for the Holocene and LGM (~18 to 22 ka, thousand years ago) are similar, but the G-

78   IG transition displays $\delta^{13}C$ minima at ~12 ka and during the Holocene at ~7.4 ka (Fig. 2b).

79   *Globigerina bulloides* shell weights are heavier during glacial times (Fig. 2c). There is also a

80   clear difference in *G. bulloides* $\delta^{11}B$ values, with Holocene $\delta^{11}B$ about 2 ‰ lower than in the

81   LGM (Fig. 2d). Alkenone-based SST estimates show a G-IG change of ~4.1°C with a

82   minimum of 8.2°C at ~21.4 ka, followed by post-glacial warming to 13.9°C at ~11 ka and

83   cooling to ~13°C over the past ~6 kyr (Fig. 2e). The most recent samples (~2.6 to 2 ka) show

84   deviations in $\delta^{18}O$, shell weight and $\delta^{11}B$ compared to earlier Holocene values.

85   Down-core *G. bulloides* $\delta^{18}O$, $\delta^{11}B$ and shell weights co-vary with each other (Fig. 2)

86   and with atmospheric CO_2 over the last 25 kyr (Fig. 3b). This co-variation is interpreted here

87   to arise from G-IG evolution of surface water temperature and chemistry[23-28]. Because

88   MD972106 was recovered at a depth above and close to the modern calcite saturation horizon

89   (Supplementary Fig. 2), it is important to consider the possible effects of post-depositional

90   calcite dissolution on shell weights[27,29], particularly when considering G-IG lysocline

91   changes versus primary calcification driven by surface water carbonate ion concentration

92   ($[CO_3^{2-}]$). Holocene core-top *G. bulloides* shell weights indicate that the foraminiferal

93   lysocline at the South Tasman Rise is at ~3,600m water depth[30]. Carbonate preservation

94   indicators, percent calcium carbonate and percent whole foraminifera (Supplementary Fig. 3),

95   suggest that seafloor calcite dissolution did not play a significant role in changing shell

96   weights over the past 25 kyr at this site.

Reconstructing seawater pH and pCO_2

Past variations in sea-surface water pH at the MD972106 core-site are calculated from the δ^{11}B-pH relationship for *G. bulloides*[31] and from the alkenone SST record (see Methods). Estimated pH shows a decline from LGM values of ~8.38 to Holocene values of ~8.16 (Fig. 3a). By comparison, the modern anthropogenic-influenced surface water pH at the MD972106 site was 8.11 in 2001 CE (Supplementary Note 1). Variations in surface water pCO_2 (Fig. 3b) over the past 25 kyr can be estimated using the SST alkenone record, the δ^{11}B surface water pH record and estimates of either alkalinity or DIC (see Methods). There is close agreement between pCO_2 calculated using estimates of pH combined with either (1) estimates of alkalinity or (2) DIC (Fig. 3b). Methods (1) and (2) both use pH estimated from *G. bulloides* δ^{11}B, and hence any differences result from the assumptions underlying estimates of the alkalinity and DIC parameters. These calculations show surface water pCO_2 rose from ~165 ppmv at the LGM to ~280 ppmv in the early Holocene (Fig. 3b). The interval ~6.3 to 4.2 ka is marked by elevated pCO_2 of ~315 to 360 ppmv that decreases to ~270 ppmv at ~2 ka (Fig. 3b). The 2001 CE surface water pCO_2 at this site was ~330 ppmv, broadly consistent with the known anthropogenic rise in atmospheric CO_2 (Supplementary Note 1).

The difference between the estimated pCO_2 of the surface water and the atmosphere (ΔpCO_2) can be calculated by using ice core CO_2 data from Antarctica[1] (Fig. 3b). Estimated ΔpCO_2 (Fig. 3c, 5e) indicates that surface waters near MD972106 were a net sink for atmospheric CO_2 during the LGM (ΔpCO_2 = -25 ppmv) and during the G-IG transition until ~12 ka, when surface waters became a net source of CO_2 during the early Holocene (ΔpCO_2 = 15 ppmv). Between ~6.3 and 4.2 ka the surface waters were a strong net source for CO_2 (ΔpCO_2 ~50 to 90 ppmv), before returning to acting as a weak net sink (ΔpCO_2 ~ -6 ppmv) at

121   ~2 ka (Fig. 3c, 5e). In addition, past surface seawater $[CO_3^{2-}]$ calculated from estimates of

122   pH, SST and alkalinity (and DIC) show $[CO_3^{2-}]$ falling from ~265 µmol kg^{-1} in the LGM to

123   ~190 µmol kg^{-1} for most of the Holocene (Fig. 4a). The anthropogenically perturbed surface

124   water $[CO_3^{2-}]$ at this site is ~183 µmol kg^{-1} whereas the pre-industrial $[CO_3^{2-}]$ is estimated to

125   be ~212 µmol kg^{-1} (Supplementary Note 2), which is within the uncertainty of the most

126   recent Holocene $[CO_3^{2-}]$ (Fig. 4a).

127   The shell weight-$[CO_3^{2-}]$ relationship[26] was also applied to the MD972106 data to

128   reconstruct $[CO_3^{2-}]$ for surface waters over the past 25 kyr (Fig. 4b). The close agreement

129   between estimated surface water $[CO_3^{2-}]$ derived from these two independent proxies (*G.*

130   *bulloides* $\delta^{11}B$ values and shell weight) reinforces our findings that $\delta^{11}B$ of *G. bulloides*

131   yields reliable reconstructions of seawater pH.

132   **Southern Ocean contribution to atmospheric CO$_2$ change**

133   Our reconstruction is consistent with the hypothesis that the G-IG modulation of the Southern

134   Ocean carbon balance likely arose from changes in SST, biogeochemistry and ocean

135   circulation, specifically: 1) colder LGM seawater increased CO_2 solubility; 2) a stronger

136   'biological pump' during the LGM reduced the DIC in surface waters; and 3) surface water

137   pH and $[CO_3^{2-}]$ were higher during the LGM.

138   Two hypotheses involving the Southern Ocean have been offered to explain G-IG

139   cycles in atmospheric CO_2. The first invokes increased strength of the biological (or 'soft-

140   tissue') pump in the high-latitude Southern Ocean during the LGM[6,9] in response to an

141   increase in nutrient utilisation, possibly through iron fertilisation[32], in sub-Antarctic surface

142   waters. This is supported by studies indicating that export production in the area between the

143   STF and Polar Front were higher during the LGM than the Holocene[12,33-35]. The second

144   invokes decreased exchange between surface waters and the deep-ocean south of the Polar

145 Front[36-38]. The increased stratification reduces upwelling and exchange of nutrient and CO_2

146 rich deep-waters with the surface ocean. This is supported by increased nutrient utilisation as

147 shown by $\delta^{15}N$ records[36], reduced ventilation of the deep Southern Ocean[39], and subsequent

148 increase in ocean CO_2 storage[15,17] during the LGM. No single mechanism[40] can explain the

149 full glacial draw-down in atmospheric CO_2, although a combination of mechanisms has been

150 proposed[2,12,14].

Zonal asymmetry of deglacial change in the Southern Ocean

152 Our full deglacial SAZ pH and pCO_2 reconstruction can be compared to a reconstruction of

153 late deglacial pH and pCO_2 in the Atlantic-sector SAZ of the Southern Ocean[13] to provide

154 further insights into the sub-Antarctic role in CO_2 change. That reconstruction of surface

155 ocean pCO_2 for the Atlantic-sector SAZ, spanning ~16-2 ka and also utilising $\delta^{11}B$ and $\delta^{13}C$

156 of *G. bulloides*[13], was undertaken at a similar latitude to MD972106. That study, while not

157 spanning the full deglacial amplitude of CO_2 change, suggested surface waters in that sector

158 were in approximate equilibrium with the atmosphere at ~16 ka and became a strong net

159 source of CO_2 to the atmosphere (ΔpCO_2 of ~50 ppmv; Fig. 5e) by ~15 ka, before declining

160 intermittently to reach approximate atmospheric equilibrium at ~4 ka. This pattern was

161 interpreted to reflect enhanced upwelling of deep waters in the Atlantic sector of the SAZ

162 during the deglaciation.

163 At our site south of Tasmania, surface waters were a net sink for atmospheric CO_2

164 (ΔpCO_2 = -25 ppmv) during the LGM (Fig. 3c, 5e). The northward migration of the STF at

165 the LGM[21] resulted in an expansion of the Southern Ocean water masses, and coincided with

166 increased delivery of bioavailable dust-borne iron to the ocean[32]; both of these processes

167 would also lead to the expansion of the zone of high biological production in the Southern

168 Ocean. At the same time, the stratification of the deep Southern Ocean during the LGM

169   reduced the contribution of upwelling of dissolved CO_2 to surface waters. At the site of

170   MD972106, the $\delta^{13}C_{adj}$ for *G. bulloides* (adjusted for temperature and $[CO_3^{2-}]$ effects; see

171   Methods for details), and the $\delta^{13}C$ gradient between planktonic and benthic foraminifera

172   ($\Delta\delta^{13}C$ gradient), were largest during the LGM (Fig. 5a, c), indicating high primary

173   productivity[41]. Similarly, alkenone concentrations (Fig. 5d) were highest during the LGM

174   and provide qualitative information on past productivity of coccolithophorid algae[42].

175   Together, the alkenone concentrations (Fig. 5d) and ΔpCO_2 (Fig. 5e) show that CO_2

176   degassing was suppressed when there was maximum biological production in this region.

177   Our data suggests the biological pump was stronger during the LGM (i.e. the DIC gradient

178   between surface and deep ocean increased), possibly through iron fertilisation[32,43], and

179   steadily decreased over the last deglaciation. Changes in the strength of the biological pump

180   could also be related to changes in circulation[44], via a more isolated deep ocean, in particular

181   south of the Polar Front[36].

182   The $\delta^{13}C$ of *G. bulloides* in the Atlantic sector of the SAZ decreased by ~1.5 ‰ from

183   the LGM to the onset of maximum CO_2 degassing at ~11 ka (not shown)[13], while the

184   MD972106 site shows a smaller $\delta^{13}C$ decrease of ~0.3 ‰ (Fig. 2b) over the same period.

185   The inferred increase in upwelling in the Atlantic sector is not reflected in the reconstructed

186   ΔpCO_2 record at MD972106 (Fig. 3c, 5e). Instead, the surface waters at MD972106 during

187   the last deglaciation remained a net sink for CO_2 (average ΔpCO_2 = -25 ppmv; Fig. 3c, 5e).

188   The steadily decreasing $\delta^{13}C_{adj}$ (Fig. 5a) and $\Delta\delta^{13}C$ gradient (Fig. 5c) during the deglaciation

189   is consistent with a progressive increase in the contribution of upwelling and advection of

190   'old' CO_2-rich (and ^{13}C-depleted) Circumpolar Deep Water (CDW) to sub-Antarctic surface

191   waters. Nevertheless, surface waters remained a net sink for atmospheric CO_2 during this

192   period, suggesting that productivity (draw-down of CO_2) likely kept pace with any

193 augmented nutrient supply, and compensated for any increased CO_2 from upwelling in the

194 MD972106 region. Alkenone concentrations (a proxy for coccolithophorid algae primary

195 production, Fig. 5d) show enhanced biological productivity was maintained during this

196 interval. There is compelling evidence for a build-up of carbon in the deep Southern Ocean

197 towards the LGM[10,15,17], and subsequent release and ventilation[39] of this deep carbon store

198 during the last deglaciation, which is consistent with the rise in atmospheric CO_2 (refs. [15,17]).

199   The interval between ~6.3 and 4.2 ka, when surface waters at MD972106 were a net

200 source of CO_2 ($\Delta p CO_2$ of ~50 to 90 ppmv; Fig. 3c, 5e), coincides with a period of

201 strengthened Southern Hemisphere westerly winds (SWW) inferred from analysis of

202 terrestrial records[45,46]. Changes in the latitude and intensity of the SWW are potential drivers

203 of changes in atmospheric CO_2, as suggested by modelling[8] and opal burial rates[47], and is in

204 agreement with past changes in equatorial and Antarctic seawater carbon isotope variations[48].

205 Intensification of the SWW increases the contribution of upwelled CO_2-rich CDW (with low

206 $\delta^{13}C$) to surface waters within the Antarctic Zone. The $\delta^{13}C_{adj}$ of *G. bulloides* at MD972106

207 reaches a minimum at ~7.4 ka (Fig. 5a) and the $\Delta\delta^{13}C$ gradient falls below the Holocene

208 average gradient (Fig. 5c). Our data are thus consistent with the hypothesis that the net CO_2

209 source during this period resulted from increased upwelling of CO_2-rich CDW within the

210 Antarctic Zone that advected northward to SAZ surface waters by the strengthened

211 SWW[45,46].

212   The deviations in the most recent *G. bulloides* samples ($\delta^{18}O$, shell weight and $\delta^{11}B$;

213 Fig 2.) stand in contrast to earlier Holocene values, and reflect changing surface water CO_2

214 dynamics. Surface waters at ~2 ka were a weak CO_2 sink ($\Delta p CO_2$ = -6 ppmv) that likely

215 resulted from a changing balance between a stronger 'biological pump' and a corresponding

216 decrease in the contribution and/or intensity of upwelling and advection of CO_2-rich CDW.

217 The increasing $\delta^{13}C_{adj}$ and $\Delta\delta^{13}C$ gradient (Fig. 5a, c), and the corresponding increase in

218 alkenone concentrations (Fig. 5d) from ~4.1 to 2 ka, are indicative of increased primary

219 productivity, corresponding to a decrease in SWW strength from ~4 to 1 ka[45,46].

220   Our findings demonstrate the interplay and changing balance between removal of CO_2

221 by biological production in surface waters and CO_2 outgassing via circulation changes during

222 the last G-IG rise in atmospheric CO_2. The modern Southern Ocean shows considerable

223 zonal variability in annual and seasonal air-sea CO_2 flux[49], so such spatial heterogeneity in

224 past ocean-atmosphere CO_2 exchange is perhaps not surprising. This study provides

225 evidence that the CO_2 dynamics of Holocene surface waters in the Southern Ocean are

226 dependent on competing factors such as the ocean's biological pump and changes in the

227 location and intensity of the SWW. The evolving relationship between atmospheric

228 dynamics and carbon exchange is critically important for understanding the role of Southern

229 Hemisphere winds in modulating the uptake of anthropogenic CO_2 (refs. [50,51]).

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Author contributions

363   A.D.M. and W.R.H. designed the study with input from M.R.P. and J.B. The manuscript was

364   written by A.D.M., W.R.H., M.R.P. and J.B. with contributions from M.J.C., E.C., C.P.,

365   M.K.G., and T.B.C. Analysis and interpretation of the measurements was completed by

366   A.D.M., W.R.H., M.R.P., J.B., M.J.C., E.C., C.P., M.K.G., and T.B.C. All authors

367   contributed to improving the final manuscript.

Competing Interests

369   The authors declare no competing interests.

370   **Supplementary Information** is available for this paper at

371

Figure captions

373   **Figure 1. Location of sediment core MD972106 and modern positions of Southern**

374   **Ocean water masses and fronts**. MD972106 (blue dot) is located at 45°09'S, 146°17'E

375   (water depth 3310 m). STF, Sub-Tropical Front; SAF, Sub-Antarctic Front; PF, Polar Front;

376   SB, southern boundary of the Antarctic Circumpolar Current (ACC). Arrows indicate ACC

377   direction. Dashed red line shows WOCE SR3 repeat hydrographic transect between

378   Tasmania and Antarctica along ~140° E. Figure adapted after Trull *et al.*, (ref. [19]).

379
380   **Figure 2. δ^{18}O, δ^{13}C, shell weight and δ^{11}B for the planktonic foraminifer, *Globigerina***

381   ***bulloides*, and SST estimates from alkenones in sediment core MD972106.** Measured *G.*

382   *bulloides* **a**, δ^{18}O (green, with Y-axis reversed); **b**, δ^{13}C (red); **c**, shell weight (blue) and **d**,

383   δ^{11}B (purple). **e**, SST estimates from alkenone unsaturation ratios ($U_{37}^{K\prime}$) (orange). Age model

384   was constructed using calibrated ^{14}C ages (black triangles, Methods). Error bars represent 1σ

16

385   uncertainties for $\delta^{18}O$, $\delta^{13}C$, and shell weight, and 2σ uncertainties for $\delta^{11}B$ based on replicate

386   measurements (Methods).   Error bars on SSTs represent 2σ analytical uncertainties for

387   replicate measurements on a homogenous laboratory standard (Methods).

388

389   **Figure 3. Reconstructed surface water pH and pCO$_2$ at the MD972106 site and**

390   **atmospheric CO$_2$ over the past 25,000 years. a,** Surface water pH (red diamonds, with Y-

391   axis reversed). **b,** pCO$_2$ calculated from pH, alkenone SST and alkalinity (Method 1, solid

392   blue circles) and from pH, alkenone SST and DIC (Method 2, open blue circles); atmospheric

393   CO$_2$ record (Antarctic ice core CO$_2$ composite[1], green diamonds). **c,** ΔpCO$_2$ is the difference

394   between reconstructed surface water pCO$_2$ and atmospheric CO$_2$ (ref. [1]) (Method 1, solid

395   black squares; Method 2, open black squares).   Error bars in **a, b** and **c** represent 95%

396   confidence intervals around the Monte Carlo mean, where 2σ uncertainties on the individual

397   input variables and other carbonate system parameters are propagated via the Monte Carlo

398   simulation (n = 10,000) in the program R (Methods).

399

400   **Figure 4. Reconstructed surface water carbonate ion concentration. a,** [CO$_3^{2-}$] calculated

401   from $\delta^{11}B$-pH estimates, alkenone SST and alkalinity (Method 1; solid green circles) and

402   from $\delta^{11}B$-pH estimates, alkenone SST and DIC (Method 2; open green circles). **b,** [CO$_3^{2-}$]

403   calculated from shell weight data (blue squares) using the shell weight-[CO$_3^{2-}$] relationship[26].

404   Error bars in **a** represent 95% confidence intervals around the Monte Carlo mean, where 2σ

405   uncertainties on the individual input variables and other carbonate system parameters are

406   propagated via the Monte Carlo simulation (n = 10,000) in the program R (Methods).

407

408   **Figure 5. Planktonic and benthic foraminiferal $\delta^{13}C$, $\Delta\delta^{13}C$ gradient, alkenone**

409   **concentrations and ΔpCO$_2$ over the past 25,000 years. a,** $\delta^{13}C_{(adj)}$ for *G. bulloides* (red); **b,**

410   benthic $\delta^{13}C$ for *Cibicidoides spp.* (green); **c,** $\Delta\delta^{13}C$ gradient ($\delta^{13}C$ planktonic$_{(adj)}$ – $\delta^{13}C$

411   benthic foraminifera, blue); dashed line shows the average Holocene $\Delta\delta^{13}$C gradient; **d**,

412   alkenone concentrations (orange circles); **e,** ΔpCO$_2$ is the difference between surface water

413   pCO$_2$ and atmospheric CO$_2$ (ref. [1]) as in Figure **3c**. Also shown in **e** is the calculated ΔpCO$_2$

414   for the Atlantic sector SAZ[13] (sediment core PS2498-1 at 44.15°S, 14.23°E, 3,783m water

415   depth; grey open diamonds and error bars are the 95% uncertainty bounds). In **a**, δ^{13}C for *G.*

416   *bulloides* are temperature and [CO$_3^{2-}$] adjusted (Methods). Error bars in **a** and **b** represent 1σ

417   uncertainties based on replicate measurements; error bars in **d** represent 2σ for replicate

418   extractions and measurements on a homogenous laboratory standard, and error bars in **e**

419   represent 95% confidence intervals around the Monte Carlo mean, based on 2σ uncertainties

420   on the individual input variables and other carbonate system parameters are propagated via

421   the Monte Carlo simulation (n = 10,000) in the program R (Methods).

422

Methods

423   **Methods**

424   **Materials and methods.** Sediment core MD972106 (45°09'S, 146°17'E, water depth 3310

425   m) is a 32 m long piston core collected using the CALYPSO Kullenberg corer on board the

426   RV *Marion Dufresne* in 1997 (in this paper, we present data from the top 2.4m of the core)

427   and was recovered from the northern flank of the South Tasman Rise. The MD972106 site is

428   located at the southern edge of the Sub-Tropical Front (STF) (Fig. 1) and modern bottom

429   water covering the South Tasman Rise is Circumpolar Deep Water, a mixture of high δ^{13}C

430   (low nutrient) North Atlantic Deep Water (or northern source deep-water) and re-circulated

431   low δ^{13}C (high nutrient) deep-water from the Indian and Pacific Oceans (Supplementary Fig.

432   1).

433   MD972106 was sampled every 5 cm on board RV *Marion Dufresne*. Raw sediment

434   samples were oven dried at 60°C, and then disaggregated in distilled water at the ACE CRC,

435   University of Tasmania. Water saturated sediment samples were wet sieved through a >150

436   µm mesh. The dried >150 µm fraction was sieved to isolate the 300-355 µm fraction from

437   which ≥50 planktonic foraminifera (*Globigerina bulloides*) were picked. We selected *G.*

438   *bulloides* as this species shows a seasonal range in $\delta^{18}O$ values in this region of the Southern

439   Ocean that is consistent with calcification in near-surface waters[52], and comparisons between

440   flux-weighted sediment trap and surface sediment $\delta^{18}O$ values indicate the sedimentary

441   record retains the seasonal isotopic imprint for *G. bulloides*[52].

442   Each batch of foraminifera was ultrasonically cleaned in methanol and oven dried at

443   60°C. Any broken tests were discarded. The cleaned samples were used to determine the

444   average shell weights and isotopic compositions ($\delta^{18}O$, $\delta^{13}C$ and $\delta^{11}B$), with the shells under-

445   going further cleaning prior to determination of their $\delta^{11}B$ values. Average shell weight, $\delta^{18}O$

446   and $\delta^{13}C$ measurements were conducted at 5 cm intervals. Determinations of $\delta^{11}B$ were

447   made at 20 cm resolution.

448   **Age model.** Age control for MD972106 is based on accelerator mass spectrometry (AMS)

449   radiocarbon (^{14}C) dating of the planktonic foraminifer, *Globorotalia inflata*. Five published

450   AMS ^{14}C dates for MD972106 (ref. [53]) were recalibrated to calendar ages using the Calib 7.1

451   program[54] with the Marine13 data set[55]. Ages were corrected for the local ^{14}C reservoir

452   correction (ΔR) for surface waters in this region of the Southern Ocean using a constant ΔR

453   regional mean value (ΔR = 107±13 yr) calculated for the Chatham Islands from the marine

454   reservoir correction database[56]. The ΔR (107±13 yr) incorporates the measured ^{14}C age of

455   560±40 yrBP obtained from gastropods[57]. Using a different and older ΔR for the ^{14}C dates at

456   16.1 ka and 23.5 ka would slightly change the chronology, but this would not affect the

457   conclusions of our study for the LGM and early deglacial periods. For example, using a ΔR

458   = 900 yr for the ^{14}C dates at 16.1 ka and 23.5 ka would change the chronology by ~0.8 - 0.9

459   kyr, and using a ΔR = 900 yr for the ^{14}C date at 16.1 ka and a ΔR = 1500 yr for ^{14}C date at

460   23.5 ka, would change the chronology by ~0.8 to 1.4 kyr. The average sedimentation rate at

461   MD972106 was ~9.3 cm kyr^{-1} over the past 25 kyr.

462   **Planktonic foraminifera shell weights.** *G. bulloides* shell weights were determined by

463   picking 50 or more whole individual shells from the 300-355µm size fraction. The cleaned

464   whole shells were counted and weighed on a microbalance (precision = 0.1 µg). The average

465   shell weights were calculated by dividing the measured weight by the total number of whole

466   foraminifera. Replicate shell-weight measurements were determined by selecting a separate

467   aliquot of 50 or more shells from the same sample. The mean difference of replicate shell

468   weights is ±1.2 µg (1σ; *n* = 55).

469   **Stable isotope analyses.** Oxygen (δ^{18}O) and carbon (δ^{13}C) isotope ratios were determined

470   for the planktonic foraminifera, *G. bulloides* (300–355 µm), and the benthic foraminiferal

471   taxa *Cibicidoides spp.* (>150 µm size fraction). Measurements of δ^{18}O and δ^{13}C were

472   conducted on an automated individual–carbonate reaction Kiel Device coupled to a Finnigan

473   MAT-251 isotope ratio mass spectrometer at the Research School of Earth Sciences, ANU.

474   Calcite samples weighing ~200 µg were reacted with 103% phosphoric acid at 90°C to

475   liberate sufficient CO_2 for isotopic analysis. The δ^{18}O and δ^{13}C values are reported as per mil

476   (‰) deviations relative to the Vienna Peedee Belemnite (VPDB) standard. The results have

477   been normalised on the VPDB scale such that the NBS-19 calcite standard yields δ^{18}O VPDB

478   (−2.20 ‰) and δ^{13}C VPDB (+1.95 ‰) and NBS-18 yields δ^{18}O VPDB (−23.0 ‰) and δ^{13}C

479   VPDB (−5.0 ‰). The 2σ uncertainties for replicate in-run measurements of NBS-19 (n=197)

480   were ±0.05 ‰ and ±0.02 ‰ for δ^{18}O and δ^{13}C, respectively. The average standard deviation

481   for repeat measurements of two planktonic samples was ±0.17 ‰ for δ^{18}O and ±0.09 ‰ for

482   δ^{13}C, and for benthic samples was ±0.05 ‰ for δ^{18}O and ±0.12 ‰ for δ^{13}C.

20

483   Boron isotope (δ^{11}B) values were determined for the planktonic foraminifera, *G.*

484   *bulloides* (300-355 μm) at Southampton University using previously described methods[58-60].

485   Oxidative cleaning procedures followed those in Barker *et al.*, (ref. [61]). We analysed ten *G.*

486   *bulloides* (150–250 μg of calcite) for each in-run measurement and this provided ~2–3 ng of

487   boron. The average 2σ in-run measurement precision was <0.2 ‰. The average agreement

488   of repeat measurements on separate sample aliquots was ±0.4 ‰ (*n* = 7) and the average

489   external 2σ precision is, at most, ±0.4 ‰. Foraminiferal cleaning procedures[61] were verified

490   for all samples by Al/Ca ratios <100 μmol mol^{-1} and this provides a sufficient screen against

491   clay contamination[62].

492   **Palaeo sea surface temperature (SST) and alkenone concentrations**. Alkenones were

493   analyzed at Geoscience Australia following the methods of Calvo *et al.*, (ref. [63]) and, with

494   them, SST estimates were obtained from the alkenone unsaturation ratio ($U_{37}^{K\prime}$ index).

495   Alkenone concentrations were quantified by using *n*-hexatriacontane as an internal standard.

496   The standard deviation for alkenone concentrations is 50 ng g^{-1} (2σ; replicate extractions and

497   measurements of a homogenous laboratory sediment standard). Alkenone-derived SSTs were

498   reconstructed using the $U_{37}^{K\prime}$-SST relationship of Müller *et al.*, (ref. [64]) where $U_{37}^{K\prime}$ = 0.033 x

499   SST + 0.044 for annually averaged SSTs. $U_{37}^{K\prime}$ measurements were completed at 10 cm

500   sample resolution. The standard deviation for replicate measurements of a homogenous

501   laboratory standard is, at the most ±0.6 °C (2σ). The standard error of SST estimates from

502   the $U_{37}^{K\prime}$-SST calibration[64] is ±1.5 °C. Long-term climate data from the World Ocean Atlas

503   2013 (WOA13; 0.25°)[65] gives a modern annual SST of 12.3 °C at the MD972106 locality,

504   which is close to the most recent core-top sediment $U_{37}^{K\prime}$ derived SST of 13.0 °C.

505   **Reconstruction of surface water *p*CO$_2$.** Seawater *p*CO$_2$ can be calculated from

506   temperature, salinity and pressure, and knowledge of two out of the six main carbonate

507   system parameters (free aqueous carbon dioxide ($CO_{2(aq)}$), bicarbonate ion (HCO_3^-),

508   carbonate ion (CO_3^{2-}), hydrogen ion (H^+), dissolved inorganic carbon (DIC), and total

509   alkalinity (TA)). Accordingly, past changes in seawater pCO$_2$ can be calculated using

510   estimates of seawater pH and either DIC or TA. Here, we use an alkenone-based proxy for

511   seawater temperature, planktonic foraminiferal δ^{11}B to estimate pH, planktonic foraminiferal

512   δ^{13}C to estimate DIC, and salinity derived seawater alkalinity to constrain major parameters

513   of the seawater carbonate system. Past variations in sea surface water pH at the site of

514   MD972106 are calculated from a recently published δ^{11}B-pH relationship for *G. bulloides*[66]

515   and the alkenone SST record. The δ^{11}B-pH relationship for *G. bulloides*[66] expands on the

516   previously published δ^{11}B-pH relationship for the same species[67]. The δ^{11}B-pH relationship[66]

517   is similar to and within error of a previously published δ^{11}B-pH relationship[67]. Even though

518   the calibration uncertainty for Martínez-Botí *et al.*, (ref. [67]) is considerably lower than

519   Raitzsch *et al.*, (ref. [66]), we used the extended δ^{11}B-pH relationship data set for *G. bulloides*[66].

520   Variations in surface water pCO$_2$ (Fig. 3b) over the past 25 kyr are estimated using

521   the SST alkenone record, the δ^{11}B surface water pH record and estimates of either alkalinity

522   or DIC. One set of estimates is derived from δ^{11}B-based pH and seawater alkalinity,

523   assuming that past variations in alkalinity were proportional to salinity, which can be

524   estimated from past sea level [58,68] (Method 1) (Fig. 3b). An alternative set of estimates is

525   derived from δ^{11}B-based pH, and foraminiferal δ^{13}C-based DIC (Method 2) (Fig. 3b). Both

526   approaches use a Monte Carlo method to calculate pCO$_2$ from pH, DIC, salinity and

527   temperature. This method generates quasi-normally distributed errors around central values

528   with 10,000 repetitions, and sea water carbonate system calculations using the R-based[69]

529   seacarb package[70]. 2σ uncertainties on the individual input variables and other carbonate

530   system parameters are included to the end; δ^{11}B (± 0.4 ‰), $U_{37}^{K'}$-derived SST (± 0.6 °C),

22

531   salinity ($\pm$ 3psu), ALK (±200 μmol kg^{-1}), and DIC (±76 μmol kg^{-1}). A disequilibrium

532   uncertainty ±20 ppm (2σ) is also included. Although we note the importance of propagating

533   all the uncertainties, we also note that pH is by far the dominant variable on pCO$_2$, and that

534   pH is well constrained by δ^{11}B alone[71]. Thus we are very confident that the change in pCO$_2$

535   forcing over this time is much more robust than the pCO$_2$ change in terms of absolute

536   uncertainty[71]. The average pCO$_2$ difference between calculations using Method (1) and (2) is

537   ~7 ppm (Fig. 3b).

538   Surface water pCO$_2$ and hence ocean circulation and productivity exerts an important

539   control on atmospheric CO$_2$ levels. However, the difference between the two (ΔpCO$_2$) is also

540   affected by terrestrial components of the carbon cycle such as (re-) growth of biomass or the

541   dynamics of (coastal) permafrost. Hence, more important than the absolute magnitude of

542   ΔpCO$_2$ is the change in this value, because this provides direct information as to whether a

543   particular area of the ocean was more or less important in driving the direction of

544   atmospheric change. Thus, while there are intervals in our record where the analytical and/or

545   age uncertainties preclude us from being certain whether our study area was acting as source

546   or sink of CO$_2$ to the atmosphere, we can be confident that the change in surface water

547   ΔpCO$_2$ levels in this area of the Southern Ocean made an important contribution to the last

548   deglacial atmospheric CO$_2$ rise.

549   We used the total pH scale, equilibrium constants for the dissociation of carbonic acid

550   from Dickson (ref. [72]) and the boron isotope equilibrium constant from Klochko (ref. [73]).

551   Modern silicate and phosphate values were applied to the calculations but they had very little

552   effect on the final results[74]. The proxies recorded in *G. bulloides* and in coccolithophorid

553   alkenones predominantly reflect austral spring conditions in the region, because this is the

554   seasonal maximum of production for both taxa[52,75]. Thus, the estimates of pCO$_2$ likely reflect

555   austral spring conditions.

556   The calculated pCO$_2$ from boron isotope-based pH estimates and DIC (Method 2)

557   utilizes an estimate of surface water DIC over time and requires a DIC estimate for the most

558   recent sediment sample. The WOCE SR3 repeat hydrographic transect between 44° S and

559   46° S (refs. [76-78]) indicates a modern surface water DIC of ~2061 µeq kg^{-1} at this site, where

560   *G. bulloides* are known to calcify[52]. Estimates of DIC are then varied over time as a function

561   of *G. bulloides* δ^{13}C, with the difference between modern surface- and deep-water DIC

562   derived via the difference between planktonic and benthic foraminiferal δ^{13}C (i.e. ΔDIC$_{SW-DW}$

563   is proportional to $\Delta\delta^{13}$C $_{planktonic-benthic}$). The biological drivers of surface-water δ^{13}C are

564   mainly modulated by organic carbon production; carbonate precipitation does not

565   significantly fractionate surface-water DIC. Therefore, any changes in the CaCO$_3$:C$_{org}$ rain

566   ratio would have a minor effect on DIC. Studies of the mechanisms modulating DIC in

567   surface waters in this region (e.g. ref. [79]) and of the Southern Ocean more broadly (e.g. ref.

568   [80]), suggest the CaCO$_3$:C$_{org}$ rain ratio is very low, with only a minor effect on surface DIC

569   and surface δ^{13}C$_{DIC}$. Any changes to the rain ratio would also affect surface-water pH, which

570   we estimate through boron isotopes. Modern surface and deep water DIC are from WOCE

571   SR3 repeat hydrographic transect between 44° S and 46° S (refs. [76-78]), δ^{13}C$_{SW}$ from King and

572   Howard (ref. [81]) and δ^{13}C$_{DW}$ are from Moy *et al.*, (ref. [53]).

573   **Temperature- and [CO$_3^{2-}$]-adjustments on *G. bulloides* δ^{13}C (δ^{13}C$_{adj}$).** Temperature and

574   carbonate ion concentration ([CO$_3^{2-}$]) have an additional, often neglected, effect on

575   planktonic foraminiferal δ^{13}C (refs.[81-83]). For Method 2, temperature and [CO$_3^{2-}$] adjustments

576   on *G. bulloides* δ^{13}C used to estimate DIC do not significantly change the pCO$_2$ estimates.

577   The average difference in pCO$_2$ estimates calculated from (a) boron isotope-based pH

578   estimates and DIC (where $\delta^{13}C$ for *G. bulloides* is not temperature and $[CO_3^{2-}]$-adjusted) and

579   (b) boron isotope-based pH estimates and DIC (where $\delta^{13}C$ for *G. bulloides* is temperature-

580   and $[CO_3^{2-}]$-adjusted) is ~2 ppm (Supplementary Fig. 4).

581   *G. bulloides* $\delta^{13}C$ values are adjusted for temperature using the $\delta^{13}C$ disequilibrium-

582   temperature relation 0.11‰ °C^{-1} (ref. [83]). The $\delta^{13}C$ disequilibrium-temperature[83] relation we

583   apply here is similar to the relationship estimated from a Southern Ocean sediment trap field

584   study[81]. Temperature adjustments are made using the alkenone-based SST estimates in

585   MD972106. *G. bulloides* $\delta^{13}C$ values are also adjusted for the so called carbonate ion ($[CO_3^{2-}]$

586   ]) effect using the relationship between $\delta^{13}C$ disequilibrium and $[CO_3^{2-}]$ (-0.014‰ $[CO_3^{2-}]^{-1}$)

587   (ref. [82]). Estimates of $[CO_3^{2-}]$ are from surface water pCO$_2$ calculations that use boron

588   isotope-based pH estimates and estimates of seawater alkalinity (Method 1). The 'close

589   agreement' between the $[CO_3^{2-}]$ outputs from Method 1 and 2 (Fig. 4a) would yield a similar

590   adjustment to *G. bulloides* $\delta^{13}C$ in terms of $[CO_3^{2-}]$ adjustments.

591

592   **Data availability**

593   All data are archived at the Australian Antarctic Data Centre (https://data.aad.gov.au/) and

594   are publicly accessible at https://doi.org/10.26179/5d5df822acf6c.

595

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135°E   150°E   165°E

120°E

Australia

180°

Sub-Tropical Zone

30°S

NZ

MD972106

STF

Sub-Antarctic Zone

45°S

SAF

Polar Frontal Zone

PF

Antarctic Zone

60°S

Zone south of the ACC

SB

Antarctica

75°S