

1 **Two modes of change in Southern Ocean productivity over the past million years**

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12 **Export of organic carbon from surface waters of the Antarctic zone of the**
13 **Southern Ocean decreased during the last ice age, coinciding with declining**
14 **atmospheric CO₂ concentrations, signaling reduced exchange of CO₂ between**
15 **the ocean interior and the atmosphere. In contrast, in the Subantarctic Zone,**
16 **export production increased into ice ages coinciding with rising dust fluxes**
17 **and thus suggesting iron fertilization of Subantarctic phytoplankton. Here, a**
18 **new high-resolution productivity record from the Antarctic zone is compiled**
19 **with parallel Subantarctic data over the last million years. Together, they fit**
20 **the view that the combination of these two modes of Southern Ocean change**
21 **determines the temporal structure of the glacial/interglacial atmospheric CO₂**
22 **record, including during the interval of “lukewarm” interglacials between 450**
23 **and 800 thousand years ago.**

24

25 Antarctic ice core measurements reveal that regional air temperatures and
26 atmospheric $p\text{CO}_2$ were tightly correlated over glacial-interglacial cycles of the past 800
27 kyrs (1). Many studies have inferred a dominant role for the Southern Ocean in
28 modulating glacial-interglacial variability of atmospheric $p\text{CO}_2$ ((2) and references
29 therein). The central role of the Southern Ocean is thought to reflect its leverage on the
30 global efficiency of the biological pump, in which the production, sinking, and deep

31 remineralization of organic matter sequesters carbon in the ocean interior, lowering
32 atmospheric CO₂. Dense subsurface water masses outcrop in the Southern Ocean,
33 providing exchange pathways between the deep ocean and the atmosphere. Vertical
34 exchange of water causes deeply sequestered CO₂ and nutrients to be mixed to the
35 surface, fueling high rates of phytoplankton productivity. Today, the Southern Ocean is
36 the principal leak in the biological pump, because export production is inadequate to
37 prevent the evasion of deeply sequestered carbon when waters are exposed to the
38 atmosphere. The polar CO₂ leak can be directly inhibited during glacial stages by factors
39 such as increased sea-ice cover (3) and/or changes in buoyancy forcing and convection
40 (4, 5). In addition, the glacial CO₂ reduction associated with these mechanisms would
41 have been amplified by iron fertilization of the Subantarctic Zone (SAZ) of the Southern
42 Ocean (6, 7) and associated alkalinity feedbacks (8).

43 Export production records from the Antarctic Zone (AZ) have been used to trace
44 changes in the rate of Southern Ocean overturning through time (9, 10). However, these
45 records only cover the last glacial cycle, restricting our understanding of the evolution of
46 the Antarctic component of this two-mode system by which the Southern Ocean regulates
47 the transfer of carbon between the ocean interior and the atmosphere over previous
48 climatic cycles. Here, we report a high-resolution relative elemental concentration record
49 from Ocean Drilling Program (ODP) site 1094 (53.2°S, 05.1°E; water depth 2,850 m)
50 (Fig. 1), which traces changes in AZ export production over the past million years (SOM,
51 Figs S1 & S2). The time resolution achieved here rivals the measurement density typical
52 for Antarctic ice-core records. These observations are complemented with reconstruction
53 of ²³⁰Th-normalized biogenic particle flux to the seafloor covering the last two glacial
54 terminations (Fig. 2).

55 The pelagic sediment analyzed in this study is dominantly composed of
56 diatomaceous opal and terrigenous detritus, the latter of which is mostly ice-rafted, with a
57 minor contribution from aeolian material (11). Assuming that sedimentary iron (Fe) is of
58 detrital origin, barium (Ba) abundance normalized to Fe yields an estimate of the
59 sedimentary concentration of biogenic (or excess) Ba (bioBa), which serves as a tool to
60 reconstruct changes in the integrated flux of organic matter to the sediment (12).
61 Normalization by Fe assumes that the detrital fraction has not varied significantly in

62 space and time, supported by provenance studies, indicating that the tephra-rich
63 terrigenous material at this site is consistently derived from the South Sandwich volcanic
64 arc, with negligible contribution from Bouvet Island and possibly the Antarctic Peninsula
65 (11). Calcium (Ca) normalized to Fe indicates the sedimentary concentration of biogenic
66 carbonate (CaCO_3). The records of Fe and Ti show almost identical trends in amplitude,
67 but XRF signals are better for Fe, which is thus used for normalization. In these opal-rich
68 sediments, elemental spectrum processing does not allow proper quantification of Al
69 because of the overlapping Si peaks, precluding the use of Al as a normalizing agent.

70 The Ba/Fe record shows a strong climate-related signal (Fig. 3C), with high
71 values during interglacials and lower values during cold stages. The Ba/Fe record is in
72 good agreement with the ^{230}Th -normalized flux of bioBa (Fig. 2C), supporting the use of
73 Ba/Fe to infer bioBa throughout the record. The large-scale Ba variations cannot be
74 explained as the result of bacterially-mediated sulfate reduction and associated diagenetic
75 barite (BaSO_4) dissolution because no significant sulfate reduction is observed in the
76 interstitial water of Pleistocene sediments of ODP site 1094 (13). Indeed, the ^{230}Th -
77 normalized flux of bioBa is similar to that of opal and chlorophyll transformation
78 products (chlorins) measured in the same sediment core (Fig. 2). Preservation of these
79 independent paleo-productivity proxies is favored in different sedimentary environments.
80 While the preservation of bioBa can be compromised by reducing conditions, the
81 preservation of organic matter in general, and chlorins in particular, is enhanced when
82 oxygen content is low (14). The preservation of opal is unrelated to the redox state of
83 sediments but primarily driven by the total sedimentation rate (15). The correlation
84 between opal fluxes and excess $^{231}\text{Pa}/^{230}\text{Th}$ at the same core site during the last 25 kyrs
85 (9) and the correlation between opal fluxes and bioBa over the last 150 kyrs reported here
86 indicate that the reconstructed opal fluxes most likely represent variable production by
87 diatoms.

88 Consequently, the sedimentary Ba/Fe is interpreted to indicate lower bioBa
89 accumulation and thus less export of organic matter from the surface ocean during cold
90 periods, with the lowest bioBa concentrations coinciding almost exclusively with the
91 glacial maxima, consistent with measurements elsewhere in the Southern Ocean, south of
92 the polar frontal zone ((16) and references therein) (Fig. S3). Sea-ice has the potential to

93 directly alter export production, by blocking sunlight vital for phytoplankton to undertake
94 photosynthesis; however, sea-ice was only present at this site during the winters of glacial
95 periods (17), not during the summer growing season. Rather, changes in export imply a
96 reduced supply of nutrients to the surface ocean. Phytoplankton growth is inhibited by the
97 lack of bioavailable Fe in most parts of the Southern Ocean. Vertical mixing and
98 upwelling (rather than atmospheric fluxes) appear to dominate the supply of Fe to the
99 Antarctic surface ocean at present (18). Thus, glacial decrease in productivity may have
100 been driven by a reduction in this deep water-derived iron supply.

101 While various physical mechanisms have been proposed for a reduction in this
102 deep water exposure, they all involve reduction of wind-driven upwelling, wintertime
103 vertical mixing, or both (4, 5, 19). Upwelling could be lowered by weaker westerlies
104 and/or by a more northerly position for them, while wintertime vertical mixing is
105 sensitive to upper ocean density stratification. Various processes can affect this
106 stratification, including upwelling, which strips away the freshwater cap (halocline) that
107 maintains vertical stability.

108 Of the nitrate imported into the Antarctic surface today, only a portion derives
109 from Ekman upwelling, with the remaining deriving from wintertime vertical mixing
110 (20). Given that the data suggest many fold lower export production during peak ice ages,
111 we infer that these changes in productivity likely require both a reduction in wind-driven
112 upwelling and an increase in density stratification. This is significant in that the latter
113 change would affect deep water formation, through which the Antarctic has its greatest
114 direct leverage on atmospheric CO₂ (21, 22).

115 Upon glacial terminations, large pulses of export production coincide with
116 prominent increases in atmospheric CO₂ concentrations reconstructed from Antarctic ice
117 cores (Figs. 2 & 3). Flux determinations of three independent export production proxies
118 suggest that the export of organic matter increased by more than an order of magnitude
119 across the two last climate transitions (Fig. 2). Reconstruction of past silicon and nitrogen
120 dynamics suggest that relative nutrient utilization did not rise sharply at the last glacial
121 termination (23), such that the rise in Ba and opal flux was a response to a large increase
122 in the nutrient supply to the euphotic zone. These increases in export were accompanied
123 by summer sea-surface temperature (SST) overshoots and abrupt disappearances of

124 winter sea-ice (17). Summer SSTs increased by more than 4°C in less than 5 kyrs for the
125 last five glacial terminations (17). While the sequence of deglacial events remains to be
126 resolved (9), the systematic and repeated glacial-to-interglacial rises in biogenic flux
127 (Fig. 3) point to a robust pattern of enhanced Southern Ocean overturning during
128 interglacials.

129 Moreover, we show that these glacial-to-interglacial export production increases
130 were accompanied by short-lived CaCO₃ spikes in these otherwise carbonate-poor
131 sediments (Fig. 3D). We note that the preservation spike observed for the last glacial
132 termination is muted at this site, for reasons that remain unclear. The near-absence of
133 CaCO₃ in most of the record suggests that seafloor preservation of the CaCO₃ rain
134 regulated the bimodal character of the record. Although intervals with higher sedimentary
135 CaCO₃ concentrations could in principle reflect increased local CaCO₃ export, the abrupt
136 increases and the transient nature of the CaCO₃ spikes compared to export production
137 proxies argue instead for a deepening of the lysocline, as expected if CO₂ was lost from
138 deep waters at this time.

139 The decrease in deep water exposure following peak interglacial conditions,
140 indicated by declining export production, leads to CO₂ reduction, and this mechanism
141 appears to apply in particular to the early stages of glaciation. As a general rule, elevated
142 Antarctic export occurs during the peak interglacials, giving way to a major decline in the
143 early stages of glaciation (Fig. 3 C), coinciding with the first half of the CO₂ decline into
144 each glacial period, 40-50 ppm (Fig. 3A, reaching ~225 ppm). Remarkably, this is a
145 similar, if slightly greater, reduction to the estimate from numerical models for the CO₂
146 decline that should result from a strong reduction in Antarctic overturning (Brovkin et al.,
147 2007; Hain et al., 2011). While further declines in Antarctic export production occur later
148 in the glacial progression (Fig. 3C), the associated CO₂ reduction associated with this
149 mechanism should have nearly saturated (2). However, based on data from ODP Site
150 1090 in the Subantarctic Zone (SAZ) to the north of ODP Site 1094, it appears that the
151 later stages of glaciation and climate cross a threshold at which the SAZ undergoes a
152 dramatic rise in productivity (Fig. 3F) (6, 24) coincident with increased dust-borne iron
153 supply to the SAZ from continental regions upstream in the westerly wind field (Fig. 3E;
154 (7)). Iron fertilization in the SAZ would have permitted biological productivity in this

155 region to sequester additional regenerated carbon in the abyssal ocean, which would have
156 further lowered atmospheric CO₂ (16, 25). It is again notable that numerical model
157 simulations of Subantarctic iron fertilization predict roughly the observed CO₂ declines
158 of ~ 40 ppm that occur later in the glacial progressions (21, 25, 26). In the modern ocean,
159 there is upper ocean mixing across the fronts separating the AZ and SAZ (27). Thus,
160 during peak ice conditions, iron fertilization in the SAZ may have further depleted the
161 AZ of surface nutrients, contributing to the continued decline of AZ export production to
162 its glacial minimum. In any case, it is a remarkable characteristic of the two records that
163 the SAZ biological response begins when AZ productivity has reached the lower half of
164 its range (Fig. 3C and F), with relatively little correlated variation between the AZ and
165 SAZ (Fig. 4), and that the major changes in each correspond to roughly half of the
166 observed CO₂ variation (Fig. 4). In summary, the paleoceanographic records from both
167 the AZ and SAZ merge with the numerical model estimates of Southern Ocean to provide
168 a coherent two-part Southern Ocean mechanism for the amplitude and timing of glacial
169 interglacial CO₂ change.

170 The potential for these two modes of the Southern Ocean to have different roles in
171 glacial/interglacial CO₂ change, first recognized in the context of the last glacial cycle (2,
172 16), is bolstered by the data reported here for the period of the “lukewarm” interglacials
173 (MIS 13-19). The lukewarm interglacials are characterized by reduced amplitude of the
174 ice-core δD and CO₂ records (Fig. 3) and a general decrease in global interglacial
175 temperatures that appears to be more pronounced in Southern Ocean SST records (28).
176 Given the potential dependencies of westerly wind position (29) and polar ocean water-
177 column stability (30) on global temperature, the muting of the pCO₂ increase during the
178 lukewarm interglacials might have been linked to a reduced dynamic range of Antarctic
179 overturning, with the abyssal ocean thereby maintaining a larger reservoir of regenerated
180 carbon than in more recent interglacials (31). This hypothesis is supported by the
181 Antarctic Ba/Fe record (Fig. 3C), which shows markedly reduced amplitude for the Ba/Fe
182 maxima associated with the lukewarm interglacials (Fig. 4, squares with open circles
183 along the x axis). Furthermore, this interval also generally has reduced deglacial CaCO₃
184 peaks (Fig. 3D), which would suggest that proportionally less CO₂ was released from the
185 deep ocean. The expression of interglacials in the SAZ record is indistinguishable

186 between the period containing the lukewarm interglacials and the rest of the record (Figs.
187 3 & 4) (7, 24), suggesting that the cessation of SAZ iron fertilization occurred during the
188 lukewarms as in other interglacials.

189 In contrast to the lukewarm interglacials, MIS 21 and 25 were characterized by
190 full-amplitude export production peaks in the AZ accompanied by large CaCO₃
191 preservation events, suggesting an increase in upwelling and deep-ocean CO₂ release
192 during Terminations X and XI (Fig. 3), consistent with planktic foraminiferal pH
193 estimates that suggest that both interglacials had *p*CO₂ values as high as recent
194 interglacials (32). This observation further argues that the subsequent lukewarm
195 interglacials represented a distinct period. Our observations thus indicate a strong
196 coupling between Antarctic deep-to-surface exchange and the magnitude of the CO₂
197 release from the ocean interior, which is consistent with observed changes in atmospheric
198 *p*CO₂ even beyond the interval covered by the Antarctic ice-core records.

199 There is much uncertainty and debate regarding the response of Southern Ocean
200 overturning to ongoing global warming, as well to its impact on the oceanic uptake of
201 anthropogenic CO₂ (33). The paleoclimate data reported here argue strongly for a robust
202 sensitivity of Antarctic overturning to global climate, in which overturning increases
203 under warmer conditions. As the physical mechanism of this coupling is not yet clear,
204 one cannot be confident that it will apply on the decadal to centennial scale and under the
205 specific conditions of anthropogenic global warming. Nonetheless, the finding of stronger
206 overturning under warmer climates, taken at face value, suggests a similar sense of
207 change in the warmer future ocean.

208

209 **Figure captions**

210

211 **Fig. 1** Core locations represented on the January-March sea-surface temperature field.
212 The black line delineates maximum winter sea-ice extent (using the 90% winter sea-ice
213 concentration line) based on the Hadley Center sea-ice concentration data 1978-2010
214 (34).

215

216 **Fig. 2** Biogenic particle flux reconstructed by ²³⁰Th-normalization for four independent

217 proxies covering the last two glacial terminations. Discrete measurements for the upper
218 25 kyrs have been performed on TN-57-13PC. (A) atmospheric $p\text{CO}_2$ (1, 35); (B)
219 comparison between CaCO_3 flux and Ca/Fe; (C) comparison between bioBa flux and
220 Ba/Fe; (D) chlorin flux; (E) biogenic opal flux. Blue shadings highlight ice ages, whereas
221 red shadings indicate interglacials. The two arrows highlight the two step-transition into
222 ice ages.

223

224 **Fig. 3** Records of (A) atmospheric $p\text{CO}_2$ (1), (B) ODP 1094 planktic foraminifera $\delta^{18}\text{O}$
225 (36, 37), (C) ODP 1094 Ba/Fe (data smoothed by a five-point running mean), (D) ODP
226 1094 Ca/Fe (data smoothed by a five-point running mean), (E) Fe flux to subantarctic
227 core ODP1090 (7), and (F) ODP 1090 sedimentary alkenone concentration (24) covering
228 the past 1 Myr. Red/grey shadings highlight intervals were Antarctic (AZ)/subantarctic
229 (SAZ) processes, respectively, are dominantly controlling the partitioning of CO_2
230 between the ocean interior and the atmosphere.

231

232 **Fig. 4** Comparison between ODP 1094 Ba/Fe and ODP 1090 sedimentary alkenone
233 concentration (24). Symbol colour indicates $p\text{CO}_2$. Filled circles illustrate the period 0-
234 450 kyrs, filled squares the lukewarm interval (450-800 kyrs) and the open squares the
235 interval 800-1000 kyrs for which $p\text{CO}_2$ reconstruction do not yet exist.

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237 **References and Notes**

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References

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