

**Title:****Carbon isotope constraints on the deglacial CO<sub>2</sub> rise from ice cores****Authors:**

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24 **Abstract:**

25 The stable carbon isotope ratio of atmospheric CO<sub>2</sub> ( $\delta^{13}\text{C}_{\text{atm}}$ ) is a key parameter to decipher  
26 past carbon cycle changes. Here we present  $\delta^{13}\text{C}_{\text{atm}}$  data for the last 24,000 years derived  
27 from three Antarctic ice cores. We conclude that a pronounced 0.3‰ decrease in  $\delta^{13}\text{C}_{\text{atm}}$   
28 during the early deglaciation can be best explained by upwelling of old, carbon-enriched  
29 waters in the Southern Ocean. Later in the deglaciation, regrowth of the terrestrial  
30 biosphere, changes in sea surface temperature, and ocean circulation governed the  $\delta^{13}\text{C}_{\text{atm}}$   
31 evolution. During the Last Glacial Maximum,  $\delta^{13}\text{C}_{\text{atm}}$  and CO<sub>2</sub> were essentially constant,  
32 suggesting that the carbon cycle was in dynamic equilibrium and that the net transfer of  
33 carbon to the deep ocean had occurred before then.

34

35 **One Sentence Summary:**

36 High-resolution ice core records of stable carbon isotopes in atmospheric CO<sub>2</sub> constrain  
37 carbon cycle changes during the Last Glacial Maximum, the early deglacial, and the  
38 transition into the Holocene.

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40

41

42 **Main Text:**

43 During the last 800,000 years (800 kyr), atmospheric CO<sub>2</sub> concentrations have varied in  
44 close relation to Antarctic temperatures (1, 2) and the general waxing and waning of  
45 continental ice sheets. In particular, CO<sub>2</sub> rose from a stable level of 190 parts per million by

46 volume (ppmv) during the Last Glacial Maximum to about 280 ppmv in preindustrial times,  
47 showing pronounced differences in atmospheric CO<sub>2</sub> rates of change in the course of the  
48 last glacial/interglacial transition (3). Many processes have been involved in attempts to  
49 explain these CO<sub>2</sub> variations, but it has become evident that none of these mechanisms  
50 alone can account for the 90 ppmv increase in atmospheric CO<sub>2</sub>. A combination of  
51 processes must have been operating (4, 5), with their exact timing being crucial. However,  
52 a unique solution to the deglacial carbon cycle changes has not been yet found.

53

54 In this respect, high-resolution and precise  $\delta^{13}\text{C}_{\text{atm}}$  records from Antarctic ice cores are  
55 needed to better constrain the evolution of carbon cycle changes during the last  
56 deglaciation. On millennial time scales,  $\delta^{13}\text{C}_{\text{atm}}$  is primarily influenced by the  $\delta^{13}\text{C}$  of  
57 dissolved inorganic carbon (DIC) ( $\delta^{13}\text{C}_{\text{DIC}}$ ) and sea surface temperature (SST), which  
58 controls the isotopic fractionation during air/sea gas exchange. The continuous rain of  
59 isotopically light organic material to the interior of the ocean draws down carbon from the  
60 surface layer to intermediate and deep waters, where the organic carbon is remineralized.  
61 Consequently, a vertical  $\delta^{13}\text{C}_{\text{DIC}}$  gradient is established, controlled by the interplay of the  
62 ocean circulation with this so-called “biological pump”. The more intense the circulation,  
63 the smaller the gradients are for  $\delta^{13}\text{C}_{\text{DIC}}$ , DIC, oxygen and nutrients. Superimposed on these  
64 marine carbon cycle processes are climate-induced changes in terrestrial biosphere carbon  
65 storage, which result in a net change in the carbon isotopic composition of the  
66 ocean/atmosphere system. On orbital time scales, weathering and sedimentation of CaCO<sub>3</sub>  
67 affect  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\delta^{13}\text{C}_{\text{atm}}$  and atmospheric CO<sub>2</sub> as well.

68

69 Until recently (6), analytical constraints represented the fundamental limitation on the  
70 utility of  $\delta^{13}\text{C}_{\text{atm}}$  ice core records (7, 8). Here we provide evidence (Fig. 1) about possible  
71 causes of carbon cycle changes with measurements of  $\delta^{13}\text{C}_{\text{atm}}$  from two Antarctic ice cores  
72 (EPICA (European Project for Ice Coring in Antarctica) Dome C and Talos Dome),  
73 performed with three independent methods in two different labs (referred to as Bern  
74 sublimation, Bern cracker and Grenoble mill data) (6, 9). One of our records is based on a  
75 sublimation method (10) that avoids the effects associated with incomplete gas extraction  
76 and thus yields more precise results (see Supporting Online Material (SOM)). A stringent  
77 residual analysis of the three data sets shows virtually no offset between the two Bern data  
78 sets and only a small systematic offset between the Bern and Grenoble data of 0.16‰,  
79 which can be explained by a method-dependent systematic fractionation. After correction  
80 of this offset, we combined the three  $\delta^{13}\text{C}_{\text{atm}}$  records over the last 24 kyr using an error-  
81 weighted Monte Carlo bootstrap approach. This method showed that all three data sets are  
82 essentially compatible within their analytical uncertainties. To make full use of the  
83 resolution and precision of the data, the inclusion of all three data sets is required, although  
84 all our conclusions are also supported by the individual records. The final data set consists  
85 of 201 individual measurements, each reflecting typically 2 to 4 replicates and with an  
86 analytical  $1\sigma$  error between 0.04 and 0.12‰. Since the resulting Monte Carlo Average  
87 (MCA) removes most of the analytical uncertainties, it contains less high-frequency  
88 variability compared to the raw data. This is in line with the centennial-scale low-pass  
89 filtering inherent to the bubble enclosure process at Dome C. Accordingly, the retained

90 variability can be regarded as the signal most representative of millennial  $\delta^{13}\text{C}_{\text{atm}}$  changes  
91 (see SOM for details regarding the MCA and its uncertainty).

92

93 Our  $\delta^{13}\text{C}_{\text{atm}}$  data is in good agreement with previously published lower-resolution records  
94 (6, 9). Our record shows a very stable level between 24 and ca. 19 kyr before present (BP,  
95 where present is defined as 1950), with an average  $\delta^{13}\text{C}_{\text{atm}}$  of -6.45‰ (Tab. S1 and S2),  
96 similar to the -6.35‰ of the Late Holocene (Fig. 2B). Given the fact that a large set of  
97 environmental parameters such as atmospheric  $\text{CO}_2$ , global SST, terrestrial carbon storage,  
98 and ocean circulation have varied between the LGM and the Late Holocene, almost  
99 identical  $\delta^{13}\text{C}_{\text{atm}}$  values indicate that opposing effects must have offset each other (11). This  
100 becomes clear if we look at three first-order effects on  $\delta^{13}\text{C}_{\text{atm}}$ : A SST rise of 1 K translates  
101 into a 0.1‰ increase in  $\delta^{13}\text{C}_{\text{atm}}$ , due to temperature-dependent fractionation between  
102 atmospheric  $\text{CO}_2$  and marine DIC species (12). Assuming a global LGM-to-Holocene SST  
103 rise of 3 K would result in about 0.3‰ higher  $\delta^{13}\text{C}_{\text{atm}}$  for the Holocene, provided that SST  
104 distribution and  $\text{CO}_2$  gross flux exchange patterns remained constant. This effect is further  
105 augmented by the uptake of isotopically light carbon by the land biosphere and  
106 counterbalanced by the smaller vertical gradient in  $\delta^{13}\text{C}_{\text{DIC}}$  in the Holocene ocean,  
107 supported by marine data (13). The fact that both  $\delta^{13}\text{C}_{\text{atm}}$  and  $\text{CO}_2$  show little variation from  
108 24 to 19 kyr BP points to the carbon cycle being essentially in dynamic equilibrium at that  
109 time. As can also be seen in Fig. 2, the climate variations related to Heinrich stadial 2  
110 (HS2) and Dansgaard-Oeschger event 2 (DO2) had little effect on the global carbon cycle  
111 during this time interval. However, given the opposing trends for reconstructed atmospheric

112  $\Delta^{14}\text{C}$  ( $\Delta^{14}\text{C}_{\text{atm}}$ ) (14, 15) and the expected  $\Delta^{14}\text{C}_{\text{atm}}$  evolution (16) based on variations in  $^{14}\text{C}$   
113 production rate (17, 18), the global  $^{14}\text{C}$  budget was not balanced (Fig. 2A).

114

115 After a very small increase in  $\delta^{13}\text{C}_{\text{atm}}$  at the very end of the glacial, a sharp drop in  $\delta^{13}\text{C}_{\text{atm}}$   
116 starting at 17.5 kyr parallels the onset of increasing atmospheric  $\text{CO}_2$ . Taken at face value,  
117 this would point to an early SST rise that preceded the onset of the  $\text{CO}_2$  increase. When we  
118 apply a crude SST correction to our  $\delta^{13}\text{C}_{\text{atm}}$  data based on a global estimate of SST  
119 temperature changes during the transition (see SOM), this  $\delta^{13}\text{C}_{\text{atm}}$  increase vanishes (Fig.  
120 2B). Note, however, that this 0.06‰ excursion is within the uncertainties of our data and  
121 that other effects could also lead to this small enrichment in  $\delta^{13}\text{C}_{\text{atm}}$ . The 0.3‰ drop in  
122  $\delta^{13}\text{C}_{\text{atm}}$  after the onset of the transition at 17.5 kyr BP is accompanied by a  $\text{CO}_2$  increase of  
123 about 35 ppmv and a 190‰ drop in  $\Delta^{14}\text{C}_{\text{atm}}$  (19), which has been attributed to a release of  
124 old carbon from the deep ocean. This coeval drop in  $\delta^{13}\text{C}_{\text{atm}}$  and  $\Delta^{14}\text{C}_{\text{atm}}$  during the so-  
125 called “mystery interval”, 17.5 – 14 kyr BP (19), is arguably the most enigmatic carbon  
126 cycle change in the course of the transition and will be discussed in more detail below.

127

128 After the broad  $\delta^{13}\text{C}_{\text{atm}}$  minimum is reached at about 16 kyr BP,  $\delta^{13}\text{C}_{\text{atm}}$  increases slightly  
129 by 0.1‰ during the pronounced Bølling-Allerød (BA) warming. Other than circulation  
130 changes in the Southern Ocean (20), the regrowth of the terrestrial biosphere in the northern  
131 hemisphere could contribute to this increase in  $\delta^{13}\text{C}_{\text{atm}}$  (4). However, since the SST-  
132 corrected  $\delta^{13}\text{C}$  evolution (Fig. 2B) does not show any increase, a robust process attribution  
133 requires precisely dated SST reconstructions and transient carbon cycle modeling.

134

135 An almost linear rise by 0.06‰ per kyr follows the second  $\delta^{13}\text{C}_{\text{atm}}$  minimum at 12.2 kyr  
136 BP, leading to maximum values of -6.33‰ at around 6 kyr BP. This rise might be largely  
137 explained by the continuing regrowth of the terrestrial biosphere (21), in concert with  
138 smaller contributions from SST warming and changes in circulation and export production  
139 (9, 22). From this mid-Holocene maximum,  $\delta^{13}\text{C}_{\text{atm}}$  values decline slightly to reach values  
140 of -6.35‰ at 0.5 kyr BP, as previously reported (6).

141

142 As mentioned above, the carbon cycle changes during the mystery interval have been a  
143 matter of intense debate (19, 20, 23). Our high-resolution  $\delta^{13}\text{C}_{\text{atm}}$  record together with other  
144 records of carbon cycle changes and insights from models may help to constrain hypotheses  
145 put forward to explain the mystery interval. The rise in  $\text{CO}_2$  and the decline in  $\delta^{13}\text{C}_{\text{atm}}$  and  
146  $\Delta^{14}\text{C}_{\text{atm}}$  between 17 and 15 kyr BP fit the concept of bringing DIC-rich waters with old  
147 carbon into exchange with the atmosphere. Indicative  $^{14}\text{C}$  signals of upwelling of old,  $\text{CO}_2$ -  
148 enriched deep water were found in Pacific intermediate waters (24), but others (23) ruled  
149 out such old water in the northeast Pacific, and evidence for a  $^{14}\text{C}$ -depleted glacial deep  
150 ocean remains elusive (19, 23, 25). These  $\Delta^{14}\text{C}$  studies were usually confronted with  
151 variable reservoir age between benthic and planktonic foraminifera. A study using deep sea  
152 corals now circumvents this problem by applying absolute U-Th dating and shows that the  
153 deep glacial Southern Ocean indeed ventilated its  $^{14}\text{C}$ -depleted reservoir during the mystery  
154 interval (26).

155

156 The constant  $\delta^{13}\text{C}_{\text{atm}}$  values during the late glacial indicate that the build-up of such an old,  
157 DIC-rich reservoir must have occurred before 24 kyr BP. A large number of records mark  
158 the start of the deglaciation around 17 kyr BP (Fig. 2). Within the uncertainty in marine and  
159 ice core age scales, the  $\text{CO}_2$  increase, the pronounced  $\Delta^{14}\text{C}_{\text{atm}}$  drop (15), the resumption of  
160 vigorous Southern Ocean upwelling as recorded in intense deposition of biogenic opal (20),  
161 and the launch of ice-rafted debris layers at the beginning of the Heinrich 1 stadial (27) all  
162 occurred simultaneously. Interestingly, our  $\delta^{13}\text{C}_{\text{atm}}$  record shows its largest deviation of  
163 0.3‰, i.e. the entire  $\delta^{13}\text{C}_{\text{atm}}$  decrease from the LGM to the Preboreal (PB), within the first 2  
164 kyr after the start of the deglaciation. Within the same interval,  $\text{CO}_2$  rose by 30 ppmv from  
165 190 ppmv to 220 ppmv, i.e. only 35% of the LGM-PB rise. Together with the trend reversal  
166 in  $\delta^{13}\text{C}_{\text{atm}}$  towards the end of the mystery interval, this indicates that only a fraction of the  
167 glacial/interglacial  $\text{CO}_2$  increase can be explained by an intensification of deep ocean  
168 ventilation bringing isotopically depleted and carbon-rich water to the surface of the  
169 Southern Ocean. Our new, high-resolution  $\delta^{13}\text{C}_{\text{atm}}$  data constrain the period of this release  
170 of isotopically depleted carbon from the deep ocean to the atmosphere to between 17.4 kyr  
171 BP and 15 kyr BP. This interpretation of the proxy records is quantitatively in line with  
172 dynamical ocean model results that link deep ocean ventilation, atmospheric  $\text{CO}_2$ ,  $\delta^{13}\text{C}_{\text{atm}}$ ,  
173  $\delta^{13}\text{C}_{\text{DIC}}$ , opal burial, and radiocarbon (28).

174

175 Alternative hypotheses (29, 30) invoking the release of old carbon from permafrost or  
176 carbon locked under continental ice sheets are unlikely to explain the carbon cycle changes  
177 in the mystery interval because the amount of terrestrial carbon needed to account for the



178  $^{14}\text{C}$  drop is very large, at 5000 Gt (25), and would conflict with the moderate 30 ppmv rise  
179 in atmospheric  $\text{CO}_2$ . Moreover, it would lead to an overall decline in  $\delta^{13}\text{C}_{\text{DIC}}$ , which is not  
180 observed in benthic foraminifera in the deep ocean (13, 22). Also, a carbonate dissolution  
181 event at the sea floor that would have to accompany such a large terrestrial carbon release  
182 into the atmosphere/ocean system is not imprinted in the deglacial marine  $\text{CaCO}_3$  record  
183 (31)

184

185 Consequently, despite the fact that the search for an extremely  $^{14}\text{C}$ -depleted deep water  
186 mass in marine records has thus far not been successful (23) and might not even essential to  
187 explain the  $\Delta^{14}\text{C}_{\text{atm}}$  anomaly (26), the release of carbon from the deep ocean remains the  
188 most plausible scenario to explain the early deglacial drop in our new  $\delta^{13}\text{C}_{\text{atm}}$  record.  
189 Furthermore, model results suggest that a  $\delta^{13}\text{C}_{\text{atm}}$  decrease of 0.3‰ and a  $\text{CO}_2$  increase of  
190 about 30 ppmv can be accommodated by relatively small (about 20‰) and spatially  
191 complex changes in deep ocean  $\Delta^{14}\text{C}$  (28). These changes may remain undetected in the  
192 search for the old abyssal water using benthic foraminifera (19, 25). However, they are also  
193 too small to explain the reconstructed  $\Delta^{14}\text{C}_{\text{atm}}$  decline in the mystery interval. Based on  
194 these considerations, the currently available marine and ice core information cannot be  
195 reconciled with the atmospheric radiocarbon record in a straightforward manner. One  
196 possibility to resolve this issue is to also reconsider a larger change in  $^{14}\text{C}$  production  
197 between the Holocene and the glacial, and to work towards independent verification of the  
198  $\Delta^{14}\text{C}_{\text{atm}}$  history.

199

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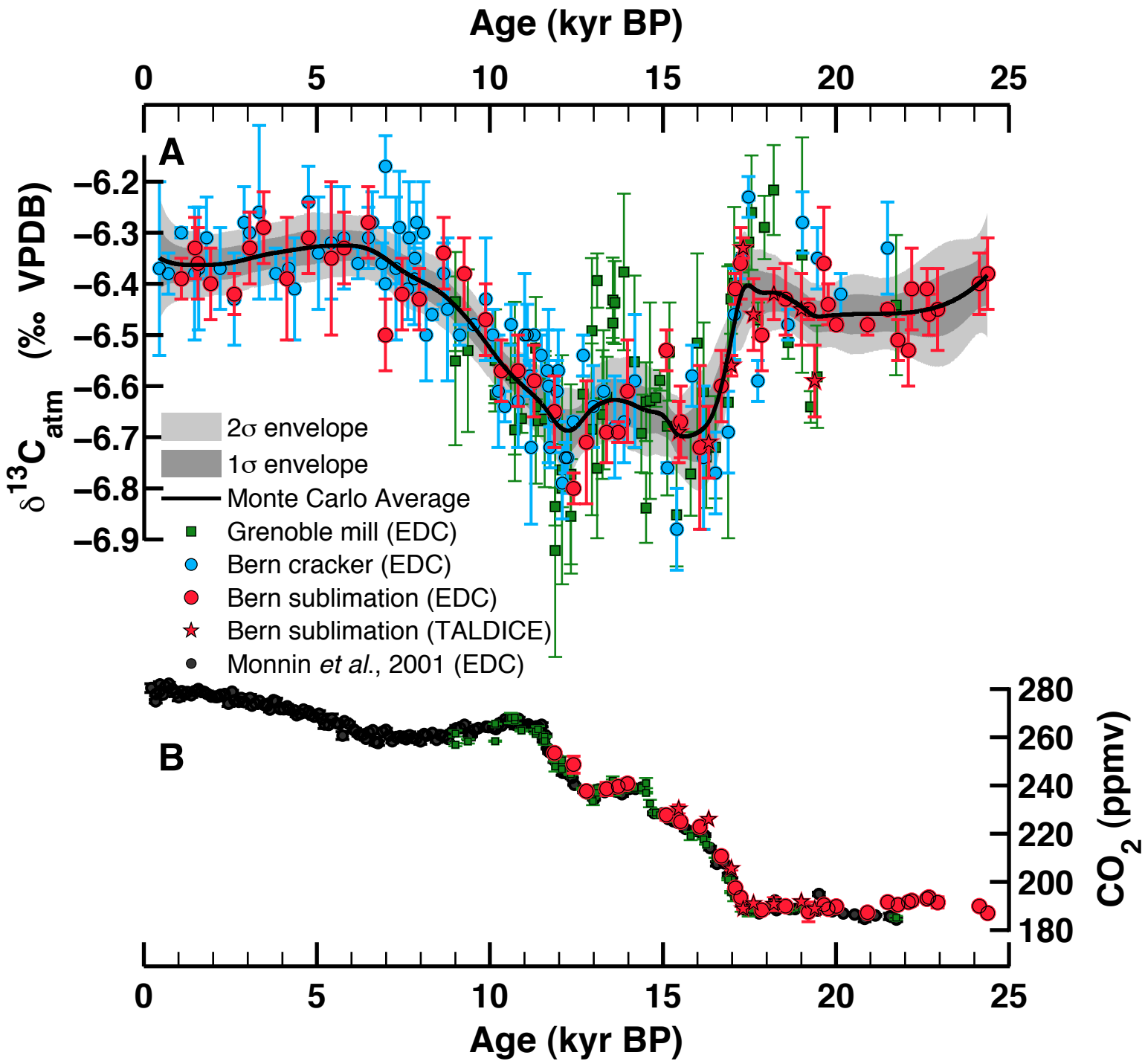
### 258 **Acknowledgements:**

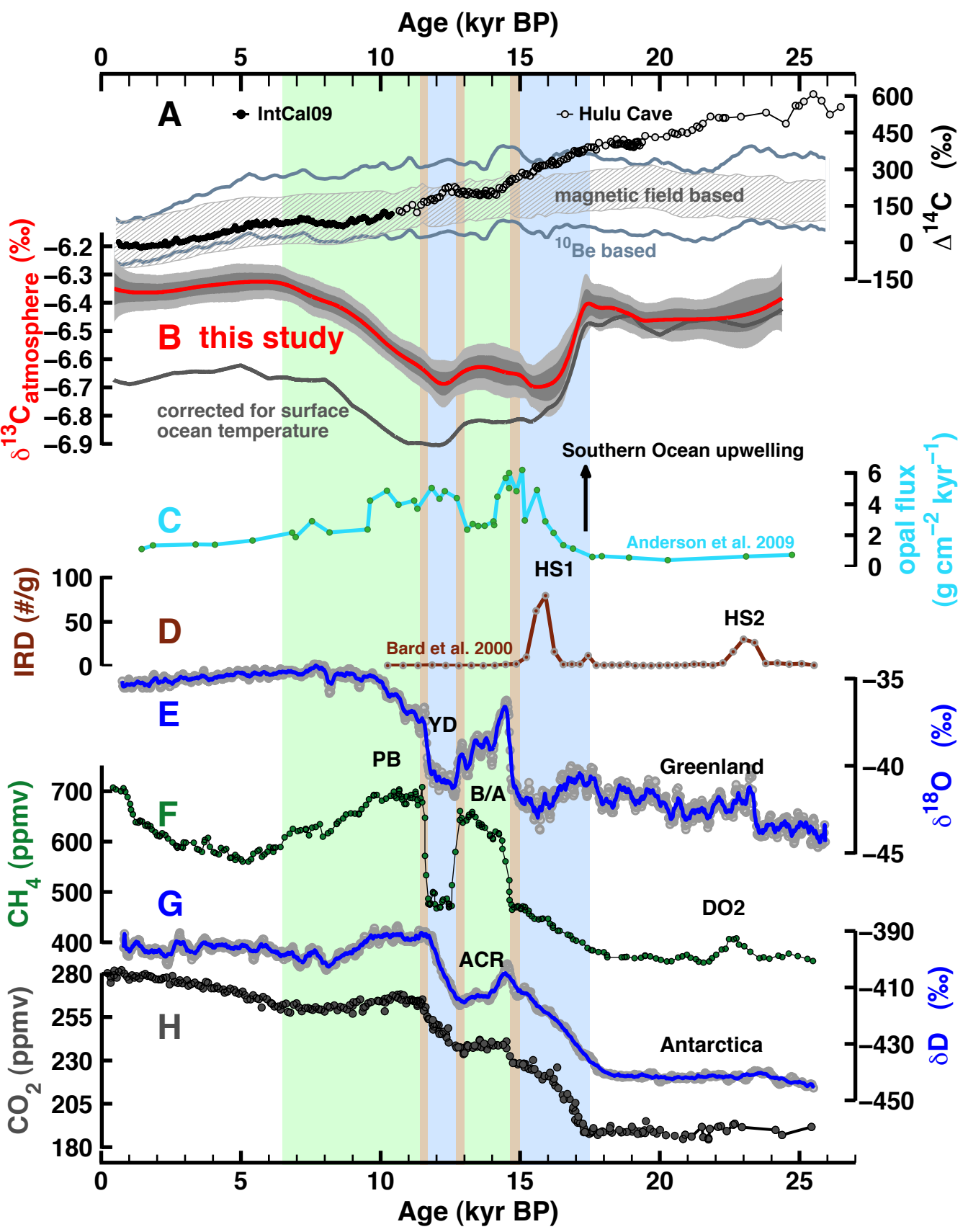
259 We thank two anonymous reviewers for carefully reviewing the manuscript. Financial  
 260 support for this study was provided in part by Deutsche Forschungsgemeinschaft (DFG),  
 261 Helmholtz Gemeinschaft, and Schweizerischer Nationalfonds (SNF). This work is a  
 262 contribution to the “European Project for Ice Coring in Antarctica” (EPICA), a joint  
 263 European Science Foundation/European Commission (EC) scientific program, funded by  
 264 the EC under the Environment and Climate Program and by national contributions from  
 265 Belgium, Denmark, France, Germany, Italy, The Netherlands, Norway, Sweden,  
 266 Switzerland, and U.K. The main logistic support at Dome C was provided by the Institut  
 267 Polaire Français – Paul Emile Victor (IPEV) and PNRA. Ice core material was also used  
 268 from the Talos Dome Ice Core Project (TALDICE), a joint European program led by Italy  
 269 and funded by national contributions from Italy, France, Germany, Switzerland and the  
 270 United Kingdom. The main logistical support at Talos Dome was provided by PNRA. This  
 271 is EPICA publication No. 284. The data is accessible online at  
 272 <http://doi:10.1594/PANGAEA.772713>.

273 **Fig. 1.** Ice core reconstructions of atmospheric  $\delta^{13}\text{C}$  and  $\text{CO}_2$  concentration covering the  
274 last 24 kyr. **(A)**  $\delta^{13}\text{C}_{\text{atm}}$  of atmospheric  $\text{CO}_2$  measured with three different methods on two  
275 different ice core drill sites. Blue circles: Bern cracker data, green squares: Grenoble mill  
276 data (9) after offset correction, red circles: Bern sublimation data. Red stars indicate values  
277 from the sublimation method but measured on Talos Dome Ice Core (TALDICE). Error  
278 bars represent the standard deviation of replicate measurements. The black line is the result  
279 of 4000 Monte Carlo simulations representing an error-weighted average of the different  
280  $\delta^{13}\text{C}_{\text{atm}}$  data sets. The light and dark shaded areas represent the  $2\sigma$  and  $1\sigma$  error envelope  
281 around the Monte Carlo Average (see SI). **(B)**  $\text{CO}_2$  concentration. Black circles represent  
282 earlier measurements on EDC (3), other symbols are the same as in panel **A**. Note: All ice  
283 core records are plotted on a synchronized age scale (32).  
284

284 **Fig. 2.** Ice core reconstructions and marine records illustrating the evolution of major  
285 components of the Earth climate system over the last 24 kyr. **(A)** Reconstructed  $\Delta^{14}\text{C}_{\text{atm}}$   
286 from IntCal09 (14) and the  $^{230}\text{Th}$ -dated Hulu Cave  $\Delta^{14}\text{C}_{\text{atm}}$  record (15) compared with  
287 modeled (16)  $\Delta^{14}\text{C}_{\text{atm}}$  assuming a constant carbon cycle under pre-industrial conditions but  
288 considering temporal changes in  $^{14}\text{C}$  production (either based on  $^{10}\text{Be}$  (18), upper and lower  
289 estimates enveloped in gray lines, or on paleomagnetic field intensity (17), hatched area).  
290 **(B)** Monte Carlo simulations (this study) of the evolution of  $\delta^{13}\text{C}_{\text{atm}}$  before (red line  
291 represents the MCA,  $2\sigma$  and  $1\sigma$  envelopes are in gray) and after SST correction (gray line;  
292 see SI) **(C)** Opal flux in the Southern Ocean as a proxy for local upwelling (20). **(D)** Record  
293 of ice rafted debris (IRD) in the North Atlantic associated with Heinrich stadials (HS1 and  
294 HS2) (27). **(E)** Greenland temperature proxy  $\delta^{18}\text{O}$  (33). **(F)** Reconstructed atmospheric  $\text{CH}_4$   
295 concentration (34) **(G)** Antarctic temperature proxy  $\delta\text{D}$  from the EDC ice core (35). **(H)**  
296 Compilation of reconstructed  $\text{CO}_2$  shown in Fig. 1B. Green bars indicate intervals with a  
297 strong net terrestrial carbon build-up, blue bars indicate intervals where sequestered deep  
298 ocean  $\text{CO}_2$  was released back to the atmosphere. Note: Ice core records are plotted on a  
299 synchronized age scale (32), other records are plotted on their individual age scales.

300







## Supporting Online Material for

### Carbon isotope constraints on the deglacial CO<sub>2</sub> rise from ice cores

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## Materials and Methods

### Analysis of $\delta^{13}\text{C}$ on ice core samples

The measurement of  $\delta^{13}\text{C}$  on ice core samples follows well-established protocols which have been applied in other studies (6, 9, 10, 35). In short, all three methods rely on four main steps. First, enclosed atmospheric air from the ice sample is released using a dedicated extraction device (sublimation, needle cracker and a ball mill for the respective data sets: Bern sublimation, Bern cracker and Grenoble mill). In a second step, the  $\text{CO}_2$  from the released ice core air is separated from the bulk air ( $\text{N}_2$ ,  $\text{O}_2$  and Ar) using cryogenic trapping. Third, a gas chromatographic column purifies the  $\text{CO}_2$  sample from other trace gases such as  $\text{N}_2\text{O}$ . Finally, the stable carbon isotopic ratio of the  $\text{CO}_2$  sample is measured against a bracketing standard using an isotope ratio mass spectrometer. The typical measurement reproducibilities of the three methods are 0.05‰ - 0.07‰ for the Bern sublimation (6, 10), 0.07‰ for the Bern cracker (6), and 0.10‰ for the Grenoble mill data set (9). Note that the method used for the Bern sublimation data set employs a novel sublimation technique (10). Besides a somewhat better precision, this technique offers the unique advantage of a quantitative gas extraction from the ice sample. The two other methods use conventional mechanic extraction devices (mill or cracker techniques), which extract only around 80% of the enclosed air in samples consisting of bubbly ice (usually the upper part, i.e. <600 m depth, of a deep ice core). This may become more problematic for ice from the bubble clathrate transition zone, where fractionation between different gases has been observed for incomplete gas extraction (36). Here we use only deglacial ice from Dome C located in the pure bubble zone and no gas extraction effects are to be expected for any extraction method used.

### Gravitational correction of the $\delta^{13}\text{C}$ data

Since gases and their isotopes become fractionated in the diffusive firn column due to gravitational fractionation, the measured  $\delta^{13}\text{C}$  values must be corrected for gravitational enrichment to derive the atmospheric signal ( $\delta^{13}\text{C}_{\text{atm}}$ ). To do this, measured  $\delta^{15}\text{N}$  on  $\text{N}_2$  serves as a proxy for the gravitational enrichment of the stable carbon isotopes of  $\text{CO}_2$ . This approach can be used because the isotopic composition of  $\text{N}_2$  was constant over the covered time interval, and the gravitational fractionation is only dependent on the mass difference,  $\Delta m$ , of the molecules, i.e.  $\Delta m = 1$  for both  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ . The three data sets (Bern sublimation, Bern cracker, and Grenoble mill) were corrected using the same measured  $\delta^{15}\text{N}$  data set provided by Dreyfus (37) and by following previously published procedures (6, 9, 35). The typical gravitational enrichment for the EDC core ranges between 0.42‰ for glacial samples and 0.52‰ for Holocene samples. The reproducibility of the  $\delta^{15}\text{N}$  measurements is about 0.01‰ (37).

As the  $\delta^{15}\text{N}$  measurements and  $\delta^{13}\text{C}$  measurements are not carried out on exactly the same ice core sample nor at the same temporal resolution, an interpolation step must

first be performed. To prevent all measurement noise of  $\delta^{15}\text{N}$  data from being transferred to the reconstructed  $\delta^{13}\text{C}_{\text{atm}}$  record, a spline interpolation is used, which is superior to a point-to-point interpolation for reasons discussed by Elsig (35). A second approach makes use of an empirical relation between  $\delta^{15}\text{N}$  and the water isotopic composition  $\delta\text{D}$ , which serves a proxy for relevant firn processes, i.e. accumulation rate, thickness of the diffusive column height and firn temperature (38). This  $\delta^{15}\text{N}$ - $\delta\text{D}$  relation must be applied for time periods where  $\delta^{15}\text{N}$  measurements are not available, which is the case for the time interval between 24 kyr and 22 kyr. As the glacial-interglacial shift of  $\delta^{15}\text{N}$  for the EDC ice core is only 0.1‰ and the  $\delta^{15}\text{N}$ - $\delta\text{D}$  relation explains 88% of the variability (38), the differences between the two approaches to correct for gravitational fractionation are negligible compared to the reproducibility of the  $\delta^{13}\text{C}$  measurement. Since the measurement reproducibility of  $\delta^{15}\text{N}$  is with 0.01‰ much lower than for  $\delta^{13}\text{C}$ , the introduced error is between 0.01 and 0.02‰ and mainly due the interpolation procedure described above.

The ice core measurements and the calculated Monte Carlo Average are available at:  
<http://doi:10.1594/PANGAEA.772713>

### Extracting the atmospheric signal

The following procedure describes the stepwise statistical data analysis to combine the three individual data sets (“residual analysis”) and to derive a robust atmospheric signal (“Monte Carlo spline process”). These steps make use of a bootstrap procedure to account for the specific measurement precision among the data sets and to allow for identification of outliers, i.e. data points which are incompatible with the common atmospheric signal in the data set.

### Residual analysis

In the main text, we combine three independently measured  $\delta^{13}\text{C}_{\text{atm}}$  data sets of different precision, accuracy and resolution for the last 24 kyr. A unified  $\delta^{13}\text{C}_{\text{atm}}$  time series of the three individual time series has to account for offsets among the records as well as for the individual measurement precision.

In the following, we quantify the overall differences in accuracy between the records. As our sublimation data (6) agree well with measurements from the Law Dome ice core (39), which have an overlap with firn air reconstructions and archived air from the Cape Grim air archive, we set the sublimation data as the reference (for details see discussion in Schmitt et al., 2011 (10)). To account for this agreement with the Law Dome record (39), the overlapping period of the Law Dome record is added to the combined data set for the Monte Carlo spline routine as additional data point (see Fig. S4). In the first step, the potential offsets between the Bern sublimation data to the Bern cracker data and the data from the Bern sublimation to the Grenoble mill are analyzed and quantified. As the procedure is the same for the Bern cracker and Grenoble mill data sets, we generally outline an offset calculation for the Bern sublimation to a 'non-

sublimation' data set. In principle, residual  $\delta^{13}\text{C}$  values between two datasets are determined where they overlap. The resulting mean systematic difference is called offset and represents the difference in the accuracy of the methods. However, the individual ice samples of the three data sets are not measured at exactly the same depth, hence gas age, which complicates direct calculation of the  $\delta^{13}\text{C}$  residuals. For each data point of a non-sublimation record, we choose the nearest available Bern sublimation data point in time. The overall mean time difference between compared points is  $\Delta t = 29 \pm 171$  years for the Bern cracker and  $\Delta t = 34 \pm 175$  years for the Grenoble mill data set (Fig. S1B and S2B). This  $\Delta t$  is sufficiently small compared to the width of the gas age distribution in EDC and Talos Dome ice (40, 41). This is also illustrated in Fig. S1B and S2B, which show that the absolute values of the residuals do not increase with larger  $\Delta t$ . Hence, we can safely assume that the differences in the compared data points arise essentially from differences in the accuracy and precision in all three methods. The calculated individual  $\Delta\delta^{13}\text{C}$  residuals are sorted into bins and plotted in a histogram.

Performing a Gaussian fit yields the mean offset and the standard deviation between sublimation and non-sublimation data set. To account for the relatively small sample number for the residual distribution we performed a Monte Carlo procedure to determine the mean and standard deviation of the distribution. In a first Monte Carlo iteration, the procedure is repeated 100 times, randomly varying the input data within their  $1\sigma$  standard deviation. From each of the obtained 100 Monte Carlo runs, a Gaussian fit is calculated providing a mean offset and  $1\sigma$  standard deviation after averaging over the 100 runs. Figure S3 shows the histogram of the residuals for the Bern cracker (A) and the Grenoble mill (B) data set. On top of the histogram, a Gaussian distribution is drawn using the average mean and standard deviation from the fitted distributions of the 100 Monte Carlo runs.

If the residuals are only due to the stochastic measurement errors in the two methods compared, then their distribution has to be Gaussian with the width of the distribution given by the propagated error of both methods. This is perfectly fulfilled for the residuals between the Bern sublimation and Bern cracker data (Fig. S3A). For the Bern cracker record, the calculated offset of  $-0.01\text{‰} \pm 0.11\text{‰}$  to the sublimation record is very small and in line with a similar analysis done on the Holocene data set (6). The distribution of the residuals is Gaussian, and its width can be entirely explained by error propagation of the individual measurement error of both methods. For the Grenoble mill data the distribution is reasonably Gaussian but the width is slightly larger than expected from the propagated measurement errors. An offset of  $0.16\text{‰} \pm 0.17\text{‰}$  between the Grenoble mill data and the Bern sublimation data is observed and correcting for this offset improves the combined record. To apply a constant offset correction, the offset has to be constant with time. Therefore, we performed a second analysis for the case of the  $\Delta\delta^{13}\text{C}$  residuals varying with time. Fig. S1A and Fig. S2A show these residuals as a function of the age of the respective data point. The Bern cracker data shows no temporal dependence of the offset, the Grenoble mill data shows a slight tendency to higher offsets for younger ages (higher  $\text{CO}_2$  concentrations), however, this trend is statistically not significant. Due to the small sample number available for the residual analysis we refrained from correcting this insignificant trend. Instead we only shifted the Grenoble data set by its mean offset relative to the Bern sublimation data. The three involved labs in Bern and Grenoble also

conducted a round-robin exercise with three cylinders with working standards to identify possible scale differences among the labs. For the cylinders, we also measured offsets which range in the observed differences among Bern and Grenoble ice core data. We could not completely identify the reasons for these small differences. Note that in view of the complex analytical systems and the differences in the referencing strategy of the three methods, the observed systematic offsets are to be expected, rather small and reproducible.

We acknowledge that the posteriori offset procedure introduces a systematic additional error to the Grenoble data set. However, we did not add this “offset error” to the measurement error since the Monte Carlo procedure would then put even less weight onto this data set and the calculated spline would be more biased towards the Bern data sets. Note that the outcome of the Monte Carlo spline procedure described below, is not significantly affected by the inclusion of the Grenoble mill data and that all of the conclusions drawn in our paper also hold, if that data set were to be excluded. However, inclusion of all three data sets is essential to obtain the highest temporal resolution possible for the  $\delta^{13}\text{C}_{\text{atm}}$  record.

#### Calculating Monte Carlo splines of the combined record

In a second step after the offset correction, cubic splines (42) of the combined  $\delta^{13}\text{C}_{\text{atm}}$  time series were calculated. To exclude the high frequency measurement noise, splines with a cut-off period of 375 years were selected (see Fig. S4 showing 400 sample splines). This value was chosen as for the ice cores used in this study, variability on shorter time periods is strongly dampened in gas reconstructions due to the low-pass filtering of the primary atmospheric signal by the continuous bubble enclosure process in the firn column (43). The spline calculation is repeated 4000 times, with the input data randomly picked from their  $1\sigma$  error range. For replicate samples, the  $1\sigma$  standard deviation of these specific data points is used. In the case that the  $1\sigma$  standard deviation for replicate samples is better than the mean reproducibility of the method, the mean standard deviation of the data set is used. The same applies for points where only one ice sample was measured. Assigning the mean standard deviation of the data set to those data points prevents unjustified pinning of the spline evolution at these positions. As can be seen in Fig. S4 and S5, regions where data points have small error bars tend to pin the spline evolution (e.g., compare spline evolution in Fig. S4 at position (D) and the respective distribution in Fig. S5D). The arithmetic average, here called the Monte Carlo Average (MCA), is calculated from the 4000 splines. Due the variability of the individual splines, the calculated MCA is smoother than the individual splines (Fig. S4). This additional smoothing of the MCA is a function of the measurement precision of a data point and its temporal distance to its neighbors (i.e. temporal resolution). Since neither the individual records nor the combined data set are equidistant and the measurement error varies among the data sets and with time, the additional smoothing of the MCA varies with time (Fig. S4). In other words, the MCA cannot be characterized by a defined cut-off period. Instead, our procedure removes high frequency components of the splines at positions where these were not robust enough as measurement error and temporal resolution did not allow to constrain the individual splines sufficiently. On the other

hand, for time intervals with small error bars and dense data coverage, the individual splines are pinned. Here, the resulting distribution is narrow, and the high frequency components were retained (Fig. S5D). This procedure is superior to approaches calculating only one spline with a fixed cut-off period, hence constant smoothing characteristic, as the MCA can account for inhomogeneous measurement error and variable temporal resolution, a common feature of our data sets. Finally, the dark gray (light gray) shaded envelopes in Fig. 1 and 2 are obtained, marking the  $1\sigma$  ( $2\sigma$ ) confidence interval of the Monte Carlo average. As the distributions of the splines at a given point in time are not truly Gaussian (see example histograms in Fig. S5), the  $1\sigma$  and  $2\sigma$  confidence intervals serve as approximations for the true spline variability at each point in time. Table S3 provided digitally in the supplement lists the MCA and the  $1\sigma$  envelope on the synchronized age scale (31).

To investigate the robustness of the chosen approach to combine the three data sets, we also calculated MCAs for subsets of the combined data. Four cases are selected and shown in Fig. S6. In case A we tested if the outlier detection does actually improve or alter the MCA (see discussion below). As illustrated in Fig. S6A this is not the case. Case B is calculated without the TALDICE samples (which have a different gas age distribution than Dome C samples) and shows that removing this subset does not change the MCA. Removing the Grenoble subset in case D leads to only minor changes in the MCA between 12-15 kyr BP. When the MCA is calculated from the sublimation data only, the spline routine produces more wiggles as the temporal resolution of the sublimation data alone is not sufficient for this cut-off period. However, also in this extreme case the general shape of the MCA is still preserved and the MCAs agree within their  $2\sigma$  envelopes. This analysis shows that combining the two Bern data sets and the Grenoble data set is a beneficial approach as it increases the temporal resolution and provides a more robust result but does not create spurious trends.

#### Outlier detection with bootstrapping

Atmospheric stable carbon isotope measurements on the EDC ice core over the Holocene report a significant measurement outlier at 170 m depth, that can neither be explained by a climatic excursion nor by poor measurement precision, but is likely caused by problems during the ice core drilling (6). To test for further outliers in the combined data set, the above described Monte Carlo procedure is repeated, but each time one data point is excluded. If the calculated  $2\sigma$  confidence interval of the MCA does not overlap with the  $2\sigma$  error of the excluded data point, this data point is assigned as an outlier and excluded from the final spline calculation. This test is done for all data points, resulting in only four measurements excluded from the data set. Note that for this bootstrap procedure, all individual measurements were used instead of the replicate mean. In a last step, the bootstrap procedure was repeated using also the replicate means instead of the individual replicates. No data point was identified as an outlier during this final step. Since only four individual measurement points were identified as outlier, the calculated MCA is not dependent on whether the outliers are included or excluded during the Monte Carlo procedure as the respective MCA and  $2\sigma$  confidence intervals nicely overlap (Fig. S6A). In summary, if a data point cannot be identified a priori as an artifact

due to either measurement problems or during drilling (e.g. the 170 m depth outliers in the Holocene section) the bootstrap procedure does not improve the MCA. In other words, the observed scatter in the combined data set can be explained already by the combined measurement error and errors due to offset corrections.

### Correction for SST changes

With changing sea surface temperature (SST), not only the partial pressure of dissolved CO<sub>2</sub> in water (pCO<sub>2</sub>) but also the isotopic fractionation during the gas exchange is altered. The δ<sup>13</sup>C of atmospheric CO<sub>2</sub> becomes isotopically heavier by roughly 0.1‰ per 1 K increase as the fractionation factor decreases (12, 44, 45). In the following, we attempted to roughly quantify this effect of changing SST on δ<sup>13</sup>C<sub>atm</sub> over the transition.

The temperature at 19 kyr BP is set as a reference point, as changes in global mean sea surface temperature at earlier glacial times are small compared to the variations during the glacial termination. The isotopic ratio of atmospheric CO<sub>2</sub> Δt years after 19 kyr BP is calculated according to:

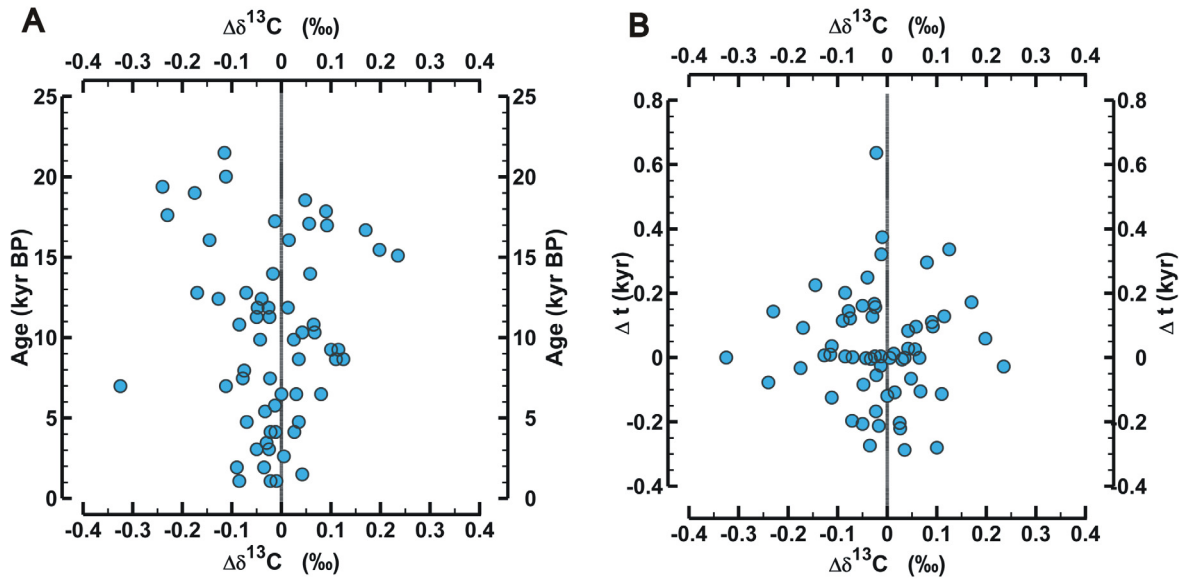
$$\delta^{13}\text{C} (19 \text{ kyr BP} + \Delta t) = \delta^{13}\text{C} (19 \text{ kyr BP}) + \Delta(\delta^{13}\text{C}), \quad (1)$$

where

$$\Delta(\delta^{13}\text{C}) = \alpha \Delta T, \text{ with } \alpha = 0.1\text{‰/K}. \quad (2)$$

The evolution of the past global mean SST can be approximated from direct marine proxies, such as alkenones or Ca/Mg ratios. For regions and time periods without marine proxy records, scaled temperature evolutions of Greenland and Antarctica serve as crude representations of the surrounding oceans. In the course of this work, we use the estimations compiled by Köhler et al. (4) that have been used in other modeling studies (11). In this compilation, the surface ocean is divided into five regions (corresponding to the surface boxes used in Köhler et al. (4)): the North Atlantic, the Equatorial Atlantic, the Southern Ocean, the Equatorial Indo-Pacific and the North Pacific. For each box, temperature proxies are used to account for the change in SST. The stable water isotopic signal δ<sup>18</sup>O from the GISP2 (46) and δD from the EDC (47) ice cores were rescaled to a glacial/interglacial amplitude of 4 K and used to quantify the SST evolutions of the Northern boxes and the Southern Ocean, respectively. Temperature changes in lower latitude boxes were adapted from foraminifera records (48). The SST approximations for the five surface boxes are shown in Fig. S7B (equatorial boxes) and Fig. S7C (high latitude boxes), together with the area-weighted temperature average (gray curve in Fig. S7B). Note that gas exchange and thus the isotopic fractionation are largely inhibited for sea-ice covered areas. Therefore, only areas dominated by open water were used for the calculation of the area-weighted SST average. These areas are calculated internally within the BICYCLE model (4). Accounting for the change in sea-ice area leads to a difference of only 0.8 K in the area-weighted SST estimate over the period between 19 kyr and 10 kyr. The total shift from 19 kyr BP to the Holocene in this reconstruction is 2.8 K.

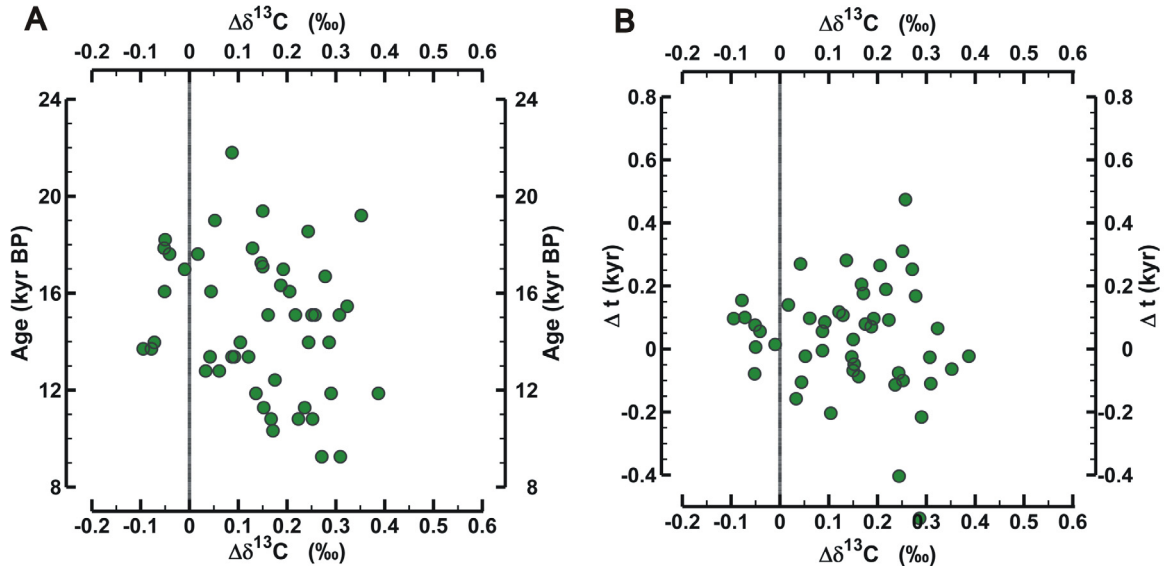
This global SST record is used to calculate the SST-corrected evolution of  $\delta^{13}\text{C}_{\text{atm}}$  according to equations (1) and (2) (gray line in Fig. S7A) by subtracting the SST-induced  $\delta^{13}\text{C}$  change from the Monte Carlo Average (red line in Fig. S7A). We note that our temperature approximation introduces further error to the one and two sigma confidence interval of the SST corrected record. However, a detailed error propagation analysis is beyond the scope of the overall approximation since the purpose of this correction was to provide only a rough estimate of the global SST change on our  $\delta^{13}\text{C}_{\text{atm}}$  record, i.e. to show that global SST changes likely shift the  $\delta^{13}\text{C}_{\text{atm}}$  by approximately 0.3‰ from the LGM to the Holocene. Note also that the proxies used for our crude SST reconstruction are on their individual age scales; therefore, interpretations on the submillennial timescale are not possible. For illustration purposes, we also assumed a simple linear SST increase of 2.8 K between 19 kyr and 10 kyr and a constant SST during the Holocene (Fig. S7B). The resulting  $\delta^{13}\text{C}$  anomaly was subtracted from the  $\delta^{13}\text{C}_{\text{atm}}$  evolution of the MCA, and this simple linear SST rise correction (Fig. S7A blue and orange line) is compared with the proxy-based SST correction. As the proxy based mean SST evolution during the deglaciation is already rather linear with only small deviations during the YD-BA oscillation, the two SST reconstructions are similar as well. In summary, our SST correction serves as an illustration of the effect of an overall glacial/interglacial warming, while small scale features in the corrected  $\delta^{13}\text{C}_{\text{atm}}$  record on sub-millennial time scale should not be interpreted.



**Fig. S1.**

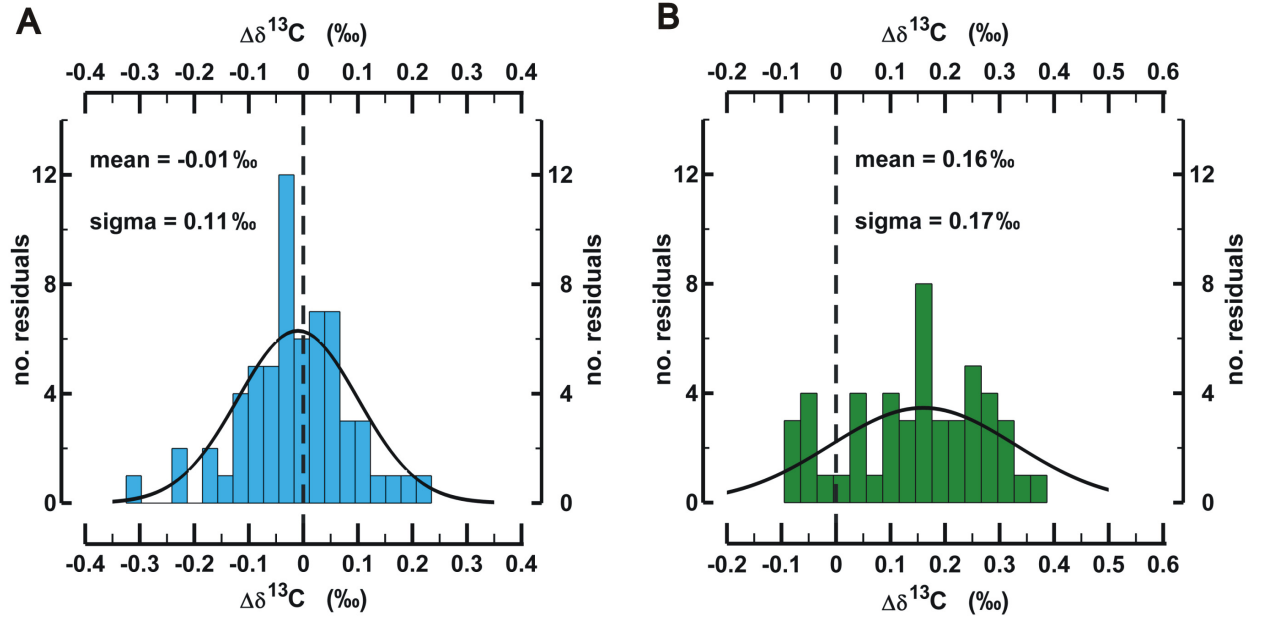
Residual plots for the Bern cracker data set. **(A)** Residuals plotted against the absolute age of the Bern cracker measurements. The data points are randomly scattered around the zero line showing no trend with time. However, the scatter shows a tendency to become larger for glacial ice with lower  $\text{CO}_2$  concentration. **(B)** Residuals plotted against  $\Delta t$ , i.e. the temporal difference between a Bern cracker measurement to its nearest neighbor in the Bern sublimation data. Most  $\Delta t$  values lie between +0.2 kyr and -0.2 kyr, with no trend of larger  $\Delta\delta^{13}\text{C}$  residuals for larger  $\Delta t$  differences.





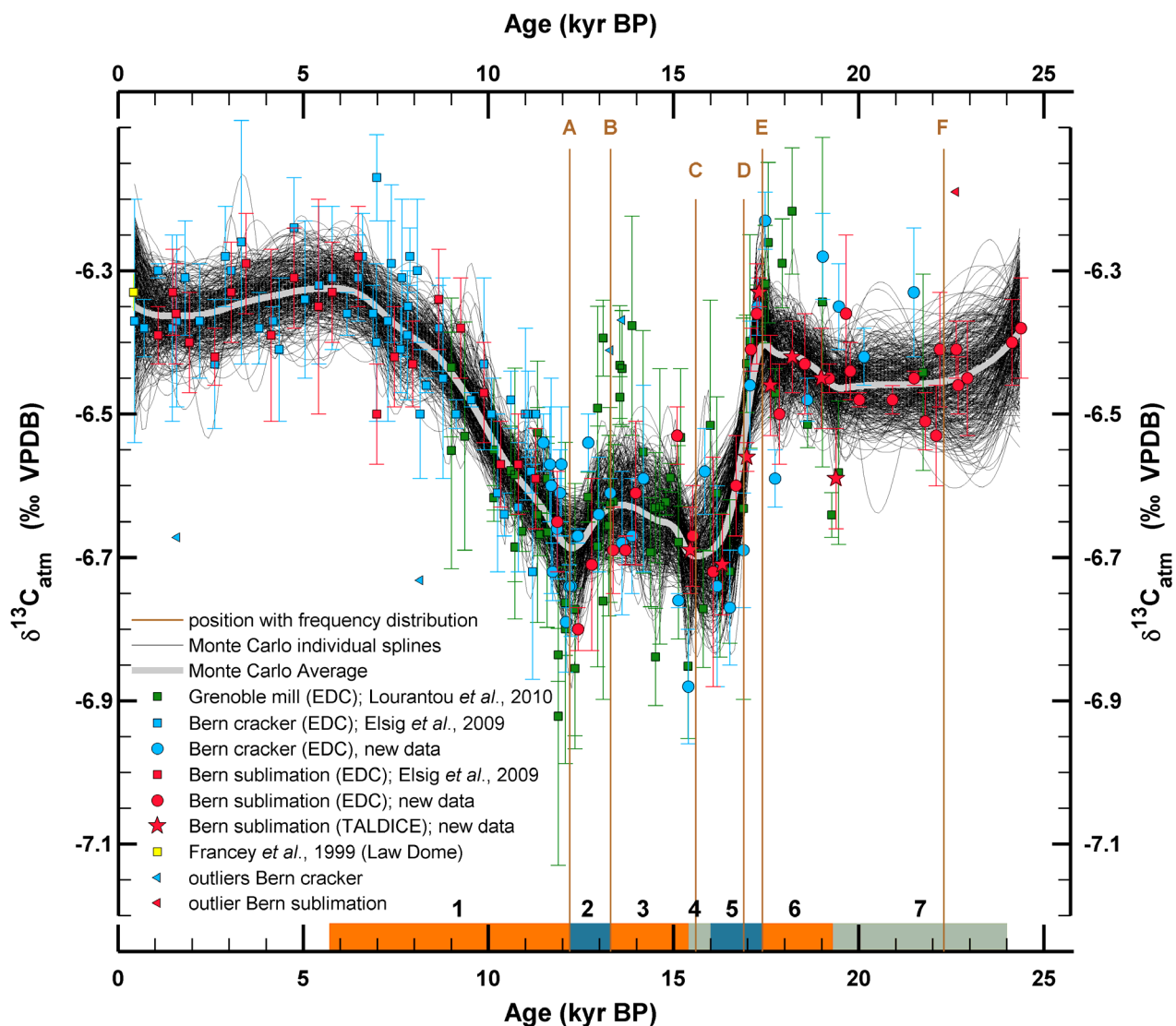
**Fig. S2**

Residual plots for the Grenoble mill data set. **(A)** Residuals plotted against the absolute age of the Grenoble mill measurements. The data points are randomly scattered but show an offset to the zero line. **(B)** Residuals plotted against  $\Delta t$ , i.e. the temporal difference between a Grenoble mill measurement to its nearest neighbor in the Bern sublimation data. Most  $\Delta t$  values lie between +0.2 kyr and -0.2 kyr, with no trend of larger  $\Delta\delta^{13}\text{C}$  residuals for larger  $\Delta t$  differences.



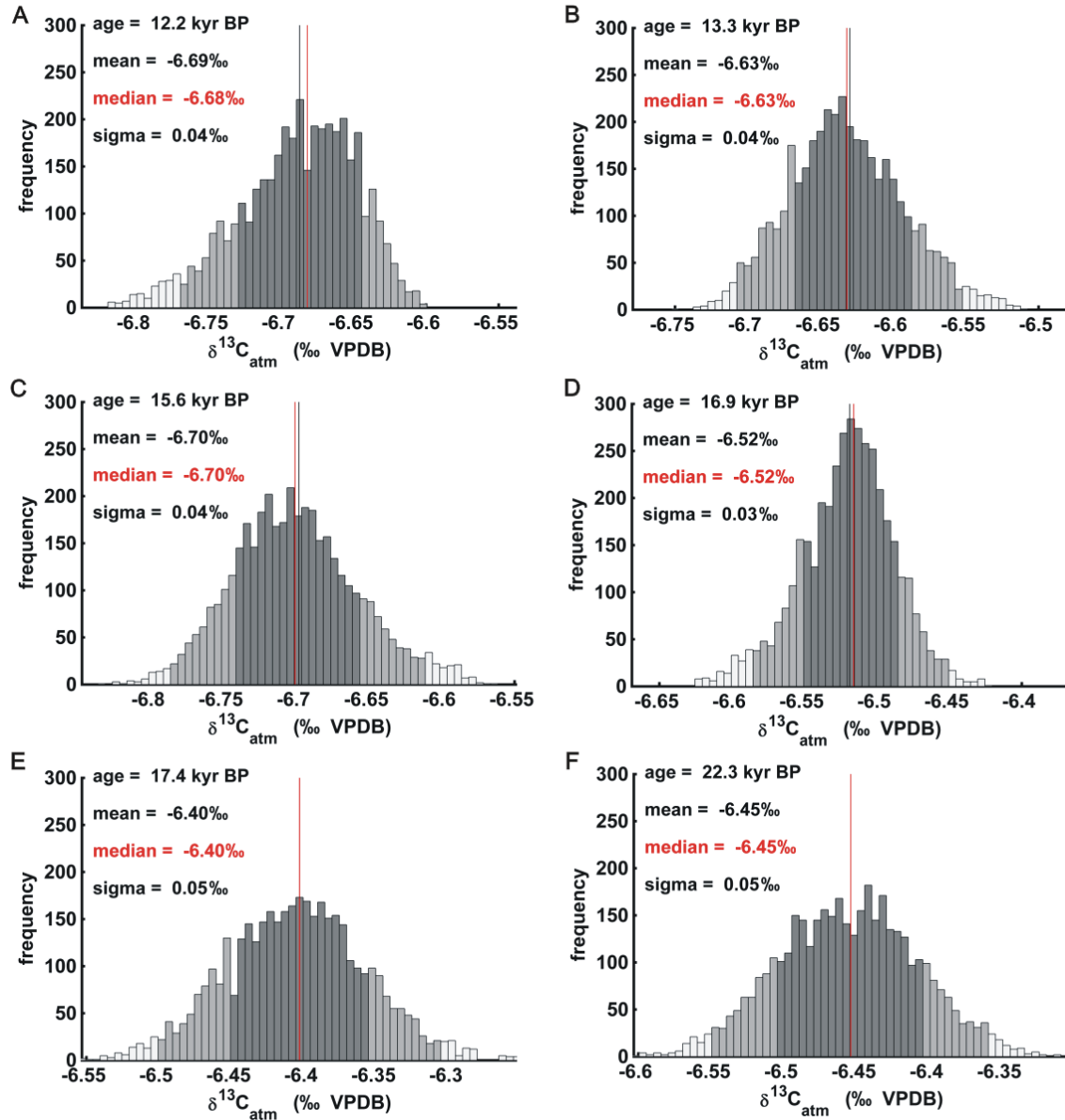
**Fig. S3**

Histograms showing the offsets among the data sets: The histograms show the residuals of the measured mean value at a given sample depth for the Bern cracker **(A)** and the Grenoble mill **(B)** data sets to its nearest neighbor in the Bern sublimation data. The output of a Monte Carlo procedure (see text) was used to determine the mean and standard deviation of the Gaussian curve (black line).



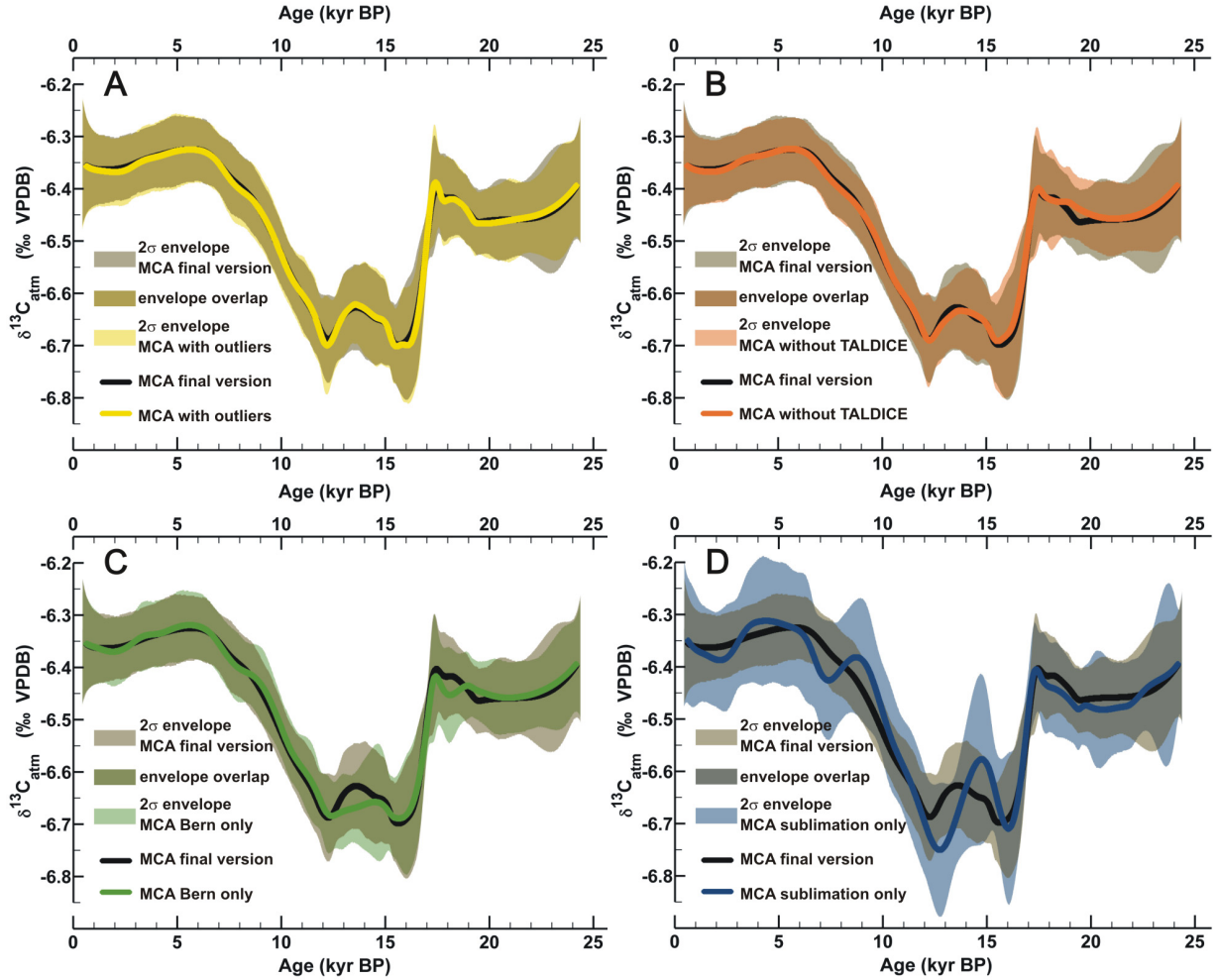
**Fig. S4**

Individual Monte Carlo splines: Compilation showing the color-coded  $\delta^{13}\text{C}_{\text{atm}}$  measurements. Squares indicate published data, circles new measurements, and triangles denote individual data points which were detected as outliers in the bootstrap routine. The Monte Carlo Average is plotted in gray and in black a sample of 400 Monte Carlo splines with a cut-off period of 375 years. Latin letters A to F connected to vertical lines denote time intervals where the frequency distribution of the 4000 splines is shown in Fig. S5. Numerals from 1-7 at the bottom axis mark the time intervals shown in Tab. S2. All  $\delta^{13}\text{C}_{\text{atm}}$  records from this study are on a synchronized age scale (31); only the reference data point at 0.42 kyr from the Law Dome record (39) is on its original age scale.



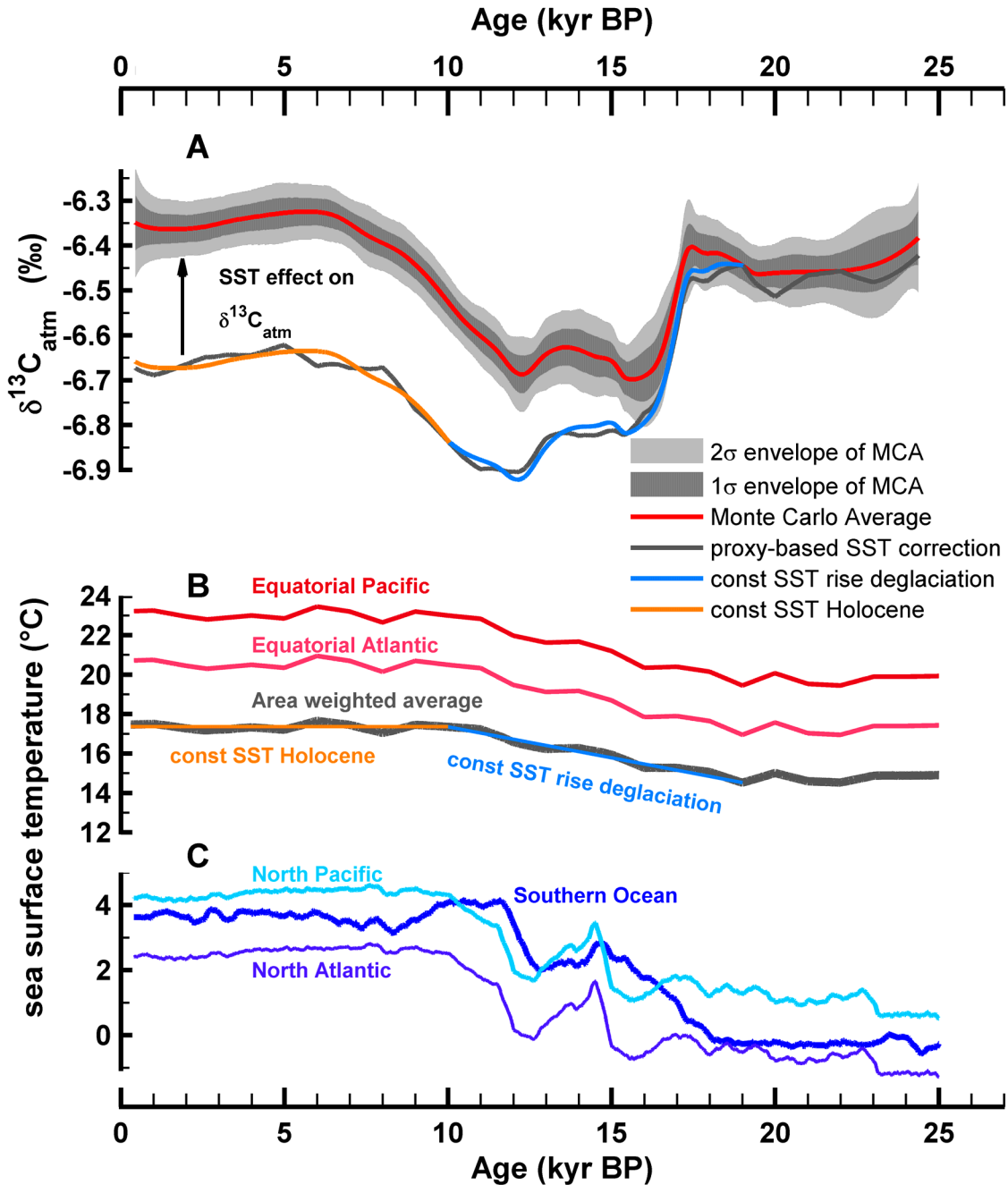
**Fig. S5**

Frequency distributions of the Monte Carlo splines at selected points in time: Histograms showing the distributions of the 4000 splines at selected points of our  $\delta^{13}\text{C}_{\text{atm}}$  time series (positions marked in Fig. S4 with brown Latin letters). Bars in dark gray mark the  $1\sigma$  interval, light gray the  $2\sigma$  interval, and white bars are outside the  $2\sigma$  interval. The black (red) vertical line marks the mean (median) of the distribution. Note that some distributions are not Gaussian but have a broader shape; therefore, mean and standard deviation do not entirely describe the frequency distributions.



**Fig. S6**

Comparison of Monte Carlo Averages for different data sets included. Each panel shows the final MCA in black, i.e. the MCA which is used in the main figures Fig. 1 and Fig. 2 of the paper and on which the interpretations are based. The individual MCAs in the sub-panels **A-D** are plotted in colors. The  $2\sigma$  envelope of the final MCA is in gray and the  $2\sigma$  envelopes of sub-panels **A-D** are colored and overlapping  $2\sigma$  envelopes are in the respective mixed tones. **A** All three data sets but with the five outliers detected in the bootstrap routine included. **B** TALDICE samples excluded **C** Only Bern cracker and Bern sublimation data (i.e. Grenoble ball mill data excluded) **D** Bern sublimation data only. While the calculated MCA is insensitive to the outliers and the TALDICE samples, removing the Grenoble ball mill data and Bern cracker data has an effect on the MCA. In case of removing the Grenoble data, the calculated MCA deviates somewhat from the final MCA between 12 and 14 kyr, where there is the largest disagreement among the three data set. However, the overall shape is retained. When only the sublimation data is used, the MCA becomes unstable and pinned at individual data points, since the resolution is insufficient for the applied cut-off period of 375 years. All exclusion experiments show that the respective  $2\sigma$  envelopes overlap and thus record the same robust  $\delta^{13}\text{C}_{\text{atm}}$  atmospheric features seen in the final MCA.



**Fig. S7**

SST correction of the  $\delta^{13}\text{C}_{\text{atm}}$  MCA evolution. A proxy-based SST reconstruction is compared with a linear temperature increase during the deglaciation. **(A)** Evolution of  $\delta^{13}\text{C}_{\text{atm}}$  (red line) and proxy-based SST corrections (gray line) compared with a linear rise of 2.8 K between 19 kyr and 10 kyr (blue line) followed by constant SST during the Holocene (orange line). **(B)** SST evolution of the equatorial boxes (red lines) and the area-weighted average of all five surface boxes (gray), the latter being used for the proxy based SST correction above, **(C)** SST evolution of the three high latitude surface boxes (blue lines).



**Table S1.**

Selected points of the Monte Carlo Average and their respective mean, median, and  $1\sigma$  standard deviation as used to calculate the time intervals shown in Tab. S2.

interval boundary (kyr BP)	mean $\delta^{13}\text{C}_{\text{atm}}$ (‰)	median $\delta^{13}\text{C}_{\text{atm}}$ (‰)	$1\sigma$ (‰)
5.7	-6.32	-6.33	$\pm 0.03$
12.2	-6.69	-6.68	$\pm 0.04$
13.3	-6.63	-6.63	$\pm 0.04$
15.4	-6.70	-6.70	$\pm 0.04$
16.0	-6.69	-6.69	$\pm 0.06$
17.4	-6.40	-6.40	$\pm 0.05$
19.3	-6.46	-6.46	$\pm 0.03$
24.0	-6.40	-6.40	$\pm 0.05$



**Table S2.**

Time intervals listing the trends in mean  $\delta^{13}\text{C}_{\text{atm}}$  and median  $\delta^{13}\text{C}_{\text{atm}}$  between two interval boundaries as listed in Tab. S1 and marked in Fig. S4. As a conservative estimate of the confidence of these differences, the last column lists the sum of both  $1\sigma$  standard deviations of  $\delta^{13}\text{C}_{\text{atm}}$  at the interval boundaries. Note that interval 1, 2, 3, 5 and 7 represent the differences between local minima and maxima positions on the MCA. In contrast, intervals 4 and 7 were selected to represent relatively flat plateaus. Intervals 1 and 5 are indicated in bold to indicate that most of the  $\delta^{13}\text{C}_{\text{atm}}$  variability is concentrated in these two intervals.

interval	interval boundaries	$\Delta$ mean $\delta^{13}\text{C}_{\text{atm}}$	$\Delta$ median $\delta^{13}\text{C}_{\text{atm}}$	$\Sigma 1\sigma$
#	(kyr BP)	(‰)	(‰)	(‰)
<b>1</b>	<b>12.2 - 5.7</b>	<b>0.37</b> ↑	<b>0.35</b> ↑	<b>±0.07</b>
2	13.3 - 12.2	0.06 ↓	0.05 ↓	±0.08
3	15.4 - 13.3	0.07 ↑	0.07 ↑	±0.08
4	16.0 - 15.4	0.01 ↓	0.01 ↓	±0.10
<b>5</b>	<b>17.4 - 16.0</b>	<b>0.29</b> ↓	<b>0.29</b> ↓	<b>±0.11</b>
6	19.3 - 17.4	0.06 ↑	0.06 ↑	±0.08
7	24.0 - 19.3	0.06 ↓	0.06 ↓	±0.08

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