Changes in atmospheric CO₂ and its carbon isotopic ratio during the penultimate deglaciation

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The largest natural increases in atmospheric CO₂ concentration as recorded in ice cores occur when the Earth climate abruptly shifts from a glacial to an interglacial state. Open questions remain regarding the processes at play, the sequences of events and their similarities along different glacial–interglacial transitions. Here we provide new combined data of atmospheric CO₂ and its carbon isotopic ratio (δ¹³CO₂) for the penultimate glacial–interglacial transition (Termination II) from the Antarctic EPICA Dome C ice core. Together with the strongest Antarctic warming, this transition bears the largest CO₂ increase (104 ppmv) of the last nine Terminations, ending with an overshoot of 21 ppmv occurring within ~300 y and leading to higher levels than those of the late pre-industrial Holocene. The full CO₂ rise is accompanied by an overall decrease of the δ¹³CO₂ minimum values, on which three positive excursions are superimposed. Peak-to-peak δ¹³CO₂ changes in our record can reach ~11‰. The ice core atmospheric δ¹³CO₂ appears more depleted by ~0.2‰ during Termination II compared to Termination I, paralleling a similar carbon isotopic depletion recorded in marine data. During both terminations, most of CO₂ and δ¹³CO₂ variations are attributed to southern ocean stratification breakdown and decreased efficiency of the biological pump. Compared to Termination I, Termination II ice core data point to different timings of decrease in iron supply and sea-ice extent, suggesting that they could account for distinct patterns of the carbon cycle.

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1. Introduction

The EPICA Dome C (EDC) East Antarctic ice core provides 800 ky of climate and atmospheric composition history, corresponding to the last eight climatic cycles (Jouzel et al., 2007; Lambert et al., 2008; Loulergue et al., 2008; Lüthi et al., 2008). The overall Antarctic temperature record deduced from water isotopic measurements in ice (Masson-Delmotte et al., 2010) reveals nine saw-tooth curves with “rapid” temperature rises followed by slower temperature decreases leading to the next glacial maximum. Such pattern coincides with the δ¹⁸O signal of benthic foraminifera, depicting ice volume changes and defining the Terminations, T (Sarnthein and Tiedemann, 1990). Each Termination exhibits the most dramatic natural changes of atmospheric CO₂ mixing ratio over this time scale, both in terms of magnitude and rate of change, ranging from 45 to 100 ppmv (parts per million by volume).

Several processes are involved in these large carbon-cycle variations, whose relative contributions and timing over a glacial (G)—interglacial (IG) transition are still a matter of debate. The main processes involve physical and biological mechanisms in the oceans, with a major contribution from the Southern (S) Ocean. Productivity changes could be related to fluctuations of iron supply (Archer et al., 2000; Röthlisberger et al., 2004), of the silica inventory (Ridgwell et al., 2002) or of the ratio of inorganic to organic carbon burial (rain rate ratio) in ocean sediments (Archer et al., 2000; Ridgwell, 2003). Sea surface temperature, sea-ice cover (Stephens and Keeling, 2000), the strength of the oceanic overturning circulation (Schmittner et al., 2007) in connection with upwelling changes of the S. Ocean (Anderson et al., 2009), the long-term effect of carbonate compensation (Archer et al., 2000) and the changes in terrestrial carbon storage (Joos et al., 2004) are other important candidates modulating atmospheric CO₂ on this time scale. Until now, box models (e.g. BICYCLE, Köhler et al., 2005;
models of intermediate complexity (e.g. CLIMBER-2, Brovkin et al., 2007) or models of intermediate complexity (e.g. CLIMBER-2, Brovkin et al., 2007) have achieved in reconstructing the G-IG CO2 rise, only by combining all above processes. At G-IG timescales, the main carbon reservoirs interacting with the atmosphere lie in the ocean and the continental biosphere. The concomitant evolution of the stable carbon isotopic ratio $\delta^{13}C$ of atmospheric CO2 ($\delta^{13}CO_2$) helps in disentangling contributions of major CO2 sources. For instance, enhanced biological productivity removing CO2 from the atmosphere would lead to increased atmospheric $\delta^{13}CO_2$ values, associated with a preferential capture of the light carbon isotope during photosynthesis in the terrestrial and/or marine biosphere. An intensified vertical mixing in the S. Ocean (for instance associated with reduced buoyancy-driven Atlantic Meridional Overturning Circulation, AMOC, in the North (N.) Atlantic) would deplete atmospheric $\delta^{13}CO_2$ and cause CO2 to increase, as it would bring at the surface CO2-enriched waters poor in $\delta^{13}C$ (e.g. Köhler et al., 2006; Schmittner et al., 2007). An increase in sea surface temperature enriches the atmosphere in $\delta^{13}CO_2$ and in CO2 due to solubility effects (e.g. Heinze et al., 1991; Köhler et al., 2005). Still, the net effect on atmospheric $\delta^{13}CO_2$ through time of any carbon-cycle mechanism is usually rendered more complex due to the buffering effect of the ocean reservoir on the isotopic ratio in the atmosphere. Carbon-cycle models are thus best adapted for quantitative interpretation of the $\delta^{13}CO_2$ signal (Köhler et al., 2010).

Analyzing the same EDC ice core, Lourantou et al. (2010) produced the first detailed record of changes in the atmospheric $\delta^{13}CO_2$ covering the last deglaciation (T-I) with unprecedented accuracy and time resolution. These data nicely confirm the ~80 ppmv CO2 increase throughout T-I, occurring in two steps interrupted by a plateau (Minnin et al., 2001). Combined with carbon-cycle box-modeling and compared with marine records, these new data have led to the conclusion that the first step of atmospheric CO2 increase mostly involved processes in the S. Ocean, such as the stratification breakdown (releasing old carbon stored in the deep ocean) and a decreased biological pump. The CO2 plateau is attributed in a large part to terrestrial biosphere buildup (Lourantou et al., 2010). This work aims at testing if a similar sequence of events is at play for Termination II.

Initial drivers of Terminations are thought to be changes in the Earth’s orbit, with a major role either of precession (Huybers and Wunsch, 2003), obliquity (Huybers and Wunsch, 2005; Drysdale et al., 2009) or their phasing (Schulz and Zeebe, 2006). The onset and the shape of deglaciations show similarities with the millennial-scale Antarctic Isotope Maximum events (AIM, EPICA Community Members, 2006), occurring during glacial conditions, which but do not lead to glacial terminations due to the interruption caused by Dansgaard–Oescher events in the N. Hemisphere (Wolff et al., 2009). Such scenario is corroborated by the occurrence of a rapid jump of atmospheric CH4 usually marking the end of the Termination and thought to be associated with the resumption of the AMOC (Petit et al., 1999; Loulergue et al., 2008). One may thus expect differences between Terminations, depending on the timing of the AMOC resumption, itself possibly modulated by the ice sheet extent in the N. Hemisphere during the preceding glacial maximum (Wolff et al., 2009). As AMOC strength and the atmospheric CO2 mixing ratio are connected through the S. Ocean ventilation, the differences between Terminations should also show up in the CO2 signal and its isotopic signature.

T-II is known to be one of the most rapid and abrupt terminations of the late Quaternary. It is associated with the largest G-IG Antarctic temperature increase over the last 800 ky (Jouzel et al., 2007). The optimum of the subsequent interglacial (MIS 5e), is warmer than the Early Holocene by 2–5 °C in the S. Hemisphere (Bianchi and Gersonde, 2002; Jouzel et al., 2007; Masson-Delmotte et al., 2010) and by 4–5 °C in Greenland ice (North Greenland Ice Core Project Members, 2004) and in the Arctic region during summer (CAPE Last Interglacial Project Members, 2006). Higher CO2 mixing ratios (+7 ppmv Petit et al., 1999; +13 ppmv Fischer et al., 1999) are recorded in the Vostok ice core during the MIS 5e optimum, compared to the pre-industrial Holocene (taken at 280 ppmv).

In the following, we focus on the comparison between T-I and T-II. T-II occurs under higher eccentricity and precession than T-I (Imbrie et al., 1984), leading to a more intense N. Hemisphere summer insolation maximum, preceded by a stronger S. Hemisphere summer insolation maximum (Broecker and Henderson, 1998; Schulz and Zeebe, 2006). This may explain some of T-II specificities of climatic patterns, for instance the sea level increase preceding the 65°N June maximum insolation at 127 ky BP (e.g. Waelbroeck et al., 2008). Termination I is unusual due to the occurrence of the Antarctic Cold Reversal-Bølling/Allerød/Younger Dryas sequence (Petit et al., 1999; Monnin et al., 2001; Jouzel et al., 2007), which is preceded by a major Ice Rafted Debris (IRD) event, H1. An IRD deposit is also observed during T-II, H11 (Robinson et al., 1999), but of lower intensity than H1. Dating uncertainties are significant for H11, varying from 128 to 131 ky (Lototskaya andרגן, 1999; Müller and Kukla, 2004; Pahnik et al., 2007; Skinner and Shackleton, 2006). We also note that at some sites of the N. Atlantic, H11 appears to cover much of the transition from 140 to 128 ky BP (McManus et al., 1994; Oppo et al., 2006; Skinner and Shackleton, 2006), instead of a narrow episode just before the MIS 5e early climatic optimum (Masson-Delmotte et al., in press).

Although some continental records in the N. Hemisphere suggest standstill — like conditions in the course of T-II (e.g. Sánchez-Goñi et al., 1999), in the marine realm there are indications that the AMOC was reduced during much of T-II, in contrast with T-I where it resumed at the start of the Bølling/Allerød period, possibly explaining the T-I oscillation occurrence (Carlson, 2008). Ice core records provide indicators of regional/global significance, which are directly relevant to the possible occurrence during Terminations of millennial events such as the Antarctic Cold Reversal-Bølling/Allerød/Younger Dryas sequence. The facts that throughout T-II the CH4 signal does not oscillate and that CO2 and δD do not show a plateau, are clear indications that T-II differs from T-I and misses such sequence at global scale. More depleted $\delta^{13}C$/$^{12}C$ ratios during T-II than T-I are observed in carbon of planktic and benthic foraminifera from different ocean basins (e.g. Ninnemann and Charles, 1997; Spero and Lea, 2002; Banakar, 2005; Pena et al., 2008), with a difference amounting to ~0.4‰. An interpretation lies upon the generally reduced strength of the AMOC during T-II compared to T-I, increasing the prevalence of old deep waters and thus depleting the average carbon isotopic composition of the global ocean (Duplessy and Shackleton, 1985). An alternative explanation involves a large change in the global wind pattern affecting the supply of terrestrial light carbon to the ocean (Banakar, 2005).

Few CO2 mixing ratio data are available over T-II, while no ice core $\delta^{13}CO_2$ record exists yet for this period. With this study, we provide the first T-II CO2 results from the EDC core, combined with the first T-II $\delta^{13}CO_2$ data. Thanks to similar data obtained on T-I (Lourantou et al., 2010), we can qualify the similarities and differences between the two deglaciations. Such intercomparison benefits from several facts: (i) both datasets have been obtained with the same analytical system and protocol (Lourantou, 2009), (ii) they have a consistent age scale EDC3 (Loulergue et al., 2007) and (iii) they rely on the same ice core with comparable gas trapping conditions between the two Terminations. One fundamental difference relates to the physical state of gas molecules in the EDC ice covering both Terminations: while T-I
samples are located in EDC ice at depths of 345–580 m, where gas is entrapped in the form of air bubbles, T-II lies at depths of 1670–1870 m where gas is only present as air hydrates (clathrates) due to the hydrostatic pressure increase with depth. This may have potential implications on gas extraction as discussed below (Section 3.2).

After presenting the methods used in our reconstruction and the main signal features, we will evaluate to what extent the new T-II and old T-I CO₂ and δ¹³CO₂ signals bear similarities and differences with other signals notably obtained on the EDC ice core. In absence of sufficient proxy data over T-II allowing one to run carbon-cycle box-model simulations similar to those performed by Lourantou et al. (2010) for T-I, we will use a Keeling plot approach and the comparison with other proxies in ice and marine cores to propose a scenario of carbon-cycle mechanisms able to explain both CO₂ and δ¹³CO₂ patterns in the course of T-II and the start of MIS 5e.

2. Materials and methods

We used the same analytical method and protocol as in Lourantou et al. (2010). A detailed description is provided in Lourantou (2009). In short, 40–50 g of ice are placed under vacuum and crushed in a stainless steel ball mill. The extracted gas is then expanded in a 10 cm³ sample loop. From there, an ultra pure helium stream flushes the gas through a glass trap where CO₂ is frozen out at −196 °C. The trapped CO₂ is then transferred into a low flow rate helium stream, to be cryofocused on a small volume glass capillary tubing also at −196 °C. The subsequent warming of the capillary allows the gas transfer through a gas chromatograph to separate the CO₂ from residual impurities such as N₂O and its introduction in the isotope ratio mass spectrometer IRMS (Finnigan MAT 252). The CO₂ mixing ratio in the ice samples is deduced from a linear regression between standard gas injections (CO₂ = 260.26 ± 0.2 ppmv in dry air, δ¹³CO₂ = −6.40 ± 0.03‰ versus VPDB) at different pressures and the corresponding CO₂ peak amplitude measured by the IRMS. Each sample or external standard introduction in the IRMS is bracketed with injections of a pure CO₂ standard reference gas (internal standard, ATMO MESSER, δ¹³C of −6.5 ± 0.1‰ versus VPDB). Each ice core gas sample result consists of the mean of three consecutive measurements of the same sample gas stored in the extraction container and expanded three times. For this analytical series on T-II EDC samples, the pooled standard deviation associated with the average value of three replicate measurements of the same extracted gas amounts to 1.9 ppmv for CO₂ and 0.1 ‰ for δ¹³CO₂. Pooled standard deviations of δ¹³CO₂ are therefore similar for samples from T-I and T-II. However, they appear slightly larger for T-II CO₂ data compared to T-I (Lourantou et al., 2010; Table 1). These analytical observations will be discussed further in the Section 3.2 dealing with possible artifacts associated with clathrated versus bubbly ice.

On a daily basis, a systematic correction (on average −0.3 ‰) is applied on the carbon isotopic ratios obtained on ice samples, based on the deviation observed between several external air standard measurements and the reference CSIRO value. Ice core results are also corrected for gravitational fractionation taking place during gas diffusion between the atmosphere and the close-off depth where gas gets entrapped into bubbles. This fractionation is proportional to the mass difference between the involved gases, the one between ¹³CO₂ and ¹²CO₂ being identical to ¹⁵N versus ¹⁴N of N₂. Therefore δ¹⁵N of N₂ data from the EDC core could be used to correct δ¹³CO₂ for gravitational fractionation. However, EDC measurements of δ¹⁵N of N₂ are not yet available at sufficient resolution for T-II. We therefore rely on an empirical relationship observed between EDC δ¹⁵N of N₂ and δD (Dreyfus et al., 2010) to estimate δ¹⁵N of N₂ and to correct both CO₂ and δ¹³CO₂ data. The difference between both δ¹⁵N corrections amounts to less than 0.01 ‰ for δ¹³CO₂ (see Supplementary material). For CO₂, the gravitational correction varies from 1.2 to 2.6 ppmv, while for δ¹³CO₂ it lies between 0.4 ‰ (MIS 6) and 0.6 ‰ (MIS 5e).

3. Results

3.1. Data description

We measured a total of 37 depth levels, two of them being duplicated. The new dataset provides an average 4m-depth resolution, translating into a mean time resolution of ~520 y over T-II (excluding the three MIS6 data before T-II). The resulting CO₂ and δ¹³CO₂ data are shown in Fig. 1a, c, together with CH₄ data from the same core (Loulergue et al., 2008, Fig. 1b). Similar to Monnin et al. (2001) for T-I, we divide T-II and the start of MIS 5e into seven sub-periods corresponding to observed changes in the CO₂ rate of increase/decrease.

Our new data confirm the CO₂ pattern already revealed from the Vostok and Dome Fuji ice cores throughout T-II (cf. Supplementary material), characterized by a gradual increase over ~12 ky ending up with a rapid jump toward the optimum at the start of MIS 5e. The better precision of our EDC record furthermore reveals that the abrupt CO₂ rise takes place within only ~300 yr and is

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Pooled standard deviations of CO₂ and δ¹³CO₂ calculated out of three expansions on each sample, for both deglaciation analytical series. n corresponds to the number of samples analyzed.

![Fig. 1. Evolution of (a) CO₂, (b) CH₄ and (c) δ¹³CO₂ in the EPICA Dome C ice core throughout the penultimate deglaciation (i.e. from MIS6 to MIS 5e). CH₄ data from Loulergue et al. (2008); CO₂ and δ¹³CO₂ data from this study; mean value of error bars added as min and max dotted lines. Vertical lines mark the limit between different sub-periods, each one corresponding to a specific CO₂ rate of change. The gas time scale is EDC3_gas, a (Parrenin et al., 2007; Loulergue et al., 2007).](image-url)
synchronous with the CH₄ overshoot. We show that the CO₂ overshoot is accompanied by a rapid drop of δ¹³CO₂, while throughout the entire deglaciation the isotopic signal shows a decreasing trend of its minimum values of 0.8‰ accompanying the CO₂ rise, on which three maxima are superimposed.

In the following, we detail the structure of both signals. We first compare the glacial (140 ky, n = 2) and interglacial (128 ky, n = 3) CO₂ optima defining T-II boundaries in our record. With our current time resolution, minimal (maximal) CO₂ levels amount to 185 ± 3 ppmv (289 ± 3 ppmv) whereas the corresponding δ¹³CO₂ values are −6.7 ± 0.1‰ (−7.4 ± 0.1‰), leading to a full CO₂ increase of 104 ppmv, i.e. the largest deglacial CO₂ increase of the last 9 Terminations. The full glacial–interglacial δ¹³CO₂ magnitude is only reached later, with the most depleted values found just after the CO₂ overshoot, leading to a full δ¹³CO₂ decrease of 0.8‰.

Based on the division into sub-periods related with the CO₂ rate of change, the two signals present the following trends:

1. A ~16 ppmv decrease of CO₂ and a 0.3‰ rise of δ¹³CO₂ take place at the end of MIS6 (n = 3). Given the small amount of data for the time period between 153 and 141 ka, there might exist higher variability in CO₂ and δ¹³CO₂ in-between, which cannot be resolved with the current dataset.

2. From 141 to 134 ky, CO₂ increases slowly by 26 ppmv while δ¹³CO₂ first declines by about 0.2‰ and then shows a ~0.3‰ positive peak over a duration of ~2 ky.

3. The following ~4 ky (from 134 to 130 ky) are characterized by a more rapid CO₂ rise of ~50 ppmv accompanied by another positive δ¹³CO₂ peak with an amplitude of ~0.3‰ superimposed on a slightly lower δ¹³CO₂ background compared with the previous sub-period.

4. Between 130 and 129 ky, the CO₂ mixing ratio barely increases by 8 ppmv (60% of this increase occurring within the last 350 y), while δ¹³CO₂ reveals two sharp peaks with an amplitude reaching 0.6‰.

5. The following ~1 ky is first marked by an unusually abrupt and large CO₂ increase (overshoot of 21 ppmv in ~300 y). The corresponding rate of increase, of 0.06 ppmv/y, is two to three times larger than the most rapid increases observed during T-I, at the beginning of the Bolling–Allerød, and at the end of the Younger Dryas (Monnin et al., 2001), and ten times larger than the rate of increase accompanying the ~20-ppmv rise observed during rapid events of the last glaciation, such as the AIM events (Ahn and Brook, 2008). It is however much lower than during the Anthropocene (~2ppmv/y). Such rate of increase may be slightly underestimated due to the time resolution of our measurements and due to the smoothing of atmospheric variations by the enclosure process of air into ice at Dome C (interglacial width of age distribution of ~200 y, Joos and Spahni, 2008), being close to the time resolution of the depicted overshoot. The overshoot is followed by a CO₂ plateau at 289 ± 3 ppmv during ~700 y, at a level significantly larger than observed during the pre-industrial Holocene. Such feature is also observed during MIS 9 (Petit et al., 1999). The overshoot and the subsequent plateau are accompanied by a strong negative δ¹³CO₂ excursion of ~0.7‰ reaching the most negative values observed throughout the Termination, i.e. ~7.5‰.

6. From 128 to 127 ky, CO₂ reveals a 20-ppmv decline, taking place in two steps: an initial rapid decline of 10 ppmv within 160 y followed by a slower one of 10 ppmv within ~900 y. The rapid decline is accompanied by a very large δ¹³CO₂ increase of ~0.8‰ reaching again the largest level observed throughout the Termination.

7. The last ~1.6 ky of our record progressing into MIS 5e show a slow 10-ppmv rise accompanied with a negative δ¹³CO₂ oscillation of ~0.3‰.

CH₄ shows similar patterns as CO₂ for T-II, with no apparent anticorrelation, contrary to what was observed during the last two sub-periods of T-I (Monnin et al., 2001; Lourantou et al., 2010). An important difference is encountered after 126 ky, where they follow opposing trends (increase for CO₂ and decrease for CH₄, Fig. 1a,b). The atmospheric δ¹³CO₂ signal experienced salient peaks and troughs within all defined sub-periods (Fig. 1c), features which are not always associated with a major change in CO₂ mixing ratio or its rate of increase/decrease, contrary to observations of Lourantou et al. (2010) over T-I. The δ¹³CO₂ changes over T-II also appears larger than during T-I. The δ¹³CO₂ signal reveals no apparent correlation with CH₄ throughout T-II (Fig. 1b,c), contrary to what is found in the end of T-I (Lourantou et al., 2010).

3.2. Bubbly against clathrated ice

In the depth range of the T-II EDC ice samples, the trapped gases only exist in the form of clathrates. Clathrates are strongly linked with the molecular network of the ice matrix. The dissociation of CO₂ clathrates into free gas plus H₂O is impeded compared with e.g. CH₄ clathrates (Circone et al., 2003). One could hypothesize that dry extraction methods applied on ice cores (i.e. mechanical ice grinding at negative temperature) could eventually fractionate the CO₂ mixing ratio between released and unreleased gases from clathrates, depending for instance on the final grain size of the grinded ice powder. Due to the different equilibrium pressure of pure hydrates made of different CO₂ isotopologues, such fractionation might also affect δ¹³CO₂ in the released gases. Lower 5D has been reported on guest CH₄ and CH₄H6 molecules in clathrates compared with the residual free gas (Hachikubo et al., 2007), thus confirming the possibility of isotopic fractionation between clathrates and free gas. In general, the crushing process easily releases atmospheric gases trapped in structural voids in the ice (such as bubbles or cracks) but can be less effective in releasing gases which are encaged in the molecular structure of the ice (Anklin et al., 1997; Wilson and Long, 1997; Stauffer and Tschumi, 2000).

This phenomenon indeed clearly shows up when comparing the extraction efficiency of our method on T-I and T-II EDC samples (data of T-I taken from Lourantou et al., 2010). In Fig. 2, we compare the amount of gas released from the EDC samples with our extraction technique (expressed in cm³ STP of dry air per g of ice, see appendix for the calculation) with the air content of neighboring EDC samples measured with an absolute method involving melting and refreezing of the ice (Lipenkov et al., 1995; Raynald et al., 2007). The amount of gas released with the dry extraction method is lower by more than 20% on T-II EDC samples compared with the T-I ones (on average 0.047 ± 0.006 cm³/g against 0.060 ± 0.005 cm³/g for T-II and T-I, respectively), whereas the true air content of the ice slightly increases by ~3% (mean of 0.992 ± 0.003 cm³/g vs. 0.989 ± 0.003 cm³/g for T-II and T-I, respectively, Fig. 2). We deduce a grinding efficiency (ratio between released gas and air content) of 62% for the ice samples covering the T-I period, and of only 52% for the T-II samples. The dry extraction method is thus less efficient on 100% clathrated ice than on 100% bubbly ice, as previously proposed (Wilson and Long, 1997) and as observed on NGRIP samples using the Bern needle cracker (Stauffer and Tschumi, 2000).

We then need to evaluate if this reduced efficiency affects the composition of the released air compared with the trapped gases. Table 1 compares the scattering calculated on the three consecutive
expansions of the extracted gas on ice samples for both CO2 and $\delta^{13}$CO2 measured over T-I and T-II. The CO2 dispersion is higher by $\sim$50% on T-II samples compared with T-I, with a tendency for CO2 to slightly increase with subsequent expansions, whereas the $\delta^{13}$CO2 scattering between the two sets of samples is comparable. Recent experiments were conducted with the LGGE dry extraction system, comparing 100% bubbly ice from the Berkner Antarctic ice core with EDC ice of the same gas age but in which trapped gases co-exist as clathrates and free gas in bubbles (transition zone known as "brittle ice"). These tests have shown a significant depletion of CO2 in the gas released from the EDC ice, by $\sim$12 ppmv (Schaefer et al., in preparation). They also revealed a large CO2 dispersion (by more than 100%) compared to T-I data. On the other hand, no significant differences were detected for $\delta^{13}$CO2 results. Such artifact observed on brittle ice, affecting the CO2 mixing ratio but not its $\delta^{13}$C, cannot be directly translated to the case of 100% clathrated ice; it could nevertheless provide an upper limit of the possible bias due to the gas extraction technique. Recently, CO2 analyses of 100% clathrated EDC ice were also performed in deeper layers of the core using two techniques: our dry extraction one and the Bern sublimation technique (providing 100% extraction efficiency, and thus not affected by bubble-hydrate transformation).

We conclude that even if the extraction efficiency of our method is lower on 100% clathrated ice compared to 100% bubbly ice, this may induce a slight underestimation in the measurement of CO2 mixing ratio in ice, but should not affect the $\delta^{13}$CO2 signal. In the following, the main structure of both signals throughout T-II is thus assumed to be valid and is further discussed in terms of carbon-cycle mechanisms and climate dynamics.

4. Discussion

4.1. Comparison of CO2, CH4 and $\delta^{13}$CO2 patterns during Terminations I and II

The three gas signals can be directly compared in terms of phasing and shape, as they are obtained on the same matrix. CH4 is closely related to Greenland and more generally N. Hemisphere climate (e.g. Chappellaz et al., 1993; Brook et al., 1996); in addition, model simulations show that Greenland climate was largely modulated by AMOC changes (e.g. Otto-Bliesner and Brady, 2010 and references therein). The comparison of CH4 with CO2 and $\delta^{13}$CO2 thus possibly brings hints into the carbon-cycle processes related to AMOC dynamics. An intensified hydrological cycle producing more CH4 on the continents (Fischer et al., 2008) should also be associated with a stronger carbon uptake through continental biomass buildup, notably in peatlands (Frolking and Roulet, 2007). Throughout T-II, CH4 depicts two distinct features: a slow and regular increase from 141 to 129 ky, and a rapid increase during the $\sim$300 y preceding the optimum of MIS 5e. Such evolution goes in line with the scenario where the AMOC was dampened during much of T-II and strengthened very rapidly at 129 ky (Carlson, 2008). Parallel to the CH4 evolution, CO2 increases in a similar manner which can be schematized as a long and relatively steady increase (albeit with some fluctuations highlighted by the sub-periods) culminating with the overshoot at 129 ky. It thus bears resemblance with the first half of T-I (from 17.6 to 14.7 ky) with a slow increase of both signals leading to the Bolling/Allerod warming and the first CH4 and CO2 rapid jumps, but on a $\sim$fourfold longer duration and a much larger amplitude: 55 ppmv for the first half of T-I versus 104 ppmv for the entire T-II.

The full T-II amplitude of change for CO2 and CH4 is also much larger than T-I (Fig. 3a,b): 104 ppmv (385 ppbv) compared with 82 ppmv (335 ppbv) (Loulergue et al., 2008; Lourantou et al., 2010). The overall CO2 rise throughout T-II is accompanied by a large decline of the $\delta^{13}$CO2 minimum values, culminating at the time of the CO2 overshoot. It bears resemblance with the first half of T-I as well, albeit with much larger amplitude: 0.8‰ instead of 0.6‰ during the first half (and throughout, as well) of T-I (Fig. 3g).

Although $\delta^{13}$CO2 exhibits a large variability during both Terminations, we observe a statistically significant difference of its average value, the mean $\delta^{13}$CO2 during the time period 125–140 ky BP being 0.2‰ more depleted than during the time period 9–22 ky BP. Such feature of more $^{13}$C-depleted carbon in the atmosphere during the penultimate deglaciation than the most recent one goes in parallel with a similar $^{13}$C depletion in the oceanic reservoir, seen in planktic and benthic foraminifera from different ocean basins (Duplessy and Shackleton, 1985; Seidenkrantz et al., 1996; Ninnemann and Charles, 1997; Hendy and Kennett, 2000; Molyneux et al., 2007; Pena et al., 2008), albeit with a larger amplitude of $\sim$4‰. The oceanic $^{13}$C depletion was interpreted as resulting from an even more reduced AMOC strength during T-II, increasing the prevalence of old deep waters and depleting the average carbon isotopic composition of the global intermediate ocean (Duplessy and Shackleton, 1985). The fact that it parallels a $^{13}$C depletion in the atmospheric reservoir suggest that T-II and the preceding glacial maximum experienced an even more reduced carbon storage on the continents, compared with T-I and the LGM, thus transferring more $^{13}$C-depleted carbon in the two other reservoirs.

The CH4, CO2 and $\delta^{13}$CO2 comparison between the two Terminations reinforce the scenario of reduced AMOC during T-II until the abrupt increase of both greenhouse gases at the very end of the Termination, when AMOC would have intensified. This is in line with the sequence of events discussed by Monnin et al. (2001) for interpreting the T-I CO2 evolution, and in accordance with modeling studies on the impact of AMOC perturbations on atmospheric CO2 under initial pre-industrial conditions (Meniel et al., 2008).

4.2. Comparison with other ice and marine core records

In our previous work on T-I, we had compared atmospheric composition records with marine data which document in detail...
the evolution of some of the key players coupling atmospheric CO₂ and global climate. Dating uncertainties and fewer available records render a similar implementation difficult on T-II. In Fig. 3, we take advantage of the different proxies from marine and ice core realm and compare them between both deglaciations. The temporal evolution of these signals can be compared, keeping in mind absolute dating uncertainties which reach 3 ky for the EDC ice core over T-II (Parrenin et al., 2007) and 1 ky between the gas and ice signals (Loulergue et al., 2007).

Fig. 3a shows a co-variation of CO₂ with δD (reflecting high southern latitude temperature) throughout T-II. This suggests that CO₂ changes are controlled by the S. Ocean during the penultimate deglaciation, as was deduced from the co-variation over T-I (Monnin et al., 2001). The EPICA Dome C ice core also provides records of dust (nss-Ca²⁺, Fig. 3d) and sea-ice extent (ss-Na⁺, Fig. 3f). These proxy records show systematic sequences of events with Antarctic temperature (δD) during all glacial terminations (Röthlisberger et al., 2008). All the ice core records exhibit differences in magnitude and structure between T-I and T-II (Fig. 3a, e–g).

Regarding amplitudes of change characterizing T-II, we observed the following compared to T-I: in addition to the +22 ppmv for CO₂ (Fig. 3a), +50 ppbv for CH₄ (Fig. 3b) and –0.2‰ for δ¹³CO₂ (Fig. 3g) mentioned before, δD increases by an additional 18‰ (Fig. 3a), δ-excess by +1.2‰ (Fig. 3c), and ss-Na⁺ rises by an extra 270 µg/m²/y (Fig. 3f). Only does the range of dust flux, whatever the proxy used (dust, iron, nss-Ca²⁺, Fig. 3d,e) appear weaker for T-II than T-I, probably due to warmer S. Hemisphere temperatures, related to the reduced AMOC.

As seen for CO₂, δD does not depict an Antarctic Cold Reversal-like feature during T-II, but it differs from the CO₂ evolution during
the late part of T-II, with a monotonic increase whereas CO2 shows first a slowing-down of its rate of increase and then an abrupt jump at 129 ky BP. On the other hand both signals peak at approximately the same time (Fig. 3a). The rapid CO2 jump parallels a similar feature in the d-excess record, a proxy of moisture source which suggests a shift toward lower latitudes associated with weakened westerlies (Masson-Delmotte et al., in press). The parallelism between both signals suggests that the CO2 overshoot could find in part its origin in abruptly reduced westerlies associated with a shift in moisture source as well. The direction of westerlies shifts on a G–IG transition is, however, highly controversial: Zharkov and Nof (2008) support a northward G–IG shift, in contrast to Toggweiler et al. (2006) who assume a poleward movement. The latter assumption enhances upwelling and therefore could be responsible for propagating the deep ocean signal to the atmosphere, under the condition that there is no sea-ice impeding this process. Fig. 3f shows the lowest fluxes of the sea-ice proxy (Na+) at exactly that time frame, while in Fig. 3i, planktic δ13C data show a minimum at the same time, possibly reflecting enhanced upwelling (Spero and Lea, 2002). Since the upwelling may drive a large atmospheric CO2 rise and δ13CO2 decline, our data are thus in line with the Toggweiler et al. (2006) scenario to explain at least partly the ~20 ppmv CO2 overshoot at the start of MIS 5e.

Although the amplitude of dust change appears less important during T-II than T-I whatever the proxy used (dust, iron, nss-Ca2+), elevated dust levels persist longer during T-II than T-I. The dust supply in the S. Ocean has been active during 10 ky for T-II, corresponding to a CO2 increase of 50 ppmv, to compare with the 4-ky duration of the elevated dust concentration during T-I associated with a 35-ppmv CO2 rise (Fig. 3d). The Fe fertilization effect (Martin, 1990) could thus account for a significant part of the initial CO2 increase, associated with negative atmospheric δ13CO2 trend, observed during T-II as well as the early part of T-I (Lourantou et al., 2010). The benthic δ13C profile from the Iberian margin, shown in Fig. 3h, reflects changes in deep-water ventilation in the N.E. Atlantic (Skinner and Shackleton, 2006). The W-pattern seen for T-I, as in the atmospheric δ13CO2 signal, is absent during T-II. An abrupt decline, followed by a more gradual increase is observed for T-II, whereas the atmospheric δ13CO2 signal shows more abrupt shifts.

The whole atmospheric δ13CO2 decreasing trend is punctuated by three peaks, the older two not being clearly associated with an important CO2 feature apart from the small change in its rate of increase. These peaks might have been related to abrupt sea surface temperature changes (Fig. 3y), as discussed below.

4.3. Scenarios of carbon-cycle evolution

The comparison above between CO2, δ13CO2 and other proxies relevant to the carbon-cycle evolution during T-II suggests that similar mechanisms as during the first half of T-I took place to generate first a gradual increase of CO2 and decrease of δ13CO2, and then a CO2 overshoot ending the δ13CO2 decrease: a reduced AMOC (even more reduced than during T-I) favored stronger ventilation of the S. Ocean, releasing δ13C-depleted CO2, a mechanism accompanied by sea-ice retreat but also by a decrease in iron aeolian input extending through a longer part of T-II than observed during T-I (reducing the biological pump strength). At the end of the Termination, the AMOC strengthening would have taken place in parallel to a poleward shift of the westerlies, resulting into the rapid CO2 jump. In order to evaluate such scenarios, a useful — albeit limited — approach consists in using a Keeling plot and comparing with its equivalent for T-I (Lourantou et al., 2010). In a two-reservoir system, Keeling plots allow one to deduce the carbon isotopic composition of the source adding CO2 in the second reservoir, i.e. the atmosphere, when plotting δ13CO2 and CO2 evolution during T-I and T-II. The continuous (T-II) and dashed (T-I) lines indicate linear regression through the selected data (green lines in the upper graph). The value of the y-intercept is given next to each regression line, together with the number of data points used. b. Right panel: Co-evolution of δ13CO2 and CO2 sources/sinks depending on different carbon-cycle mechanisms simulated in the course of T-I with the carbon box-model BICYCLE (Köhler et al., 2005, figure adapted from simulations presented in Lourantou et al., 2010). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
—15‰, i.e. a relatively narrow range for both deglaciations, suggesting a common mechanism behind the corresponding CO2 phases of increase. Lourantou et al. (2010), using the BICYCLE box-model, associated these “Keeling-plot” signatures with a physical mechanism (the breakdown of S. Ocean stratification), combined with a biological process (a decreased biological pump) for the first step of δ13CO2 reduction. The Keeling plot approach suggests that such mechanisms could also explain a large part of the T-II CO2 increase. Only the physical processes can be invoked during the rapid jump of CO2 at 129 ky BP, as the dust/iron levels in EDC already reached interglacial low levels before this particular CO2 event.

Still, a stringent observation in the CO2–δ13CO2 co-evolutions during T-II is the occurrence of three δ13CO2 peaks superimposed on its large decline, accompanied by only small changes in the rate of CO2 increase for two of them. Such feature seems present also during sub-period II of the last deglaciation, when H1 occurred, with two small δ13CO2 peaks when the CO2 rate of increase also shows minor changes. These positive δ13CO2 peaks produce a much more positive y-intercept in the Keeling plot (not shown in Fig. 4). Fig. 4b gives the combined evolution of δ13CO2 and the CO2 source/sink resulting from different carbon-cycle mechanisms, simulated in the course of T-I with the carbon-box model BICYCLE (Köhler et al., 2005, graph adapted from carbon-cycle mechanisms, simulated in the course of T-I with the model BICYCLE (Köhler et al., 2005, graph adapted from simulations in Lourantou et al., in press). Among them, three processes are able to associate a CO2 increase with a positive δ13CO2 anomaly: (1) increasing SSTs, (2) decreasing sea-ice cover and (3) sea level rise. The last one is probably too slow to generate δ13CO2 anomalies at timescales of 2 ky or less, as observed during T-II. It thus seems plausible that positive excursions in our δ13CO2 reflects periods of rapidly changing sea surface conditions in areas of important CO2 exchange.

In summary, although the lack of proxy data from the marine and continental realms and of carbon-cycle modeling applied to T-II seriously limits the strength of our conclusions, the combination of CO2 and δ13CO2 evolutions in the course of the penultimate deglaciation suggests that S. Ocean stratification breakdown and decreased biological pump could well explain the main features observed in the two signals. In particular the delayed decrease (compared to T-I) of dust input and sea-ice cover suggested by the EDC ice proxies points toward a relatively stronger contribution of associated carbon-cycle mechanisms. Such delay could potentially be related to the differences in orbital configuration (e.g. Broecker and Henderson, 1998) and ice sheet extent (e.g. Govin et al., submitted for publication), affecting the strength of AMOC, notably reduced during MIS 6 and T-II compared with MIS 2 and T-I, as suggested by δ13C records in the world oceans. This could justify why the amplitude of the CO2 increase and δ13CO2 decrease are much larger than T-I and (2) the CO2 increase ends up with a large 21-ppmv jump in ~300 y. The latter could find an additional contribution through intensified upwelling, due to a poleward shift of the westerlies which contributes as well to the extent of tropical wetlands, leading to concomitant and rapid increases of both CO2 and CH4.

Positive δ13CO2 excursions superimposed on the long-term decrease along T-II suggest that rapid changes in sea surface temperature and sea-ice extent could also have contributed to the 104 ppmv rise. It is only after the CO2 optimum of MIS 5e, when CO2 decreases by ~10 ppmv and δ13CO2 increases back to its highest level (sub-period 6), that the co-evolution of both signals goes in line with a possible contribution from vegetation buildup, taking away CO2 from the atmosphere and leaving a more enriched δ13C signature, as suggested by Lourantou et al. (2010) for the Bolling/Allerød sequence during T-I.

5. Conclusions

The new dataset of CO2 and δ13CO2 from the EDC ice core over the penultimate deglaciation presented here, provides important quantitative constraints on climate/carbon-cycle interactions during this major climatic event. It confirms that the CO2 increase (of 104 ppmv in our record) is the largest observed over the last 9 Terminations. This increase takes place in two major steps: a long increase from 141 to 129 ky BP, accompanied by minor changes in the rate of increase, and a rapid jump (21 ppmv in ~300 y) toward the MIS 5e maximum, taking place at 129 ky BP. This is accompanied by large variations of δ13CO2, which can be sketched as a progressive decrease of the minimum values through time, culminating when CO2 jumps to its maximum at 129 ky BP, and three positive excursions superimposed on the long trend. The larger amplitudes encountered in our atmospheric signals are also seen in other ice core proxy records. The more depleted (by 0.2‰) average atmospheric δ13CO2 signal during T-II compared with T-I is also witnessed in marine sediments, and suggests a larger transfer of 13C-depleted carbon from the terrestrial reservoir to the ocean–atmosphere ones before and during T-II.

A first attempt to interpret these records using Keeling plots, and a comparison with other ice core and marine data covering the past two deglaciations, suggest that S. Ocean upwelling combined with reduced biological pump could have been the two dominant factors controlling CO2 levels throughout T-II as during the first half of T-I. The continental biosphere would have left an imprint in both CO2 and δ13CO2 only after the optimum of MIS 5e. The main differences between the two Terminations could be summarized as: (1) a delayed response of dust and sea-ice decreases in the course of T-II and a reduced AMOC, contributing to increase even more CO2 in the atmospheric reservoir and (2) the lack of a millennial-scale event similar to the Antarctic Cold Reversal–Bølling/Allerød-Younger Dryas sequence, most probably due to different boundary conditions of ice sheet extents. Additional proxy information from high-resolution sediment records covering this critical period (e.g. more detailed records on the occurrence of H11 event and the final AMOC resumption), as well as the use of carbon-cycle models will help in verifying the above assumptions and better deciphering the mechanisms at play. Lastly, even if there is no indication that the dataset presented here would be affected by any known artifact, future measurements performed using different techniques and on different ice cores will be helpful to confirm the main features seen in our record.

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m

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V / m = \frac{V_m - V_{\text{ice}}}{T_{m,1}} + \frac{V_l}{T_{l,1}} \times \frac{P_o - m}{P_{\text{H}_2O}} \times (P_1 - P_{\text{H}_2O})
\]

where \(V\) represents the amount of air released, \(m\) represents the sample mass, \(T\) the temperature, \(P\) the extraction pressure, \(P_{\text{H}_2O}\) the pressure of water vapour, \(T_0 = 273 K\) and \(P_0 = 1013\) hPa (standard conditions). The subscript \(i\) corresponds to the extraction line, \(m\) to ice mill, and the number “1” indicates the 1st sample expansion.

**Appendix. Supplementary material**

Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.quascirev.2010.05.002.

**References**


