Supplemental Material

Methods:

The analytical methods for CO_2 measurements used at the University of Bern and at LGGE in Grenoble are based on dry extraction techniques followed by laser absorption spectroscopy and gas chromatography, respectively. In Bern, four to six samples (2.3 x 2.3 x 1.6 cm; 8 grams) from each depth level (every 55 cm) in the ice core are measured in random order (two on the same day; the following two after all depth intervals have been measured twice). The samples are crushed by a cooled needle cracker under vacuum conditions. The sample container is connected to a cold trap for several minutes in order to avoid fractionation due to a slower release of CO_2 relative to N_2 and O_2 from clathrates. Afterwards, the air is expanded to a measuring cell, where a laser is tuned six times over the absorption line of a vibration-rotation transition of the CO_2 molecule. For calibration, we use a CO_2 in air standard gas with a concentration of 251.65 ppmv calibrated to the WMO mole fraction scale.

The blank level is evaluated using bubblefree ice samples. After the evacuation CO_2 in air standard gas is introduced into the crusher and the routine protocol is run. The amount of standard gas is chosen so that the amount of CO_2 in the cell is similar to the amount usually extracted from ice core samples. These test measurements have been performed using CO_2 in air standard gas with concentrations of 197.65 ppmv, 251.65 ppmv and 321.1 ppmv. An uncertainty of the device of 1.5 ppmv has been derived.

1237 samples from 289 depth levels have been measured including remeasurements in the part published earlier[29]. The average standard deviation of the mean of four to six samples is 1.3 ppmv over the whole record. Four validation measurements have been done by extracting the air by a sublimation device similar to the one described by Güllük et al.[30].

The 61 (14 below and 47 above 3190 m) Grenoble measurements have been done with a method slightly modified compared to Barnola et al.[31]. On every depth level one to three samples of about 40 g of ice are crushed under vacuum conditions. About 20 minutes later, the extracted gas is expanded in the sample loop of the gas chromatograph and analysed. Depending on the amount of the extracted air, three to five successive analyses are performed. In order to avoid the possible influence of the water vapour injected with the gas, the CO_2 ratio is calculated as the ratio between the CO_2 peak and the air (O_2+N_2) peak. The calibration is conducted using an Air Liquide® standard scaled on three CSIRO standards (260,3 ppmv, 321,1 ppmv and 172,8 ppmv).

Comparison of the Bern and Grenoble CO_2 data:

Figure S1 shows all CO_2 data from the clathrate zone of Dome C measured in both labs consisting of values of MIS 11[29] (11 values) and MIS 16 – 19 (47 values). The Bern values have been interpolated to the depth levels of the samples measured in Grenoble. The characteristics of the mean regression line are summarized in ST1.

Considering all common data, the slope of the regression line is significantly different from 1, indicating a possible non-linearity in at least one of the analytical systems. Furthermore, the Grenoble measurements average 3.1 ppmv higher than the values obtained at Bern. Standard gas measurements, however, performed at both labs, conducted using the same procedure with the same standard gases for calibration as during the usual ice sample measurements, do not support these observations (see ST2). An extended intercomparison study will be done to examine differences in the two labs. The proposed nonlinearity and offset between Bern and Grenoble measurements do not question any of the conclusions in the main text.

Lowest CO_2 concentrations ever measured in an ice core:

The lowest CO_2 concentration measured at Bern (172 ppmv, 667 kyr BP) is not confirmed to the full extent by the laboratory in Grenoble (178 ppmv). Comparing Bern and Grenoble results for MIS 11, 16 and 19 in the Dome C ice core has shown that Bern gets slightly lower values for samples with low CO_2 concentration. This raises the question whether measurements in Bern would be lower than those from Grenoble during the Vostok interval (last 440 kyr BP).

The lowest CO_2 concentration found in the Vostok ice core is 182 ppmv 20 kyr BP[32]. This age has also been measured on Dome C[33] and Taylor Dome ice[34], respectively, by the University of Bern (Figure S2). In fact, Bern measurements are slightly higher than those of Grenoble in both ice cores (184 and 188 ppmv). Furthermore, preliminary measurements on Dome C ice during MIS 6 performed at the University of Bern show similar concentrations as measured on the Vostok ice core in Grenoble. Taking this into account, we conclude that the CO_2 values during MIS 16 (172 ppmv) and MIS 18 (177 ppmv) are the lowest values ever found in ice cores and this with a difference of 10 ppmv.

Time relationship between CO_2 and Antarctic temperature:

Determination of the exact timing of CO_2 versus temperature changes is complicated by the age of the occluded air being younger than the surrounding ice[35] by up to 5200 years. This so called Δage can be calculated with a densification model. Comparison of ice and gas records of the EPICA cores suggests that the computed Δage for low accumulation sites has probably previously been overestimated by up to a few hundred years[36]. Applying the new EDC3 ice age time scale[37] and the currently best estimate for the gas age scale (EDC3_gas_a)[36] alters the lag of CO_2 for terminations VII and VI from 2800 and 1600[29] to 900 and 1900 yr, respectively, and turns the one for termination V from 800 yr into a lead of CO_2 of 300 yr. Similar calculations for the new data yield a lag of 400 and 2300 yr for terminations IX and VIII, respectively. Compared to the time scales of glacial cycles, these time lags are small and do not question the important role of CO_2 as an amplifier of the large temperature rise during deglaciations. A special case remains MIS 14.2 (about 550 kyr BP) when CO_2 preceded changes in deuterium by about 2000 ± 500 yr (EDC2 timescale)[29]. Using the new timescales, this lead reduces to 1100 ± 500 yr. Again unknown processes during firnification may affect Δage during MIS 14.2.

Choice of the intervals for the calculation of mean values of CO_2:

Figure S3 illustrates the accuracy of the mean values due to the choice of the interval definition. The initial and end points of the intervals shown as dashed black lines in figure 2 and in figure S3 below are centred in every second glacial period including two interglacials. The accuracy of the choice of the intervals is calculated by a Monte Carlo simulation randomly shifting the interval boundaries by ± 10 kyr (except for 799 kyr BP: only - 10 kyr). The statistical results are listed in table ST4 and included as grey areas in figure S3 demonstrating the independence of the result from the choice of the intervals position. The splines according to Enting[38] with a cut-off period of 200 kyr indicate the trends discussed in the paper.

CO_2 and isotopic changes during ice age terminations:

Figure S4 shows a compilation of δD and CO_2 results across termination I to IX. Together with the lags of CO_2 against deuterium, two significantly different patterns of transitions are found: The one between 796 and 787 kyr BP (T_{IX}), with its more or less linear CO_2 increase of about 8 ppmv/kyr, resembles those observed during the last five terminations (7.8 - 12 ppmv/kyr), all of them with a strong coupling to deuterium reaching the top without longer lasting interruptions (except the Antarctic cold reversal during termination I). The CO_2 increases of T_{VI} - T_{VIII} show a different pattern with two distinct intervals: First (interval I) CO_2 rises rapidly at a rather constant rate of 9 - 14 ppmv/kyr during 3 - 4 kyr with a similar relationship to the temperature as discussed for terminations I - V and IX. In a second interval (II), with stable or slowly rising Deuterium values, CO_2 increases for an other couple of 1000 years gradually at a mean rate of 1.2 - 1.9 ppmv/kyr (a more detailed discussion will be presented elsewhere).

References

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Tables:

Equation	1σ of the slope	1σ of the axis intercept (ppmv)	R^2	X_{mean} (ppmv)	Y_{mean} (ppmv)	Y_{mean} - X_{mean} (ppmv)
y=0.938x+17.22 ppmv	0.020	4.66	0.974	227.57	230.64	3.07 ± 1.01 (2σ)

ST1: Characteristics of the mean regression line shown in figure S1. R^2 is the squared coefficient of correlation of the Bern and Grenoble values. X_{mean} is the average of the interpolated Bern data, Y_{mean} the average of the Grenoble data. Y_{mean} - X_{mean} is the mean difference between Grenoble and Bern values.

Lab	Standard	Theoretical value (ppmv)	Measured value (ppmv)	Standard deviation (1σ)
Bern	SIO 197	197.11	198.2	1.03
Bern	SIO 251	251.65	251.5	0.82
Bern	SIO 321	321.1	321.5	0.92
Bern	Grenoble 233	233.5	234.3	0.64
Grenoble	Bern SIO 251	251.65	251.2	0.69
Grenoble	CSIRO 1630	321.1	321.0	0.8
Grenoble	CSIRO 1657	172.8	172.7	0.62
Grenoble	CSIRO 1677	260.26	260.0	0.72

ST2: Results of CO_2 in air standard gas measurements performed at the University of Bern with laser absorption spectroscopy and at LGGE in Grenoble by gas chromatography. For the calibration, SIO 251 is used at Bern and 233.5 ppmv standard is used at Grenoble. The measured values are averages of 10-20 single measurements. The standard deviation is calculated for a single measurement.

	Marine Isotope Stage 3				**MIS 18**		
Event	AIM 8	AIM 12	AIM 14	AIM 17	A	B	C
Δtemp (°C)	2.27	2.77	2.28	3.14	2.12	2.19	1.99
ΔCH_4 (ppbv)	137	74	97	112	77	65	96
ΔCO_2 (ppmv)	15.0	16.7	14.5	12.3	15.5	14.3	16.7
Δt CH_4 rise (years)	830	648	488	896	638	462	616

ST3: Comparison of the AIM events during MIS 3 and the found events during MIS 18. Magnitudes (Δtemp, ΔCH_4 and ΔCO_2) are calculated taking the difference between the maximum of each event and the mean of the preceding and the following minimum value. Δt CH_4 rise is the duration of the main CH_4 rise. This duration is influenced by the smoothing time of the low accumulation record of Dome C and, hence, can not be compared with results of other ice cores.

Temperature							
Interval	**Initial point**	**End point**	**Mean (°C / ppmv)**	**Standard deviation (1σ)**	**Minimum (°C / ppmv)**	**Maximum (°C / ppmv)**	**Δ (°C / ppmv)**
I	50,000	270,000	- 5.5	0.08	- 5.7	- 5.3	0.4
II	270,000	450,000	- 4.9	0.14	- 5.1	- 4.4	0.7
III	450,000	650,000	- 5.1	0.10	- 5.3	- 4.8	0.5
IV	650,000	799,000	- 5.5	0.14	- 5.9	- 5.2	0.7
CO_2							
I	50,000	270,000	221.6	0.8	220.2	223.6	3.4
II	270,000	450,000	233.8	1.6	232.2	239.9	7.7
III	450,000	650,000	226.9	1.3	223.5	229.6	6.1
IV	650,000	799,000	211.9	1.2	210.0	212.6	2.6

ST4: Results of the Monte Carlo simulation randomly shifting the initial and end points within ± 10 kyr (except for 799 kyr BP: only within 0 and -10 kyr; 10,000 iterations).

Figures:

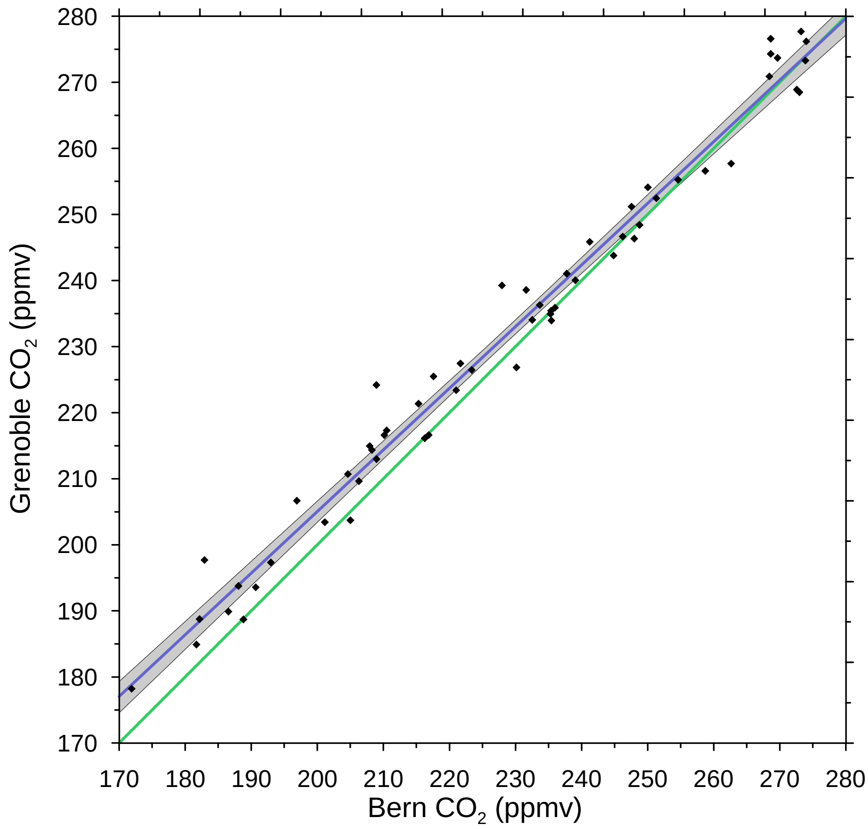

Figure S1: Comparison of Bern and Grenoble measurements. Black full diamonds: Dome C CO_2 values of MIS 11[29] and MIS 16-19 measured at LGGE in Grenoble plotted against the ones measured at the University of Bern (interpolated on the depth levels of the Grenoble samples). The grey area visualizes the Monte Carlo simulation results (10,000 realisations) for a possible range of regression lines calculated for Bern and Grenoble values fluctuating within the 2σ-uncertainty of 2.6 ppmv and 3 ppmv, respectively. The blue line is the mean regression line whereas in green the 1:1 line is given.

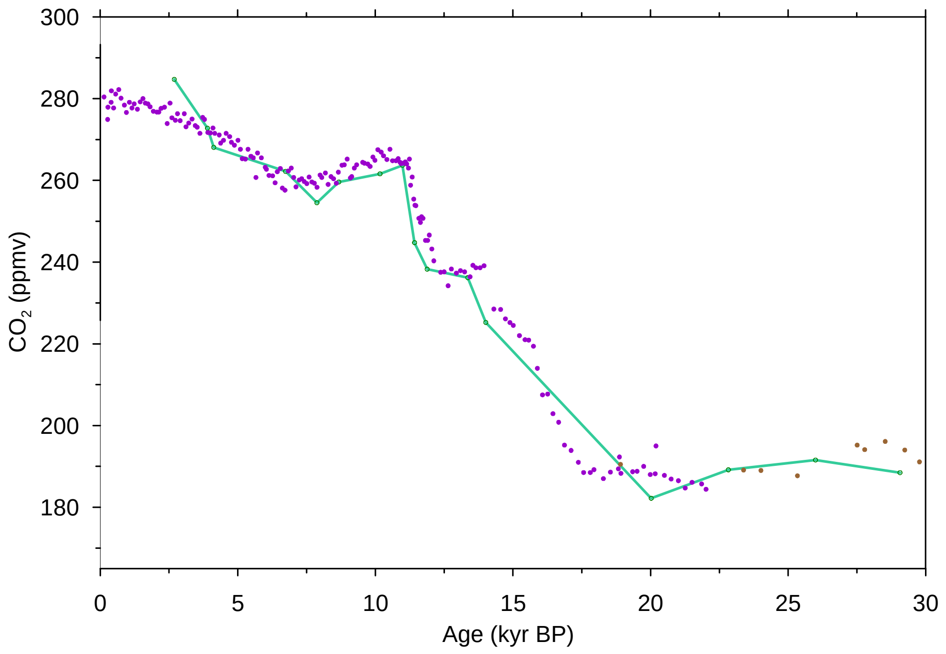

Figure S2: Lowest atmospheric concentration of CO_2 ever measured on the Vostok ice core[32] (green; 182 ppmv at 20 kyr BP; obtained at LGGE in Grenoble) compared to values measured on Dome C[33] (pink) and Taylor Dome ice[34] (brown), respectively, at the University of Bern.

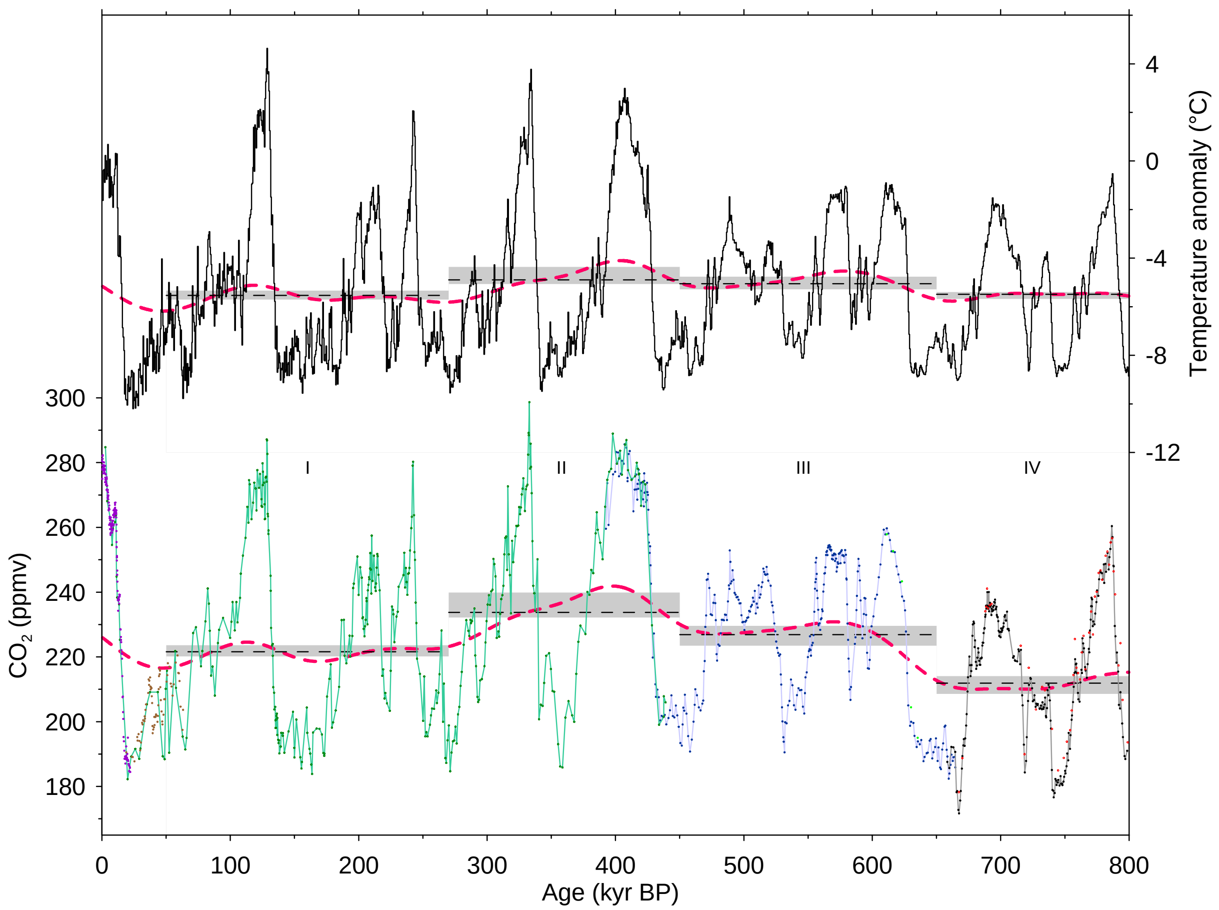

Figure S3: The Dome C temperature anomaly record with respect to the mean temperature of the last millennium[39] (original data interpolated to a 500-yr resolution), plotted on the EDC3 timescale[37], is given as a black line. Purple solid circles: Dome C CO_2 measurements of Monnin et al.[33]; brown: CO_2 measured on Taylor Dome ice[34]; green: Vostok CO_2[32, 40, 41]; blue: Dome C CO_2[29]; light green (650 - 600 kyr BP) and black solid circles: Dome C CO_2 data of this work measured in Bern; red open circles: Dome C CO_2 data of this work measured at LGGE in Grenoble. All CO_2 values are on the EDC3_gas_a age scale[36]. The dashed black lines (also shown in figure 2) are mean values of CO_2 and temperature anomaly of the intervals represented by Roman numerals (799-650, 650-450, 450-270 and 270-50 kyr BP). The grey area illustrates the mean values calculated shifting the initial and end point of the intervals by ± 10 kyr randomly (Monte Carlo simulation; 10,000 iterations; for the initial point of interval IV (799 kyr BP) only - 10 kyr). The red dashed lines are splines according to Enting[38] with a cut-off period of 200 kyr.

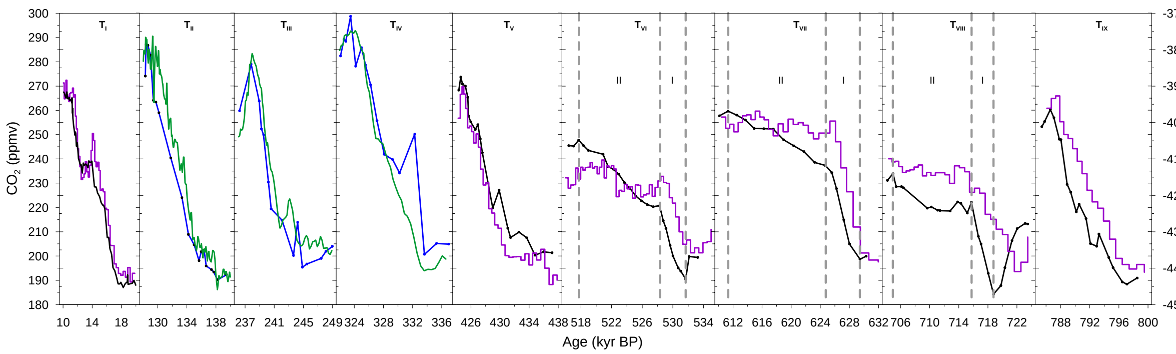

Figure S4: Compilation of δD and CO2 values across nine glacial-interglacial transitions (terminations I to IX, T_I to T_{IX}). The purple step curves in termination I and V-IX indicate Dome C Deuterium[39] (δD, proxy for local temperature); The black curve represents the Dome C CO_2 concentrations; termination I[33]: mean of six samples plotted on the EDC3_gas_a age scale[36]; terminations V-VII[29]: mean of four to six samples (EDC3_gas_a age scale); terminations VIII and IX: mean of four to six samples (this work; EDC3_gas_a age scale). Vostok Deuterium[32] with an offset of + 40 ‰ (because of different distances to the open ocean, elevations and surface temperature of Vostok and Dome C) is given by the green curve and Vostok CO_2 is shown in blue curves[32], all of them plotted on the GT4 gas and ice time scale. The dashed grey lines indicate the two different intervals with respect to the CO_2 increase during terminations VI-VIII.