

Table 1. Experimental (28) and theoretically estimated (Brownian dynamics) bimolecular rate constants k_2 ($M^{-1} s^{-1}$) for the cytochrome b_5 self-exchange ET as a function of ionic strength μ .

μ (M)	k_2 ($M^{-1} s^{-1}$)	
	Experiment	Theory
0.1	2.6×10^3	1.0×10^3
0.3	4.6×10^3	2.4×10^4
0.6	1.6×10^4	7.6×10^4
1.0	2.8×10^4	1.1×10^5
1.5	4.5×10^4	1.7×10^5

extended-Hückel approach to electronic coupling calculation is certainly dependent on its parameterization.

The existence of multiple tunneling regimes also provides insight into several recent (and otherwise puzzling) experimental and theoretical observations in biological ET reaction kinetics. Winkler, Gray, and co-workers found that ET across protein-protein interfaces in protein crystals mediated by three water molecules is nearly as rapid as unimolecular ET is over the same distance (7). Canters and co-workers showed that water dimers between covalently cross-linked azurin complexes could substantially enhance the intermolecular ET kinetics (15). Similarly, Klinman and co-workers investigated the copper-to-copper ET over about 7 Å in the hydroxylating domain of peptidylglycine α -amidylating monooxygenase and found an unusually large electronic coupling mediated, apparently, by water rather than by the protein or substrate (17). Using Pathways-level analysis, Onuchic and co-workers found that water molecules mediate the dominant ET coupling routes between cytochrome c_2 and the photosynthetic reaction center (18). Cave and co-workers showed that water molecules between model D and A pairs substantially enhance intermolecular ET rates as well (19). All of these recent observations support our conclusion that a small number of structured water molecules interposed between the donor and the acceptor cofactors can substantially enhance ET rates.

The influence of aqueous tunneling pathways on interprotein ET kinetics has remained a key open issue in biological ET for some time. Single-exponential decay models fail to describe water-mediated ET reactions properly. The existence of multiple tunneling mediating regimes identified above is evinced by a body of recent experimental and theoretical observations. Most importantly, the structured water coupling regime may provide an important mechanism to facilitate ET reactions in the critical near-contact distance range relevant to biological ET kinetics. We hypothesize that water may be a particularly strong tunneling mediator when it occupies a sterically constrained space between redox cofactors with strong organizing forces that favor

constructively interfering coupling pathways. It will be particularly interesting to use both theory and experiment to explore how the water-mediated coupling between proteins varies with protein-protein shape complementarity, surface charge and polarity, and dynamical fluctuations of the proteins and of the organized water at the interface.

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Supporting Online Material

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SOM Text
Figs. S1 to S6
References

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Stable Carbon Cycle–Climate Relationship During the Late Pleistocene

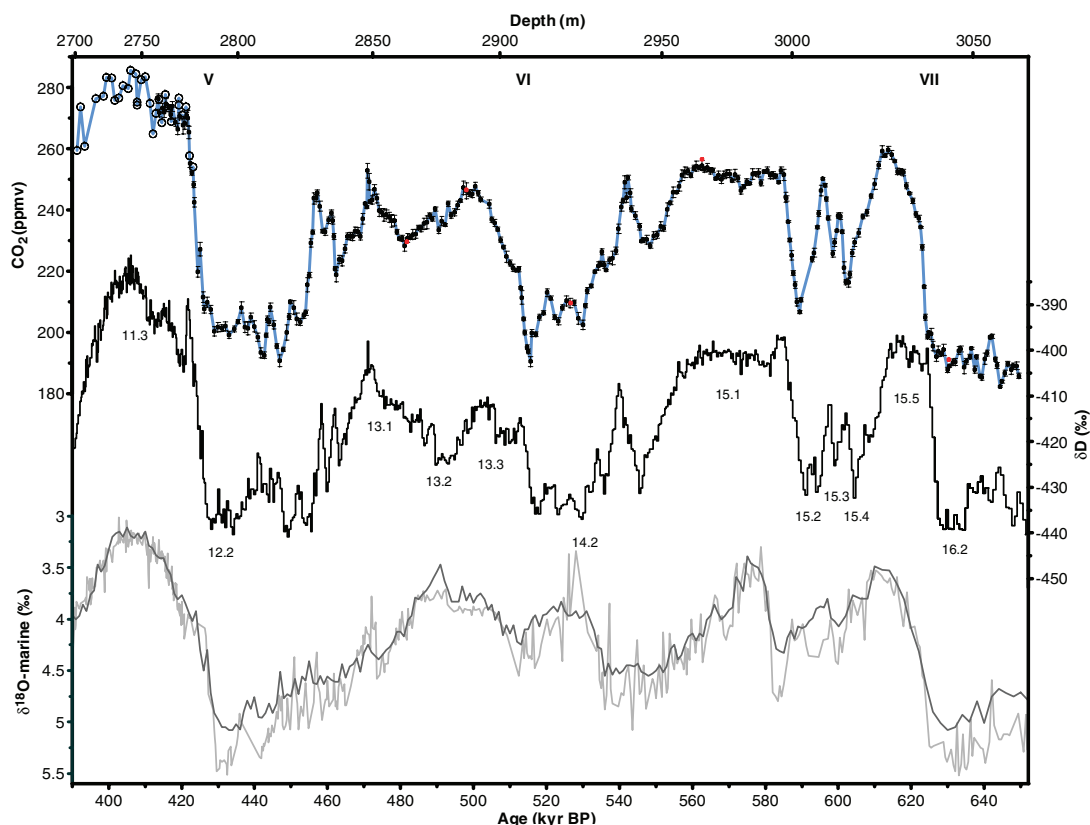
Urs Siegenthaler,¹ Thomas F. Stocker,^{1*} Eric Monnin,¹
Dieter Lüthi,¹ Jakob Schwander,¹ Bernhard Stauffer,¹
Dominique Raynaud,² Jean-Marc Barnola,² Hubertus Fischer,³
Valérie Masson-Delmotte,⁴ Jean Jouzel⁴

A record of atmospheric carbon dioxide (CO_2) concentrations measured on the EPICA (European Project for Ice Coring in Antarctica) Dome Concordia ice core extends the Vostok CO_2 record back to 650,000 years before the present (yr B.P.). Before 430,000 yr B.P., partial pressure of atmospheric CO_2 lies within the range of 260 and 180 parts per million by volume. This range is almost 30% smaller than that of the last four glacial cycles; however, the apparent sensitivity between deuterium and CO_2 remains stable throughout the six glacial cycles, suggesting that the relationship between CO_2 and Antarctic climate remained rather constant over this interval.

The European Project for Ice Coring in Antarctica (EPICA) recovered two deep ice cores from East Antarctica. One of the cores, located

at Dome Concordia (Dome C) (75°06'S, 123°21'E, altitude of 3233 m above sea level, and mean annual accumulation rate of 25.0

Fig. 1. Dome C CO₂ Bern data (black solid circles) are the mean of four to six samples, including the data from 31 depth intervals over termination V of (7); error bars denote 1σ of the mean. Red solid circles are test measurements with the use of the sublimation extraction technique. Dome C CO₂ Grenoble data are shown as black open circles. Dome C CO₂ measurements are connected with a blue line, and the high-resolution deuterium record is given as a black line (18). Benthic δ¹⁸O stack and benthic δ¹⁸O record from ODP site 980 are shown as a dark gray line (19) and a light gray line (19–22), respectively. The EDC2 time scale for Dome C is the same as in (7) (the depths at the top of the figure are only valid for the CO₂ record). Glacial terminations are given in roman numerals; marine isotope stages are given in arabic numerals according to (17).



kg m⁻² year⁻¹), is the only ice core covering at least eight glacial cycles (1), four cycles longer than previously available from ice cores. This has allowed us to reconstruct the record of the concentration of atmospheric CO₂ much further back in time than was possible before. Here, we report results from the interval between 390 and 650 kyr B.P. (kyr B.P. is thousand years before the present, i.e., before A.D. 1950).

Analyzing the air extracted from ice cores is the only way to directly determine atmospheric greenhouse gas concentrations for times before routine atmospheric measurements were begun. Antarctic ice cores are very suitable for CO₂ measurements because of their low temperatures and low concentrations of impurities, which minimize the risk of artifacts. Data from different Antarctic ice cores (2–13) and drilled at sites with different temperatures, accumulation rates, and impurity concentrations [except

cores with summer melting (14) and where elevated CO₂ values by up to 20 parts per million by volume (ppmv) are found] demonstrate that Antarctic ice cores are reliable recorders of atmospheric CO₂.

The concentrations of atmospheric CO₂ during the past four glacial cycles measured in the Vostok ice core vary between glacial and interglacial values of 180 ppmv and 280 ppmv, respectively (7). Including the data from Petit *et al.* (7), Fischer *et al.* (5) and Kawamura *et al.* (10), the lowest and highest values measured during a glacial cycle are on average 182 ± 4 ppmv (±1 standard deviation) and 296 ± 7 ppmv, respectively. This stable range of natural CO₂ variations on glacial-interglacial time scales led to the suggestion that feedbacks in the climate influence on the global carbon cycle maintain the rather narrow range observed (15).

The Dome C CO₂ record [mean sampling resolution of 731 years; details about the methods and the sampling are given in (16)] is plotted in Fig. 1, together with the δD record (Antarctic temperature proxy) of Dome C (18) [both records are shown on the EDC2 time scale (1)], a stack of benthic δ¹⁸O records from globally distributed sites (19), and a high-resolution benthic δ¹⁸O record from Ocean Drilling Project (ODP) site 980 (55°29'N, 14°42'W) (19–22). There is an excellent overall correlation between δD and benthic δ¹⁸O, a proxy of global ice volume (19).

First, we discuss the main features of the CO₂ record from Dome C from 650 to 390 kyr B.P. Our measurements begin at 650 kyr B.P., close to the lowest value for the entire record of 182 ppmv at 644 kyr B.P.. At marine isotope stage (MIS) 16, the CO₂ concentration is about 190 ppmv before the onset of termination VII. The entire transition between glacial and interglacial δD values occurred rapidly, within 3 kyr (ky) with the EDC2 dating. As expected from firmification processes, the corresponding CO₂ increase occurred deeper in the ice core, so there is no indication for an ice flow disturbance at this depth of about 3040 m, as has been observed at certain depths in the lowest 10% of some ice cores (7, 23). After emerging slowly out of the baseline band, the CO₂ increase can be divided in two intervals. The first increase of 35 ppmv up to a CO₂ concentration of 235 ppmv takes less than 2 ky, whereas the second increase of another 20 ppmv takes about 5 ky. Although the CO₂ trend at the beginning of the interglacial MIS 15.5 does not show an early CO₂ peak as during the past four interglacials, this second CO₂ increase is very similar in magnitude (20 ppmv) and duration (5 ky) to the Holocene one, although evolving with generally lower CO₂ values by about 25 ppmv. Therefore, the Holocene increase during the last 8 kyr is not an anomalous trend in comparison to other interglacials as postulated recently (24); instead it is a likely response of the carbon cycle

¹Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland. ²Laboratoire de Glaciologie et de Géophysique de l'Environnement (CNRS), 54 Rue Molières, 38402 St. Martin d'Hères Cedex, France. ³Alfred Wegener Institute for Polar and Marine Research (AWI), Columbusstrasse, D-27568 Bremerhaven, Germany. ⁴Institut Pierre Simon Laplace/Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS 1572, CE Saclay, Orme des Merisiers, 91191 Gif-sur-Yvette, France.

*To whom correspondence should be addressed. E-mail: stocker@climate.unibe.ch

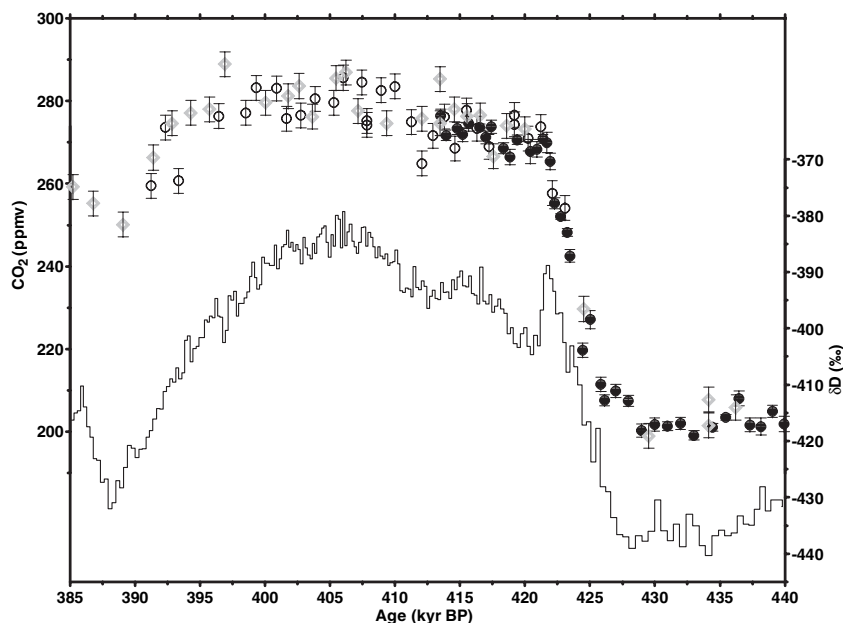


Fig. 2. CO₂ results of entire MIS 11, including end of MIS 12. Dome C CO₂ Bern data (solid circles) from EPICA community members (7) and this work; error bars, 1 σ of the mean. Dome C CO₂ Grenoble data are indicated by open circles; error bars, accuracy of 2 σ = 3 ppmv. High-resolution deuterium record is shown as a black line (18). Vostok CO₂ Grenoble data are indicated by gray open diamonds; error bars, accuracy of 2 σ = 3 ppmv on the corrected time scale (28).

to large changes in biomass (25). At the end of MIS 15.5, CO₂ attains its local maximum of about 260 ppmv, which is the highest concentration in the record before MIS 11 but substantially lower than the interglacial concentrations measured during the last four glacial cycles. At MIS 15.4 and MIS 15.2, the deuterium record indicates near-glacial conditions, only interrupted by two peaks at MIS 15.3. During the time interval of MIS 15.4 to 15.2, CO₂ shows rather large variations, with values between 207 ppmv and 250 ppmv and with two peaks during MIS 15.3 that are very similar to the deuterium peaks. The lowest values are close to glacial CO₂ concentrations, which raise the question of whether MIS 15 was a single continuous interglacial or multiple ones.

The increases of CO₂ and δ D into MIS 15.1 are very uniform and take 4 to 5 ky for each component. An unexpected feature is the very stable and long-lasting MIS 15.1. In contrast to the increasing global ice volume suggested by the benthic records of marine sediments (Fig. 1) (19), all indicators from Dome C exhibit almost constant values during MIS 15.1. This is observed in the records of deuterium (1), of CH₄ (26), and of aerosols (27) of the Dome C ice core but is most pronounced in our CO₂ results. We find a stable 251.5 ± 1.9 ppmv (± 1 standard deviation) CO₂ concentration from 585 kyr B.P. to 557 kyr B.P. on the EDC2 time scale, which is unprecedented in any other time interval covered by previous CO₂ measurements on ice cores. This result suggests that the global carbon

cycle operated in an exceptionally stable mode for many millennia. The current estimate for the duration of MIS 15.1, on the basis of the EDC2 time scale, is 28,000 years. Accordingly, this interval is a prime target for developing a better understanding of the influence of orbital geometry on climate and the global carbon cycle. However, we cannot, at this stage, exclude the possibility that at least part of the exceptionally long duration of stable conditions could be due to an exceptionally low thinning rate of the corresponding ice layer.

The decrease in δ D from the end of MIS 15.1 to the start of MIS 14.2 is interrupted by a double peak, the older of which is most pronounced with a corresponding peak in the CO₂ record and with elevated values by more than 20 ppmv. The phase relationship between CO₂ and deuterium for this event is discussed later in the text. The deuterium increase to the maximum value of MIS 13.3 ("termination" VI) evolves in two steps, with a rather stable concentration in between and a difference between glacial and interglacial values that is smaller in comparison to any other termination during the past 650 ky. The CO₂ increase can be divided again into two intervals, as for termination VII. The first increase of 30 ppmv takes 3 ky, whereas the duration for the second increase of 20 ppmv is more than 8 ky. During MIS 13, CO₂ values are in the range of about 230 to 250 ppmv, with a minimum at 481 kyr B.P. This minimum lags the deuterium minimum by about 10 ky. The decrease to MIS 12.2 is

interrupted by another prominent set of deuterium and CO₂ double peaks. During MIS 12.2 (and also MIS 16.2) we find pronounced millennial CO₂ fluctuations of 10 to 20 ppmv. They are comparable in duration and amplitude to the distinct CO₂ peaks observed during the past four Antarctic warm events (A1 to A4) during the last glacial (4, 8).

A detailed comparison with Vostok data (28) during MIS 11, an interglacial period that occurred some 400,000 years ago and lasted for about 30,000 years, is shown in Fig. 2 in order to examine the consistency of CO₂ values measured in this deep ice. Both records agree within the error limits and show interglacial CO₂ concentrations in MIS 11 similar to those found in the Holocene. Accordingly, we are confident that the Dome C data in the pre-Vostok era reflect true atmospheric CO₂ concentrations.

The coupling of CO₂ and δ D is strong. The overall correlation between CO₂ data and Antarctic temperature during the time period of 390 to 650 kyr B.P. is $r^2 = 0.71$. Taking into account only the period 430 to 650 kyr B.P., where amplitudes of deuterium and CO₂ are smaller, the correlation is $r^2 = 0.57$. Corrections for changes in the temperature and δ D of the water vapor source, which also affect δ D of the ice, have not been made yet. The strong coupling of CO₂ to Antarctic temperature confirms earlier observations for the last glacial termination (9) and the past four glacial cycles (7) and supports the hypothesis that the Southern Ocean played an important role in causing CO₂ variations.

δ D as a function of CO₂ from the Vostok (MIS 1 to MIS 11) and Dome C ice cores [MIS 12 to 16, Holocene (11), and termination I (9)] is shown in Fig. 3. The offset in the deuterium values of Dome C and Vostok is due to the different distances to the open ocean, elevations, and surface temperatures of the two sites (29). It is remarkable that the slope of the three records is essentially the same. This suggests that the coupling of Antarctic temperature and CO₂ did not change substantially during the last 650 ky.

Another important parameter elucidating the coupling of atmospheric CO₂ and Antarctic temperature is their relative phasing. Because of the enclosure process of air in ice, the phase relationship of CO₂ and δ D is associated with uncertainties. Because the enclosed air is younger than the surrounding ice (30), CO₂ is plotted on a gas age chronology, whereas deuterium is plotted on an ice age chronology. For Dome C and the period under investigation, the gas age/ice age difference (Δ age) is in the range of 1.9 to 5.5 ky (fig. S1). The estimated uncertainty of Δ age in the upper 800 m of

the Dome C ice core is about 10% (31), neglecting uncertainties in the thinning rate. Deviations from the modeled thinning would introduce systematic errors in Δ age.

By shifting the time scales of the entire CO_2 and deuterium records between 390 and 650 kyr B.P. relative to each other, we obtained the best correlation for a lag of CO_2 of 1900 years. This lag is significant considering the uncertainties of Δ age. Over the glacial terminations V to VII, the highest correlation of CO_2 and deuterium, with use of a 20-ky window for each termination, yields a lag of CO_2 to deuterium of 800,

1600, and 2800 years, respectively. This value is consistent with estimates based on data from the past four glacial cycles. Fischer *et al.* (5) concluded that CO_2 concentrations lagged Antarctic warmings by 600 \pm 400 years during the past three transitions. Monnin *et al.* (9) found a lag of 800 \pm 600 years for termination I, and Caillon *et al.* (32), with use of the isotopic composition of argon in air bubbles instead of deuterium, calculated a value of 800 \pm 200 years for termination III. Overall, the estimated lags over the entire Dome C record between 390 and 650 kyr B.P. and over the three ter-

minations in this time period are small compared with glacial-interglacial time scales and do not cast doubt on the strong coupling of CO_2 and temperature or on the importance of CO_2 as a key amplification factor of the large observed temperature variations of glacial cycles.

An apparent exception of the lag of CO_2 to deuterium observed over most of the record occurs around 534 to 548 kyr B.P., where CO_2 seems to lead δD by about 2000 \pm 500 year. We cannot conclude with certainty whether the observed lead of CO_2 at this time is real or an artefact in the EDC2 time scale. To make the CO_2 and the δD peaks simultaneous, we would need to increase the modeled depth offset of the gas record and the ice record (Δ depth) from 4.3 m to 7 m (fig. S2). This can be achieved by a reduced thinning rate, an increased accumulation rate, a decreased temperature, or a combination of them. However, because accumulation and temperature are strongly positively correlated at present (33), the required change in accumulation or temperature, or a change of both, is rather unlikely. An anomalously low thinning rate is therefore the more likely way to produce such an artefact in the EDC2 time scale.

A composite CO_2 record over six and a half ice age cycles back to 650,000 yr B.P. is shown in Fig. 4, created from a combination of records from the Dome C, Taylor Dome, and Vostok ice cores. This record shows the differences in amplitudes of CO_2 and deuterium before and after 430 kyr B.P. and demonstrates, within the resolution of our measurements, that the atmospheric concentration of CO_2 did not exceed 300 ppmv for the last 650,000 years before the preindustrial era.

Fig. 3. Correlation between δD , a proxy for Antarctic temperature, and CO_2 for three data sets. The new data from Dome C cover the beginning of MIS 12 to MIS 16 (black solid circles; black line is the linear fit $\delta\text{D} = 0.44\text{‰ ppmv}^{-1} \times \text{CO}_2 - 517.75\text{‰}$, $r^2 = 0.57$), and the period from MIS 1 to MIS 11 is covered by data from the Vostok ice core [gray solid circles (7); gray line is linear fit, $\delta\text{D} = 0.50\text{‰ ppmv}^{-1} \times \text{CO}_2 - 575.86\text{‰}$, $r^2 = 0.70$] and Dome C Holocene and termination I [black open circles (9, 11); black dashed line is the linear fit, $\delta\text{D} = 0.50\text{‰ ppmv}^{-1} \times \text{CO}_2 - 529.87\text{‰}$, $r^2 = 0.84$]. The offset in the δD values from these two cores is due to the different distances to the open ocean, elevations, and surface temperatures of the two sites (29).

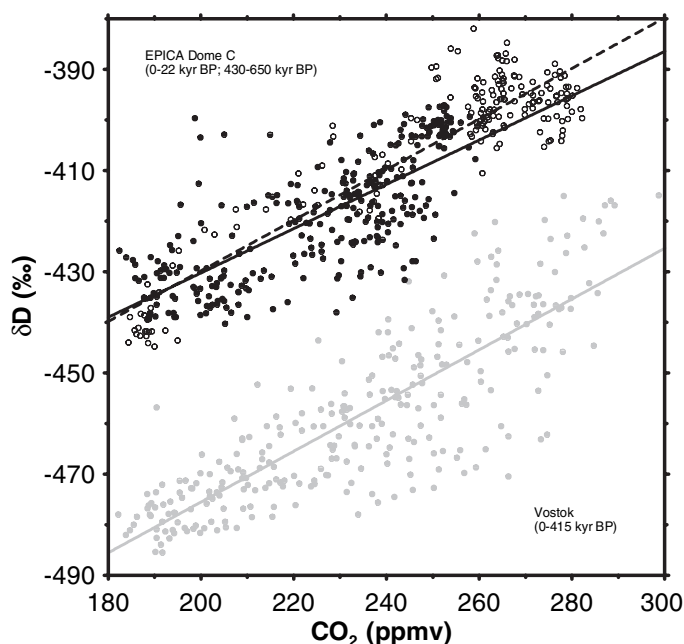
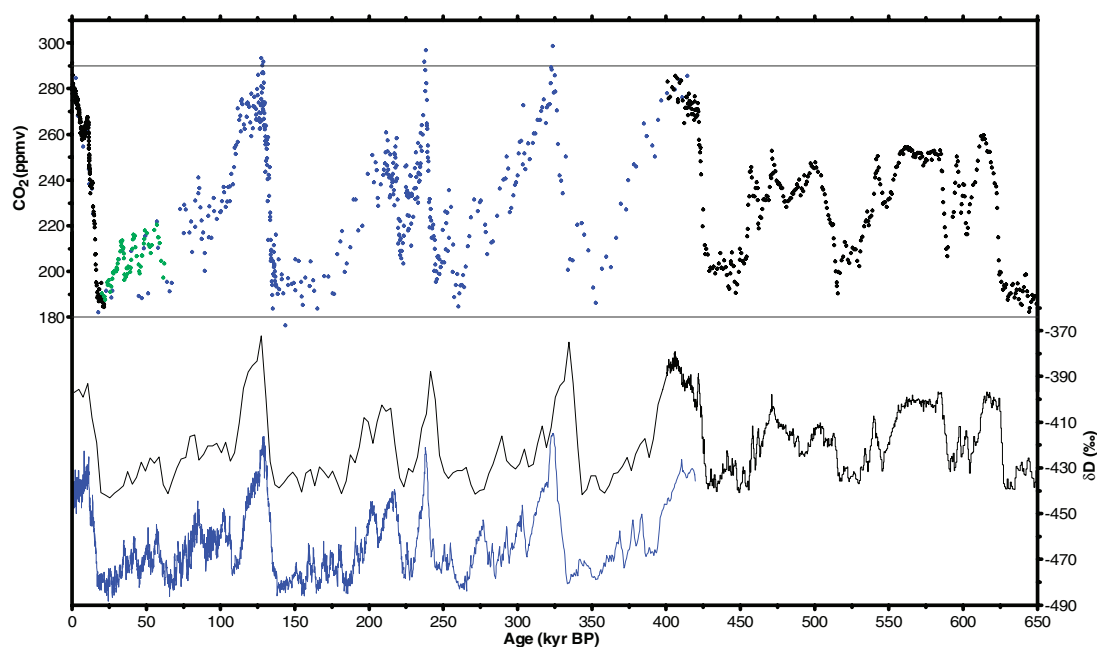


Fig. 4. A composite CO_2 record over six and a half ice age cycles, back to 650,000 years B.P. The record results from the combination of CO_2 data from three Antarctic ice cores: Dome C (black), 0 to 22 kyr B.P. (9, 11) and 390 to 650 kyr B.P. [this work including data from 31 depth intervals over termination V of (7)]; Vostok (blue), 0 to 420 kyr B.P. (5, 7), and Taylor Dome (light green), 20 to 62 yr B.P. (8). Black line indicates δD from Dome C, 0 to 400 kyr B.P. (1) and 400 to 650 kyr B.P. (18). Blue line indicates δD from Vostok, 0 to 420 kyr B.P. (7).



The CO₂ record from the EPICA Dome C ice core reveals that atmospheric CO₂ variations during glacial-interglacial cycles had a notably different character before and after 430 kyr B.P. Before MIS 11, the amplitude of temperature was lower, and the duration of the warm phases has been much longer since then. In spite of these differences, the significant covariation of δD and CO₂ is valid in both periods. Before MIS 11, CO₂ concentrations did not exceed 260 ppmv. This is substantially lower than the maxima of the last four glacial cycles. The lags of CO₂ with respect to the Antarctic temperature over glacial terminations V to VII are 800, 1600, and 2800 years, respectively, which are consistent with earlier observations during the last four glacial cycles.

Our measurements have revealed an unexpected stable climate phase (MIS 15.1) during which the atmospheric CO₂ concentration was 251.5 ± 1.9 ppmv for many millennia (28,000 years, based on the EDC2 time scale), although the duration of MIS 15.1 is uncertain because of possible inaccuracies in the Dome C EDC2 time scale between MIS 12 and 15. However, the roughly 30,000-year duration of MIS 11 (and possibly MIS 15.1) demonstrates that long interglacials with stable conditions are not exceptional. Short interglacials such as the past three therefore are not the rule and hence cannot serve as analogs of the Holo-

cene, as postulated recently (24). Examining δD as a function of CO₂, we observe that the slope during the two new glacial cycles compared to the last four cycles is essentially the same. Therefore, the coupling of Antarctic temperature and CO₂ did not change significantly during the last 650 kyr, indicating rather stable coupling between climate and the carbon cycle during the late Pleistocene.

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Materials and Methods

Figs. S1 and S2

References

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Atmospheric Methane and Nitrous Oxide of the Late Pleistocene from Antarctic Ice Cores

Renato Spahni,¹ Jérôme Chappellaz,² Thomas F. Stocker,^{1*} Laetitia Loulergue,² Gregor Hausammann,¹ Kenji Kawamura,^{1,†} Jacqueline Flückiger,^{1,‡} Jakob Schwander,¹ Dominique Raynaud,² Valérie Masson-Delmotte,³ Jean Jouzel³

The European Project for Ice Coring in Antarctica Dome C ice core enables us to extend existing records of atmospheric methane (CH₄) and nitrous oxide (N₂O) back to 650,000 years before the present. A combined record of CH₄ measured along the Dome C and the Vostok ice cores demonstrates, within the resolution of our measurements, that preindustrial concentrations over Antarctica have not exceeded 773 ± 15 ppbv (parts per billion by volume) during the past 650,000 years. Before 420,000 years ago, when interglacials were cooler, maximum CH₄ concentrations were only about 600 ppbv, similar to lower Holocene values. In contrast, the N₂O record shows maximum concentrations of 278 ± 7 ppbv, slightly higher than early Holocene values.

Earth's climate during the late Pleistocene was characterized by ice age cycles with relatively short warm periods (interglacials) and longer cold periods (glacials) (1). The Vostok ice core provided an archive of climate and atmospheric composition over

the past four climatic cycles back to marine isotope stage (MIS) 11, about 420 thousand years before the present (420 kyr B.P.) (2). That record demonstrated the high correlation of temperature changes with greenhouse gas concentration changes in the atmo-

sphere in the past. The European Project for Ice Coring in Antarctica (EPICA) Dome Concordia (Dome C) ice core (75°06'S, 123°21'E, 3233 m above sea level) provides an ice core archive much longer, spanning eight climatic cycles over the past 740 thousand years (ky) (3). It demonstrates that the oldest four interglacials were cooler but lasted longer than the younger interglacials. Such findings raise the question whether the greenhouse gases CH₄ and N₂O behaved differently before MIS 11. Here, we present CH₄ and N₂O records derived from the EPICA Dome C ice cores reaching back to 650 kyr B.P.

¹Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland. ²Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE, CNRS-UJF), CNRS, 54 Rue Molières, 38402 St. Martin d'Hères, Grenoble, France. ³Institut Pierre Simon Laplace/Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS 1572, CE Saclay, Orme des Merisiers, 91191 Gif-sur-Yvette, France.

*To whom correspondence should be addressed: stocker@climate.unibe.ch

†Present address: Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0244, USA.

‡Present address: Institute of Arctic and Alpine Research, University of Colorado at Boulder, 450 UCB Boulder, Colorado 80309-0450, USA.

Stable Carbon Cycle–Climate Relationship During the Late Pleistocene

Urs Siegenthaler, Thomas F. Stocker, Eric Monnin, Dieter Lüthi, Jakob Schwander, Bernhard Stauffer, Dominique Raynaud, Jean-Marc Barnola, Hubertus Fischer, Valérie Masson-Delmotte and Jean Jouzel

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