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Atmospheric CO_2 concentration from 60 to 20 kyr BP from the Taylor Dome ice core, Antarctica

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Abstract. A high–resolution record of the atmospheric CO_2 concentration from 60 to 20 thousand years before present (kyr BP) based on measurements on the ice core of Taylor Dome, Antarctica is presented. This record shows four distinct peaks of 20 parts per million by volume (ppmv) on a millennial time scale. Good correlation of the CO_2 record with temperature reconstructions based on stable isotope measurements on the Vostok ice core (Antarctica) is found.

Introduction

The concentration of atmospheric CO_2 is increasing since the beginning of industrialization from its pre-industrial value of about 280 ppmv to its present value of about 365 ppmv [*Neftel et al.*, 1985; *Keeling and Whorf*, 1994] by fossil-fuel burning and changes in land use. In order to understand the impact of this strong perturbation to climate it is important to know the relation carbon cycle–climate system on different time scales.

Records from polar ice cores document that Antarctic temperature and atmospheric CO_2 concentration varied in phase on a 100'000 yr time scale [*Petit et al.*, 1999]. A synchronization between the CO_2 ice core record from Byrd Station (West Antarctica) and the $\delta^{18}O$ record (a proxy for air temperature) from the GRIP ice core (Central Greenland) revealed that the atmospheric CO_2 concentration varied only during the most prominent reorganisations of climate in the North Atlantic region in the last glacial (Dansgaard-Oeschger (D–O) event 8 and 12) [*Stauffer et al.*, 1998]. These most prominent warming features in Greenland have counterparts in Antarctic stable isotope records; the warming in Antarctica preceded the onset of D–O events 8 and 12 (36 kyr BP and 44 kyr BP on the GRIP time scale) [*Blunier et al.*, 1998]. The question arises whether these warming events in Antarctica could have had an influence on the concentration of atmospheric CO_2 and what could have been the mechanisms.

Here we confirm the findings of *Stauffer et al.* [1998] by new measurements on the Taylor Dome ice core (Antarctica) in principle, showing that the CO_2 concentration parallels the Antarctic warmings. We extend the detailed CO_2 record to 60 kyr BP and show that the 20 ppmv oscillations of the atmospheric CO_2 concentration are synchronous with warming events in Antarctica.

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Samples and chronology

In order to reconstruct the atmospheric CO_2 concentration from 60 to 20 kyr BP, we analyzed the ice core from Taylor Dome (TD), Antarctica (77°47S, 158°43E; elevation 2365 m above sea level). A total of 438 samples have been measured at 73 different depth intervals (10 to 15 cm length) from 380 to 471 m depth. For each interval six neighboring samples have been measured. Measurements on bubble-free single crystal ice, to which reference gas is added, yield an estimate of ±1.5 ppmv for the analytical uncertainty of the device. The analytical protocol is described in *Indermühle et al.* [1999]. The measurements are corrected in order to account for daily drifts (the corrections are on the order of 1 ppmv).

In order to discuss our record and to compare it with other paleodata, an accurate chronology has to be established. Air which is enclosed in bubbles has a younger age than the surrounding ice; the age difference will be denoted as Δage. Δage depends on the accumulation rate $\dot{b}$ and the annual mean temperature $\overline{T}$ at the drill site. In principle there are two methods to calculate the age of the air (gas age). First, the age of the ice (ice age) can be estimated from annual layer counting, ice flow modelling and wiggle-matching of climate parameters. The gas age scale can then be established by calculating Δage if $\dot{b}$ and $\overline{T}$ are known with sufficient accuracy. Second, the gas age scale of one ice core can be obtained by synchronizing suitable parameters entrapped in the air with the same parameters measured in a reference ice core. These parameters must be globally well mixed in the atmosphere which is the case for $\delta^{18}O(O_2)$ [*Sowers and Bender*, 1995] and CH_4. Methane permits a synchronization with higher accuracy due to its fast changes during the last glacial and the transition to the Holocene [*Blunier et al.*, 1998].

The gas age scale for the TD ice core for the last 36 kyr is based on a synchronization of the CH_4 and $\delta^{18}O(O_2)$ records from TD and GISP2 [*Brook et al.*, 1999]. For older ages, only three points for the gas age, which are not very well constrained, existed so far [*Steig et al.*, 1999]. Therefore, we need to establish a new gas age scale for our record.

We use the synchronization method, choosing the Vostok GT4 time scale [*Petit et al.*, 1999] as a reference. The reason for this choice will become apparent below. For the TD record younger than about 36 kyr BP (D–O event 8) we synchronized the CH_4 records from TD [*Brook et al.*, 1999] and Vostok [*Petit et al.*, 1999]. For the older part we synchronized the CO_2 records from TD and Vostok [*Barnola et al.*, 1991]. The CO_2 record from Vostok shows two dis-

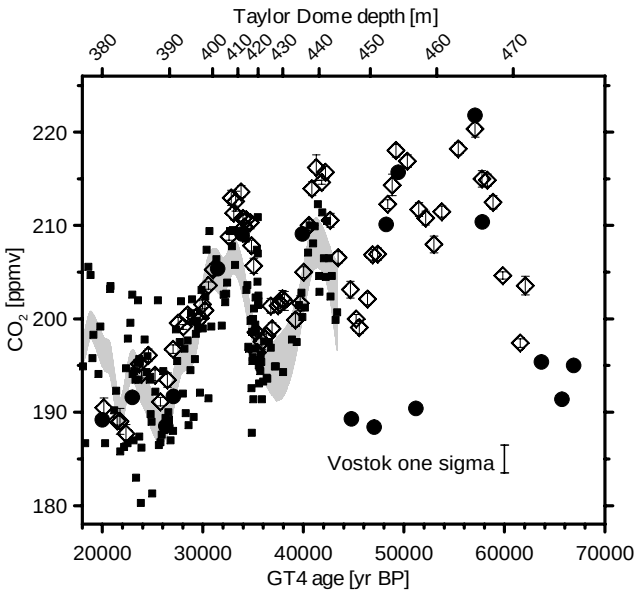

Figure 1. CO_2 mean values from Taylor Dome (open diamonds; error bars: 1-σ of the mean), Vostok (large dots, *Barnola et al.*, 1991) and Byrd Station (small squares [*Neftel et al.*, 1988]; shaded area: 2-σ spline) versus the Vostok GT4 age scale [*Petit et al.*, 1999] and Taylor Dome depth (only valid for the Taylor Dome record).

tinct peaks at 49.4 kyr BP and 57 kyr BP which we used as control points. An additional constraint on the synchronization is given by a ^{10}Be peak found in the two cores [*Steig et al.*, 1999] which has an age of 65.6 kyr BP in the GT4 time scale. For this peak a Δage of $1400 \pm 200\,yr$ has been calculated using the Herron-Langway firn densification model [*Herron and Langway*, 1980] with the parameters $\overline{T} = (-47 \pm 2)^\circ$C, $\dot{b} = (3.5 \pm 0.5)$ cm ice/yr and close-off density $\rho_{co} = (820 \pm 10)\,kg/m^3$. The age scale for the TD CO_2 record then resulted from a polynomial fit (degree 5) to the control points. The accuracy of the synchronization is about $\pm$500 yr for the part younger than 36 kyr BP, where rapid variations of CH_4 occur, and about $\pm$2000 yr for the older part. In order to compare the CO_2 record from Byrd Station (BS henceforth) [*Neftel et al.*, 1988] with the TD and Vostok records, we converted the gas age scale from *Stauffer et al.* [1998] to the GT4 time scale comparing the two time scales of the Vostok CH_4 record.

Results

The CO_2 records from TD (open diamonds), Vostok (large dots) and BS (small squares) are plotted in Fig. 1 versus age (Vostok GT4 time scale) and depth (only valid for the TD CO_2 record). The error bars denote the reproducibility for TD (i. e. one standard deviation of the mean) which is about 1 ppmv. In the TD record, there are four well-defined CO_2 oscillations with a peak-to-peak amplitude of about 20 ppmv superimposed on a long-term decreasing trend. The CO_2 values from BS are plotted without error bars to obtain a clearer graph. The two-σ band (shaded area in Fig. 1) for the BS record has been calculated using a Monte Carlo simulation and a smoothing spline [*Enting*, 1987]. There is reasonable agreement between the measurements from Taylor Dome and the general trend of the record from BS. The minimum values in the Vostok record at about 45 and 51 kyr BP are not found at TD. A poor quality of the ice in this part of the core is reported [*Barnola et al.*, 1991]. Therefore, we consider the record from Taylor Dome as more reliable.

The possibility of CO_2 enrichment in the air bubbles by chemical reactions has been discussed [*Anklin et al.*, 1995; *Smith et al.*, 1997; *Tschumi and Stauffer*, 1999]. The main possibilities are acid–carbonate reactions and oxidation of organic matter. The probability of such reactions is – in addition to physical properties – dependent on the concentration of the causing impurities in the ice. In the GRIP ice core, the CO_2 concentration is about 40 ppmv higher during D–O events (high δ^{18}O values) than during cold episodes. Such elevated CO_2 concentrations are not observed in Antarctic ice cores [*Anklin et al.*, 1997; *Stauffer et al.*, 1998]. Moreover, samples from the GRIP ice core show a scatter between neighboring samples which can neither be explained by atmospheric CO_2 variations nor by the analytical uncertainty. During the D–O events the ice can become acidic whereas it is alkaline during cold periods as indicated by the Electric Conductivity Method (ECM, *Wolff et al.*, 1997). This points to an acid–carbonate reaction as the main contributor to the elevated values and large scatter in the GRIP CO_2 record, but oxidation of organic matter could have contributed also.

The ice in the TD core is generally slightly acidic, as revealed by ECM (K.C. Taylor, unpublished data). However, there is no correlation between the CO_2 and ECM records. In the GRIP ice core, the acidity and not the concentration of carbonate (as indicated by the high concentration of Ca^{++}) is assumed to be the limiting compound for a CO_2 production [*Anklin et al.*, 1997]. This may be different in the TD ice core, where the concentration of Ca^{++} is at least one order of magnitude lower than in the GRIP core. If the observed CO_2 peaks were produced by an acid–carbonate reaction we may therefore expect a positive correlation of the Ca^{++} and the CO_2 concentrations. We found in fact a negative correlation between the interpolated Ca^{++} [*Steig et al.*, 1999] and the CO_2 data. Thus, as there are no positive correlations between Ca^{++} or ECM and CO_2 data and the scatter of neighboring samples is in agreement with the analytical uncertainty, we conclude that our record most likely represents the atmospheric CO_2 concentration with good reliability.

Discussion

Based on measurements of the ice core from BS, *Stauffer et al.* [1998] have shown that the atmospheric CO_2 concentration varies significantly with large iceberg discharges (Heinrich events H4 and H5) which precede the most prominent D–O events (8 and 12), whereas the variations of CO_2 during the less pronounced D–O events are only small (< 10 ppmv). With the new measurements these findings are confirmed and extended to the effect that the variation of CO_2 during the less pronounced D–O events is < 2 ppmv. *Blunier et al.* [1998] have shown a lead of the Antarctic warming events A1 and A2 relative to D–O events 8 and 12, respectively. A synthesis of these two publications reveals that the increases of the atmospheric CO_2 concentration parallel A1 and A2. The question now arises whether

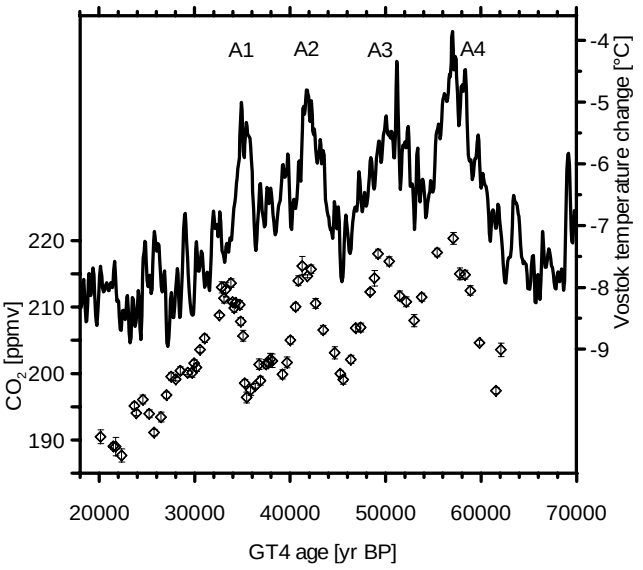

Figure 2. Top: Air temperature record at Vostok (temperature change relative to modern temperature based on measurements of the isotopic composition of the ice, *Petit et al.*, 1999), running mean (3 points). A1 and A2 are Antarctic warm events according to *Blunier et al.* [1998]. Bottom: CO_2 data from Taylor Dome.

this apparent connection between Antarctic warming events and CO_2 oscillations also appears beyond A2.

Similar to the CO_2 record, the temperature record from Vostok (based on measurements of the isotopic composition of the ice, *Petit et al.*, 1999) shows four distinct peaks (solid line, denoted A1 to A4 in Fig. 2) with inferred temperature changes of 2°C superimposed on a decreasing trend over the time interval 65 to 20 kyr BP. Strong climatic connections should exist between Antarctica and the Southern Ocean (SO), as the SO exports latent and sensible heat to Antarctica. The broad features of the Vostok temperature record are thought to be representative of a large area (Antarctica and parts of the Southern Hemisphere), at least qualitatively [*Petit et al.*, 1999]. The similarities between SO sea surface temperature (SST) and Vostok temperature are striking for the long-term features [*Jouzel et al.*, 1987; *Pichon et al.*, 1992; *Waelbroeck et al.*, 1995] and similar structures are also present on shorter time scales. The TD $\delta^{18}O$ record, on the other hand, suggests near-synchronous changes with the Greenland ice cores during the last termination. However, isotopic temperatures at near coastal drill sites such as TD may be influenced on a millennial time scale by further processes, such as wind-driven convection and ocean-atmosphere heat exchange in the near Ross Sea [*Steig et al.*, 1998]. Therefore, we consider the Vostok temperature record as the better indicator for SO SST.

In order to compare the CO_2 and temperature records, we carried out the following procedure: We calculated the correlation coefficient of the CO_2 and temperature records using the mean temperature over ~ 300 yr (3 data points) to every corresponding CO_2 data point. This value is justified by the age distribution of ~ 300 yr of the air in the bubbles due to the slow enclosure process. The correlation coefficient is $R = 0.66$. Shifting the time scale of the CO_2 record in steps of 100 yr yields a maximum value of $R = 0.83$ at a time lag of CO_2 of 900 yr. In order to test the sensitivity of this lag to the uncertainty of the control points and of Δage of the Vostok ice core (1000 yr, *Petit et al.*, 1999), we performed a Monte Carlo simulation (2000 runs) where the ages of the control points have been varied randomly within estimated uncertainties (Gaussian propagation of the uncertainties of the control points and of Δage). In each run, *i*) a new chronology for the CO_2 record was established using a polynomial fit (degree 5), *ii*) the time scale of the CO_2 record has been shifted in steps of 100 yr and, *iii*) the lag was calculated for which the correlation coefficient of the CO_2 record and the corresponding temperatures values reached a maximum. The simulation yields a lag of (1200 ± 700) yr. This value is roughly in agreement with findings by *Fischer et al.* [1999] who reported a time lag of CO_2 to the Vostok temperature of (600 ± 400) yr during early deglacial changes in the last 3 transitions glacial–interglacial. However, these results have to be considered as preliminary.

Different SST reconstructions from the Indian sector of the Southern Ocean report variations in summer SST of up to 2°C from 65 to 20 kyr BP [*Waelbroeck et al.*, 1995; *Pichon et al.*, 1992]. Such changes in SST in the ocean area between 30-70°S can only explain about 5 ppmv of the CO_2 changes by changes of its solubility [*Takahashi et al.*, 1993]. Therefore, additional mechanisms have to be taken into account.

Petit et al. [1999] suggest that the glacial–interglacial changes of the atmospheric CO_2 concentration are driven by either changes of the input of iron, following the hypothesis of *Martin et al.* [1990] or by changes in the deep ocean circulation and sea ice extent in the SO. High dust values during periods of low CO_2 support both scenarios. If these scenarios are applicable also for the small CO_2 changes from 65 to 20 kyr BP, then an anti-correlation of the dust (used as an indicator for iron or sea-ice extent, respectively) and CO_2 records is expected. The dust record shows only small variations which are at the limit of significance (the uncertainty of the data is high in this time interval due to bad core quality, J.R. Petit, pers. comm.) and therefore, these hypotheses cannot yet be tested.

Marchal et al. [1998] simulated the evolution of the atmospheric CO_2 concentration in response to a freshwater induced collapse of the thermohaline circulation (THC) using a coupled ocean circulation–biogeochemical model. In their simulation, a THC shut-down leads to an increase of the CO_2 concentration due to a warming of the SO (the so called 'seesaw effect', *Broecker*, 1998; *Stocker*, 1998) which over-compensates the North Atlantic cooling. Changes in alkalinity and dissolved inorganic carbon concentration in the North Atlantic surface, mainly due to dilution, amplify the increase. Sensitivity studies reveal that the response of the temperature in the North Atlantic and the SO and of the atmospheric CO_2 concentration are dependent on the amount, duration and geographic location of freshwater input (i.e. iceberg discharge, see Fig. 12 in *Marchal et al.*, 1998). That would explain the fact that some D–O events are preceded by an Antarctic warming and an increase of atmospheric CO_2 and others are not [*Stocker and Marchal*, 1999].

Conclusions

We present a new high-resolution record of the atmospheric CO_2 concentration which shows 4 oscillations with

an amplitude of about 20 ppmv between 60 to 20 kyr BP. The record correlates with reconstructed air temperature based on stable isotope measurements on the Vostok ice core. A further interpretation of the CO_2 record requires a more accurate chronology in order to discuss leads and lags relative to Greenland and Antarctic ice cores.

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