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A record of atmospheric CO_2 during the last 40,000 years from the Siple Dome, Antarctica ice core

Jinho Ahn,[1] Martin Wahlen,[1] Bruce L. Deck,[1] Ed J. Brook,[2] Paul A. Mayewski,[3] Kendrick C. Taylor,[4] and James W. C. White[5]

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[1] We have measured the CO_2 concentration of air occluded during the last 40,000 years in the deep Siple Dome A (hereafter Siple Dome) ice core, Antarctica. The general trend of CO_2 concentration from Siple Dome ice follows the temperature inferred from the isotopic composition of the ice and is mostly in agreement with other Antarctic ice core CO_2 records. CO_2 rose initially at ~17.5 kyr B.P. (thousand years before 1950), decreased slowly during the Antarctic Cold Reversal, rose during the Younger Dryas, fell to a local minimum at around 8 kyr B.P., and rose continuously since then. The CO_2 concentration never reached steady state during the Holocene, as also found in the Taylor Dome and EPICA Dome C (hereafter Dome C) records. During the last glacial termination, a lag of CO_2 versus Siple Dome isotopic temperature is probable. The Siple Dome CO_2 concentrations during the last glacial termination and in the Holocene are at certain times greater than in other Antarctic ice cores by up to 20 ppm (μmol CO_2/mol air). While in situ production of CO_2 is one possible cause of the sporadic elevated levels, the mechanism leading to the enrichment is not yet clear. *INDEX TERMS:* 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1610 Global Change: Atmosphere (0315, 0325); 1615 Global Change: Biogeochemical processes (4805); *KEYWORDS:* CO_2, paleoclimate, Siple Dome

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1. Introduction

[2] Understanding how the atmospheric concentration of CO_2 changed in the past in response to other changes in the climate system provides us with a better understanding of how current and future changes in the carbon cycle will influence our future climate. The concentration of CO_2 in the atmosphere during previous times can be determined by measurements made on the air trapped in ice cores [e.g., *Delmas et al.*, 1980; *Neftel et al.*, 1982; *Fischer et al.*, 1999; *Petit et al.*, 1999]. CO_2 records from Antarctic ice cores are considered to be representative of paleoatmospheric concentrations. Greenland ice cores are not useful for determining the paleoatmospheric concentration because of in situ production of CO_2 due to high dust content [*Barnola et al.*, 1995; *Anklin et al.*, 1995, 1997; *Smith et al.*, 1997a, 1997b; *Tschumi and Stauffer*, 2000].

[3] The Siple Dome ice core from West Antarctica was drilled from 1997 to 1999. The site is at 81.66°S, 148.82°W, at an altitude of 621 meters asl, with an annual mean temperature of −25.4°C and an accumulation rate of 12.4 g cm^{-2} yr^{-1} as water equivalent (Figure 1 and Table 1). The total depth of the core is 1003.8 m. The high accumulation rate at Siple Dome allows rapid climate changes to be more accurately preserved and permits more accurate assessment of the relative timing between ice-isotopic variations and of variations in occluded gases compared to the low accumulation rate sites like Vostok, Dome C, or Dome Fuji (Table 1). In this study, we compare the CO_2 record from the Siple Dome ice core for the last 40,000 years with CO_2 records from other Antarctic ice cores using common time scales based on the GISP2 gas age and correlation to Antarctica using CH_4 concentrations variations. We also examine the relative timing of the CO_2 increase and temperature change. The highest resolution CO_2 record from Law Dome covering only the last thousand years [*Etheridge et al.*, 1996], and the recent Dome Fuji CO_2 record over the last 320 kyr [*Kawamura et al.*, 2003] measured by the wet extraction method are not discussed.

2. Method and Timescales

[4] Measurements were made on 462 samples from 86 depths in the top 832 meters in the Siple Dome ice core.

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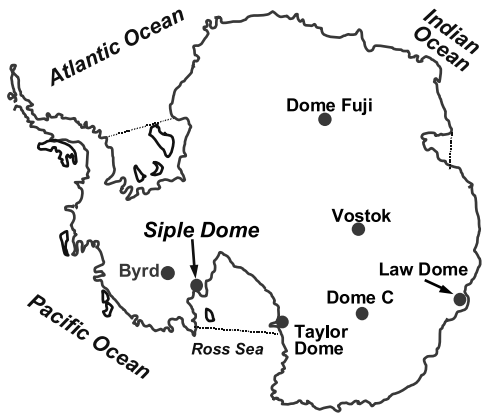

Figure 1. Location map of Antarctic ice cores referred to in the text.

These measurements span over the last 40,000 years. The ice core has a diameter of 13 cm. The outer 0.5 to 2 cm of the samples was removed with a band saw to reduce the possibility of contamination from present atmospheric CO_2 or postdrilling chemical reactions. The Siple Dome core samples contain bubbles and did not contain clathrates. Post collection temperature monitoring confirmed that the ice was kept below −15°C from the time it was removed from the drill site to arrival at Scripps Institution of Oceanography (SIO). The storing, cutting, and loading of samples into a mechanical crusher at SIO was done at −25°C. At most depths four to six ice samples, taken from a depth interval spanning 1 to 3 cm (mostly less than several years in ice age), were analyzed for each reported data point. At some depths samples of 6 to 12 cm depth intervals were used because of poor quality (extensive fracturing in the ice). Many fractures were observed below 500 m and the samples were more extensively trimmed in this region to assure sampling of unfractured ice. Contamination through undetected fractures results in higher CO_2 values due to high CO_2 concentration in the ambient air.

[5] For outliers in a group of samples cut from the same depth interval, we applied Grubb's test at the 95% confidence level to the suspected data. In this test a ratio of the difference between the outlier and the mean and the standard deviation of the data for the group was compared to a critical value [*Iglewicz and Hoaglin*, 1993]. We rejected results from 12 individual ice samples (usually the highest values) out of the total of 462 analyzed.

[6] The gas extraction and IR spectroscopic methods used are well established [*Wahlen et al.*, 1991; *Smith et al.*,1997a, 1997b; *Fischer et al.*, 1999]. Occluded air was dry extracted by mechanical crushing of samples in a double walled crusher cooled using an ethanol-liquid nitrogen mixture at about −50°C. The liberated air was collected in cold traps chilled by closed cycle He refrigerators to a temperature of about 32 K. The frozen air samples held in the cold traps were liberated by heating and transferred to an IR absorption cell held at a constant pressure and temperature. IR absorption measurements were made several times on each gas sample with a tunable diode laser by scanning a single vibrational-rotational CO_2 absorption line at Doppler resolution in the R branch of the 4.3 μm CO_2 absorption band. To calibrate the instru on, measurements were made with three air standards of precisely known CO_2 concentrations of 163, 240, and 330 ppm (±0.01 ppm, C. D. Keeling, personal communication) that were introduced over three of the crushed ice samples, thus duplicating the crushing procedure. This calibration procedure was performed each day. A group of samples from the same depth interval were measured on the same day. The average standard deviation of the data of the samples from the same depth interval measured on the same day (5.9 ppm) is greater than the daily internal precision (1.7 ppm) measured on crushed ice samples with reference gas added. Considering the daily uncertainty in calibration and the reproducibility, we expect the internal precision to be better than 2 ppm when measured on different days for a group of samples from the same depth interval with constant CO_2 concentration among the samples. Directly introduced standards (not over ice) were run to check laser linearity and performance.

[7] The gas age dating of the Siple Dome core over the time period of 40 to 8.2 kyr B.P. is established by correlation of CH_4 data with those of the GISP2 ice core [*Taylor et al.*, 2004b; E. Brook et al., manuscript in preparation, 2004]. The methods for CH_4 measurements are described by *Brook et al.* [2000, manuscript in preparation, 2004]. For ice younger than 8.2 kyr B.P. the age of the ice was determined by counting annual layers and the corresponding gas ages were assigned by subtracting the ice age – gas age difference (Δage) from the ice ages [*Taylor et al.*, 2004a]. The Δage was calculated with a firn densification model (Brook et al., manuscript in preparation, 2004). The Δage is about 280 ± 80 years in the early Holocene, increasing to about 750 ± 220 years during the Last Glacial Maximum (LGM). The gas age of bubble ice varies according to ice bubble close-off depth. We estimate that the width of the age distribution is on the order of 10% of the Δage value [*Goujon et al.*, 2003].

3. Results

3.1. Data Quality

[8] Measurements were made over a period of 2.5 years at random depth intervals to eliminate the possibility that

Table 1. Characteristics of the Antarctic Ice Cores From Which CO_2 Gases Have Been Measured

Core Name	Mean Annual Temperature, °C	Mean Accumulation Rate as Water Equivalent, g cm^{-2} yr^{-1}	Elevation, m
Law Dome	−22 ∼ −19[a,b]	60 ∼ 110[b]	1390[b]
Siple Dome	−25.4[c]	12.4[d]	621[e]
Byrd[f]	−28	16	1530
Taylor Dome	−42[g]	7[h]	2374[h]
EPICA Dome C	−54[i]	3[j]	3233[k]
Vostok[f]	−55.5	2.3	3490
Dome Fuji[l]	−58	3.2	3810

[a] *Etheridge and Wookey* [1989].
[b] *Etheridge et al.* [1996].
[c] *Severinghaus et al.* [2001].
[d] *Hamilton* [2002].
[e] *Taylor et al.* [2004b].
[f] *Raynaud et al.* [1993].
[g] *Waddington and Morse* [1994].
[h] As unit of cm ice equivalent per year [*Steig et al.*, 1998].
[i] *Schwander et al.* [2001].
[j] *EPICA Dome C 2001-02 Science and Drilling Teams* [2002].
[k] *Tabacco et al.* [1988].
[l] *Dome-F Deep Coring Group* [1998].

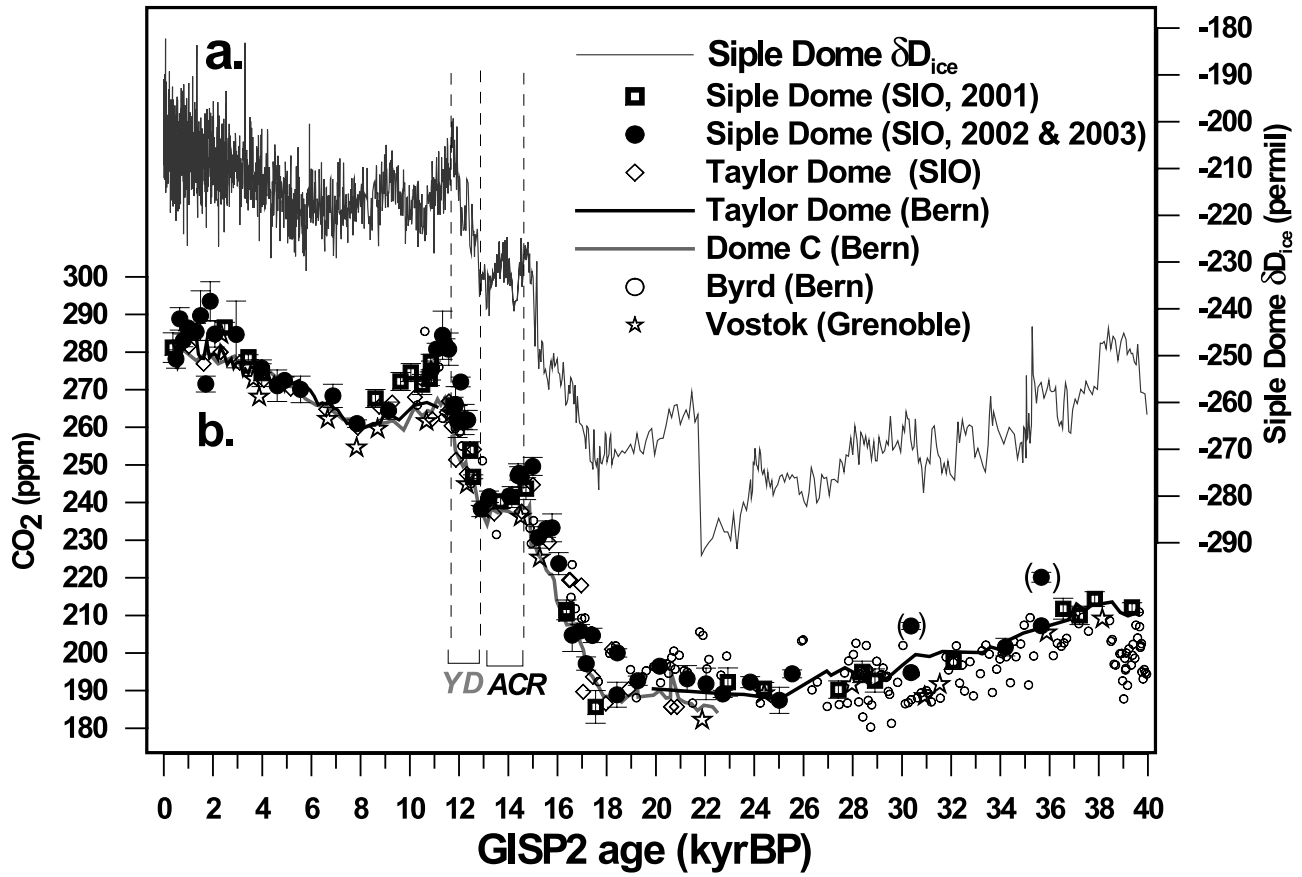

Figure 2. Antarctic ice core CO_2 plotted on GISP2 gas age scale. (a) Siple Dome δD_{ice} on ice age scale. (b) Ice core CO_2 records on synchronized gas age scale with GISP2 via CH_4. Shown are Vostok data [*Petit et al.*, 1999], EPICA Dome C [*Monnin et al.*, 2001; *Flückiger et al.*, 2002], Taylor Dome [*Indermühle et al.*, 1999, 2000; *Smith et al.*, 1999], and Byrd [*Neftel et al.*, 1988; *Staffelbach et al.*, 1991] and Siple Dome (this study). Error bars represent one standard error deviation of the replicate measurements at the same depth interval. The brackets indicate averages of two anomalously high values of the six samples from the same depth intervals. Taylor Dome gas ages of 40 to 20 kyr B.P. are from *Brook et al.* [2000]; Byrd gas ages are from *Blunier and Brook* [2001]; Vostok gas ages for 40 to 10 kyr B.P. are from *Blunier et al.* [1998]. The Vostok GT4 timescales [*Petit et al.*, 1999] are younger than those of GISP2 by about 1 kyr for the latter of the last termination and by up to 5 kyr during 40 to 20 kyr B.P. The Holocene depth-gas age scales of Vostok and Dome C are linearly interpolated between the youngest age points and synchronized gas age points in the early Holocene. Dome C gas ages for 17.2 to 11 kyr B.P. are synchronized with GISP2 in this study and for 22.5 to 17.2 kyr B.P. are extended from the synchronized gas age at 17.2 kyr B.P. by adding the depth-gas age intervals of the original paper [*Monnin et al.*, 2001]. YD, Younger Dryas; ACR, Antarctic Cold Reversal.

unnoticed analytical changes would create trends in the data. Measurements of Siple Dome CO_2 made in 2001 (black open squares) at SIO agree well with those made in 2002 and early 2003 (solid circles) as shown in Figure 2b.

[9] The results can be compared to other Antarctic ice cores as shown in Figure 2b. The CO_2 concentration of Dome C, Taylor Dome and Byrd cores were measured in Bern [*Monnin et al.*, 2001; *Flückiger et al.*, 2002; *Indermühle et al.*, 1999, 2000; *Neftel et al.*, 1988; *Staffelbach et al.*, 1991] and compare well with the SIO data. This is expected because Bern's gas extraction method (dry crushing) is similar to that at SIO.

[10] High accumulation rate provides a small width of gas age distribution and therefore a record of high temporal resolution. Similarly, t of small pieces of ice potentially also improves temporal resolution. On the other hand, this potentially increases the scatter in the data since inhomogeneities are not smoothed out as they are in larger samples covering longer intervals of time [*Smith et al.*, 1997a]. The accumulation rate at Siple Dome is two and five times larger than that at Taylor Dome and Dome C, respectively. Thus the high accumulation rate at Siple Dome (Table 1) and the small sample size (4 to 6 cm^3) used in the measurement at SIO may increase the scattering of the Siple Dome data. Sample sizes used in the Siple Dome CO_2 study at SIO are half of those used for Taylor Dome and Dome C at Bern. Some Taylor Dome samples were also measured at SIO (Figure 2b) and there is good agreement between the SIO and the Bern results, even though the volume of samples for a depth interval used at SIO was about one

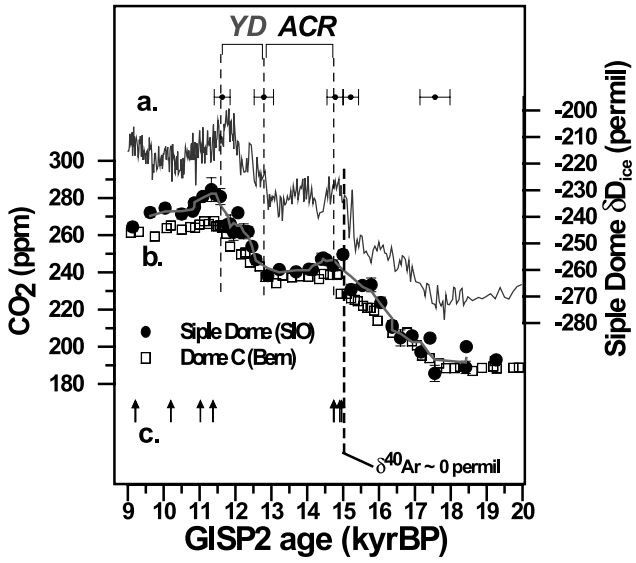

Figure 3. CO_2 change during the last Termination. (a) Siple Dome δD_{ice} on ice age scale. (b) CO_2 records from Siple Dome (solid circles) and Dome C (open squares) [*Monnin et al.*, 2001]. The line between Siple Dome CO_2 is the running average of three adjacent points. (c) Melt layers (vertical arrows) [*Das*, 2003]. The horizontal bars at top are gas age ranges around age tie points based on CH_4 records between Siple Dome and GISP2. The thick vertical dashed bar indicates where the argon and nitrogen isotopic anomaly occurs [*Severinghaus et al.*, 2003]. YD, Younger Dryas; ACR, Antarctic Cold Reversal.

fourth of what was used at Bern, where calibration was routinely done using reference gases from SIO at 251.7 ppm and 321.06 ppm [*Indermühle et al.*, 1999].

3.2. Trend of the Siple Dome CO_2 Record

[11] In general, the trends in the Siple Dome CO_2 record (solid circles and open squares in Figure 2b) follow temperature trends, indicated by δD_{ice} (Figure 2a), which is taken as a proxy for local temperature. The general time series of Siple Dome CO_2 concentration confirms previous studies in Antarctic ice cores (Figures 2 and 3). The Siple Dome CO_2 record shows a continuous decrease from 214 ppm at 38 kyr B.P. to 186 ppm at LGM (~18 kyr B.P.) and then a rapid increase up to 247 ppm during the early part of the last termination. It is important to note that the CO_2 increase is reversed during the Antarctic Cold Reversal (15 to 13 kyr B.P.) reaching a local minimum of 239 ppm, which has been observed in the Dome C, Taylor Dome and Byrd records. After the Antarctic Cold Reversal, Siple Dome CO_2 increases again reaching up to 284 ppm at the beginning of the Holocene (11.5 kyr B.P.). This increase occurs during the Younger Dryas interval as shown in the Dome C record [*Monnin et al.*, 2001]. During the Holocene, the Siple Dome CO_2 concentrations decrease to a local minimum of 261 ppm at about 8 kyr B.P., and then increase to 285 ppm in the late Holocene (mean of the scattered values). There is good agreement of this local minimum at about 8 kyr B.P. between the different Antarctic cores from Siple Dome, Taylor Dome, Dome C and Vostok. The CO_2 concentration never re steady state during the Holocene after the end of the last termination as was also found in the Taylor Dome and Dome C records [*Indermühle et al.*, 1999; *Flückiger et al.*, 2002].

[12] Figure 3 shows an enlarged portion of Figure 2 covering the last termination. Again, Siple Dome CO_2 follows the temperature proxy (δD_{ice}) as seen in other Antarctic ice cores. For most of the record, the Siple Dome CO_2 time trend is almost the same as that of the high resolution Dome C record.

[13] However, at the depth (677.61 m) corresponding to around 15 kyr B.P., CO_2 in Siple Dome is higher than in Dome C by about 21 ppm. We believe that this anomalous CO_2 value is suspicious as an atmospheric CO_2 record because of the following two reasons. First, near the depth of the anomalously high CO_2 value (~20 cm apart in depth), the $\delta^{40}Ar$ and $\delta^{15}N$ of N_2 values reach atmospheric values, indicating there was no diffusive column and a possible hiatus in deposition [*Severinghaus et al.*, 2003]. Second, the difference of 21 ppm is too large to be explained by age uncertainties. The anomaly occurs at a greater depth than that corresponding to the beginning of Antarctic Cold Reversal (defined by the rapid increase in CH_4 concentration from Siple Dome ice, as defined in the Dome C ice core, where abrupt CO_2 and CH_4 increases happened [*Monnin et al.*, 2001]). Thus the age uncertainty at this depth does not affect the CO_2 difference between Siple Dome and Dome C significantly (<5 ppm).

[14] Except for this anomalous period, we calculate the rates of CO_2 change and time lag of CO_2 compared to temperature. During the last termination, CO_2 changed at the rate of 19.1 ppm/kyr from 17.7 to 15 kyr B.P., −5.2 ppm/kyr during the Antarctic Cold Reversal (15 to 13 kyr B.P.) and 26.8 ppm/kyr from 13.0 to 11.3 kyr B.P., respectively. These values are similar to CO_2 changes in the Dome C record [*Monnin et al.*, 2001].

3.3. Phase Relationship Between Changes in CO_2 and Siple Dome Temperature

[15] To compare the phasing of changes in CO_2 and surface temperature (using δD_{ice} as a temperature proxy), we interpolated the CO_2 and δD_{ice} data on a 10-year spacing. We calculated the change in CO_2 and δD_{ice} (dCO_2/dt and $d(\delta D_{ice})/dt$) for 10-year intervals and smoothed them by averaging over time windows ranging from 0 to 500 years. The correlation coefficient between the dCO_2/dt and $d(\delta D_{ice})/dt$ was then calculated for different lag times and for different degrees of smoothing. The maximum correlation coefficients were obtained with a 210 ~ 330 year lag of dCO_2/dt behind $d(\delta D_{ice})/dt$ with a smoothing of 200 ~ 500 years as shown in Figure 4a. Several maxima in correlation coefficients for different time lags are observed over less than 200-year windows, possibly due to the average spacing of 230 years in the CO_2 data. To check the sensitivity of the time lag by the uncertainties in CO_2 concentration and Δage, we carried out Monte Carlo simulations for CO_2 concentrations in two conditions, namely maximum Δage (estimated Δage + uncertainty) and minimum Δage (estimated Δage − uncertainty). For each situation, we produced 3000 different sets of CO_2 concentrations, which vary randomly with Gaussian propagation in their uncertainties. After interpolation and smoothing both dCO_2/dt and $d(\delta D_{ice})/dt$ with

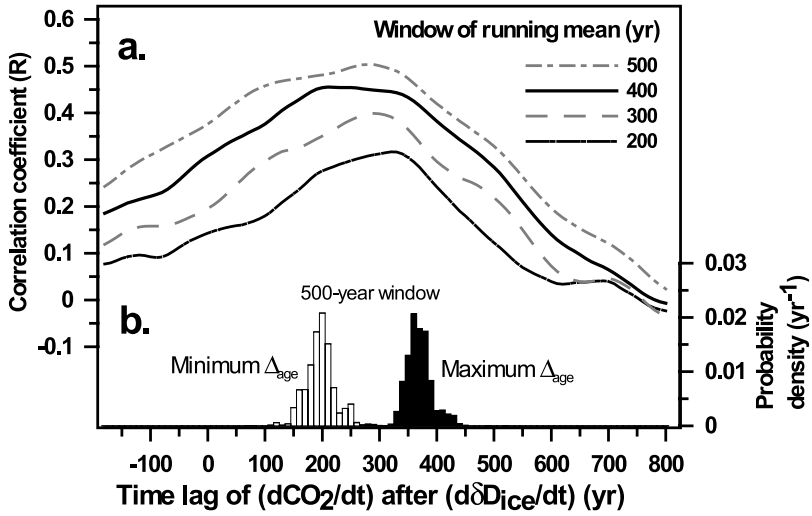

Figure 4. Time lag analysis of (dCO_2/dt) after ($d\delta D_{ice}/dt$) in the Siple Dome ice core during the last termination. (a) Correlation coefficients for different time lags after averaging data with windows of 200 $\sim$ 500 years. (b) Histograms of the time lags after Monte Carlo simulation for CO_2 concentrations in two situations, maximum Δage and minimum Δage. For each situation, 3000 different sets of CO_2 concentrations were generated and used. The derived dCO_2/dt and $d(\delta D_{ice})/dt$ were smoothed with 500-year window for each data set.

500-year window, maximum correlation coefficients were obtained with a 369 ± 23 years lag (mean ± 1σ) for maximum Δage and 196 ± 25 (mean ± 1σ) for minimum Δage as seen in Figure 4b. The time lags for CO_2 behind temperature are greater than the uncertainty of the Δage of 80 years at the end of the last termination but close to 220 years at LGM. The time lags roughly agree with those of *Fischer et al.* [1999] (600 ± 400 years during the last three terminations in Byrd, Taylor Dome and Vostok records) and are slightly less than the value proposed by *Monnin et al.* [2001] (410 years during the last termination in Dome C record). *Indermühle et al.* [2000] found higher values (1200 ± 700 years) for the period 60 to 20 kyr B.P. in the Taylor Dome record, as did *Caillon et al.* [2003] (800 ± 200 years) across termination III in the Vostok record. Although the correlation method discussed above suggests that changes in surface temperature at Siple Dome could lead changes in the concentration of atmospheric CO_2 by $\sim$300 years, this lead is small relative to both our sampling interval and possible systematic error in Δage, for example due to inaccuracies in estimating past accumulation rates, which are derived from a thermodynamic model employing temperatures calculated from the δD_{ice} record (Brook et al., manuscript in preparation, 2004). Our main conclusion is therefore that a lead of CO_2 versus Siple Dome temperature is unlikely, a lag of CO_2 versus Siple Dome temperature is likely, and that our results provide strong support for previous suggestions of a close link between Antarctic temperature and CO_2 change during the deglaciation.

4. Possible Mechanisms for In Situ CO_2 Production

[16] In some depth intervals the CO_2 concentrations in Siple Dome ice are than in the Vostok, Taylor Dome and Dome C cores (Figures 2 and 3). These differences are up to 20 ppm greater (e.g., at around 11 kyr B.P.). One possible explanation for these differences is uncertainty in the age scales, particularly at times when CO_2 was changing. For example, during the two periods of rapid CO_2 increase during the last termination, an offset of 300 years between otherwise identical records would produce a CO_2 difference of 10 ppm. This effect may explain the differences between the Siple Dome versus the Dome C and Siple Dome versus the Taylor Dome cores (Figure 5c). The low CO_2 values of the Byrd ice core at about 39 kyr B.P. can be compared to low values in Taylor Dome at about 42 kyr B.P. (not shown in Figure 2) on the GISP2 age scale [*Indermühle et al.*, 2000]. However, elevated CO_2 levels in the Siple Dome at times of relatively little change in CO_2 (for example, during the Antarctic Cold Reversal or in the earliest Holocene) cannot be attributed to timescale uncertainties. Interestingly, most of the cold period (40 $\sim$ 23 kyr B.P.) CO_2 data from the Siple Dome ice shows little difference in CO_2 when compared to other cores.

[17] As mentioned above, large variations of atmospheric CO_2 concentrations between Antarctic ice core sites are unlikely, prompting us to search for another explanation for the differences between the Siple Dome CO_2 and other records. To examine the possibility and the mechanisms of CO_2 production, we check the CO_2 difference between Siple Dome and Taylor Dome or Dome C (Figure 5c). We call this "excess CO_2" although we cannot rule out the possibility of CO_2 consumption in other ice cores by the interaction between CO_2 in the bubbles and the carbonates in the ice (i.e., $CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$) [*Neftel et al.*, 1982].

[18] The excess CO_2 is high at depth of 100 to 330 m (0.4 to 3.5 kyr B.P.) and 560 to 640 m (9.5 to 12.5 kyr B.P.) but is within the experimental uncertainty at depths >708 m

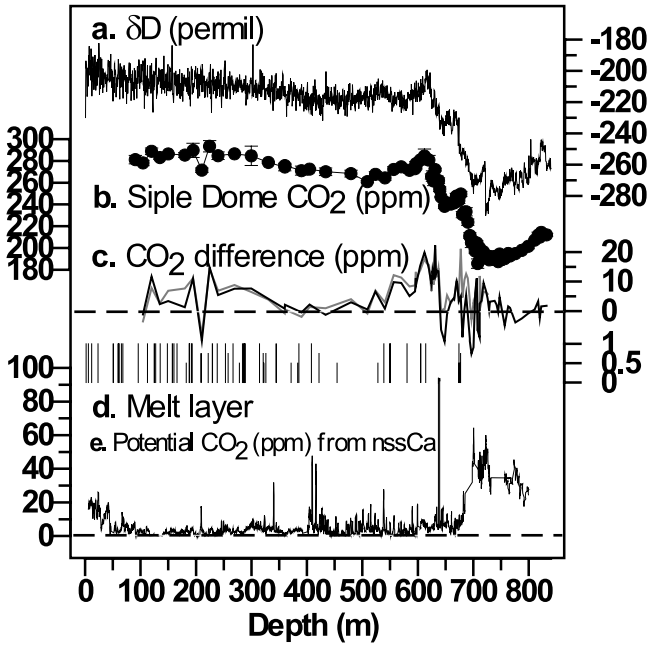

Figure 5. Comparison of possible processes of the excess CO_2 in Siple Dome ice cores on depth scale. (a) Siple Dome δD_{ice}. (b) Siple Dome CO_2. (c) CO_2 difference between Siple Dome and Taylor Dome (solid line) or Dome C (shaded line). The dashed horizontal line represents 0. (d) Melt layers [*Das*, 2003]. The lengths of bars indicate the confidence level. 1, sure; 0.75, probable; 0.5, possible. (e) Potential CO_2 from acid-carbonate reaction. The dashed horizontal line represents 0. Non-sea-salt Ca (nssCa) was assumed to have been in the form of $CaCO_3$ and totally reacted with excess H^+. Considering total gas content in the unit gram of ice [*Severinghaus et al.*, 2003], the CO_2 produced by the reaction was converted to a concentration change of CO_2.

(17.5 kyr B.P.). The Siple Dome ice samples are more fractured than Taylor Dome samples below about 500 m (about 8 kyr). One possibility is that the CO_2 in the core might be compromised by air entering fractures in the core that reseal after the ice reaches the surface, during transportation and storage. However, there are high excess CO_2 values in the late Holocene Siple Dome ice where fracturing is minor, and low excess CO_2 in glacial ice where Siple Dome ice is highly fractured. Moreover, correlations between the scattering of data from adjacent samples and excess CO_2 does not support the possibility of ambient air contamination. The above observations imply the possibility that some of the artifacts in Siple Dome CO_2 records are related to in situ CO_2 production in the ice.

[19] Possible CO_2 production mechanisms include (1) carbonate-acid reaction [*Delmas*, 1993; *Anklin et al.*, 1995, 1997; *Barnola et al.*, 1995; *Smith et al.*, 1997a, 1997b], (2) oxidation of organic compounds abiologically [*Tschumi and Stauffer*, 2000], or biologically [*Campen et al.*, 2003], and (3) snowmelting-refreezing [*Neftel et al.*, 1983; *Stauffer et al.*, 1985].

[20] We have calculated the potential CO_2 produced by the carbonate-acid reac etween $CaCO_3$ and H^+ [*Neftel et al.*, 1988], as shown in Figure 5e, using the non-sea-salt Ca (nssCa) ion content assuming all of the nssCa is from $CaCO_3$ and that all $CaCO_3$ reacts to produce CO_2. This source of potential CO_2 is too low to produce the excess CO_2 observed during the Holocene and shows little correlation with the excess CO_2 data (Figure 5c). Moreover, electric conductivity measurements (ECM, proxy for H^+) do not show any significant change at the depth intervals of high excess CO_2 in Figure 5c. Thus it is unlikely that a carbonate-acid reaction has affected the Siple Dome CO_2 record.

[21] Oxidation of organic compounds has been proposed to be at least as important as acid-carbonate reactions for CO_2 production (e.g., $2H_2O_2 + HCHO \rightarrow 3H_2O + CO_2$) [*Tschumi and Stauffer*, 2000]. Organic acid concentrations in Siple Dome ice core have not yet been reported. H_2O_2 is one of the important oxidants of organics in ice. The top 100 m of Siple Dome ice core shows concentrations near or below the detection limits of $\sim$0.02 μM H_2O_2 except at the 0 to 2.5 m depth [*McConnell*, 1997]. This H_2O_2 concentration corresponds to a potential CO_2 production of less than 5 ppm assuming an adequate supply of organic acids, which does not easily explain the 20 ppm excess CO_2. CH_3COO^- and $HCOO^-$ can act as other oxidants [*Tschumi and Stauffer*, 2000]. Another possible CO_2 production mechanism is respiration of microorganisms (consuming organic acids and producing CO_2) within the ice [*Campen et al.*, 2003]. Natural organic acids and other organic materials have much lower values of $\delta^{13}CO_2$, approximately -25‰, compared to atmospheric $\delta^{13}CO_2$ (preindustrial value of about -6.5‰) and $CaCO_3$ ($0 \sim 4$‰). Thus precise $^{13}CO_2$ values could be used to investigate the sources of excess CO_2. For example if the early Holocene CO_2 record has excess CO_2 values of 20 ppm derived from organic materials, it would reduce the $\delta^{13}CO_2$ value by about 1‰. However, $^{13}CO_2$ analyses in the Siple Dome ice core have been hampered by the contamination of the ice by drilling fluid, n-butyl acetate, which in the mass spectrometer lead to fragmentation interference with m/z = 45 [*Ahn et al.*, 2001].

[22] CO_2 can be considerably enriched in frozen melt layers due to the high solubility of CO_2 in meltwater [*Neftel et al.*, 1983]. At Dye 3, Greenland, melt layers contribute about 7% by volume at today's climate conditions and show mean CO_2 concentration as much as 1500 ppm [*Stauffer et al.*, 1985]. The annual mean snow temperature of Siple Dome is -25.4°C, the highest among the Antarctic ice cores discussed in this paper [*Severinghaus et al.*, 2001], and occasional surface melting occurs during the summer, resulting in thin bubble free layers in the ice core. These melt layers can be detected visually, see arrows in Figures 3c and bars in Figure 5d [*Das*, 2003]. The ice samples measured for the Siple Dome CO_2 did not include visible melt layers. However, it is likely that small melt layers would not be detected visually, particularly deeper in the core where ice flow has thinned the layering. The mode of excess CO_2 is only weakly associated with that of melt layers (Figures 5c and 5d). Alternative possibilities beside warm temperature and the coastal location of the Siple Dome (Figure 1 and Table 1) include higher ambient temperatures during the austral summer (often being substantially higher than the mean annual temperature of

−25.4°C), combined with high sea salt content, resulting in CO_2 contamination.

5. Conclusion

[23] We present the CO_2 record of air occluded over the last 40,000 years in the Siple Dome ice core, Antarctica. The general time series of Siple Dome CO_2 concentration is similar to previous studies in other Antarctic ice core CO_2 records. Siple Dome ice also shows that surface temperature inferred from δD_{ice} correlates well with CO_2 concentration as shown in other Antarctic ice cores. During the last termination, it is likely that the change of the Siple Dome CO_2 concentrations lags the Siple Dome temperature change. Despite similarities with other Antarctic ice cores, the Siple Dome ice shows higher CO_2 concentrations than those in other Antarctic ice cores at some depth intervals, which may be due to in situ production in the ice. The cause of these elevated concentrations is not known with certainty. CO_2 production due to surface melting is the leading hypothesis, but the evidence is not definitive.

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