CO_2 record between 40 and 8 kyr B.P. from the Greenland Ice Core Project ice core

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Abstract. CO_2 ice-core records show an increase in the atmospheric concentration of 80-100 parts per million by volume (ppmv) from the last glacial maximum (LGM) to the early Holocene. We present CO_2 measurements performed on an ice core from central Greenland, drilled during the Greenland Ice Core Project (GRIP). This CO_2 profile from GRIP confirms the most prominent CO_2 increase from the LGM, with a mean concentration of 200 ppmv, to the early Holocene with concentrations between 290 and 310 ppmv. Some structures of the new CO_2 record are similar to those previously obtained from the Dye 3 ice core (Greenland), which indicated a dilemma between Greenland and Antarctic CO_2 records [*Oeschger et al.*, 1988]. Both Greenland cores show high CO_2 values for rather mild climatic periods during the last glaciation, whereas CO_2 records from Antarctica do not show such high CO_2 variations during the glaciation and, furthermore, the CO_2 values in the early Holocene are about 20-30 ppmv higher in the GRIP record than in Antarctic records. There is some evidence that the difference could be due to chemical reactions between impurities in the ice leading to an increase of the CO_2 concentration under certain conditions. If in situ processes can change the CO_2 concentration in the air bubbles, the question arises about how reliably do CO_2 records from ice cores reflect the atmospheric composition at the time of ice formation. The discrepancies between the CO_2 profiles from Greenland and Antarctica can be explained by in situ production of excess CO_2 due to interactions between carbonate and acidic species. Since the carbonate concentration in Antarctic ice is much lower than in Greenland ice, CO_2 records from Antarctica are much less affected by such in situ-produced CO_2.

1. Introduction

CO_2 measurements on air occluded in cold polar ice have been performed on several deep ice cores covering the transition from the last glaciation to the Holocene, e.g., Camp Century and Byrd [*Neftel et al.*, 1982], Dome C [*Delmas et al.*, 1980], Vostok [*Barnola et al.*, 1987], Byrd [*Neftel et al.*, 1988] and Dye 3 [*Stauffer et al.*, 1984]. Whereas all records show lower CO_2 values during the last glacial maximum (LGM) than during the Holocene, pronounced differences occur between Antarctic and Greenland CO_2 records during periods of the glaciation between 20 and 40 kyr B.P., where the CO_2 profile from Dye 3 (Greenland) shows several fast variations of the order of 50 parts per million per volume (ppmv), while the Byrd and Vostok

CO2 profile (both from Antarctica) exhibits only small fluctuations of no more than 20 ppmv. If both profiles would reflect unadulterated atmospheric concentrations, then this implies an interhemispheric difference up to about 50 ppmv during certain periods. On the basis of the present knowledge of the atmospheric carbon cycle, such large interhemispheric concentration differences can be excluded.

High CO_2 values found in the Dye 3 core between 20 and 40 kyr B.P. are parallel with mild climatic periods, the so-called Dansgaard-Oeschger events. One possible explanation for the high CO_2 concentration during the Dansgaard-Oeschger events in the Dye 3 core is melt layers, which contain air considerably enriched in CO_2 [*Neftel et al.*, 1982]. It was one of the important goals of the Greenland Ice Core Project (GRIP) to solve the CO_2 dilemma mentioned by *Oeschger et al.* [1988]. The above explanation is not very likely because the new drill site at Summit (central Greenland) was selected also due to its current low mean annual temperature

of -32°C. In addition, the isotopic signal shows that the mean temperature during these mild periods was at least 5°C colder than the temperature during the Holocene, so that melt layers can be excluded as the reason for the elevated CO$_2$ concentrations. On the basis of observations of the visual stratigraphy, melt layers do indeed occur only exceptionally, about once a century under present climatic conditions. If the increased CO$_2$ concentrations in the Dye 3 core during the Dansgaard-Oeschger events were due to melt layers, such elevated CO$_2$ values should not be observed in the GRIP ice core because of the lower mean annual temperature of the drill site.

2. Results

The CO$_2$ analyses on the GRIP ice core have been mainly performed at the Physics Institute, University of Bern, and additional measurements for tests and calibration have been made at the Laboratoire de Glaciologie et de Geophysique de l'Environnement in Grenoble. The two laboratories use three different dry extraction methods and sample sizes to collect air occluded in the ice, as well as three different analytical methods to determine the CO$_2$ concentration of the extracted air. In Bern, the air from most of the samples has been extracted with a needle crusher and analyzed with an infrared laser spectrometric method (IRLS) (described by *Zumbrunn et al.* [1982]) and some has been extracted using a grinder crusher associated with a volumetric determination of the CO$_2$ concentration [*Moor and Stauffer*, 1984]. In Grenoble the air has been extracted with a ball crusher and analyzed by a gas chromatograph (GC) (described by *Barnola et al.* [1995]). The accuracy of a single measurement is ±3 ppmv with the IRLS and the GC methods and about ±5 ppmv with the volumetric method. With the IRLS and the volumetric methods the analytical error limits are determined by adding calibration gas to gas-free single crystal samples and then following the same crushing and analytical procedure as with the polar ice samples. Calibrations with and without single crystals show that most of the error is caused by water vapor in the extraction system. In spite of the analytical differences among these three methods, generally, they give the same results within the error limits as demonstrated by records from the Siple Station for the two methods used in Bern [*Oeschger and Siegenthaler*, 1988] and by that from Summit (EURO-CORE) for the IRLS method applied in Bern and the GC method applied in Grenoble [*Barnola et al.*, 1995].

All the CO$_2$ results obtained from IRLS, GC, and volumetric measurements from the GRIP ice core are plotted versus depth in Figure 1. Each data point represents a single CO$_2$ analysis. The GRIP CO$_2$ record, plotted versus age, is compared in Figure 2 with other CO$_2$ profiles previously obtained from Antarctica (Byrd, [*Neftel et al.*, 1988] and Vostok, [*Barnola et al.*, 1991]) and Greenland (Dye 3, [*Stauffer et al.*, 1984]), as well as

with the isotopic profile of the GRIP ice core [*Johnsen et al.*, 1992]. In Figure 2, the GRIP CO$_2$ measurements performed within depth intervals of 0.55 m are averaged to one data point. The gas age to depth relationship described by *Chappellaz et al.* [1993] has been used to date the enclosed air from the GRIP ice core. In Table 1 mean values for four different periods are given to facilitate the discussion below. The records show the following main features:

1. Between 1300- and 1500-m depth, corresponding to the time period of the early Holocene, the CO$_2$ values measured with the IRLS are considerably lower than those from Grenoble. This depth interval is characterized by the disappearance of air bubbles. The air in the bubbles transforms into air hydrates due to the hydrostatic pressure (1100-1650 m). The difference between the two laboratories is due to a fractionation effect occurring during the extraction process in Bern which has a lower extraction efficiency for ice with air enclosed in air hydrates than the other two methods. This effect can be reduced by increasing the time of extraction, as discussed in the following section. All measurements below 1500 m have been done with a prolonged extraction time and are not influenced by this fractionation effect.

2. Neglecting all measurements affected by the effect mentioned above, measurements from both laboratories show about 20 ppmv higher values during the early Holocene than the corresponding record from Byrd.

3. The increase from low to high CO$_2$ concentrations during the transition from the last glacial period to the Holocene started at about 18 kyr B.P. and ended at about 10 kyr B.P. Beside the generally increasing trend
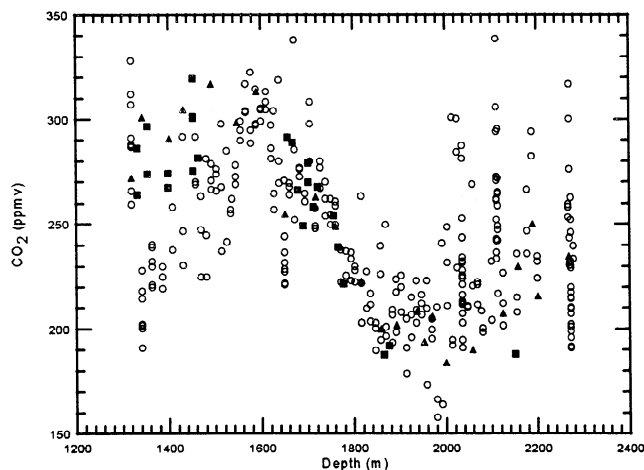
Figure 1. Single CO$_2$ measurements versus depth performed on the GRIP deep ice core. Open circles indicate measurements performed in Bern with the IRLS technique, solid triangles show the volumetric measurements, and the solid squares show GC measurements performed in Grenoble. The volumetric measurements have a smaller spatial resolution due to the larger sample size (~10 times larger than the samples for IRLS and GC measurements).
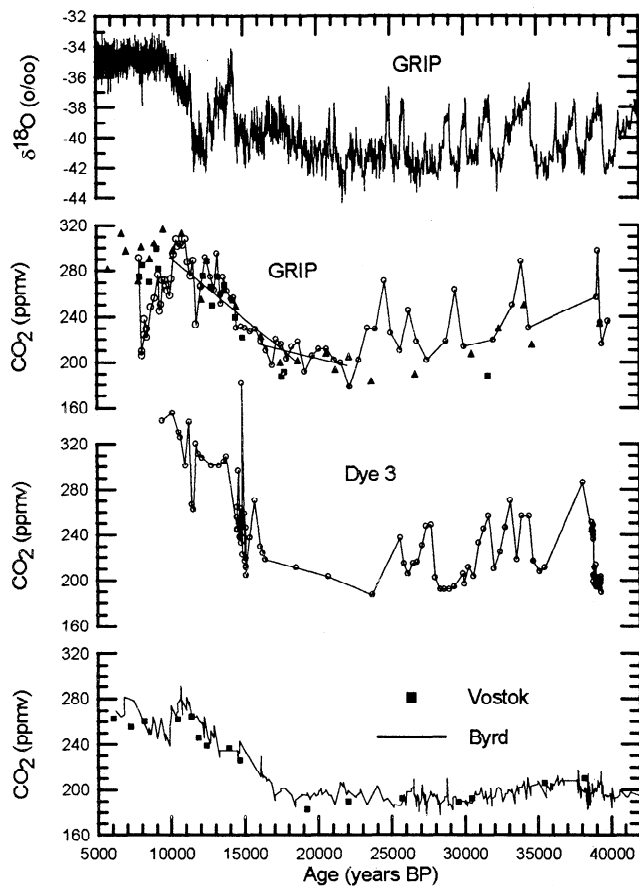
Figure 2. The $\delta^{18}O$ profile from the GRIP ice core versus ice age [*Johnsen et al.*, 1992], and CO_2 profiles from Greenland (GRIP, Dye 3) and Antarctica (Byrd, Vostok) versus gas age. Open circles (IRLS) and solid triangles (volumetric method) are mean CO_2 values obtained in Bern, and solid squares are mean values from Grenoble for both the GRIP and the Vostok ice core. All CO_2 profiles show increasing CO_2 values from the LGM at about 20 kyr B.P. to the Holocene. Elevated CO_2 concentrations are measured in the GRIP ice core during mild periods of the last glaciation as indicated by the isotopic temperature. Two linear regression lines are calculated from the CO_2 concentrations (IRLS measurements) between 16 and 10 kyr B.P. and 22 and 17 kyr B.P., respectively.

of the CO_2 concentration during this period, the CO_2 records from GRIP and Dye 3 both show decreasing concentrations during the Younger Dryas cold period,

whereas the Byrd, Dome C, and Vostok records [*Jouzel et al.*, 1992] do not show such a decrease.

4. During the LGM (23-17 kyr B.P.) the average CO_2 concentrations in the GRIP, Dye 3, and Byrd records are in good agreement, showing the same values within the error limits (Table 1).

5. Between 40 and 23 kyr B.P. the CO_2 profile from the GRIP core shows similar fluctuations as the one from Dye 3, i.e., high CO_2 concentrations during mild climatic phases, indicated by high $\delta^{18}O$ values of the ice. During this time interval, there is a good correlation between the two Greenland records, whereas there is no correlation for the short time variations between the GRIP and the Antarctic records.

2.1. Discussion of the Results Obtained in the Air Hydrate Formation Zone (1100- to 1500-m Depth)

In the upper 300 m of the GRIP ice core, CO_2 measurements from the two laboratories are generally in good agreement within the analytical error limits of ± 3 ppmv as mentioned before [*Barnola et al.*, 1995]. Also, for the lower part of the GRIP ice core, i.e., below 1500-m depth, there is generally a good agreement between the results obtained by the three different analytical methods (Figure 1). However, within the depth interval where air bubbles transform into air hydrates (1100- to 1650-m depth), large discrepancies occur between the results from the IRLS and the GC/volumetric method. These discrepancies are far beyond the usual analytical uncertainties and are caused by fractionation processes during the extraction. All three crushing methods use dry extraction techniques and their extraction efficiencies are lower for ice containing air hydrates ($\sim 45\%$) than for ice containing air bubbles ($\sim 75\%$, $\sim 60\%$ for the volumetric method). The extraction efficiency is determined by the total gas content obtained with a melting-refreezing method [*Chappellaz et al.*, 1990] and the amount of air obtained with the dry extraction methods used for the CO_2 analyses. With the IRLS a short equilibrating time of about 10 s (i.e., time between crushing and disconnection of the laser absorption cell from the crusher) was normally used to extract the air in order to keep possible interactions between water vapor and CO_2 minimal [*Zumbrunn et al.*, 1982]; in contrast,

Table 1. Mean CO_2 Concentration During Different Climatic Stages Determined From Three Deep Ice-Core Profiles: GRIP, Dye 3, and Byrd

| | Age, kyr B.P. | | GRIP, | Dye 3, | Byrd, |
	From	Till	ppmv	ppmv	ppmv
Pre-Boreal	11.5		295 $\pm$16	331 $\pm$17	275 $\pm$31
Younger Dryas	12.7	11.5	251 $\pm$31	295 $\pm$24	258 $\pm$8
Bølling-Allerød	14.5	12.7	267 $\pm$15	305 $\pm$4	238 $\pm$9
LGM	23	17	205 $\pm$19	205 $\pm$13	197 $\pm$5
Fast variations		23			197 $\pm$8
Cold periods			220 $\pm$24	204 $\pm$11	
Warm periods			261 $\pm$27	251 $\pm$12	

with the grinder or the ball crusher, a longer equilibrating time of 900 s is applied (in Grenoble the interaction with water vapor is minimized by keeping the extraction vessel at -50°C). Detailed IRLS measurements performed in Bern, after the discrepancy became evident, showed that an equilibrating time of 10 s is too short to extract air from ice within the air hydrate formation zone, as shown in Figure 3, where the pressure is plotted versus time after the crushing. The incomplete extraction in the depth interval from 1300 to 1500 m leads to a fractionation of the air composition. A similar effect has already been observed by *Neftel et al.* [1983] in the "freshly drilled" ice core from Dye 3. However, *Neftel et al.* [1983] have shown that this fractionation effect disappeared rapidly within a few months after the core has been drilled. The GRIP CO$_2$ samples have all been measured 6 months or more after the ice-core recovery. Despite the relatively long time after core recovery, fractionation effects occurred with the IRLS method using the needle crusher especially in the depth interval where air hydrates are formed if the usual equilibrating time of 10 s was applied. Tests showed that an equilibrating time of 180 s is needed for the GRIP ice core in the depth interval in which hydrates are formed (1300-1500 m) and 90 s below this depth, where all air is enclosed in hydrates. The results of the measurements done with a too short equilibrating time before the tests are included in Figures 1 and 2 to demonstrate the effect but are not used to calculate the mean values in Table 1.

2.2. Discussion of the Results Obtained Below 1500-m Depth

The following discussion is limited to those CO$_2$ results where no discrepancy between the three analytical
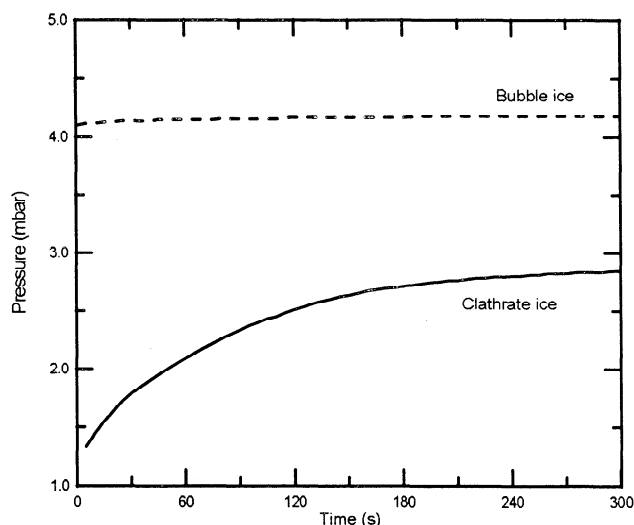

Figure 3. The pressure over a crushed ice sample versus equilibration time. The pressure rises rapidly after crushing a bubble ice sample and remains stable, whereas after crushing an air hydrate ice sample, the pressure rises only slowly and has not reached a plateau after 5 min.

methods exists, i.e., below 1500 m depth corresponding to 9600 years B.P.

Detailed CO$_2$ measurements by IRLS with a high spatial resolution, along 0.55-m-long ice-core segments of the GRIP core, show that the standard deviation within such a short depth interval is much higher for ice samples where the air is occluded in air hydrates than for samples where air is enclosed in bubbles. For bubble ice the standard deviation within a 0.55-m-long depth interval is typically 7 ppmv, whereas it is 20-30 ppmv in air hydrate ice as indicated in Figure 4. Only about 3 ppmv of these variations can be attributed to analytical uncertainties. Short-term variations shown in Figure 4 cannot reflect real atmospheric variations but must arise both from chemical reactions as discussed by *Anklin et al.* [1995] and from the generally larger scatter of the results in air hydrate ice (caused by fractionation effects due to the lower extraction efficiency). Analyses performed on the GRIP ice core 1 year and 3 years after drilling show standard deviations of about 25 ppmv and 12 ppmv, respectively, within a 0.55-m-long depth increment, indicating that the scatter decreases with increasing storage time, i.e., increasing transformation from air hydrates to bubbles. In parallel, the extraction efficiency increased by 14% during 2 years, which also indicates the ongoing transformation from air hydrates to bubbles. This indicates that CO$_2$ analyses on the GRIP ice core will have to be repeated after a few years storage time to produce a CO$_2$ profile with reduced scatter. Former CO$_2$ measurements on the Dye 3 ice core performed 1-2 years after recovery [*Stauffer et al.*, 1984] and 6 years after recovery [*Staffelbach et al.*, 1988] showed that the standard deviation of the CO$_2$ results has decreased by about 70%, whereas the mean concentration for each depth level has changed by less then 5% during the storage. The scatter of the CO$_2$ concentration within a single 55-cm-long ice-core section (representing about 10 years) is caused by an increased error due to fractionation processes as well as due to variations of the acidity and the carbonate concentration within this core section. As the mean CO$_2$ concentrations in the Dye 3 ice core have not changed much during the storage of 6 years, this indicates that the shape, mean values, and major trends in the averaged CO$_2$ profile from GRIP (Figure 2) will not change much as the core relaxes.

The CO$_2$ values observed in the early Holocene below 1500-m depth are about 20-30 ppmv higher than the corresponding values in the Byrd profile. This Greenland-Antarctica difference is larger than the one found by *Barnola et al.* [1995] during the period 1300 to 900 C.E. We assume that the reason for the difference between the GRIP and the Antarctic CO$_2$ profiles is the same for both the early Holocene and the recent millennium. Most likely, excess CO$_2$ is produced in the ice by interactions between carbonate and acidic species as suggested by *Delmas* [1993] and further discussed by *Anklin et al.* [1995]. However, the oxidation of organic
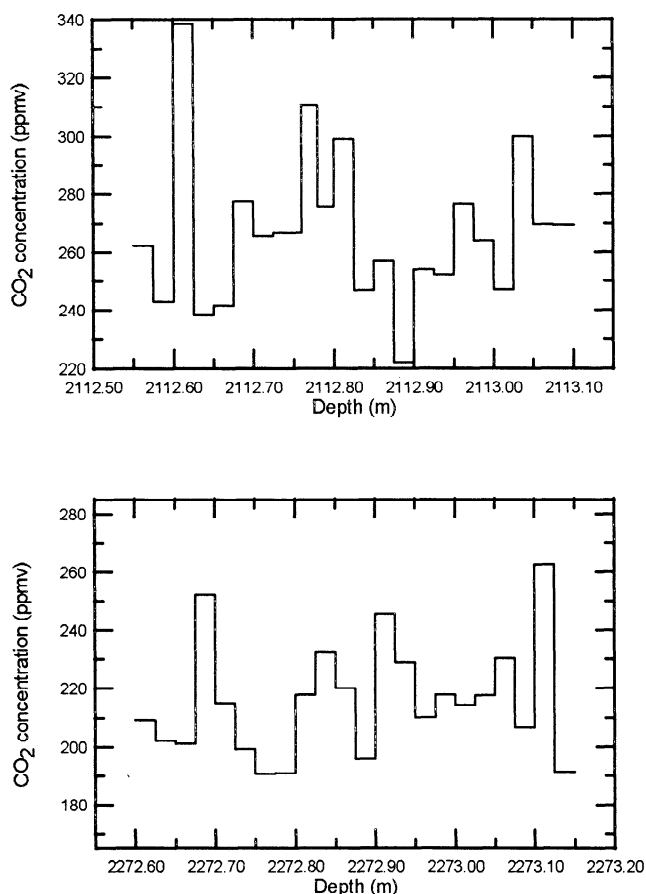
Figure 4. CO$_2$ measurements performed with the IRLS on 0.55-m-long depth sections during Dansgaard-Oeschger events. They show both a large scatter. (top) The mean CO$_2$ concentration from a mild phase is 263 ±27 ppmv. The gas age of this depth section is about 23.4 kyr B.P., and the annual layer thickness is still about 2 cm [*Johnsen et al.*, 1992]. (bottom) The mean CO$_2$ concentration of this cold phase is 216 ±20 ppmv. The gas age of this depth section is determined by *Johnsen et al.* [1992] at about 39.5 kyr and the annual layer thickness is about 1 cm.

material as a source of excess CO$_2$ cannot be excluded [*Anklin et al.*, 1995]. In the Dye 3 record, CO$_2$ measurements are disturbed by melt layers throughout the Holocene [*Neftel et al.*, 1983], explaining the about 40 ppmv higher values compared with the GRIP results.

During the climatic transition to the Holocene the CO$_2$ concentration increases by about 11 ppmv/kyr in both the GRIP and the Byrd profiles. The beginning of the CO$_2$ transition from the LGM to the Holocene is not clearly defined either in the GRIP or in the other records, though it is very important to determine the onset of the increase in order to understand the mechanisms forcing climatic changes. To estimate the beginning of the CO$_2$ increase, two different linear regression lines are applied; the first regression line shows the slope of the CO$_2$ profile between 16 and 10 kyr B.P., and the second regression line indicates the slope during the LGM, from 22 to 17 kyr B.P. (Figure 2). The point of

intersection of these two lines determines the estimated beginning of the CO$_2$ increase to the early Holocene. The onset of the CO$_2$ transition is determined by this method at 17.7 ±4 kyr B.P. for the GRIP record and at 17.8 ±1 kyr B.P. for the Byrd record. If the onset of the atmospheric CO$_2$ increase is correctly estimated at about 18 kyr B.P., this implies that the CO$_2$ increase started roughly 3000 years before the onset of the large reorganization of the thermohaline circulation in the ocean at about 14500 years B.P. [*Lehman and Keigwin*, 1992]. The larger uncertainty for the GRIP record is mainly caused by the CO$_2$ values from the Bølling-Allerød and the Pre-Boreal period, which show probably too high values due to CO$_2$ produced by chemical reactions and which could also lead to a systematic error for the determined intersection point. Furthermore, the accuracy of the timescale itself can also induce some error in the determination of the onset of the CO$_2$ increase.

A comparison of the timescale from GRIP with the one reconstructed from the Greenland Ice Core Project 2 (GISP2) ice core shows that the two timescales are in good agreement for ice younger than 14.5 kyr B.P. but deviate from each other for the older part of the cores [*Hammer and Meese*, 1993]. Similar features in the δ^{18}O record from GRIP [*Johnsen et al.*, 1992; *Dansgaard et al.*, 1993] and GISP2 [*Grootes et al.*, 1993; *Stuiver et al.*, 1995] (age-depth scale from *Meese et al.*, 1994) are dated older in the GISP2 than in the GRIP ice core, and the difference is 230 years at 14.5 kyr B.P. (GRIP age), 1600 years at 18.5 kyr B.P., 1800 years at 26 kyr B.P., and 3700 years at 34.7 kyr B.P. Using the GISP2 timescale and linear regression lines as described above, the onset of the CO$_2$ increase is determined at 18.2 kyr B.P., instead of 17.7 kyr B.P. with the GRIP timescale, which is within the uncertainties.

Both Greenland ice cores indicate also that there is a depletion of CO$_2$ during the Younger Dryas period. No such depletion can be observed in the Byrd profile. We assume that the apparent depletion in the Greenland cores is not an atmospheric signal but is induced by too high values during the Bølling-Allerød and the Pre-Boreal epoch due to CO$_2$ produced by carbonate, whereas the ice is weakly alkaline during the Younger Dryas so that no excess CO$_2$ was formed.

During the LGM, lasting from 23 to 17 kyr B.P., the mean CO$_2$ concentration in the GRIP profile is 205 ±19 ppmv, in the Dye 3 profile, it is 205 ±13 ppmv, and in the Byrd profile, it is 197 ±8 ppmv. There is no significant difference between the CO$_2$ concentrations of these three records. The good agreement in this section may be surprising considering the high carbonate concentration but is most probably due to the high alkalinity of the ice, preventing an acid-carbonate reaction.

One of the important results of the GRIP ice core is that the Dansgaard-Oeschger events during the last glacial epoch could be confirmed as climatic signals. These events are mild periods lasting 1-3 kyr with a

temperature about 5°C higher than the glacial temperature but still 5°C colder than the Holocene temperature according to the stable isotope record [*Johnsen et al.*, 1992]. During the mild phases the GRIP CO_2 record shows concentrations which are about 40 ppmv higher than the mean glacial concentration during the cold periods (Figure 2, Table 1). This finding is very similar to the CO_2 results from Dye 3 [*Stauffer et al.*, 1984] and Camp Century [*Staffelbach et al.*, 1988]; thus, the dilemma of the fast CO_2 variations during the glaciation discussed by *Oeschger et al.* [1988] remains. Antarctic CO_2 records from Byrd and Vostok never exceed 220 ppmv, and they show no CO_2 variation of this magnitude throughout the entire glaciation. In Greenland ice, excess CO_2 could be produced during the Dansgaard-Oeschger events and during the Holocene by interaction between carbonate and acidity in the ice. Excess CO_2, resulting from carbonate can only be produced under acidic conditions, i.e., in Greenland during the Holocene and during the mild periods where the ice is weakly acidic but not during the cold periods where the ice is weakly alkaline based on electrical conductivity measurements [*Taylor et al.*, 1993]. Due to the high concentration of calcium observed in the GRIP ice [*Fuhrer et al.*, 1993], we assume that during the glaciation the acidity but not the carbonate is the limiting compound for any CO_2 production. In contrast with Greenland ice, Antarctic ice is acidic throughout the entire glaciation and Holocene [*Legrand et al.*, 1988] but no carbonate above the detection limit has been found in this ice [*Legrand*, 1987]; thus excess CO_2 is unlikely to play an important role in Antarctic ice. This is at present the most probable explanation for the discrepancy between Antarctic and Greenland CO_2 records. A further indication that the CO_2 concentration measured within Dansgaard-Oeschger events in Greenland ice cores does not reflect atmospheric concentrations has been given earlier by *Staffelbach et al.* [1988], who showed that the CO_2 transition to a Dansgaard-Oeschger event parallels the $\delta^{18}O$ transition in depth in both ice cores, Dye 3 and Camp Century. Taking into account that these two sites have different accumulation rates and therefore a different time lag between age of the ice and age of the enclosed air, this would imply that the atmospheric CO_2 increase at Camp Century and Dye 3 has not occurred at the same time, which cannot be the case.

3. Summary and Conclusions

To recover air with the original, unaffected composition from air hydrate ice is more difficult than from bubble ice, but comparing measurements from Byrd bubble ice with Vostok air hydrate ice (both at the same gas age) shows similar CO_2 values, indicating that the CO_2 concentration of the extracted air does not significantly depend on the form of the air occlusion. Nevertheless, detailed CO_2 studies within a short depth in-

terval indicate both a significantly larger scatter for air hydrate ice than for bubble ice and a decrease of the scatter in air hydrate ice as the ice relaxes. The general trend of the CO_2 record obtained from the GRIP ice core is in good agreement with the trends found in the Antarctic profiles. Thus the CO_2 concentration in both hemispheres is about 200 ppmv during the LGM, and the CO_2 concentration increases by about 11 ppmv/kyr during the transition to the Holocene up to about 280 ppmv. The well-dated core allows also the determination of the start of the increase at about 18 kyr B.P. More detailed fluctuations of the record cannot be used for direct reconstruction of the atmospheric CO_2 concentration. Detailed analyses show that during the Holocene and during the Dansgaard-Oeschger events, the CO_2 values from the GRIP record are significantly higher than those from Byrd and Vostok. These deviations are most likely due to chemical reactions, which can increase the CO_2 concentration in the occluded air. We cannot exclude chemical reactions in Antarctic ice, but since the concentration of impurities is generally about 1 order of magnitude lower in Antarctica than in Greenland ice, the Antarctic CO_2 profiles are more reliable than those from Greenland. We believe therefore that the Antarctic record provides the most direct proxy record for past CO_2 changes [*Raynaud et al.*, 1993]. However, further detailed investigations on the GRIP core are needed to explain the discrepancies between Greenland and Antarctic CO_2 records.

References

Anklin, M., J.M. Barnola, J. Schwander, B. Stauffer, and D. Raynaud, Processes affecting the CO_2 concentration measured in Greenland ice, *Tellus, Ser. B, 47*, 461-470, 1995.

Barnola, J.M., D. Raynaud, Y.S. Korotkevich, and C. Lorius, Vostok ice core provides 160,000-years record of atmospheric CO_2, *Nature, 329*, 408-414, 1987.

Barnola, J.M., D. Raynaud, and Y.S. Korotkevich, CO_2 climate relationship as deduced from the Vostok ice core: A re-examination based on new measurements and on a re-evaluation of air dating, *Tellus, Ser. B, 43*, 83-90, 1991.

Barnola, J.M., M. Anklin, D. Raynaud, J. Schwander, and B. Stauffer, CO_2 evolution during the last millennium as recorded by Antarctic and Greenland ice, *Tellus, Ser. B, 47*, 264-272, 1995.

Chappellaz, J., J.M. Barnola, D. Raynaud, Y.S. Korotkevich, and C. Lorius, Atmospheric CH_4 record over the last climatic cycle revealed by the Vostok ice core, *Nature, 345*, 127-131, 1990.

Chappellaz, J., T. Blunier, D. Raynaud, J.M. Barnola, J. Schwander, and B. Stauffer, Synchronous changes in atmospheric CH_4 and Greenland climate between 40 and 8 kyr B.P., *Nature, 366*, 443-445, 1993.

Dansgaard, W., et al., Evidence for general instability of past climate from a 250-kyr ice-core record, *Nature, 364*, 218-220, 1993.

Delmas, R.J., J.M. Ascencio, and M. Legrand, Polar ice evidence that atmospheric CO_2 20,000yr B.P. was 50% of present, *Nature, 284*, 155-157, 1980.

Delmas, R.J., A natural artefact in Greenland ice-core CO_2 measurements, *Tellus, Ser. B, 45*, 391-396, 1993.

Fuhrer, K., A. Neftel, M. Anklin, and W. Maggi, Continuous measurements of hydrogen peroxide, formaldehyde, calcium and ammonium concentrations along the new GRIP ice core from Summit, central Greenland, *Atmos. Environ. Part A, 27*, 1873-1880, 1993.

Grootes, P.M., M. Stuiver, J.W.C. White, S.J. Johnsen, and J. Jouzel, Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores, *Nature, 366*, 552-554, 1993.

Hammer, U.C., and D.A. Meese, Dating ice cores, *Nature, 363*, 666, 1993.

Johnsen, S.J., H.B. Clausen, W. Dansgaard, K. Fuhrer, N.S. Gundestrup, C.U. Hammer, P. Iversen, J. Jouzel, B. Stauffer, and J.P. Steffensen, Irregular glacial interstadials recorded in a new Greenland ice core, *Nature, 359*, 311-313, 1992.

Jouzel J., et al., The last deglaciation in Antarctica: Evidence for a "Younger Dryas" type climatic event, in *Bard E., and Broecker W.S. (eds), Absolute and radiocarbon chronologies, NATO ASI Series*, pp. 229-266, Springer, Berlin Heidelberg New York, 1992.

Legrand, M., Chemistry of Antarctic snow and ice, *J. Phys. Colloq., 48*, 77-86, 1987.

Legrand, M., C. Lorius, N.I. Barkov, and V.N. Petrov, Vostok(Antarctic) ice core: Atmospheric chemistry changes over the last climatic cycle (160000 years), *Atmos. Environ., 22*, 317-331, 1988.

Lehman, S.J., and L.D. Keigwin, Sudden changes in North Atlantic circulation during the last deglaciation, *Nature, 356*, 757-762, 1992.

Meese, D.A., R.B. Alley, A.J. Gow, P. Grootes, P.A. Mayewski, M. Ram, T.C. Taylor, I.E. Waddington, and G. Zielinski, Preliminary depth-age scale of the GISP2 ice core, *CRREL Spec. Rep., 94-1*, Cold Reg. Res. and Eng. Lab., Hanover, N.H., 1994.

Moor, E., and B. Stauffer, A new dry extraction system for gases in ice, *J. Glaciol., 30 (106)*, 358-361, 1984.

Neftel, A., H. Oeschger, J. Schwander, B. Stauffer, and R. Zumbrunn, Ice core sample measurements give atmospheric CO_2 content during the past 40,000 yr, *Nature, 295*, 220-223, 1982.

Neftel, A., H. Oeschger, J. Schwander, and B. Stauffer, Carbon dioxide concentration in air bubbles of natural cold ice, *J. Phys. Chem., 87 (21)*, 4116-4120, 1983.

Neftel, A., H. Oeschger, T. Staffelbach, and B. Stauffer, CO_2 record in the Byrd ice core 50,000-5,000 years B.P., *Nature, 331*, 609-611, 1988.

Oeschger, H., and U. Siegenthaler, How has the atmospheric concentration of CO_2 changed?, in *The Changing Atmosphere. Dahlem Konferenzen 1988*, pp. 5-23, John Wiley, New York, 1988.

Oeschger, H., A. Neftel, T. Staffelbach, and B. Stauffer, The dilemma of rapid variations in CO_2 in Greenland ice cores, *Ann. Glaciol., 10*, 215-216, 1988.

Raynaud, D., J. Jouzel, J.M. Barnola, J. Chappellaz, R.J. Delmas, and C. Lorius, The ice record of greenhouse gases, *Science, 259*, 926-933, 1993.

Staffelbach, T., B. Stauffer, and H. Oeschger, A detailed analysis of the rapid changes in ice-core parameters during the last ice age, *Ann. Glaciol., 10*, 167-170, 1988.

Stauffer, B., H. Hofer, H. Oeschger, J. Schwander, and U. Siegenthaler, Atmospheric CO_2 concentrations during the last glaciation, *Ann. Glaciol., 5*, 160-164, 1984.

Stuiver, M., P.M. Grootes, and T.F. Brazuinas, The GISP2 $\delta^{18}O$ climate record of the past 16,500 years and the role of the Sun, ocean, and volcanoes, *Quat. Res., 44*, 341-354, 1995.

Taylor, K.C., C.U. Hammer, R.B. Alley, H.B. Clausen, D. Dahl-Jensen, A.J. Gow, N.S. Gundestrup, J. Kipfstuhl, J.C. Moore, and E.D. Waddington, Electrical conductivity measurements from the GISP2 and GRIP ice cores, *Nature, 366*, 449-452, 1993.

Zumbrunn, R., A. Neftel, and H. Oeschger, CO_2 measurements on 1-cm³ ice samples with an IR laser spectrometer (IRLS) combined with a new dry extraction device, *Earth Planet. Sci. Lett., 60*, 318-324, 1982.

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