# ATMOSPHERIC CARBON DIOXIDE AND METHANE CONCENTRATIONS IN THE PAST AND SYNCHRONISATION OF ICE CORE RECORDS FROM BOTH HEMISPHERES BASED ON METHANE RESULTS

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**Abstract:** In the central parts of the large polar ice sheets ice is formed by dry sintering of cold snow. The analyses of air extracted from bubbles of well dated ice samples from such locations, allow to determine the composition of the atmosphere at the time of ice formation. Of special interest are the two dominant greenhouse gases carbon dioxide and methane.

The methane concentrations are very reproducible and represent the atmospheric concentration at the time of ice formation with a good accuracy. The records show unexpected variations of this concentration during the glacial epoch as well as during the Holocene. The concentration differences measured on ice cores from Greenland and Antarctica allow to determine concentration differences between the Northern and Southern Hemispheres.

Ice core records show that the atmospheric  $CO_2$  concentration has increased steadily from about 280 ppmv in 1750 to the present value of about 355 ppmv and that the large climatic change from the last glacial to the post glacial epoch was accompanied by a naturally caused increase of the atmospheric  $CO_2$  concentration from about 200 ppmv to 280 ppmv. However, uncertainties about a possible  $CO_2$  production in the ice make the investigation of smaller variations and accurate time lags between climatic changes and changes of the atmospheric  $CO_2$  concentration especially in Greenland ice cores difficult. A synchronisation of ice core records from Greenland and Antarctica by methane results allows to compare  $CO_2$  records from Antarctica with climatic records from Greenland.

#### 1. Introduction

The properties of snow after deposition change constantly due to temperature gradients and due to small chemical potential differences caused by different curvature (COLBECK, 1983). Snow flakes transform into snow grains, larger grains grow on the expense of smaller ones which leads to a steady increase of the crystal size (Gow, 1969). Parallel to the metamorphosis of single grains the snow cover is more and more compacted so that the density increases with increasing depth. The amount of atmospheric air filling the pore space between the grains is getting smaller and smaller. At densities above 730 kg m<sup>-3</sup> more and more of the air filled channels forming an interconnected system disappear and clusters of air filled pockets are isolated from the atmosphere. At a density of about 840 kg m<sup>-3</sup> all remaining air is isolated (SCHWANDER and STAUFFER, 1984). Figure 1 shows the principle of the whole enclosure process. The air which becomes isolated is in principle of atmospheric composition. This allows



Fig. 1. Simplified schematic of the sintering of cold snow and firn to ice. The depths given are typical for Summit in Central Greenland. Bubble enclosure starts at 70m and is completed at 80m depth below surface in this example.

to determine the atmospheric composition of the past by analysing air extracted from air bubbles of well dated ice samples. However, two important questions have to be answered:

- What is the age difference between the air in the bubbles and the surrounding ice ?
- Can interactions between air and firn grain surfaces and between air and impurities in the ice be neglected ?
- Can the diffusion of air components, enclosed in bubbles or enclosed in clathrates, be neglected and is there no fractionation extracting air from ice samples where air is enclosed in clathrates?

More than 90% of the air is isolated in bubbles over a relative short depth ange (about 10 m) at the firn-ice transition (SCHWANDER et al., 1993). The depth of the lower end of the transition zone depends on temperature and accumulation rate and lies typically between 60 m and 110 m below the snow surface. The age of the ice at the transition depth can be determined by counting annual layers which can be identified by seasonal variations of isotopes or impurity concentrations. The time needed to reach the transition density can also be calculated if temperature and accumulation rates are known (HERRON and LANGWAY, 1980). The firn above the transition is open-porous and the air in it can exchange with the atmosphere. In the top few meters the air can be considered as well mixed due to wind pumping and atmospheric pressure changes. In the largest part of the firn mixing occurs by molecular diffusion (SCHWANDER et al., 1993). There might be a narrow layer just above the transition zone where firn is still permeable but intercepted by thin impermeable layers which prevent an air mixing in the vertical direction (SCHWANDER, 1996).

A fractionation of gases can occur by gravitation separation (SCHWANDER, 1989), thermal diffusion and possibly by a flow through narrow capillary like channels in the lowest firn layer (BATTLE *et al.*, 1996). All effects lead to rather small deviations from the atmospheric composition. The gravitation separation causes an enrichment of  $CO_2$ 

of about 2 ppm.

For Summit in Central Greenland the age distribution of air in the firn layer has been measured experimentally. At 70 m depth, which is near to the bubble close-off depth the mean age of  $CO_2$  is 12 years with a standard deviation of 7.5 years. The age of the ice at this depth is 220 years, so that the difference between mean age of  $CO_2$  and age of ice is about 210 years (SCHWANDER et al., 1993). The difference for other air components are slightly different due to other molecular diffusion constants. The air mixing by diffusion in the firn layer as well as the continuous enclosure of air over a depth interval of about ten meters leads to a relatively broad age distribution for the air enclosed in bubbles at a certain depth. The mixing process by molecular diffusion is dominant for this broadening. A model based on the results from Summit, allows to calculate the mean age difference between ice and enclosed air in function of temperature and accumulation rate (Schwander et al., 1997). The mean age difference varies not only from drilling site to drilling site but also within one ice core with depth respectively time due to the changing climatic conditions. This has to be taken into account for comparisons of climatic records measured on ice with such measured on air extracted from air bubbles.

The molecular solubility of the main air components  $N_2$ ,  $O_2$ , Ar and of  $CO_2$  and  $CH_4$  in the matrix of pure ice is small (UCHIDA *et al.*, 1994). However, the growth of snow crystals in the atmosphere is relatively fast and air can be enclosed by kinetic processes (MAENO and KUROIWA, 1967). The metamorphosis of snow after snow deposition acts as a purification process. Most of the ice material undergoes a recrystallisation. The growth rates during metamorphosis is generally very small so that a purification by a kind of zone refining occurs. The escaping gases are mixed with the air in the pore space of the firn. The process is most effective in the upper firn layer, so that the air in the pore space will exchange with the atmosphere.

Laboratory measurements show that physi- and chemisorption on firn grains is small (ADAMSON and JONES 1971; OCAMPO and KLINGER 1982). The best indication that interactions between air and firn grains can be neglected comes from ice cores from locations with high accumulation rates.  $CH_4$  and  $CO_2$  records from such cores allow a time overlap of ice core measurements with direct atmospheric measurements (NEFTEL *et al.*, 1985; FRIEDLI *et al.*, 1986; STAUFFER *et al.*, 1985; ETHERIDGE *et al.*, 1992; ETHERIDGE *et al.*, 1996; NAKAZAWA *et al.*, 1993).

The results agree well within the error limits. However, this agreement does not exclude possible interactions between the air and impurities in the ice after the enclosure in bubbles is completed. A depletion of  $H_2O_2$  in certain layers with increasing depth shows that chemical reactions in natural ice even at temperatures below  $-30^{\circ}C$  are possible (NEFTEL 1996). Chemical reactions could possibly only occur at triple junctions of ice crystals where certain impurities are enriched and allow that a narrow vein is liquid down to very low temperatures (MULVANEY *et al.*, 1988). This would explain that it needs a long time for such reactions between air in bubbles and impurities in triple junctions, because they can occur only when bubbles intercept accidentally such a vein.

Experiments and tests have been performed to find out whether certain air components can be enriched or depleted by chemical reactions in the ice. A straight forward way to check for such processes in nature is to analyse air of ice with the same age but from ice cores from different locations with different impurity concentrations. While the chemical composition is different the  $CO_2$  and  $CH_4$  concentrations have to be about the same because both gases are well mixed and show only small gradients in the global atmosphere. Similar analyses can also be made along one ice core by performing gas analyses with a high spatial resolution. Most impurities show seasonal or irregular short-term variations along ice cores, while the air composition is not expected to show fast variations due to the smoothing by enclosure and diffusion in the firn as discussed above. Variations of the  $CH_4$  or  $CO_2$  concentratin within one or a few annual layers, therefore, indicate an artefact caused by chemical interactions in the ice. For methane no indications have been found for a production or depletion by chemical reactions but for  $CO_2$  it seems that chemical reaction can lead to an increase of the concentration.

### 2. The Methane Records

Methane is after  $CO_2$  the second important greenhouse gas if water vapour is excluded. Of special interest are the increase during the past few hundred years due to anthropogenic influences, the natural variability and a possible link of the atmospheric CH<sub>4</sub> concentration with climate. Several ice core records showed that the atmospheric CH<sub>4</sub> concentration has increased from about 650 ppbv at the beginning of industrialisation (about 250 years B.P.) to about 1750 ppbv at present (STAUFFER *et al.*, 1985; ETHERIDGE *et al.*, 1992; NAKAZAWA *et al.*, 1993) and that the transition from the last glaciation to the Holocene was accompanied by an increase of the CH<sub>4</sub> concentration from about 350 ppbv to 650 ppbv (STAUFFER *et al.*, 1988; CHAPPELLAZ *et al.*, 1993).

Figure 2 shows the methane record measured along the GRIP ice core from Central Greenland compared with the  $\delta^{18}$ O record (CHAPPELLAZ et al., 1993). The age of the methane record is corrected for the age difference between ice and enclosed air. The record shows the features already known from previous recovered ice cores, especially a doubling of the methane concentration from 350 ppbv to about 700 ppbv during the glacial-post glacial transition. Remarkable is, that this increase was not steady and smooth but shows strong oscillations which are to a high degree synchronous to the  $\delta^{18}$ O record. Surprising were also the CH<sub>4</sub> variations during the glacial period which go parallel with the  $\delta^{18}$ O record. The isotope record is considered to be a proxy for the local temperature of the drilling site (JOHNSEN et al., 1992; DANSGAARD et al., 1993). The atmospheric  $CH_4$  concentration, on the other hand, has to be a global signal, due to the relatively short mixing time of methane in the atmosphere compared with its life Variations of the atmospheric methane concentration during the glacial epoch time. are most probably caused by changes of the production rate of methane in tropical wetlands. The fact that the hydrological cycle in tropical regions which influences the extent of wetlands and their methane productivity shows variations which go parallel with the GRIP  $\delta^{18}$ O record is a strong indication, that this record is not only a proxy for the local temperature. The conclusion is, that the fast and drastic climatic variations during the last glacial, the so called Dansgaard-Oeschger events, are of global significance.

Surprising is also that the Holocene part of the record shows much more structure than the  $\delta^{18}$ O record. The atmospheric CH<sub>4</sub> concentration shows at present, despite



Fig. 2. Methane record from Summit in Greenland according to (CHAPPELLAZ et al., 1993) compared with the  $\delta^{18}O$  record of the same core (JOHNSEN et al., 1992): The dashed lines mark the beginning of so called Dansgaard Oeschger events. For methane the age is corrected for the age difference between ice and enclosed air.

the good global mixing a latitudinal gradient, because most of the anthropogenic sources are located in the Northern hemisphere. The atmospheric  $CH_4$  concentration is at present about 140 ppbv higher in the Arctic than in the Antarctic. Natural sources are also more numerous in the Northern hemisphere. Measurements on ice cores allow to determine the interhemispheric concentration difference and to estimate based on this difference roughly the latitudinal distribution of methane sources in the past. To determine such differences records from two Antarctic ice cores have been compared with the GRIP ice core (CHAPPELLAZ et al., 1997). The two Antarctic cores are from Byrd Station in West Antarctica and from D47 of the coastal Adelie Land. The D47 core spans only the later part of the Holocene. The Byrd core reaches back in the last glacial epoch but the brittle zone covering a depth interval corresponding to the time span of about 2200 to 8700 years BP, does not allow to reconstruct a reliable detailed record for this period.

A part of the results by (CHAPPELLAZ et al., 1997) are shown in Fig. 3. The main results and conclusions of the authors of this paper are summarised in the following. The estimated mean interpolar difference of the atmospheric methane concentration for four selected time intervals are:



Fig. 3. Methane record from Summit (Greenland) compared with two records from Antarctica according to (CHAPPELLAZ et al., 1997): Mean interpolar concentration differences have been calculated for the time interval A-D. In the time interval 8700-7200 yr. BP no suitable records from Antarctic cores are available.

• 250- 1000 years B.P.	$35\pm7\mathrm{ppbv}$
• 2500- 5000 years B.P.	$50\pm3\mathrm{ppbv}$
• 5000- 7000 years B.P.	33±7 ppbv
• 9500-11500 years B.P.	44 <u>+</u> 4 ppbv

The error given with the results characterise the  $1\sigma$  (68%) uncertainty. Based on the globally averaged mixing ratios and on the interpolar concentration differences a three box model was used to calculate for four time intervals the distribution of CH<sub>4</sub> sources among the three boxes. The boxes are a Northern region (N) from the Northpole to 30° N, a Tropic region (T) from 30° N to 30° S and a Southern region (S) from 30° S to the Southpole. CHAPPELLAZ *et al.* (1997) had to make several assumptions for their simplified model:

- The CH<sub>4</sub> sink is estimated to be 20% higher than today due to a higher OH concentration in the preindustrial atmosphere. It is assumed that the total sink and the latitudinal distribution of the sinks did not change during the preindustrial Holocene. (The average global lifetime was 9.9 years according to this estimate compared with 11.9 years at present.)
- The CH<sub>4</sub> concentrations measured in Greenland today are 13% lower than in average for the N box. Most of the anthropogenic CH<sub>4</sub> sources are located in mid latitudes. It is assumed that the Greenland values were in the preindustrial time closer to the mean value in the N box than today. It was estimated that the Greenland values were 7% lower than the average value for the Nordic box.

• The source in the S box was assumed to have been on a constant low value of 15 Tg per year through the whole Holocene.

The results of the 3-box model calculation are shown in Fig. 4. The record of the mixing ratio together with the interpolar  $CH_4$  differences suggest the following development of  $CH_4$  sources during the four time intervals A-D in the Holocene:

- The time interval A (11500-9500 yr BP; Fig. 3) was the wettest period of the Holocene in the Tropics. But the CH<sub>4</sub> increase at the beginning of the Preboreal (first part of Holocene) cannot be caused by sources of the tropics alone, the interpolar difference would be smaller in that case. A strong source in mid to high latitude with a source strength of similar magnitude to that from the tropics is needed. The source could be degassing of CH<sub>4</sub>-hydrate reservoirs (THORPE *et al.*, 1996) and wetlands on new ice free areas. However, a degassing of CH<sub>4</sub>-hydrates from the permafrost in a few large dramatic bursts can be excluded based on the detailed CH<sub>4</sub> record compared with a modeled record assuming degassing bursts in the order of 4000 Tg (CHAPPELLAZ *et al.*, 1997).
- During the time interval B (7000–5000 yr BP) both the CH<sub>4</sub> mixing ratio as well as the interpolar difference decrease. This indicates that the sources in the Tropic as well as in the Nordic box decreased. In the tropics the humidity decreased, but there is no obvious reason for a decrease in the Nordic box.
- The mixing ratio in the time interval C (5000-2500 yr BP) is almost the same as in time interval B but the interpolar difference is much larger. This implies that the CH<sub>4</sub> production in the Tropics decreased while it increased in the Nordic box. This period is indeed characterised by an ongoing drying in the tropics especially in Africa and an extension of peat in high Nordic regions (especially Russia).
- In the time period D (1000-250 yr BP) the mixing ratio is as high as in the Preboreal epoch and the interhemispheric difference is rather small. This means that the CH<sub>4</sub>



Fig. 4. Emission of methane in the three boxes (North, Tropics, South) estimated according to (CHAPPELLAZ et al., 1997) for four time intervals (A: 11500– 9500 yr. BP, B: 7000–5000 yr. BP, C: 5000–2500 yr. BP, D: 1000–250 yr. BP).

production decreased in the Nordic box but increased in the Tropic box. Candidates for a natural higher  $CH_4$  production in the past millennium are the Amazons basin and possibly India. A certain early anthropogenic influence in the Tropics during this time interval cannot be excluded.

The presented scenarios are still speculative but they shall illustrate the potential of ice core analyses to reconstruct not only the climate of polar regions but to a certain extent the environmental history of the whole earth.

## 3. The CO<sub>2</sub> Records

Concerning  $CO_2$  we are not yet able to develop similar scenarios. There is a good agreement of all ice core results concerning the increase of the atmospheric  $CO_2$ concentration from about 280 ppmv at the beginning of industrialisation (1750 A.D.) to 315 ppmv in 1958 when direct atmospheric measurements started (NEFTEL et al., 1985; BARNOLA et al., 1995; ETHERIDGE et al., 1996). There is also a good agreement of values of about 200 ppmv during the Last Glacial Maximum 20000 years B.P. and an increase of the atmospheric  $CO_2$  concentration afterwards parallel to the transition from the last glacial to the Holocene epoch (NEFTEL et al., 1988; BARNOLA et al., 1987; STAFFELBACH et al., 1991). During the glacial period CO<sub>2</sub> variations with amplitudes of about 50 ppmv have been observed in Greenland ice cores (STAUFFER et al., 1984). In three different Greenland cores enhanced CO<sub>2</sub> concentrations are found during mild phases of Dansgaard-Oeschger events. Different as in the case of methane, such variations could not be observed in Antarctic ice cores. This causes a dilemma (OESCHGER et al., 1988). The atmospheric interpolar  $CO_2$  difference with the anthropogenic CO<sub>2</sub> sources concentrated in the Northern hemisphere is about 6 ppmv at present. It is not expected to have been above 5 ppmv in the past. It is assumed today that chemical reactions in the ice are causing the enhanced values in the Greenland cores (ANKLIN et al., 1995).

Already in ice representing the last millennium values from Greenland cores are during certain time intervals higher by 20 ppmv than the values from Antarctic ice cores (BARNOLA et al., 1995). Also this difference is most probably due to a production of  $CO_2$  by chemical reactions between impurities in the ice. Ice is, despite these problems, the most reliable storage container for old atmospheric air and gives the best straight forward information about variations of the atmospheric  $CO_2$  concentration in the past. Therefore, it is very urgent to identify the reactions which lead to a surplus of CO<sub>2</sub> and to obtain quantitative estimates of the amount of CO<sub>2</sub> produced in the ice after pore close off in function of the chemical impurities in the ice. Until this problem will be solved it will be difficult to get a more detailed record of the atmospheric  $CO_2$ concentration and it will be difficult to convince the public that there is no doubt on the two main findings: the anthropogenic caused increase during the industrial period and the natural caused increase at the end of the last glaciation. Reactions between carbonates and acidic components have been suggested as likely candidates for the production of CO<sub>2</sub> (DELMAS, 1993). We had the idea in our laboratory that such a production would be most probable in ice with a high concentration of carbonates and acidity and checked different segments of ice cores with sporadic enhanced  $CO_2$  values

for elevated Ca and acidity concentrations. After we found no clear correlation (ANKLIN *et al.*, 1995) we realised that Ca is possibly a bad proxy for a general carbonate concentration. The source of Ca is certainly dominantly CaCO<sub>3</sub> but during the long transport to the Greenland ice sheet it can be changed to a great part to CaSO<sub>4</sub>. Carbonate on the other hand can as well be present as MgCO<sub>3</sub> and NaCO<sub>3</sub>. We have developed a system which allows to measure the carbonate concentration of ice directly. First results of these time consuming measurements give no clear answer either. One of two records shows a good correlation of enhanced CO<sub>2</sub> values with high carbonate values the other does not. Carbonate acidic reactions are still a main candidate for a CO<sub>2</sub> production in ice and further investigations are needed but a production of CO<sub>2</sub> by the oxidation of organic substances seems to be also quite possible.

Main candidates among organic compounds for the production of  $CO_2$  are formaldehyde and organic acids (ANKLIN et al., 1995). Formaldehyde has been measured continuously along the GRIP ice core with a high spatial resolution (FUHRER et al., No depletion of formaldehyde was observed during the whole Holocene period. 1993). The measurements of the concentration of organic and fatty acids in polar ice cores have started recently (LEGRAND et al., 1992; KAWAMURA et al., 1996). No records which are detailed enough for a comparison like the one done with acidity and carbonates are available yet. It is estimated that carbon in organic acids in the ice corresponds totally to a CO<sub>2</sub> surplus of at least 100 ppm in Greenland ice and of about 10 ppm in Antarctic ice (ANKLIN et al., 1995). There seems to be an easy test with  $\delta^{13}$ C analyses to decide whether a CO<sub>2</sub> surplus originates by an acid-carbonate reaction or by the oxidation of organic material. Organic material has  $\delta^{13}$ C values in the order of -28%, carbonate at its source region values of 0%. However, it is unknown how this value of the carbonates is changed during the transport in the atmosphere. Variations of the atmospheric CO<sub>2</sub> concentration will lead also to a variation of the  $\delta^{13}C$  value of atmospheric CO<sub>2</sub> (MACHIDA et al., 1996), but the isotopic signal remains despite these uncertainties an important tool to solve the problem of  $CO_2$  production in the ice. What compound in the ice or in the air bubble is able to oxidise organic compounds ?-It is unlikely that  $O_2$  in air bubbles is able to do this. One important candidate is  $H_2O_2$ . It is known that  $H_2O_2$  is depleted in narrow layers with increasing depth in Greenland ice. About the kind of reaction which are destroying  $H_2O_2$  nothing is known yet. We will investigate with detailed analyses if there is a correlation between local  $CO_2$  surplus and narrow layers with depleted  $H_2O_2$ .

It is certain that Antarctic ice cores are less affected by a possible  $CO_2$  production than Greenland ice cores (RAYNAUD *et al.*, 1993). The impurity concentration in Greenland ice from the preindustrial Holocene is four to ten times higher than in preindustrial Antarctic Holocene ice. However, ice from the glacial epoch from Byrd station has similar impurity concentrations for certain species than Greenland Holocene ice from Summit. For Holocene ice we can expect that  $CO_2$  productions in the ice are an order of magnitude lower for Antarctic ice than for Greenland ice. For ice from the last glacial epoch we have to be more careful. Detailed measurements along short segments of the Byrd ice core show a scatter of the  $CO_2$  results of about 4 ppmv compared with an analytical reproducibility of 3 ppmv. In ice from Summit the comparable scatter is 15 ppmv. Based on the small scatter in ice from Byrd from the glacial epoch we are confident that the values represent atmospheric  $CO_2$  concentrations with a good accuracy.

### 4. Synchronisation of Ice Core Records with Methane Variations

The  $\delta^{18}$ O records of Greenland ice cores show large and fast variations, so called Dansgaard-Oeschger events. The climatic variations are most probably caused by changes of the thermohaline circulation of the ocean especially of the deep water formation in the North Atlantic. That these climatic events are not a pure North Atlantic matter is demonstrated by the synchronous methane variations discussed above. There is no clear signal of these variations in the  $\delta^{18}$ O record of Antarctic ice cores. To learn more about the global carbon cycle it is important to investigate possible  $CO_2$ changes parallel to Dansgaard-Oeschger events. In Greenland ice cores this is not possible due to the obvious production of CO<sub>2</sub> during mild phases of Dansgaard-Oeschger events. If records from Greenland and Antarctic ice cores can be synchronised precisely enough such investigations can be done on Antarctic ice cores. A first synchronisation has been done by using the global variations of  $\delta^{18}$ O of atmospheric O<sub>2</sub> (measured on air enclosed in bubbles) (BENDER et al., 1994). Methane records with their fast variations during the glacial epoch which are synchronous in Greenland and Antarctica allow an even more accurate synchronisation. First results from a comparison of the synchronised  $\delta^{18}$ O records from GRIP (Greenland) and Byrd (Antarctica) ice cores gave already interesting results concerning the transition from the last glaciation to the Holocene. In Greenland ice cores as well as in various paleoclimate archives from Europe a cold phase called the "Younger Dryas" (about 12700-11550 yeras BP) is observed during the transition from the last glaciation to the Holocene. In Antarctic ice cores a much smaller cold phase called "Antarctic Cold Reversal" (about 14400-12900 years BP) (JOUZEL et al., 1992) is observed. The synchronisation with methane results shows that the Antarctic Cold Reversal preceded the Younger Dryas by at least 1800 years (BLUNIER et al., 1997). The results show as well that the increase of the atmospheric CO<sub>2</sub> started already at about 16000 years BP and was not interrupted by a decrease during the Younger Dryas (BLUNIER et al., 1997).

The synchronisation of the two cores allows also a new interpretation of a CO<sub>2</sub> record measured earlier along the Byrd ice core (NEFTEL *et al.*, 1988). It varies in the time interval from 47000–17000 years B.P. between 180 and 220 ppmv. Because methane variations going parallel with the Dansgaard-Oeschger events are observed with a similar amplitude in the Byrd core an attenuation of CO<sub>2</sub> variations due to the lower accumulation rate at Byrd can be excluded. Therefore, variations of the atmospheric CO<sub>2</sub> concentration with an amplitude of 50 ppmv as suggested by measurements from Greenland ice cores are not possible. However, the Byrd record shows variations with an amplitude of up to 20 ppmv (Fig. 5) (STAUFFER *et al.*, 1998). Maximum values of CO<sub>2</sub> are observed where especially broad Dansgaard-Oeschger events are shown by the GRIP  $\delta^{18}$ O record. The dashed line with the  $\delta^{18}$ O record shows the so called Bond cycles (Bond *et al.*, 1993). Their beginnings characterise large discharges of ice bergs into the Northatlantic documented by ice rafted debris in deep sea cores (HEINRICH 1988). Figure 5 shows that there is a parallelism between the CO<sub>2</sub> record and these

Bond cycles. If such links between processes in the Northatlantic and the atmospheric  $CO_2$  concentration can be confirmed this will be an important step forward in our understanding of the global carbon cycle. The  $CO_2$  results from Vostok agree with the



Fig. 5. Comparison of  $CO_2$  variations and fast climatic changes according to (STAUFFER et al., 1998): the top curve gives the  $\delta^{18}O$  record of the GRIP ice core from Summit (Central Greenland) (DANSGAARD et al., 1993): The dashed saw tooth curve characterises the Bond long-term cooling cycles (BOND et al., 1993): the middle section shows the Byrd  $CO_2$  record (NEFTEL et al., 1988) on a time scale adjusted to the GRIP time scale. The lowest section shows the methane records of the GRIP (solid line) and Byrd (dashed line) ice cores. The GRIP record is plotted on the original GRIP time scale (DANSGAARD et al., 1993) (corrected for the age difference between ice and enclosed air (SCHWANDER et al., 1997)): The Byrd record is plotted on an adjusted time scale which is obtained by a Monte Carlo method maximising the correlation between the two methane records.

values of the Byrd core but their resolution does not allow to reconstruct a record showing similar variations than that of the Byrd core. Detailed  $CO_2$  records will become available by the detailed analyses of the already recovered ice cores from Taylor Dome (USA) and Dome Fuji (Japan) and from the ice cores to be drilled by EPICA at Dome Concordia and in Dronning Maud Land.

Polar ice cores provided already much information about variations of the atmospheric concentration of the two very important greenhouse gases  $CO_2$  and  $CH_4$ . There is still much more information which can be obtained by further investigations. However, it is not a field of research where a few spectacular results will give a final answer. What is needed are detailed records from ice cores from various locations.

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