4. Atmospheric CO_2 Data from Ice Cores: Four Climatic Cycles

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4.1 Introduction

Ice core records of CO_2 reach as far back as 420,000 years before present. The Vostok long-term record shows a consistent pattern of glacial-interglacial CO_2 changes over the past four climatic cycles. It is likely that the CO_2 increase started before a large northern hemispheric warming for each termination. The long-term records have a relatively low time resolution, and the propagation of the atmospheric signal is recorded significantly smoothed by the gas occlusion process. Several records with higher resolution reach back into the last glacial. The CO_2 record in the last glacial shows minor variations that parallel temperature changes in Antarctica. It is possible that this characteristic of the CO_2 record is linked to the bipolar sea-saw between northern and southern hemispheric temperature. A model study over the Younger Dryas period supports this hypothesis. Generally the CO_2 record is highly correlated with the Antarctic temperature over glacial-interglacial cycles. Detailed analyses over the last termination reveal that some characteristics of northern hemispheric climate change are imprinted in the succession of the CO_2 increase. It appears that the large CO_2 changes are dominated by southern hemispheric climate change with an overlaid northern influence.

There are still open questions about the reliability of the CO_2 record. Greenland records are evidently altered by physical or chemical processes; moreover, such effects are not completely ruled out for Antarctic records. However, even

including this possibility, the uncertainty for recent high resolution CO_2 measurements from Antarctica is about 1%. Only ice core records are able to reconstruct the atmospheric CO_2 concentration to this level of confidence.

4.1.1 Occlusion of Trace Gas Records in the Ice

Polar ice sheets are an important climate archive for atmospheric air. Snow accumulating on the ice sheet sinters to firn and finally ice under the pressure of following precipitations. This process takes place with no melting in polar regions. A layered record of past precipitation builds up. Mass-balance leads to the ice flowing from the center of the ice sheet (Dome) downwards and outwards to the ablation zone. In central Greenland the thickness of the ice sheet is about 3km. The longest reliable climate record spans about one climatic cycle, roughly 100,000 years. The ice thickness found in Antarctica is about equal. However, some sites in Antarctica have accumulation rates about one order of magnitude lower than in Greenland, and thus their climate record extends over several (four at Vostok) climatic cycles. Ice cores from Dome F and Dome C will extend the ice core climate reconstruction by several climatic cycles.

Glaciers and ice sheets are unique as they are the only paleoarchives that record atmospheric composition in the form of trapped air bubbles. The top 50–150 m of ice are comprised of porous firn (Fig. 4.1).

Atmospheric air exchanges with the air in this top layer. Air in the porous firn thus consists of a mixture of air that was last in equilibrium with the atmosphere at different times (Schwander 1996). Because of physical and (in case of reactive gases) chemical processes, at a given time the concentrations of gas species in the firn are not the same as their atmospheric concentrations. Therefore, and due to gradual air occlusion at the bottom of the firn column, air occluded in ice does not have an exact age reflecting its last contact with the atmosphere; instead, it has an age distribution, and the temporal resolution of any trace gas record from ice cores is inherently limited. This age distribution is a function of both temperature and accumulation, which are highly variable from site to site. Generally, it increases with decreasing temperature and accumulation. The width of the age distribution is as low as seven years at high accumulation/high temperature sites but can be several centuries for Antarctic low accumulation/low temperature sites (Schwander and Stauffer 1984).

In the top few meters of firn, air is well mixed by convection and thus has essentially the same composition as the atmosphere. Below this zone, the air in the firn is static and mixes mainly by molecular diffusion. An equilibrium between molecular diffusion and gravitational settling is reached for each gas component (Craig, Horibe, and Sowers 1988; Schwander 1989). As a consequence, two gas components with different molecular weights fractionate with depth relative to their initial relationship in the atmosphere. The magnitude of this fractionation is well known, allowing the construction of an accurate, corrected ice core record. The process is most important for isotope records but can be neglected when dealing with concentration records. For CO_2, the con-

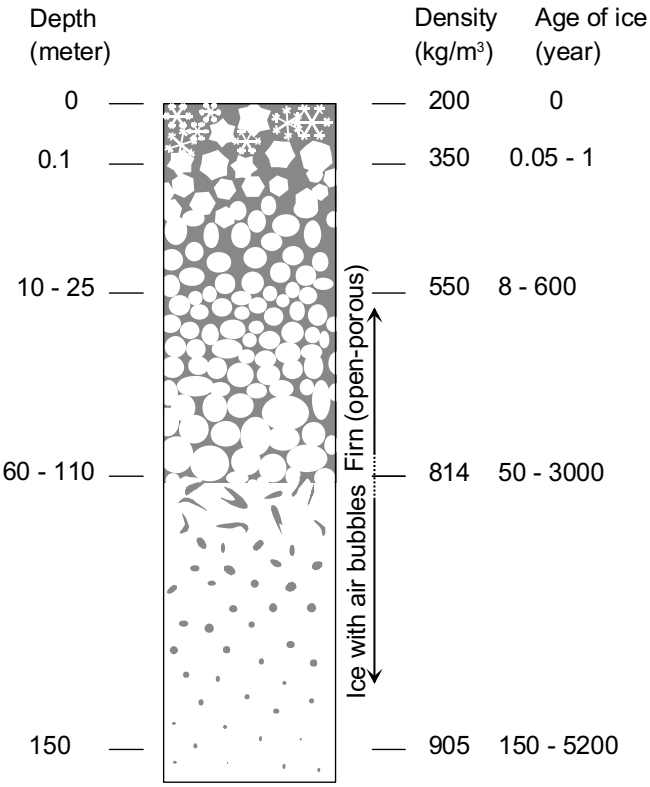

Figure 4.1. Sketch of the firn column. The indicated depth and age ranges are typical for polar ice sheets.

centration measured in ice cores is about 1% elevated compared to the true atmospheric value. This number varies slightly with temperature and the depth of the close off.

Another consequence of the air occlusion at the bottom of the firn column is that the age of the air in an occluded air bubble is less than the age of the surrounding ice. This age difference (Δage hereafter) is the difference between the age of the ice and the mean age of the air at the depth of occlusion. The age of the ice at close off is the dominant term of Δage, and Δage can be calculated using models for the firn densification process (Arnaud, Barnola, and Duval 2000; Barnola et al. 1991; Schwander 1989). Although the process is well understood, the accuracy of the calculation is limited due to uncertainty in past accumulation and temperature. However, Δage calculated with the densification model is in excellent agreement with independent measurements of Δage based on temperature diffusion processes in the firn for central Greenland ice cores (Lang et al. 1999; Leuenberger, Siegenthaler, and Langway 1999; Severinghaus

and Brook 1999; Severinghaus et al. 1998). The Δage can be substantial. Under present-day conditions Dage is on the order of decades to a few centuries for high accumulation/high temperature sites: e.g., 210 years for central Greenland (Schwander et al. 1993). At Vostok, where accumulation and temperature are low, Δage is about 3000 years (Barnola et al. 1991; Schwander and Stauffer 1984). Under colder climate conditions that are paralleled by lower accumulation, Δage increases significantly.

Below the close off zone the air bubbles shrink in size as the ice flows to deeper strata under the increasing pressure of overlying layers. When the pressure gets high enough, the gas is transformed from air bubbles into air hydrates (Miller 1969). Air hydrates constitute cage structures made up of water molecules that are fully or partially occupied by air molecules. For example, first hydrate formation has been observed at 500 m depth at Vostok and 1022 m at Summit Greenland, respectively (Shoji et al. 2000). Hydrates decompose into bubbles again once the core is recovered and relaxed. However, a full reformation of air bubbles takes several decades (Uchida et al. 1994). In the zone where bubbles and hydrates coexist, the composition of air in bubbles and hydrates deviate (Anklin et al. 1997; Ikeda et al. 1999). Fractionation takes place during hydrate formation and decomposition.

4.1.2 How Reliable Are CO_2 Data from Ice Cores?

How sure are we that the CO_2 concentration measured in ice cores represents the atmospheric concentration at trapping time? Where melting occurs, gas content and gas composition may be altered by chemical reactions taking place in aquatic systems or by physical gas exchange between the gaseous and the aquatic sections. In Greenland and Antarctica, surface melting is sporadic. At these sites the gas occlusion occurs by dry sintering of the firn described above. However, very slow chemical reactions are able to alter gas concentrations in ice cores due to the long time available for the reaction to proceed.

In specific time intervals, CO_2 from Greenland ice cores has been measured as significantly higher than Antarctic levels, too high given that atmospheric CO_2 is well mixed in the atmosphere and interhemispheric differences of more than a few ppmv are not realistic. In records from Greenland, concentrations fluctuate on the order of 50 ppmv between cold and warm phases of the last glacial (Stauffer et al. 1984), whereas no such variations are seen in Antarctic records (Indermühle et al. 2000; Neftel et al. 1988; Oeschger et al. 1988). It is now established that the elevated CO_2 concentrations in the Greenland ice cores do not represent the atmospheric concentration but are a spurious signal caused by an acid-carbonate reaction or by oxidation of organic material in the ice (Anklin et al. 1995; Delmas 1993; Tschumi and Stauffer 2000).

It has been demonstrated that the Antarctic records provide the most reliable data of changes in global atmospheric CO_2 (Raynaud et al. 1993). Antarctic results are consistent despite the fact that the coring sites have different accumulation, temperature, and impurities. CO_2 measurements made several years

apart on the same core show no significant changes. Detailed centimeter-scale CO_2 analyses of several ice cores indicate that also Antarctic ice core records may deviate systematically from the atmospheric CO_2 concentration at the time of air occlusion. However, it is unlikely that this deviation exceeds 1% of the measured concentration (Stauffer et al. 2003).

4.1.3 Extraction of Air for CO_2 Measurements

Principally there are three ways to extract air from the ice: melting, crushing, and sublimation of the ice. It is crucial to exclude alteration of the CO_2 concentration during the extraction or analysis of the gas. In light of the explanations in the previous section, it is obvious that extraction by melting is not suitable for CO_2 measurements. Carbonate reactions in the meltwater can significantly change the CO_2 concentration (Anklin et al. 1995; Delmas 1993). Where air is occluded fully or partly in hydrates, only a fraction of the gas can be extracted by the crushing method. This may cause the composition of the extracted gas to deviate from the true composition (Anklin et al. 1997; Stauffer and Tschumi 2000). The sublimation method has so far not resulted in routine measurements (Güllük, Slemr, and Stauffer 1998). Sorption processes at the apparatus walls (Zumbrunn, Neftel, and Oeschger 1982) lead to contamination of the sample that cannot be excluded so far. Reliable results are produced by the crushing methods that are used routinely in all laboratories measuring CO_2 concentrations from ice cores.

4.2 Glacial-Interglacial CO_2 Variations

Shown in Fig. 4.2 is the long-term perspective of atmospheric CO_2 changes over four glacial-interglacial cycles covering roughly the past 400,000 years. The Vostok ice core shows a remarkable correlation between temperature and greenhouse gas concentrations on glacial-interglacial scales (Petit et al. 1999). CO_2 concentrations oscillate between 180 and 200 ppmv during the coldest glacial periods; they oscillate between 280 and 300 ppmv during full interglacials.

One question regarding glacial-interglacial time scales that is still unanswered is why the atmospheric CO_2 rose by 80 to 100 ppmv during glacial to interglacial warmings. Changes in the atmospheric CO_2 concentration are driven by physical and biogeochemical changes in the ocean or in the terrestrial biosphere, which has grown between the last glacial and the Holocene (Adams and Faure 1998; Crowley 1995). Therefore, going from glacial to interglacial, the terrestrial biosphere is a sink, not a source, to the atmospheric carbon reservoir. The ocean has certainly played the dominant role, since it represents the largest pool of available CO_2 that could have been delivered to the atmosphere.

There is a third player, namely, changing rates in the weathering of silicate and carbonate rocks. Although it certainly played a role, this process is too slow to explain the rapidity of transitions seen in the Vostok record. We can therefore

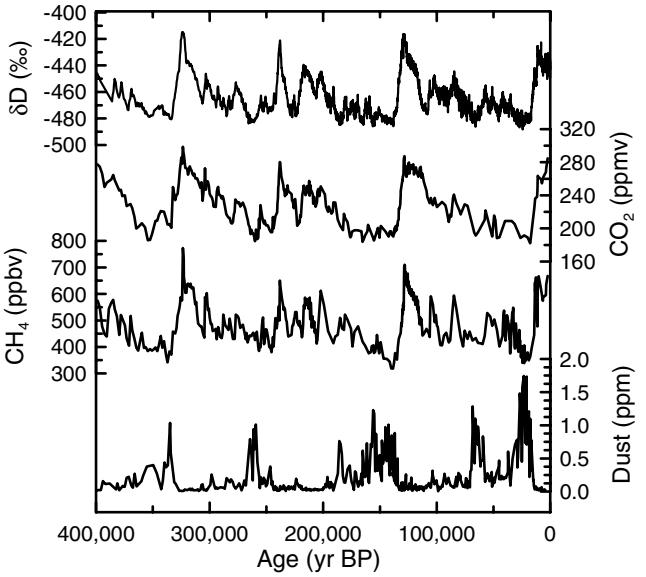

Figure 4.2. Climate records over the past 420,000 years. Deuterium (δD) is a proxy for local temperature, CO_2, CH_4, and dust from the Vostok ice core (Pépin et al. 2001; Petit et al. 1999).

assert that the 170–190 Gt of carbon that accumulated in the atmosphere during the several millennia corresponding to glacial to interglacial transitions must have been the result of a net flux out of the oceans. This is a minimum estimate, since during the same time the uptake of atmospheric CO_2 by the continental biosphere, although not well constrained, was almost certainly positive.

CO_2 is one of the major greenhouse gases. The initial forcing due to the direct radiative effect of increasing greenhouse trace gases (CO_2 + CH_4 + N_2O) during the glacial-interglacial transitions is estimated to have produced a global warming of about 0.95°C (Petit et al. 1999). This initial forcing would have been amplified by rapid feedbacks due to associated water vapor and albedo modifications (e.g., sea ice, clouds, etc.), as is also the case with the increasing load of anthropogenic greenhouse trace gases. Results from different climate simulations make it reasonable to assume that these trace gases and the associated rapid feedbacks have contributed significantly (possibly about half, that is 2–3°C) to the globally averaged glacial-interglacial temperature change (Weaver et al. 1998).

For the interpretation of the CO_2 record it is important to know the timing and the rate of the CO_2 variations with respect to other climatic records. From the long-term Vostok record we can deduce that the decrease of CO_2 to minimum values is slower than the CO_2 increases to interglacial levels. For the last glaciation, the CO_2 decrease lags the southern temperature decrease by several

thousand years (Barnola et al. 1991; Cuffey and Vimeux 2001). Generally the CO_2 decrease lags the Antarctic temperature decrease at the entrance of glacial periods (Barnola et al. 1991; Petit et al. 1999).

At the end of glacial periods, the Vostok record suggests that CO_2 and Antarctic temperature begin to increase in phase (Pépin et al. 2001; Petit et al. 1999). However, the low resolution of the Vostok profile prevents a firm statement about the precise timing of the Vostok temperature versus the CO_2 increases. Here we turn to a higher resolution record for the last termination from the Dome C core (Monnin et al. 2001). The Dome C record confirms and details earlier measurements from Antarctica over the last glacial termination (Monnin et al. 2001). We present these records in Fig. 4.3 together with records from Byrd station, Antarctica, and a $\delta^{18}O$ record from Greenland. The $\delta^{18}O$ and δD measured on ice are proxies for the local temperature. In this figure, the Dome C time scale has been adjusted so that the "global" CH_4 signals between the Greenland and the Dome C record are consistent over the Younger Dryas period.

First of all let us note that the temperature increase in Greenland and Antarctica is fundamentally different. Antarctic temperature increases steadily with a dip to colder temperatures toward the end of the transition. This dip is called the Antarctic Cold Reversal (ACR) (Jouzel et al. 1995). In contrast, Greenland temperature increases within decades from almost full glacial to Holocene temperature levels in the Bølling-Allerød period and drops back to near glacial conditions during the Younger Dryas. For the last glacial-interglacial termination, the main and fast temperature increase in Greenland lags the Antarctic temperature increase by several millennia. We now compare the CO_2 increase to the Arctic and the Antarctic temperature increases.

The CO_2 measurements highly correlate with the temperature reconstruction from Dome C. The start of the temperature increase occurs 800 ± 600 years before the increase of the CO_2 concentration confirming earlier estimates from various ice cores (Fischer et al. 1999; Neftel et al. 1988). It is likely that the start of the glacial-interglacial CO_2 increase generally lags the temperature evolution. This assumption was confirmed recently for Termination III ($\sim$240 kyr BP) on the Vostok ice core. Caillon et al. (2003) concluded, based on a temperature proxy in the air bubbles, that the CO_2 increase lagged the Antarctic temperature increase by 800 ± 200 years. However, even a time lag of a few hundred years does not cast doubt on the importance of CO_2 as an amplification factor of the temperature due to the fact that this time lag is much smaller than the 6-kyr duration of the CO_2 and temperature increase.

The rapid glacial-interglacial temperature increase observed in Greenland obviously lags the rise in CO_2 and the Antarctic temperature increase. Greenland temperature and the global CH_4 signal change in concert (at least for the main features over the last termination). Therefore we can regard the CH_4 signal recorded in the Vostok ice core as a proxy for Greenland temperature. If this analogy holds, the CO_2 increase over the last four glacial-interglacial terminations has always occurred before a major temperature increase in the Northern

Hemisphere (Pépin et al. 2001). In summary, the CO_2 increase probably lags the Antarctic temperature increase by a few hundred years but precedes the Greenland temperature increase by a few millennia as does the Antarctic temperature.

The high correlation of the CO_2 record with the Dome C temperature reconstruction (δD record) points to the Southern Hemisphere as the main driver of the CO_2 change over the last termination. Assuming that the Dome C δD record is a qualitative indicator for Southern Ocean surface temperature, one possible cause of the CO_2 increase would be a reduced solubility of the Southern Ocean surface waters owing to increasing temperatures. However, a quantitative estimate shows that the observed CO_2 increase is too large to be explained by this mechanism alone (Broecker and Henderson 1998). An additional mechanism could be an enhanced air-sea exchange in the Antarctic region due to the reduction of Antarctic sea ice that increases the deep sea ventilation (Stephens and Keeling 2000). The decrease of dust also could have influenced the atmospheric CO_2 concentration: e.g., through a decrease of iron fertilization of the Southern Ocean bioproductivity (Broecker and Henderson 1998; Martin 1990). We note, however, that the dust decrease most probably started significantly before the onset of the CO_2 increase and that the dust level already dropped to about Holocene values before 15 kyr BP.

The detailed CO_2 record from Dome C can be subdivided into four intervals over the glacial to interglacial increase. Surprisingly, the steps in CO_2 and CH_4 concentration changes are synchronous. Since the CH_4 signal is a first-order approximation for northern hemispheric temperature (Fig. 4.3), this points to a northern hemispheric influence to the CO_2 increase.

A first CO_2 increase of about 35 ppmv happens over a first moderate increase of the CH_4 concentration from about 17 to 15.5 kyr BP. Over a section of approximately 15.5 to 14 kyr BP where the CH_4 concentration is roughly constant, CO_2 increases slowly. At the sharp CH_4 increase, which parallels the sharp Greenland temperature increase into the Bølling-Allerød period, CO_2 rises almost instantaneously by about 8 ppmv. CO_2 slightly decreases over the Bølling-Allerød period, which corresponds to the ACR to finally increase by 30 ppmv to its Holocene level over the Younger Dryas period.

The slight CO_2 decrease during the Bølling-Allerød period could be attributed to the cooling in the Southern Ocean in conjunction with the ACR, but it will be difficult to find a Southern Hemisphere explanation for the sudden CO_2 increase of 8 ppmv at the beginning of this period. A cause for this sudden increase is more likely connected with the fast temperature increase observed in the Northern Hemisphere parallel with a reorganization of the formation of North Atlantic Deep Water (NADW): an enhanced NADW could increase the deep-sea ventilation and therefore increase the atmospheric CO_2 concentration (Siegenthaler and Wenk 1984; Toggweiler 1999). During the Younger Dryas, the CO_2 increase resumes again and is terminated by a sudden CO_2 rise. Simulations of Younger Dryas-type events with a global ocean circulation-biogeochemical

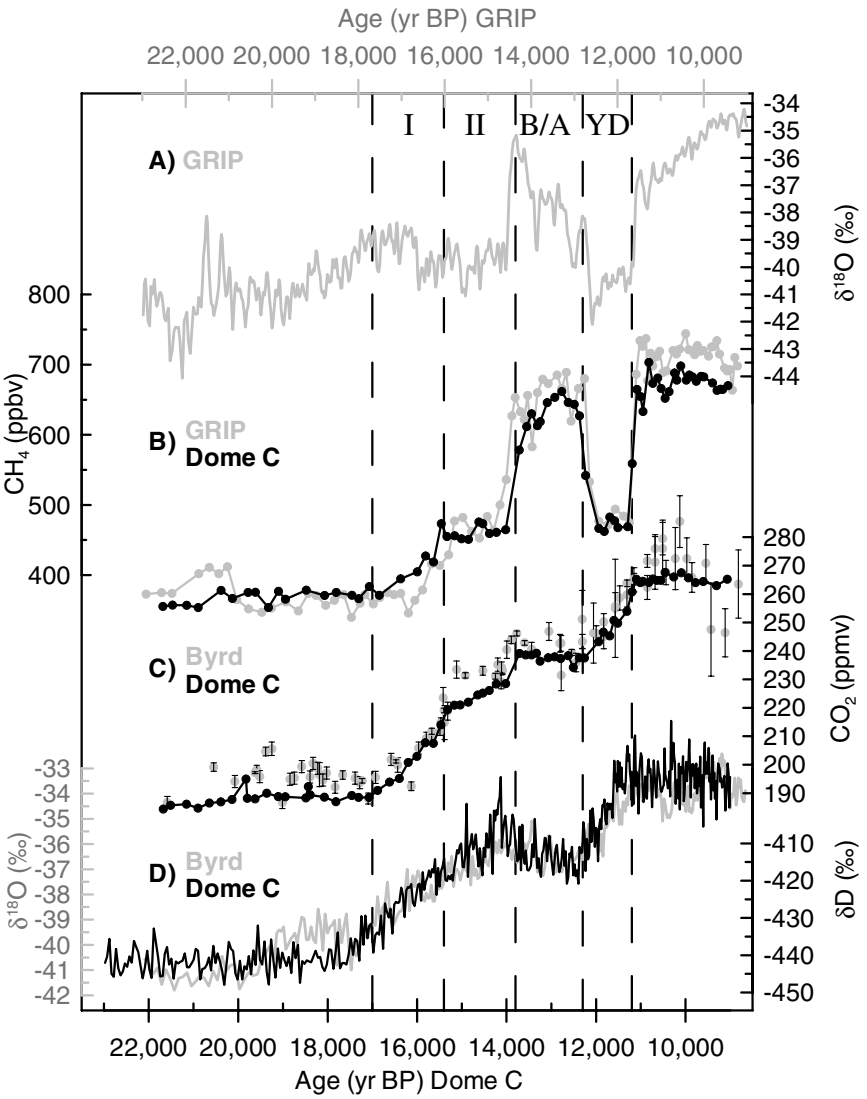

Figure 4.3. Ice core records covering the last glacial-interglacial termination. **(A)** $\delta^{18}O$ from Greenland (GRIP ice core, Dansgaard et al. 1993). **(B)** Methane from Greenland (GRIP ice core, Blunier and Brook 2001) and Antarctica (Dome C, Monnin et al. 2001). The CH_4 concentration in Antarctica is generally slightly lower than the CH_4 concentration in Greenland (Dällenbach et al. 2000). **(C)** CO_2 concentrations from Byrd station (Marchal et al. 1999) and Dome C (Monnin et al. 2001), Antarctica. **(D)** $\delta^{18}O$ from Byrd station (Johnsen et al. 1972) and δD from Dome C (Monnin et al. 2001). The GRIP and Byrd station records are plotted on the GRIP ss09 timescale (top x-axis). The Byrd station records have been synchronized to the GRIP record over the CH_4 signals (Blunier et al. 1998). Dome C records are plotted on the Dome C timescale (bottom x-axis, Schwander et al. 2001). The two timescales are adjusted so that the "global" CH_4 signal is consistent between the GRIP and the Dome C record over the Bølling-Allerød (B/A), Younger Dryas (YD) period.

model suggest that the Younger Dryas increase could have been triggered by a freshwater-induced reduction of the Atlantic thermohaline circulation (Marchal et al. 1999).

The general shape of the glacial-interglacial CO_2 increase corresponding to the Antarctic temperature points to a Southern Ocean explanation for the increase. However, the details of the CO_2 increase have some characteristics of the northern hemispheric climate change pointing to a non-negligible northern hemispheric influence on the global carbon cycle at least over the last termination. The northern hemispheric influence presumably involves changes in the NADW formation (Marchal et al. 1999).

4.2.1 Smoothing in the Vostok CO_2 Record

As pointed out above, the progression of the atmospheric gas composition is recorded smoothed in the ice. This smoothing may be significant and averages over centuries for Vostok station (Barnola et al. 1991; Rommelaere, Arnaud, and Barnola 1997; Schwander and Stauffer 1984). Would a concentration increase like the one we observe over the past few centuries be visible in the Vostok record? In Fig. 4.4 we show how the present anthropogenic CO_2 increase will be recorded at Vostok.

For the propagation of the atmospheric CO_2 concentration to the future we

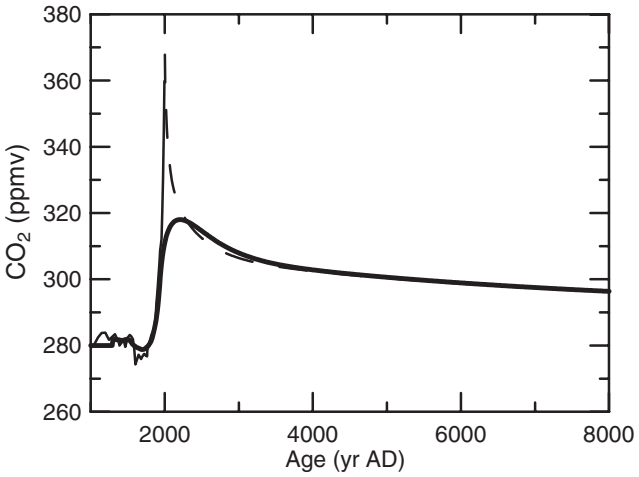

Figure 4.4. Solid line: Atmospheric CO_2 concentration from ice cores and atmospheric measurements up to the year 2000. Broken line: Propagation of the atmospheric CO2 concentration calculated with the Bern model (Joos et al. 1996) setting the hypothetical anthropogenic carbon source to zero after the year 2000. Heavy solid line: prediction of how the atmospheric signal will be recorded in the Vostok ice core, calculated with the Schwander model for gas occlusion (Schwander et al. 1993) with an extension for gradual gas occlusion over the close-off interval (Spahni et al. 2003).

are using the Bern model (Joos et al. 1996). As a lower limit for the future CO_2 concentration we set the anthropogenic CO_2 emission to zero after the year 2000. The smoothed "Vostok record" is obtained using the Schwander model for gas occlusion (Schwander et al. 1993) with an extension for gradual gas occlusion over the close-off interval (Spahni et al. 2003). The resulting concentration propagation with a maximum of about 315 ppmv and a very slow decrease to the preindustrial background clearly stands out. At no place in the Vostok record has such a high concentration with such a concentration trend been measured. Strictly speaking the Vostok record does not exclude a pulselike atmospheric CO_2 signal of few-decades duration with concentrations as high as those found today. However, this would require both a large carbon release (order 200 GtC) and an equally large uptake within only a few decades. Such an oscillation is not compatible with our present view of the global carbon cycle. We conclude that the present CO_2 concentration is unprecedented in the Vostok record.

4.3 Millennial Changes in the Last Glacial

The ice core isotopic records from Greenland (Dansgaard et al. 1993; Grootes et al. 1993) reveal 24 mild periods (interstadials) lasting 1 to 3 kyr during the last glacial, known as Dansgaard-Oeschger (D–O) events (Oeschger et al. 1984), where temperature increased by up to 15°C compared to full glacial values (Johnsen et al. 1995; Schwander et al. 1997). These millennial scale changes are observed in large portions of the world on land and in the ocean (Broecker 1994; Voelker and workshop participants 2002). What is the effect of Dansgaard-Oeschger events on the CO_2 budget?

As outlined above, the CO_2 records must originate from Antarctic records. However, central Antarctica is about the only place where millennial-scale climate change is principally different than in Greenland (Blunier and Brook 2001). Therefore, CO_2 changes recorded in Antarctic ice cores have to be compared to temperature variations recorded in Greenland to identify a potential influence of millennial-scale climate variation on the CO_2 budget.

Millennial-scale variability in Greenland is characterized by abrupt temperature increases, followed by gradual decreases and abrupt returns to baseline glacial conditions. In contrast, Antarctic warmings and coolings are gradual and fewer than in Greenland. Blunier and Brook (2001) and Blunier et al. (1998) showed that the onset of Antarctic warmings preceded by more than 1.5 to 3 kyr the onset of major D–O events, i.e., those that are longer than 2 to 3 kyr, namely, D–O events 8, 12, 14, 16/17, 19, 20, and 21 (Fig. 4.5).

In general, Greenland temperatures were cold or cooling during the gradual warmings in the Antarctic Byrd record. The Antarctic temperature rise was apparently interrupted at or near the time when Greenland temperatures rose abruptly to an interstadial state within only a few decades (Grootes et al. 1993). Subsequently, temperatures decreased in both hemispheres to full glacial level, but cooling in the Byrd record was more rapid.

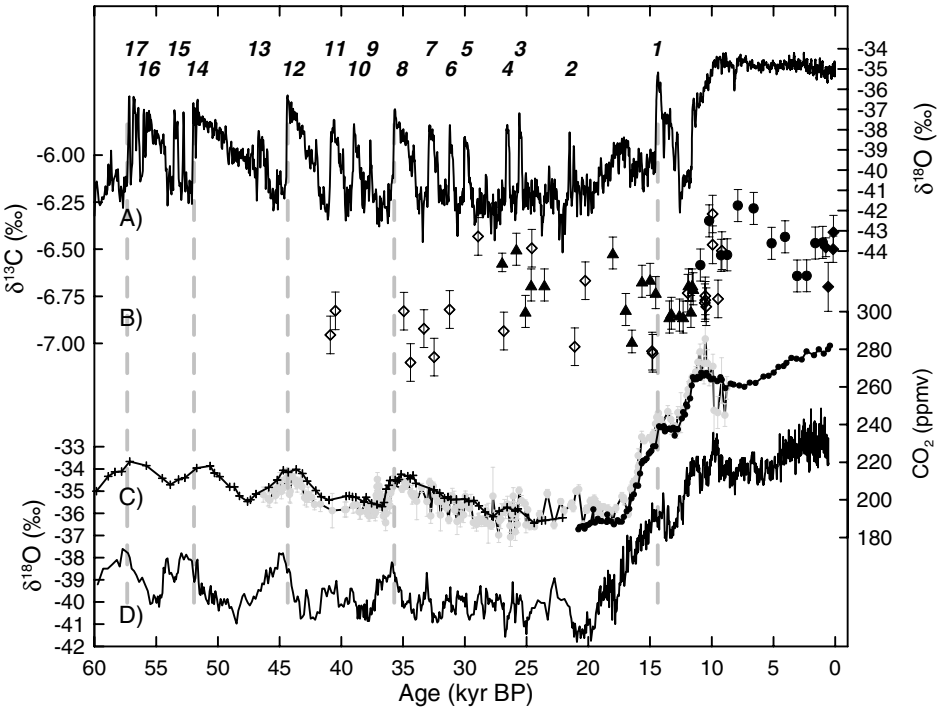

Figure 4.5. Climate records from the last glacial to the preindustrial Holocene: **(A)** $\delta^{18}O$ of the ice, a proxy for local temperature, from the GRIP ice core, Greenland (Dansgaard et al. 1993). **(B)** $\delta^{13}C$ of CO_2; dots (Indermühle et al. 1999b) and filled triangles (Smith et al. 1999) from the Taylor Dome ice core. Open diamonds are from Byrd station and filled diamonds from several ice cores covering the preindustrial Holocene (Leuenberger et al. 1992). **(C)** Composite record of atmospheric CO_2 from Antarctic ice cores. Gray dots with error bars are from the Byrd station ice core (Marchal et al. 1999; Neftel et al. 1988; Staffelbach et al. 1991) on a timescale synchronized to the GRIP temperature record over the global CH_4 record (Blunier et al. 1998; Stauffer et al. 1998). The Taylor Dome record (crosses, 60–20 kyr BP) has been adjusted to the GRIP timescale so that the relative position of CO_2 and Antarctic temperature variations is preserved from the original tie to the Vostok GT4 timescale (Indermühle et al. 2000). The CO_2 record over the last glacial termination and the Holocene (dots) is from the (EPICA) Dome C core (Flückiger et al. 2002; Monnin et al. 2001). **(D)** $\delta^{18}O$, a proxy for local temperature, from the Byrd ice core, Antarctica (Johnsen et al. 1972). $\delta^{18}O$ from Byrd station is plotted on the GRIP timescale (Blunier and Brook 2001).

High resolution CO_2 data from Byrd station (Marchal et al. 1999; Neftel et al. 1988; Staffelbach et al. 1991) span from approximately 47 to 8kyr BP. This record is well synchronized to the Greenland ice core records (Stauffer et al. 1998). The Byrd CO_2 concentration varies between about 180 and 210 ppmv during 47 to 17kyrBP (see Fig. 4.5). Two distinct millennial-scale peaks of 20 ppmv during this period correlate well with the Antarctic temperature reconstruction from Byrd station.

The high-resolution record from the Taylor Dome ice core reaches back to about 60 kyr BP (Indermühle et al. 2000). Indermühle et al. (2000) tied this record to the temperature variations at Vostok and found also a strong covariance between the CO_2 and the temperature record. We present the Taylor Dome record in Fig. 4.5. The time scale has been adjusted so that the relative position of CO_2 and Antarctic temperature variations is preserved from the initial publication (Indermühle et al. 2000).

The Southern Hemisphere warming and, apparently, the atmospheric CO_2 concentration increase occur when Greenland temperatures are lowest (Indermühle et al. 2000). Marchal et al. (1998) simulated the evolution of the atmospheric CO_2 concentration in response to a freshwater-induced collapse of the thermohaline circulation using a coupled ocean circulation-biogeochemical model. In their simulation, a thermohaline-circulation shutdown leads to an increase of the CO_2 concentration due to a warming of the Southern Ocean (the so-called see-saw effect, Broecker 1998; Stocker 1998), which overcompensates the North Atlantic cooling. Changes in alkalinity and dissolved inorganic carbon concentration in the North Atlantic surface, mainly due to dilution, amplify the increase. Sensitivity studies reveal that the response of the temperature in the North Atlantic and the Southern Ocean and of the atmospheric CO_2 concentration depend on the amount, duration, and geographic location of freshwater input (i.e., iceberg discharge, see Fig. 12 in Marchal et al. 1998). That would explain why some D-O events are preceded by an Antarctic warming and an increase of atmospheric CO_2, while others are not (Stocker and Marchal 2000).

4.4 The Holocene

The Antarctic Taylor Dome CO_2 and $\delta^{13}C$ records reveal that the global carbon cycle has not been in steady state during the Holocene (Indermühle et al. 1999b). The CO_2 record was recently confirmed by measurements on the Dome C core and shows an 8 ppmv decrease in the CO_2 mixing ratio (Flückiger et al. 2002). This decrease is paralleled by a 0.3‰ increase in $\delta^{13}C$ between 10.5 and 8.2 kyr BP. Over the following 7 kyr, a fairly linear 25 ppmv CO_2 increase is accompanied by a approximately 0.2 $\delta^{13}C$ decrease (see Fig. 4.5). Inverse methods based on a one-dimensional carbon cycle model applied to the Taylor Dome record (Indermühle et al. 1999b) suggest that changes in terrestrial biomass and sea surface temperature are primarily responsible for the observed CO_2 changes. In particular, the CO_2 increase from 7 to 1 kyr BP could correspond to a cu-

mulative continental biospheric release of about 195 GtC, in connection with a change from a warmer and wetter mid-Holocene climate to the colder and drier preindustrial conditions. This model result is not sensitive to surface-to-deep ocean mixing and air-sea exchange coefficients because of their faster time scales. Changes in the biological carbon isotope fractionation factor, which varies according to the contribution from C_3 and C_4 plants and due to environmental changes, may contribute up to 30 to 50% of the observed and modeled changes. The resulting additional uncertainty in the cumulative biospheric carbon release is ± 30 GtC at 7 kyr BP and ± 70 GtC at 1 kyr BP.

However, this model calculation is very dependent on the $\delta^{13}C$ data and the smoothing line. Better, high resolution δ^{13} data will improve our knowledge of the causes of CO_2 variations not only over the Holocene period but also in the glacial and over the glacial-interglacial transition.

4.5 The Anthropogenic Increase

A continuous record of CO_2 over the past millennium, which overlaps with the period of instrumental data, is contained in the Law Dome ice core (Etheridge et al. 1996), as shown in Fig. 4.6.

There is no doubt that the atmospheric CO_2 concentration has been increasing

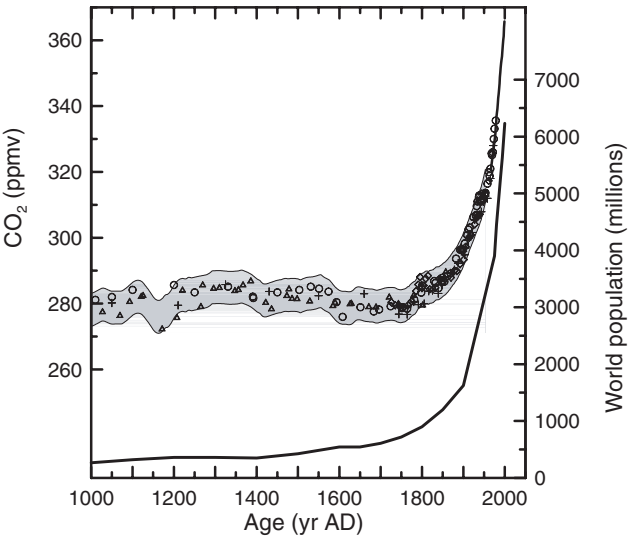

Figure 4.6. The last millennium. CO_2 data from Antarctic ice cores compiled by Barnola (1999). The ice core measurements overlap with direct atmospheric measurements, shown with the solid line (Keeling and Whorf 2000); world population (McEvedy and Jones 1979).

since the industrial revolution and reached a concentration that is unprecedented over more than 400,000 years. The CO_2 record suggests slightly increased concentrations from approximately AD 1200 to 1400, during Medieval times, and slightly reduced concentrations from approximatly AD 1550 to 1800, during the Little Ice Age. However, caution should be used in interpreting these variations as natural. Although all ice core records from different Antarctic locations show the same general picture, we cannot exclude a small contribution from chemical reactions in the ice (Barnola 1999). The pre-anthropogenic level of CO_2 during the last millennium is approximately 280 ± 10 ppmv (Etheridge et al. 1996).

4.6 Comparison of Ice Core CO_2 Data to Other Methods

The smooth increase of atmospheric CO_2 suggested by low-resolution CO_2 records has been questioned for two reasons: (1) the records did not have the resolution to exclude any fast changes (at least over some time intervals) and (2) the smoothed recording of atmospheric signals could potentially mask such fast changes. Indirect CO_2 measurements from $\delta^{13}C$ in peat (Figge and White 1995) and stomatal density and stomatal index measurements (Beerling, Birks, and Woodward 1995; McElwain, Mayle, and Beerling 2002; Wagner et al. 1999) suggest century or even decadal changes of the CO_2 concentration in the range of the Younger Dryas to the early Holocene.

The ice core CO_2 record over the last glacial termination to the Younger Dryas period has been subject to intensive studies in recent years. The results from low accumulation ice cores and high accumulation ice cores are in excellent agreement. From two ice cores we have records with a high time resolution (Byrd station $\sim$160 years; Dome C $\sim$140 years).

Besides the study from Wagner et al. (1999), which has been criticized for its calibration process (Indermühle et al. 1999a), indirect studies of CO_2 concentrations agree fairly well with ice core data on the CO_2 level. However, CO_2 records based on ice core and stomatal findings differ significantly on short-term fluctuations (Fig. 4.7).

It is intriguing that stomatal density data from various sites agree fairly well on a proposed CO_2 variation during the Younger Dryas (Beerling, Birks, and Woodward 1995; McElwain, Mayle, and Beerling 2002). Is it possible that the ice core archive did not record the variations observed in the stomatal records because of its limitations concerning the trapping of atmospheric gas? To investigate this question we treated the Span Pond CO_2 record from McElwain, Mayle, and Beerling (2002) with the smoothing function of Byrd station and Dome C. The width of the age distribution is 20 to 25 years for Byrd station and one order of magnitude larger for Dome C. The effect of the Byrd smoothing function on the stomatal record is minor. Even applying the Dome C smoothing function (see Fig. 4.7) does not remove the short-term fluctuations in the stomatal record. Therefore the disagreement between ice core and stomatal-based CO_2 reconstructions cannot be explained by the smoothing of the ice core record.

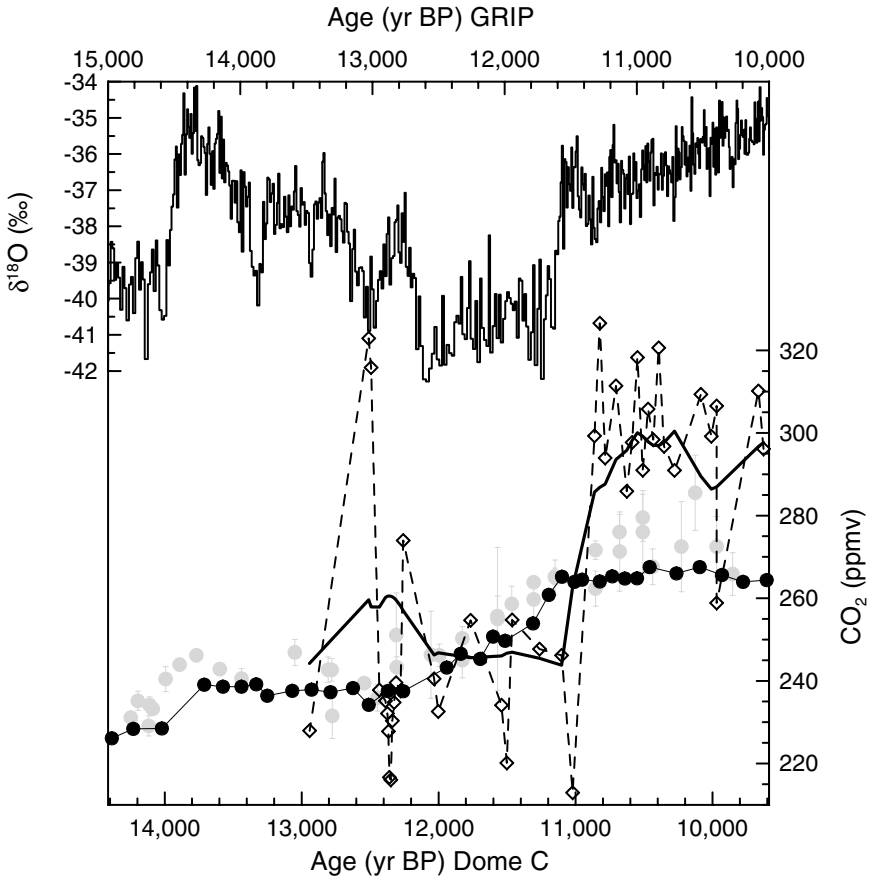

Figure 4.7. Comparison of CO_2 records from Byrd station (gray dots, Marchal et al. 1999) and Dome C (black dots, Monnin et al. 2001) with a reconstruction from stomata frequency measurements (open diamonds McElwain et al. 2002). The Dome C record is plotted on the Dome C timescale (bottom x-axis, Schwander et al. 2001); all the other records are plotted on the GRIP ss09 timescale. The two timescales are adjusted so that the "global" CH_4 signal is consistent between the GRIP and the Dome C record over the Bølling-Allerød (B/A), Younger Dryas (YD) period (see Fig. 4.3). The stomata record shows higher variability than do the ice core records. Ice core reconstructions of atmospheric gas records are smoothed in time. Smoothing the stomata record with the Byrd smoothing function barely affects the record (not shown). The smoothing in the Dome C record is one order of magnitude larger than in the Byrd station record. Still, the two records basically show the same variations. Smoothing the stomatal record with the Dome C smoothing function (heavy solid line) does not remove the suggested steep CO_2 increase around 11.2 kyr BP. The stomatal record is in discrepancy with both ice core records. The origin of this discrepancy is currently not known.

Also we are not aware of any other process during the trapping or measuring of CO_2 from ice cores that would explain the discrepancy. We are convinced that the ice cores are reliable to an uncertainty of about 1% (Stauffer et al. 2003). The advantage of the ice core based method compared to other methods to reconstruct past CO_2 concentrations is that it is the only approach that accesses the atmospheric CO_2 concentration directly as CO_2 in air.

4.7 Summary

The paleo CO_2 record from ice cores spans over four glacial-interglacial cycles. It is highly probable that the CO_2 concentration over this time period has never been as high as it is today. The Vostok CO_2 record and Antarctic temperature are correlated. This points to the Southern Ocean as the main driver for the glacial-interglacial CO_2 variations. The timing of the CO_2 variations is such that the CO_2 decreases lag Antarctic temperature decreases by a few millennia. The CO_2 increase, in contrast, lags the Antarctic temperature increase by a few centuries. This has been demonstrated over the last termination but is probably also the case for terminations II to IV. The CO_2 increase precedes by several millennia the northern glacial-interglacial temperature increase, which dominates over large portions of the world. The detailed CO_2 record over the last transition shows that the CO_2 increase can be divided into several intervals with different increase rates and fast CO_2 increases on decadal timescales. The timing of these intervals shows characteristics of northern hemispheric climate variations. The CO_2 increase over termination I shows a combination of Northern and Southern Hemisphere climate change. CO_2 variations over the Holocene show that the CO_2 budget has not been in steady state over this period. We are certain that the Antarctic CO_2 record represents the atmospheric CO_2 signal and is presently the best reconstruction available.

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