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Reconstruction of glacial/interglacial changes in the global carbon cycle from CO_2 and $\delta^{13}CO_2$ in Antarctic ice cores

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Abstract: High-resolution CO_2 and $\delta^{13}CO_2$ records from the Taylor Dome ice core, Antarctica, reveal significant changes in the global carbon cycle over the last 30000 yrs. CO_2 concentrations increase from 180 ppmv at 20 kyr before present to 275 ppmv at the start of the Holocene with an intermittent decline during the Antarctic Cold Reversal. $\delta^{13}C$ shows a net increase from the average glacial level of –6.7‰ to mean Holocene values of around –6.5‰. However, the transition period is initiated by an 0.5‰ drop at 20 kyr before present followed by an 0.7‰ increase which is interrupted by an 0.2‰ decline during the Antarctic Cold Reversal. Isotope budget considerations show that during the Holocene and the Last Glacial Maximum changes in the size of terrestrial biosphere can account for the observed changes in CO_2 and $\delta^{13}C$. In contrast changes in the atmosphere/ocean system are dominant during termination I. The size of the CO_2 increase cannot be explained by variations in ocean temperature, salinity or net transfer of carbon into the terrestrial biosphere alone. The strong temporal correlation of CO_2 and Antarctic isotope temperatures is in conflict with hypotheses to account for the missing CO_2 which are connected to sea level change or a dust induced change in the biological productivity in the Southern Ocean. Changes in the Southern Ocean sea ice cover, however, may provide a direct link to temperature which appears to be able to account for the observed changes in atmospheric CO_2 and $\delta^{13}C$.

key words: Antarctica, ice core, atmospheric CO_2, carbon cycle

1. Introduction

Substantially rising atmospheric CO_2 levels during this century have been documented in the atmosphere (Keeling and Whorf, 2000) as well as in atmospheric samples enclosed in polar ice (Neftel *et al*., 1985). These changes can be unambiguously attributed to the extensive combustion of fossil fuel since the onset of the industrialization, as reflected in the accompanying change in the carbon isotopic signature of atmospheric CO_2 (Francey *et al*., 1998). In view of the role of CO_2 as the most important anthropogenic greenhouse gas (second only to the natural water vapor content of the atmosphere) this increase has gained great attention in connection to growing evidence of an anthropogenically induced global warming during recent decades (Johannessen *et al*., 1999; Kaufmann and Stern, 1997; Mann *et al*., 1995).

In order to estimate the future development of the global carbon cycle and thus a CO_2

induced warming, various conceptual and computer models have been used (IPCC, 2001). One of the most stringent tests of such models is whether they can reproduce the naturally occurring changes in the global carbon cycle during climate variations in the past. Ice core studies show that atmospheric CO_2 varied between 180 and 280 ppmv during the last four glacial cycles (Petit *et al.*, 1999). These natural variations are approximately of the same size as the anthropogenic increase encountered during this century. A quantitative understanding and model description of natural changes in the global carbon cycle and their relationship to glacial/interglacial climate changes will greatly enhance the accuracy of our model predictions of respective changes in the future.

With respect to paleoclimatic changes the role of the global carbon cycle is twofold:

1) Atmospheric CO_2 plays an active role in the climate system by changing the radiative balance of the earth.

2) The global carbon cycle is subject to changes of climate parameters, *e.g.* ocean circulation and temperature, sea level or sea ice coverage.

Any transfer of carbon from the ocean or the terrestrial biosphere to the atmosphere (which represent the three most important carbon reservoirs on time scales on the order of 100–10000 years, which are relevant for this study, see Fig. 4) has to be initiated by some change in at least one of those climate parameters. In return, an elevated atmospheric CO_2 level is able to trap a larger amount of thermal radiation in the atmosphere and, thus, to create a respective climate feedback. Because of this intimate coupling of the climate system with the global carbon cycle, the latter also represents a very efficient diagnostic tool to test (conceptual) models of paleoclimatic changes. Any concept to explain paleoclimatic variations can only be accepted, if it is able to explain paleoclimatic temperature variations together with the accompanying changes in the carbon cycle. Accordingly, it is mainly in this respect (*i.e.* the exchange of carbon between different reservoirs in reaction to climate change) that we can learn from ice core studies about the carbon cycle and its relationship to climate and only secondarily about the climate sensitivity on future CO_2 changes.

One way to gain further insight into the relative contributions of ocean and biosphere to atmospheric CO_2 changes is the study of its carbon isotopic signature. Carbon accumulated in terrestrial biomass has a distinctively different isotopic composition ($\delta^{13}C \approx -23‰$) compared to Dissolved Inorganic Carbon (DIC) in the ocean ($\delta^{13}C \approx +1.5‰$). CO_2 released during respiration is not subject to further fractionation while CO_2 released during air/sea gas exchange has an effective isotopic signature of -6 to $-7‰$ (Mook, 1986). Consequently, carbon fluxes from each of these reservoirs into the atmosphere cause distinctively different changes in atmospheric $\delta^{13}CO_2$ (see also Fig. 4). A quantitative approach to interpret ice core results of paleoclimatic changes in CO_2 and $\delta^{13}C$ has been followed by Indermühle *et al.* (1999) for the Holocene, where boundary conditions of the carbon cycle are sufficiently constrained to employ inverse modeling techniques. This model study assumed that the ocean/atmosphere system is in equilibrium with respect to the carbon cycle, which is a reasonable assumption considering changes in atmospheric CO_2 taking place on time scales of a few thousand years. Double deconvolution of the CO_2 and $\delta^{13}C$ data from the Taylor Dome ice core, Antarctica, over the last 11000 years revealed that an initial decrease of atmospheric CO_2 by a few ppmv from 11000 yrs before present (BP) to 7000 yrs BP and a following gradual increase by more than 20 ppmv to the preindustrial level of 285 ppmv can be essentially attributed to changes in the size of the terrestrial biosphere. This implies that during the
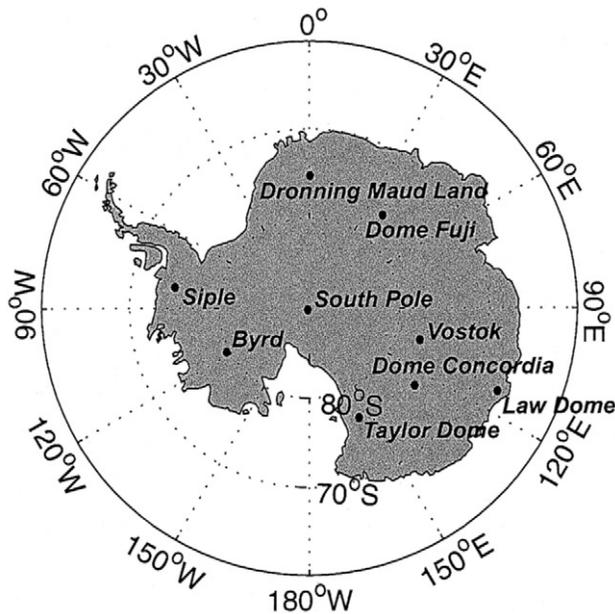
Fig. 1. Map of the Antarctic ice sheet indicating the most important ice core drill sites.

second half of the Holocene the terrestrial biosphere acted as a net (cumulative) carbon source of app. 200 Gt C, *i.e.* about one third of the net carbon release estimated for the last glacial termination (Crowley, 1995).

The study by Indermühle *et al.* (1999) showed the great potential of CO_2 reconstructions in connection with measurements of its isotopic signature which allow a more quantitative source/sink attribution of paleoatmospheric CO_2 changes. Here, paleoatmospheric changes in CO_2 and $\delta^{13}C$ from the Last Glacial Maximum (LGM) to the present derived from the Antarctic Taylor Dome and Vostok ice cores (Fischer *et al.*, 1999; Smith *et al.*, 1999) will be discussed in combination with other recently published Antarctic ice core CO_2 records from Taylor Dome (Indermühle *et al.*, 2000), Dome C (Monnin *et al.*, 2001) and Vostok (Petit *et al.*, 1999) (for an overview of the mentioned ice core drill sites see Fig. 1). Semiquantitative conclusions on the main parameters controlling the global carbon cycle during paleoclimatic changes are drawn and the influence of external parameters on the observed variations in atmospheric CO_2 during the glacial/interglacial transition are quantified. In a last step potential hypotheses to account for the remaining changes in the carbon cycle are discussed making use of other paleoclimatic and atmospheric records. In this respect the role of sea ice coverage in the Southern Ocean represents a very promising physical parameter to explain the size and temporal evolution of the CO_2 change during the last glacial cycle.

2. Methods

Samples measured for CO_2 and $\delta^{13}C$ at the Scripps Institution for Oceanography have been taken from the Taylor Dome and Vostok ice cores, Antarctica. For CO_2 concentrations ice samples of app. 4 cm³ have been taken and the gas entrapped in the air bubbles has been

dry extracted using a cooled needle crusher. Gas samples and standards over ice have been transferred to individual miniature cold traps cooled by a closed He refrigerator (25K). Then samples and standards are warmed to –70°C and individually transferred into an absorption cell for IR laser spectroscopy. The accuracy of a single measurement is better than 5 ppmv. For each depth three replicate samples have been measured and averaged. Consequently, the accuracy of CO_2 values for every given depth is better than 3 ppmv. For details concerning the laser spectroscopy method see Wahlen *et al*. (1991).

For the isotopic measurements ice samples of 200 cm^3 have been dry extracted using a larger volume ultrahigh vacuum rotary crusher inside a cold room (–20°C). CO_2 of the released gas has been cryogenically separated from water vapor and non condensable air components using –90°C and liquid nitrogen cold traps on an all glass extraction rack. CO_2 was then quantitatively collected in Pyrex glass ampoules cooled to liquid nitrogen temperature. These samples have been transferred to a VG Prism II isotope ratio mass spectrometer for $\delta^{13}C$ determination using a temperature controlled microvolume. Measurement accuracy of the mass spectrometric analysis on these very small CO_2 samples (approximately 5 μl CO_2 at standard pressure) is 0.03‰. Absolute calibration of the extraction procedure has been achieved by expanding an air standard of well known $\delta^{13}C$ over the ice sample in the crusher and extracting it the same way as the gas from the ice sample itself. Standard deviation of $\delta^{13}C$ of these air standards is 0.075‰. All values are referenced versus VPDB and have been Craig corrected (Craig, 1957). Furthermore the data have been corrected for minute levels of N_2O in the sample which are frozen out during the extraction process together with CO_2. The paleoatmospheric N_2O concentration of each sample has been estimated from data given by Leuenberger and Siegenthaler (1992) and the effect of the isobaric interference of N_2O has been corrected by calibrating the mass spectrometer using different CO_2/N_2O mixtures. After the analysis the systematic fractionation effect induced by gravitational separation in the diffusive firn column (Schwander, 1996; Sowers *et al*., 1992) has been corrected using $\delta^{15}N$ data in atmospheric N_2 measured on Taylor Dome ice samples by Sucher (1997). Since this fractionation effect is only dependent on the absolute mass difference of the respective isotopes, changes in the $\delta^{15}N$ values can be directly applied to our $\delta^{13}C$ data. Including these systematic corrections the 1 σ uncertainty of a single $\delta^{13}C$ value increases to 0.085‰ (Smith *et al*., 1999). Duplicates at an age of 2.2 kyr BP and 17.2 kyr BP and a triplicate at 27.4 kyr BP have a 1 σ uncertainty of 0.06 and 0.049‰, respectively.

3. Results and discussion

3.1. *CO$_2$ and $\delta^{13}C$ changes over the Glacial/Interglacial Transition*

Changes in atmospheric CO_2 during Termination I (see Fig. 2) are characterized by an overall increase from minimum concentrations of 180 ppmv during the Last Glacial Maximum (LGM) to approximately 280 ppmv in the course of the Holocene as previously shown by Barnola *et al*. (1987) on ice core samples from Vostok. In addition, the high-resolution Taylor Dome record as well as a recent high-resolution study by Monnin *et al*. (2001) on the Dome C ice core reveal significant fine structure in the course of the transition. The CO_2 increase has taken place in certain steps closely paralleling the concurrent changes in Antarctic isotope temperatures (Fig. 2). For instance the Antarctic Cold Reversal (ACR) at 12.5–14 kyr BP (Blunier *et al*., 1997) is accompanied by an intermittent decline in CO_2 con-
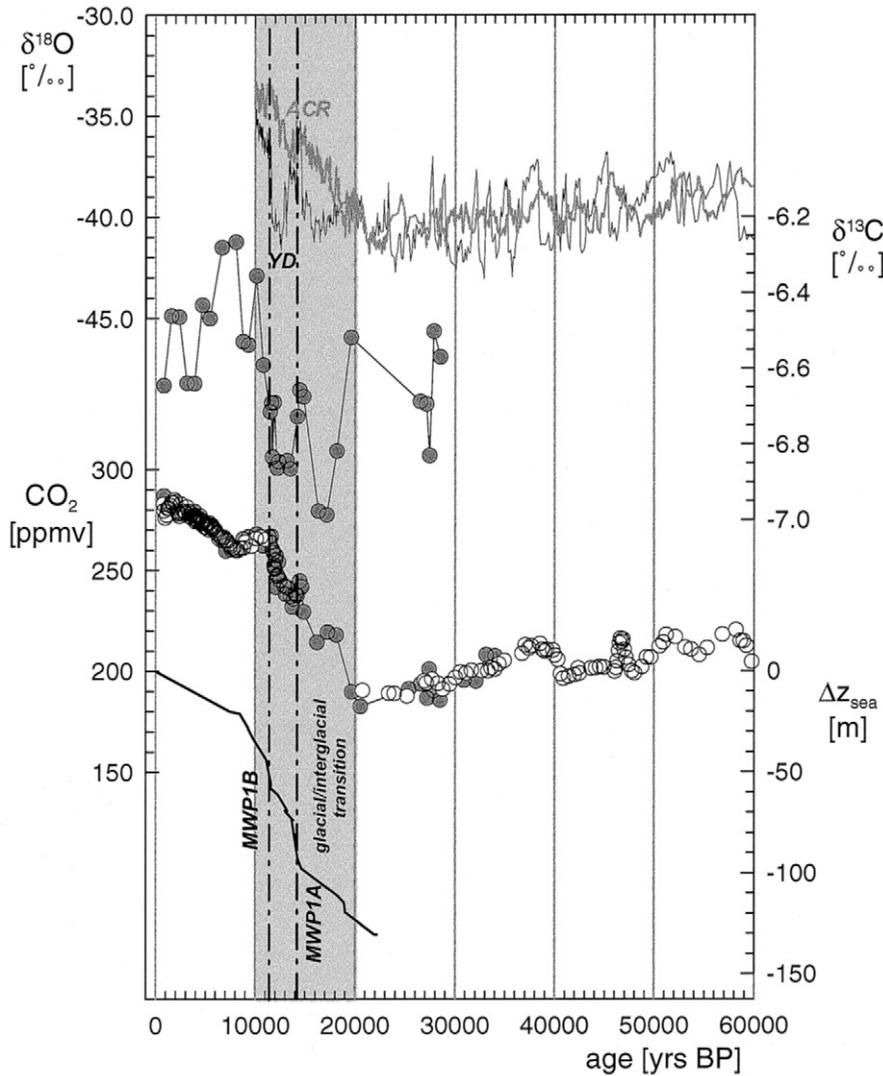
Fig. 2.   *Temporal evolution of CO₂ and δ¹³C data over the last 60000 yrs as recorded in the Taylor Dome ice core (dark grey circles derived from Fischer et al. (1999), Indermühle et al. (1999) and Smith et al. (1999) white circles from Indermühle et al. (2000) and Indermühle et al. (1999)) together with ice core climate reconstructions for Greenland (GISP2, thin black line) and Antarctica (Byrd, thick grey line) (Blunier and Brook, 2001) and the change in sea level Δz_{sea} relative to present day (Fairbanks, 1989).*

centration by a few ppmv (Fischer *et al*., 1999). Monnin *et al*. (2001) were able to show that the CO₂ increase during the first 5 kyr of the transition occurred in two phases in accordance with respective Antarctic temperature reconstructions at Dome C. The first phase shows a significantly higher CO₂ gradient than the second one, which again ended in a step increase of up to 10 ppmv just prior to the ACR.

Taking an even closer look, the high resolution CO_2 record from Taylor Dome and Vostok indicate a phase lag of the CO_2 maxima at the beginning of the last three interglacials relative to Antarctic temperature reconstructions by 600–1000 years (Fischer *et al*., 1999). While this comparison suffers from the uncertainty in the relative dating of air and ice in polar ice core records such a lag has also been found when comparing $^{36}Ar/^{40}Ar$ ratios (which most likely reflect temperature dependent changes in the thickness of the diffusive firn column) with CO_2, which are both measured on the gas archive in ice cores (Caillon *et al*., 2003). This lag implies that CO_2 is reacting on the temporal change in ocean temperature and only in return causes a climate feedback by increasing greenhouse forcing. The size of this lag is in agreement with the time scale of ocean mixing which is necessary to establish a new equilibrium in the atmosphere/ocean system.

A close relationship between CO_2 and temperature and an indication of a CO_2 lag on the order of 1000 years has also recently been found for Marine Isotope Stage 3 (Indermühle *et al*., 2000), however, the uncertainty in the ice age/gas age difference during glacial periods does not allow an unambiguous conclusion. As shown in Fig. 2 CO_2 varies by 20 ppmv on time scales of a few thousand years during this period but does not show any significant imprint of rapid climate shifts as for instance the Dansgaard-Oeschger events encountered in the northern hemisphere (Grootes *et al*., 1993; Johnsen *et al*., 1992). Note, that dating of the ice cores in Fig. 2 was accomplished by methane synchronization of Antarctic ice core records with the Greenland GISP2 ice core record (Blunier and Brook, 2001; Brook *et al*., 2000). This provides an independent check of the phase relationship between temperature and CO_2 as discussed by Indermühle *et al*. (2000) who achieved a relative dating of the Taylor Dome CO_2 record by correlation with Vostok CO_2 data. As illustrated in Fig. 2 CO_2 lags temperature around 58 and 51 kyr but leads for the maximum at 47 kyr. These variations in the phase relationship can be readily explained by the uncertainty in the synchronization as well as in the air age/ice age difference.

During MIS 3 all Antarctic ice core temperature records (Taylor Dome, (Steig *et al*., 1999); Vostok, (Jouzel *et al*., 1987; Petit *et al*., 1999); Dome Fuji, (Watanabe *et al*., 1999); Byrd, (Johnsen *et al*., 1972)) show essentially the same temporal evolution. This is also true for Termination I with exception of the Taylor Dome isotope temperature record. The latter shows a rapid rise in isotope temperature at around 15 kyr BP, resembling Greenland temperature variations in this time interval more closely. Whether this is due to spatial heterogeneity in Antarctic temperatures during the deglaciation or some artifact in the Taylor Dome ice age scale is still a matter of discussion. In summary, we conclude that temperature changes during the last glacial cycle appear to be—within the glaciological uncertainties—homogeneous all over Antarctica. In that case the temperature signal stored in the ice core records can be regarded as regionally representative for at least the Antarctic continent and most likely also for the Southern Ocean region. The ocean represents the largest carbon reservoir acting on time scales relevant for ice core records (*i.e.* 100–10000 years) and the abyssal ocean, where the majority of oceanic carbon is stored as dissolved inorganic carbon (DIC), is coupled to Southern Ocean surface waters via isopycnal transport. Therefore, the strong correlation between CO_2 and Antarctic temperatures strongly points to the Southern Ocean being the primary factor driving long-term atmospheric CO_2 changes during the last glacial cycles.

In addition to changes in the ocean, the waxing and waning of the terrestrial biosphere

caused by climate changes and variations in continental ice cover may contribute to changes in atmospheric CO_2 concentrations which should be imprinted in the carbon isotopic signature of CO_2. So far only limited data on $\delta^{13}CO_2$ from Antarctic ice cores are available. Carbon isotopic changes in our Taylor Dome data during Termination I as shown in Fig. 2 are characterized by an overall increase from an average LGM level of –6.7‰ to the mean Holocene level of –6.5‰, as has been also found in previous ice core results by Leuenberger *et al*. (1992). Generally lower isotopic values have also been documented for the LGM in studies of leaf material in macrofossil assemblages by Marino *et al*. (1992). However, these authors found $\delta^{13}C$ values to be 0.3‰ lower than in the direct atmospheric archive of Antarctic ice cores. Marino *et al*. rule out any postdepositional alteration of their organic samples. If this is the case, the difference might imply a climate dependent shift in the isotopic fractionation during carbon fixation by photosynthesis for cold climate conditions. However, in view of the lower offer of CO_2 available for photosynthesis during cold climate conditions, plants would be (if at all) expected to fractionate less against ^{13}C and accordingly $\delta^{13}C$ in plant material should be higher.

Besides this shift in $\delta^{13}C$ our Taylor Dome record represents the first data set which additionally allows to discuss the temporal evolution of this parameter in the course of the last deglaciation. As can be seen in Fig. 2 the $\delta^{13}C$ record over the transition shows two oscillations superimposed on the overall increase. The deglaciation is initiated by an 0.5‰ dip in $\delta^{13}C$ starting at 20 kyr BP followed by a rapid increase to about –6.7‰ at 14 kyr BP and an intermittent 0.2‰ lowering of $\delta^{13}C$ starting within the uncertainty in the ice age-gas age difference in parallel to the onset of the ACR but persisting about 2 kyr longer than the accompanying decline in CO_2. These variations are in temporal agreement with the results by Marino *et al*. (1992), taking the dating uncertainty and the low temporal resolution of the macrofossils study (only 4 to 5 samples during the transition) into account.

In principle the Taylor Dome data set represents the base for inverse modeling studies over Termination I comparable to the one performed by Indermühle *et al*. (1999) for the Holocene. This has not been undertaken yet, since boundary conditions imposed by other changing parameters of the global carbon cycle such as ocean circulation, biological carbon cycling in the ocean, biome composition of the terrestrial biosphere (ratio of C3 to C4 plants), air/sea gas exchange and others have to be sufficiently constrained. Although such a rigorous approach is still missing, we might at least be able to draw some semiquantitative conclusions from our data. To this end the $\delta^{13}C$ data are plotted in an isotope mixing diagram versus inverse CO_2 concentration. This representation is motivated by the carbon balance of a two component system, where carbon is added from reservoir 1 with a distinct carbon isotopic signature $\delta^{13}C_1$ (*e.g.* the terrestrial biosphere) to the reservoir which is sampled (in the case of ice cores this is the atmosphere). Accordingly the atmospheric CO_2 concentration C is

$$C = C_0 + C_1,$$

with C_0 representing the undisturbed concentrations and C_1 the difference due to carbon added from reservoir 1. For the isotopic signature $\delta^{13}C$ we find

$$C\delta^{13}C = C_0\delta^{13}C_0 + C_1\delta^{13}C_1,$$

and thus

$$\delta^{13}C = \delta^{13}C_1 + \frac{1}{C}C_0\,(\delta^{13}C_0 - \delta^{13}C_1). \tag{1}$$

As can be seen in eq. (1) $\delta^{13}C$ values are linearly dependent on the inverse CO_2 concentrations in a two reservoir system. Plotting the Taylor Dome data this way (Fig. 3) the data splits into three distinct groups according to the main climate periods covered:

• the Holocene and the LGM showing decreasing $\delta^{13}C$ values with increasing CO_2 concentrations (decreasing $1/CO_2$ values),

• the glacial/interglacial transition where $\delta^{13}C$ shows a net increase with rising CO_2 levels.

Most striking is the linear dependence of $\delta^{13}C$ *vs*. $1/CO_2$ with a y-intercept of –9.6‰ for the climatically most different periods of the LGM and the Holocene. In the case of a two component system (as described in eq. (1) above) this y-intercept could be identified with the iso-
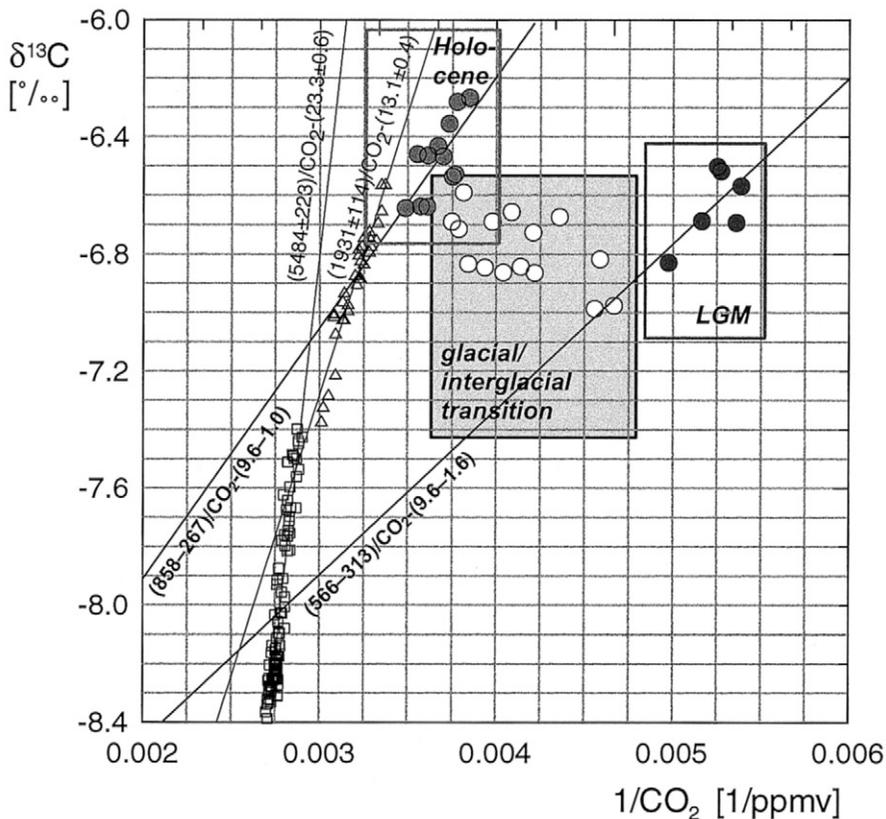

Fig. 3.   *Isotope mixing diagram for the Taylor Dome CO_2 and $\delta^{13}C$ data. Note, that the data points are grouped according to time intervals (Holocene: 10 kyr BP to present, the transition period: 20 to 10 kyr BP and the LGM: 30 to 20 kyr BP) and not according to linear relationships. Also plotted are CO_2 and $\delta^{13}C$ data over the time span 1900–1970 deduced from the Law Dome ice core (triangles) (Francey et al., 1998) and seasonally resolved data of the time interval 1990–97 from Boint Barrow (squares) (data provided by INSTAAR, University of Colorado and NOAA, CMDL, Carbon Cycle Group). The linear regression of each data subset is indicated by thin lines together with their regression parameters and respective standard errors.*

topic signature of the component added to or subtracted from the atmosphere. However, the ocean consists of various deep and surface water masses at low and high latitudes and the biosphere may be separated into various dead and living reservoirs exchanging CO_2 with the atmosphere on different time scales (see Fig. 4). Accordingly, the carbon cycle is not a two component system and a linear dependence cannot necessarily be expected. However, if we find such a linear dependence, this implies that the global carbon cycle acted in a constant mode with the relative contributions of the different participating reservoirs to the atmosphere being essentially constant. In that case the y-intercepts in Fig. 3 can be interpreted as the flux weighted mean of all components exchanging CO_2 with the atmosphere.

This effect is reflected in the size of the y-intercept of –9.6‰, which falls between the isotopic signature of the terrestrial biosphere and the ocean. Due to the permanent exchange of atmosphere and ocean, any biospheric CO_2 released will in part be taken up by the ocean which in return is replaced by CO_2 of oceanic origin as illustrated in Fig. 4. How much of the CO_2 is recycled by the ocean is dependent on the time scale of CO_2 release. For example in the case of the seasonal uptake/release of biospheric carbon the effective end member as determined according to eq. (1) for measurements performed at point Barrow, Alaska, is about –23‰, *i.e.* that of the terrestrial biosphere (Fig. 3). This implies that the ocean had virtually no time to incorporate substantial parts of the carbon taken up and released by the biosphere during summer and winter, respectively.

In contrast, CO_2 concentrations during the Holocene and the LGM change on time scales of several thousand years where the deep ocean is expected to be in equilibrium with atmospheric CO_2 (an assumption also made in the modeling study by Indermühle *et al*. (1999)). In this case a fraction x of the isotopically light CO_2 released by the biosphere is taken up by the ocean and replaced by isotopically heavier CO_2 as indicated by large arrows
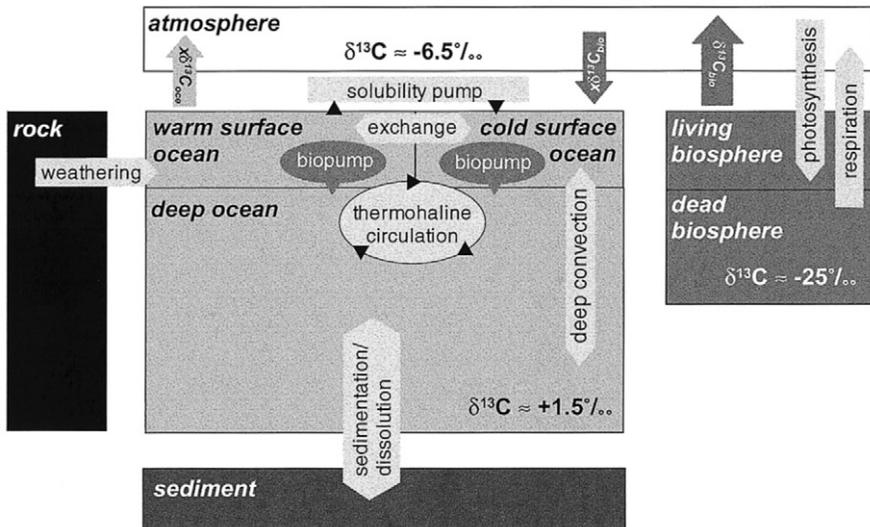

Fig. 4.   Simplified sketch of the global carbon cycle including major reservoirs and exchange processes as well as the typical carbon isotopic signature of the ocean, terrestrial biosphere and the atmosphere. Thick arrows indicate the fate of biospheric carbon released into the atmosphere and partly recycled by the ocean.

in Fig. 4. The y-intercept in Fig. 3 represents the weighted average of the isotopic signature of both the ocean and the biosphere, *i.e.*

$$(1-x)\delta^{13}C_{bio} + x\delta^{13}C_{oce} = -9.6‰. \tag{2}$$

With an effective isotopic signature of $\delta^{13}C_{oce}=-6.5‰$ and $\delta^{13}C_{bio}=-23‰$ of the ocean and the terrestrial biosphere, respectively, this results in a fraction of only 19% of biospheric CO_2 remaining in the atmosphere.

An independent estimate of this fraction can be deduced from the size of the reservoirs involved. If we assume that the whole ocean is in equilibrium with atmospheric CO_2 the fraction of additional biospheric CO_2 remaining in the atmosphere would be equal to the ratio of the carbon reservoir size of the preindustrial atmosphere (600 GtC) to total sum of the atmosphere and the ocean (app. 38000 GtC). For the uptake of additional CO_2 by the ocean the chemical buffering of the carbonate system in sea water has to be considered, which reduces the effective ocean reservoir by a factor of approximately 11.5. Using these values 15% of the extra CO_2 remain in the atmosphere which is in good agreement with the isotopic budget derived above. For the LGM, when the atmospheric carbon reservoir was significantly smaller (400 GtC) the fraction remaining in the atmosphere is reduced to about 11% (keeping both buffer factor and oceanic reservoir size constant) . This translates to an effective isotopic signature of CO_2 exchanged (y-intercept in Fig. 3) of –8.3‰, which is still well within the error limits of the regression parameters for the LGM in Fig. 3. The implications of this are twofold:

a) CO_2 variations during the LGM and the Holocene can be essentially explained by changes in the size of the terrestrial biosphere.

b) The carbon isotopic measurements on Taylor Dome ice core samples reflect true long-term variations in $\delta^{13}CO_2$, although the formal accuracy of each sample may accommodate a large spread in $\delta^{13}C$. If this would not hold, it seems to be virtually impossible to reproduce the y-intercept of –9.6‰, which has to be expected for an atmosphere/ocean carbon cycle in equilibrium

A similar semiquantitative exercise could be performed for the transition period, however, due to the only weakly defined y-intercept we refrain from doing this. Here, all we can deduce from Fig. 3 is that the biosphere is of minor importance and changes in the ocean were the most dominant factors controlling atmospheric CO_2 change and led to higher $\delta^{13}C$ with lower $1/CO_2$.

Also plotted in Fig. 3 are ice core data for the 20th century anthropogenic CO_2 increase/$\delta^{13}C$ decrease (Francey *et al*., 1998), due to combustion of fossil fuel, which is originally also of biogenic origin and carries an isotopic signature of app. –23‰. The y-intercept for this data set in Fig 3 is about –13‰, *i.e.* significantly lighter than expected for the ocean carbon reservoir to be in equilibrium with the atmosphere. As a matter of fact, the anthropogenic increase in CO_2 acts on time scales of decades, while equilibration of the ocean with the atmosphere requires a few centuries. Inserting the value of the y-intercept into eq. (2) we obtain a fraction of 39% of anthropogenic CO_2 remaining in the atmosphere. This is not such a bad guess compared to the actual value of 50% determined by carbon cycle models (Siegenthaler and Joos, 1992) considering that isotopic equilibration is faster than net uptake of CO_2, where the chemical buffering of the carbonate system is involved.

3.2. Possible factors contributing to CO_2 changes during the transition

3.2.1. The net change in CO_2 and $\delta^{13}C$

As can be seen in Fig. 3 CO_2 changes during the last glacial/interglacial transition were mainly determined by the ocean reservoir. However, significant temporal variations in $\delta^{13}C$ point to a more complex behavior of the global carbon cycle. In the following the contributions of changing physical parameters to these variations will be quantitatively assessed and potential conceptual models to explain the residual CO_2 changes as well as the temporal pattern will be discussed. The controlling factors for the glacial/interglacial CO_2 change have been recently discussed in papers by Broecker and Henderson (1998) and Sigman and Boyle (2000). While those papers try to resolve the still persistent CO_2 enigma by elaborate changes in the biological carbon pump we will additionally present another scenario based on the effect of sea-ice coverage in the Southern Ocean on the air/sea gas exchange as described by Stephens and Keeling (2000).

Both changes in the benthic $\delta^{13}C$ signature in marine sediments (Curry *et al.*, 1988) as well as estimates of changes in terrestrial biomes (Adams *et al.*, 1990) indicate an overall transfer of carbon to the terrestrial biosphere during the last deglaciation. Initial estimates differed by a factor of two, but could be improved by a reassessment by Crowley (1995). In the following we adopt the value of Crowley (1995) of app. 600 GtC for the net transfer of carbon from the atmosphere/ocean system to the terrestrial biosphere during Termination I. This translates to a net increase in atmospheric $\delta^{13}CO_2$ by dilution of this signal in the atmosphere/ocean system of

$$\Delta\delta^{13}C \approx \frac{-23\%o \cdot -600\,\text{GtC}}{(38000+600)\,\text{GtC}} = 0.36\%o,$$

and an actual decline in carbon dioxide concentrations defined by the product of this net exchange and the ratio of the atmospheric reservoir and the sum of the effective ocean carbon reservoirs and the atmosphere, *i.e.*

$$\Delta CO_2 \approx -600\,\text{GtC}\frac{600\,\text{GtC}}{(38000/11.5+600)\,\text{GtC}}\frac{280\,\text{ppmv}}{600\,\text{GtC}} = -43\,\text{ppmv},$$

where the first factor is the change in the biospheric carbon reservoir, the second the ratio of the preindustrial size of the atmosphere and the sum of atmosphere and ocean carbon stocks and the third factor the conversion factor of the atmospheric carbon stock to CO_2 concentration.

Another important physical factor is the ocean temperature controlling the solubility of CO_2 which causes a $-4.2\%/°C$ change in atmospheric CO_2 (Takahashi *et al.*, 1993). Different methods for the reconstruction of the increase of sea surface temperature during the deglaciation vary from 2°C to 5°C (CLIMAP, 1976; Guilderson, 1994). Taking into account that high latitude surface waters are close to the freezing point an average temperature change of 3°C seems to be reasonable. This implies an accompanying CO_2 change in the range of 15 to 40 ppmv (25 ppmv for a 3°C warming of SST). Additionally, the isotopic fractionation during air/sea exchange is altered by about $0.12\%o/°C$ (Mook, 1986) resulting in a $\delta^{13}C$ change of $0.24\%o$ to $0.60\%o$ for a 2 to 5°C temperature change, respectively ($0.36\%o$ for a 3°C warming).

Ocean salinity S is decreasing during the transition due to the freshwater influx con-

nected to the melting of the continental ice sheets. This freshening of ocean waters affects the solubility of CO_2 in the ocean by 10 ppmv/‰ S (Weiss, 1974). From reconstructions of the sea level change during the transition an overall salinity change of -1.4‰ could be deduced (Fairbanks, 1989). This translates to a CO_2 decrease of app. 15 ppmv, while $\delta^{13}C$ is not affected by salinity changes.

Table 1.   Summary of the effect in atmospheric CO_2 and $\delta^{13}C$ of changes in various parameters during the glacial/interglacial transition.

Process LGM→Holocene	CO_2 (ppmv)	$\delta^{13}C$ (‰)
Net change in biosphere	-43 (-32 to -97)	0.36 (0.27 to 0.80)
Increase in SST	25 (15 to 40)	0.36 (0.24 to 0.60)
Salinity decrease	-15	–
Sum	-33 (-97 to -7)	0.72 (0.51 to 1.40)
Measured	90	0.2 (0.7)

The numbers for the CO_2 effects discussed above are compiled in Table 1 showing that the net change in CO_2 and $\delta^{13}C$ amounts to -33 ppmv and $+0.72$‰, respectively. Thus, while this change in $\delta^{13}C$ is higher than the observed 0.2‰ increase of $\delta^{13}C$ from the LGM to the Holocene, the change in CO_2 concentrations leaves up to 120 ppmv unaccounted for! This gap has to be explained by changes in other parameters of the carbon cycle.

3.2.2. The temporal evolution of CO_2 and $\delta^{13}C$

Further constraints of the origin of these changes can be deduced from ice cores and high-resolution sediment records, since not only the size of the CO_2 effect has to be explained by such parameters but any scenario has also to be in agreement with the temporal evolution of the carbon cycle during the transition. The atmospheric imprint of these temporal changes are:

• a rather monotonous increase in CO_2 with intermittently reduced CO_2 levels during the ACR in close correspondence to Antarctic isotope temperatures.

• a sudden 0.5‰ drop of $\delta^{13}C$ at the start of the transition and following a 0.7‰ increase with an intermittent decrease of 0.2‰ starting at the ACR.

As indicated in Fig. 3, CO_2 concentrations during the transition are mainly determined by ocean changes and here especially by conditions in the Southern Ocean. Solubility changes caused by temperature variations must occur according to Southern Ocean temperature as reflected in Antarctic ice core isotope temperatures. The rather gradual increase in CO_2 during the transition in Fig. 2, *i.e.* from around 18 kyr BP to 10 kyr BP, supports this picture although the size of the CO_2 rise cannot be explained by solubility changes without appropriate amplification by other parameters.

In contrast, sea level changes implying salinity variations do not occur continuously over the transition but are characterized by two major melt water pulses (Fairbanks, 1989),

the first one (MWP 1A) dated between 15 and 14 kyr BP and the second one (MWP 1B) between 12 and 11 kyr BP. Keeping this in mind, salinity induced changes in atmospheric CO_2 should be focussed to these events, and most importantly start more than 3000 yr after the first rise in CO_2. The high-resolution CO_2 profile deduced by Monnin *et al.* (2001) shows a slowing of the CO_2 rise during MWP 1A. A net decline in CO_2 starts after the melt water pulse, *i.e.* during the ACR. Approximately in phase with MWP 1B, CO_2 starts to decrease into the Holocene period, however, this decline continues for another 3–4 thousand years, *i.e.* much longer than the rapid sea level change.

For the net change in the terrestrial biosphere the temporal evolution is hard to assess but most changes should occur in parallel with or after the change in sea level, when retreating ice masses allow an expansion of the terrestrial biosphere. Accordingly, major parts of the CO_2 decrease connected to the expansion of the biomass should occur in the second half of the transition. Again, no clear indication of such an effect parallel to changes in sea level can be found in the ice core records.

In order to explain the unaccounted CO_2 changes during glacial/interglacial transitions various models have been proposed. In the following the major ideas proposed in these models are discussed and compared to our CO_2 and $\delta^{13}C$ data. The close correspondence of CO_2 concentrations and Antarctic temperatures and especially the virtual lack of significant imprints of rapid North Atlantic climate variations (*i.e.* the Dansgaard-Oeschger events or the Younger Dryas, (Johnsen *et al.*, 1992)) in the CO_2 records rules out a significant influence of deep water formation in the North Atlantic on atmospheric CO_2 levels. Other hypotheses for the CO_2 change derive from the sudden release of carbon after flooding of vast shelf areas during sea level increase, which have been exposed during glacial times (Broecker, 1982). Again, these models are in contradiction with the timing of the CO_2 increase, which shows a rapid rise at the start of the transition, thus long before significant sea level change set in.

Another factor which has a long-term influence on the carbon budget is the dissolution/sedimentation of $CaCO_3$ (Archer and Maier-Reimer, 1994). Two hypotheses have been brought forward, how this process may lower glacial pCO_2 in the ocean: A shift of carbonate fixation from coral reefs to the deep ocean at sea level low stand would require a higher carbonate concentration hence a lower pCO_2 of the ocean. This option would be connected to sea level change and cannot explain the timing of the CO_2 increase. The second option invokes a change in the rain ratio between calcite and organic carbon in the sea, which would lead to enhanced calcite dissolution in sediments and thus lower pCO_2. This option in principle may explain the time scale of CO_2 change over the transition, however, the origin of the change in the rain ratio remains obscure. Assuming a constant weathering flux of Ca^{2+} into the ocean, any such change in $CaCO_3$ dissolution in the deep ocean requires a substantial change in the depth of the lysocline during climate variations. Although an increase in the lysocline depth has been observed in Pacific and Indian Ocean sediment records (Farrell and Prell, 1989) the size of this change (globally averaged about 500 m) may only explain a CO_2 change up to 20 ppmv (Broecker and Peng, 1993). Unfortunately, no time record of Ca^{2+} input into the ocean is available to date, however, an increased Ca^{2+} flux is expected if it exists parallel to the retreat of the continental ice sheets imposing a timing problem with the observed CO_2 change. Additionally, while carbonate compensation is in principle able to explain CO_2 changes on time scales of millennia it seems to be too insensitive to explain the strong correlation of CO_2 and Antarctic isotope temperature during the last four glacial

cycles.

This leaves us with hypotheses located in the Southern Ocean with possible forcing factors being dependent on SST and which are able to create the correct amplification factor of the temperature induced solubility changes. Frequently discussed are changes in the biological pump in the Southern Ocean (Volk and Hoffert, 1985), where nowadays nutrient utilization is not complete. However, enhanced biological carbon fixation during cold periods would require an equivalent increase in biological productivity and an increase in net export of carbon into the deep ocean which is not unambiguously observed in ocean sediments (Broecker and Peng, 1993). Modeling studies (*e.g.* Knox Ennever and McElroy ,1985) indicate that enhanced respiration of organic carbon would drive deep ocean waters close to anoxia, which is not observed in the sediment records. Furthermore, taking the influence of sediment respiration on carbonate compensation into account, Archer *et al*. (2000) were able to show that a CO_2 change due to productivity change without a shift in the rain ratio is approximately compensated by the sediment response. Even if there is a net increase in productivity we need a reason for the strengthened biological cycling. While most nutrients are abundant in the recent Southern Ocean, iron may possibly limit biological productivity in this region as *e.g.* indicated by recent iron fertilization experiments (Watson *et al*., 2000). The close connection of Antarctic isotope temperatures and the dust content in Antarctic ice cores points to aeolian dust input which might supply iron to Southern Ocean surface waters. Again, there exist considerable timing problems relative to the CO_2 increase. For instance late glacial dust concentrations in the Vostok record are reduced long before CO_2 starts to increase at the onset of the transition which would call for a dust threshold to explain this behavior (Broecker and Henderson, 1998). Even more important seems to us that dust is and remains low in the course of the transition while CO_2 continues to rise for at least 8000 yrs. To account for that, Broecker and Henderson (1998) hypothesize an impact of iron supply to nitrogen fixation. With a residence time of nitrate in the ocean on the order of a few thousand years, a net increase in the nitrate inventory of the ocean could then expand the time scale of an iron induced effect on CO_2. Similar to the carbonate compensation this time scale expansion, however, appears to be incompatible with the rather close response of CO_2 concentrations to Southern ocean temperature during MIS 3 (Indermühle *et al*., 2000) and the ACR (Fischer *et al*., 1999).

Another factor has been recently discussed in a modeling study by Stephens and Keeling (2000). They investigated the influence of the Southern Ocean sea ice coverage, which significantly reduces the air/sea gas exchange during glacial times. They show that a decrease of the ice-free area south of the Antarctic Polar Front (APF, today located at 55°S) to about $0.16 \cdot 10^{12} \, m^2$ would lead to a CO_2 decrease of about 70 ppmv. Most importantly this theory would not call for a substantial change in paleoproductivity or a serious reduction in deep water oxygen levels (Stephens and Keeling, 2000). Such an extent of sea ice coverage during the LGM can be well accommodated. Sediment reconstructions (Cooke and Hays, 1982; Crosta *et al*., 1998) point to an average extent of winter sea ice coverage during the Holocene to approximately 55°S. Summer sea ice is harder to assess but is believed to have a minor impact on CO_2 (Stephens and Keeling, 2000). While the box model study by Stephens and Keeling (2000) only treats the size of the CO_2 effect, the sea ice hypothesis seems to be favorable to explain the temporal evolution of atmospheric CO_2 as well. At first order sea ice coverage is expected to be directly dependent on southern ocean temperature and would be in

agreement with the gradual increase of CO_2 and its strong correlation to temperature. However, what is the effect of sea ice on the isotopic signature of CO_2? As calculated by Stephens and Keeling (2000) a decrease in sea ice cover during the transition would lead to an 0.9‰ decrease in $\delta^{13}C$, where the majority is expected to occur at the start of the sea ice retreat. While this effect is significantly larger than the 0.5‰ drop in $\delta^{13}C$ at the start of the transition, it is at least in temporal agreement with the evolution of the Taylor Dome $\delta^{13}C$ record. Accordingly, the initial drop in $\delta^{13}C$ may be attributed to the decline in sea ice and the following net increase in $\delta^{13}C$ can be quantitatively explained by the other factors discussed above (*i.e.* SST and net transfer of carbon into the biosphere).

We conclude, that sea ice coverage can act as a strong amplifier of CO_2 changes during deglaciation and as a damping mechanism during glaciation. From all hypotheses discussed in this chapter the sea ice hypothesis seems to be most compatible with the ice core and sediment records and clearly justifies further modeling and observational studies in this direction.

4. Implications

As illustrated in the discussion above the interpretation of the changes in the global carbon cycle during the glacial/interglacial transition still lacks a quantitative explanation. A net change in the biological productivity has so far failed to account for the observed changes in CO_2 together with $\delta^{13}C$ (Archer *et al*., 2000) and cannot easily be connected to the observed temporal variations in these parameters during the transition. In contrast recent box model studies (Gildor and Tziperman, 2001; Hausman and McElroy, 1999; Stephens and Keeling, 2000; Toggweiler, 1999) were able to account for the full size of the CO_2 change solely invoking changes in physical parameters such as sea ice coverage or deep sea ventilation and temperature, which may be more directly related to Southern Ocean temperature. However box model results have been questioned because of their small sensitivity on surface ocean conditions in low latitudes compared to complex ocean circulation models (Archer *et al*., 2000), which in return may overestimate diapycnal mixing in the ocean.

To date models only describe the net difference between the steady states of the carbon cycle during the Holocene and the LGM but inverse modeling as demonstrated for the Holocene by Indermühle *et al*. (1999) has not been performed for the transition. To accomplish such transient modeling, we have to compile all the available observational evidence of carbon cycle changes preserved in various marine and terrestrial climate archives. Using these data sets we hope to be able to model temporal scenarios of the carbon cycle during Termination I which will help to decide which factor or which combination of the various factors discussed above determine both the size and the temporal evolution of the observed CO_2 changes and which are in agreement with the overall change in the climate system.

Even without such model studies we were able in this study to identify the most important driving factors for carbon cycle changes during the last 30000 years using the complementary information from atmospheric CO_2 and $\delta^{13}C$ archived in Antarctic ice cores. While during the transition changes the ocean/atmosphere system appears to be most important for CO_2 changes, it appears to be the biosphere which dominates CO_2 variations during stable climate periods such as the Holocene and the LGM. During these periods the size of the terrestrial biomass was able to vary considerably (on the order of hundreds of GtC). Although

the climatic conditions between Holocene and LGM are most different, the carbon cycle acted in a comparable mode. The intimate coupling of the atmospheric CO_2 level with the size of the terrestrial biosphere also implies that the biosphere plays a crucial role in the future development of the anthropogenic rise in atmospheric CO_2. This calls for the use of coupled carbon cycle models which include both the temporal development of the ocean and of the terrestrial biosphere to predict future CO_2 levels and thus future anthropogenic warming (Cox *et al.*, 2000).

Acknowledgments

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