



## Atmospheric $\delta^{13}\text{CO}_2$ and its relation to $p\text{CO}_2$ and deep ocean $\delta^{13}\text{C}$ during the late Pleistocene

P. Köhler,<sup>1</sup> H. Fischer,<sup>1,2</sup> and J. Schmitt<sup>1,2</sup>

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[1] The ratio of the stable carbon isotopes of atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{CO}_2$ ) contains valuable information on the processes which are operating on the global carbon cycle. However, current  $\delta^{13}\text{CO}_2$  ice core records are still limited in both resolution and temporal coverage, as well as precision. In this study we performed simulations with the carbon cycle box model BICYCLE with special emphasis on atmospheric  $\delta^{13}\text{CO}_2$ , proposing how changes in  $\delta^{13}\text{CO}_2$  might have evolved over the last 740,000 years. We furthermore analyze the relationship between atmospheric  $\delta^{13}\text{CO}_2$ ,  $p\text{CO}_2$ , and deep ocean  $\delta^{13}\text{C}$  of dissolved inorganic carbon (DIC) ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in both our modeling framework and proxy records (when available). Our analyses show that mean ocean and deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  are mainly controlled by the glacial/interglacial uptake and release of carbon temporarily stored in the terrestrial biosphere during warmer climate periods. In contrast glacial/interglacial changes in  $p\text{CO}_2$  and  $\delta^{13}\text{CO}_2$  represent mainly a mixture of ocean-related processes superimposed on the slow glacial/interglacial change in terrestrial carbon storage. The different processes influencing atmospheric  $\delta^{13}\text{CO}_2$  largely compensate each other and cancel all variability with frequencies of  $1/100 \text{ kyr}^{-1}$ . Large excursions in  $\delta^{13}\text{CO}_2$  can a priori be expected, as any small phase difference between the relative timing of the dominant and opposite sign processes might create large changes in  $\delta^{13}\text{CO}_2$ . Amplitudes in  $\delta^{13}\text{CO}_2$  caused by fast terrestrial uptake or release during millennial-scale climate variability depend not only on the amount of transferred carbon but also on the speed of these changes. Those which occur on timescales shorter than a millennium are not detectable in  $\delta^{13}\text{CO}_2$  because of gas exchange equilibration with the surface ocean. The  $\delta^{13}\text{CO}_2$  signal of fast processes, on the other hand, is largely attenuated in ice core records during the firnification and gas enclosure. We therefore suggest to measure  $\delta^{13}\text{CO}_2$  with priority on ice cores with high temporal resolution and select times with rather fast climatic changes.

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### 1. Introduction

[2] Our understanding of the natural variability in the global carbon cycle is steadily increasing. Especially for the late Pleistocene both new data sets and model experiments were published recently. The atmospheric  $\text{CO}_2$  record was now measured in ice cores over the last 800 kyr [Petit *et al.*, 1999; Siegenthaler *et al.*, 2005; Lüthi *et al.*, 2008]. A carbon cycle box model applied transiently in time gave some quantitative interpretation of glacial/interglacial (G/IG) changes in the carbon cycle over these times [Köhler and Fischer, 2006]. More complex approaches, such as Earth system models of intermediate complexity or ocean circulation models provide improved insight into the processes

controlling atmospheric  $\text{CO}_2$  in the past [e.g., Brovkin *et al.*, 2007; Menviel *et al.*, 2008a, 2008b; Parekh *et al.*, 2008; Schmittner and Galbraith, 2008; Tschumi *et al.*, 2008]. The interpretation of simulation results always depends on the accuracy by which processes are implemented in the models and, thus, a more complex understanding will emerge the more feedback processes are included. However, for the very long timescales of several glacial cycles we still have to rely on the faster and simpler approach of box models.

[3] A variable which could improve our interpretation capability of changes in the global carbon cycle is the ratio of stable carbon isotopes  $\delta^{13}\text{C}$ . It gives another boundary condition on temporal variability in the carbon cycle which has to be met by modeling experiments and could further constrain which processes are responsible for observed variations in atmospheric  $\text{CO}_2$ . Isotopic fractionation is associated with any biological, chemical, or physical process, thereby enriching/depleting  $^{13}\text{C}$  relative to  $^{12}\text{C}$ . In general, reaction rates involving the light isotope  $^{12}\text{C}$  are greater than those involving the heavy isotope  $^{13}\text{C}$ , thus leading to an enrichment of  $^{13}\text{C}$  in the source, and to a depletion of  $^{13}\text{C}$  in

<sup>1</sup>Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany.

<sup>2</sup>Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland.

the sink of any exchange process [e.g., *Zeebe and Wolf-Gladrow*, 2001]. For example, terrestrial photosynthesis fractionates  $\delta^{13}\text{C}$  by  $-5\%$  to  $-27\%$ , depending on environmental conditions and photosynthetic pathway [*Lloyd and Farquhar*, 1994]. As a consequence,  $\delta^{13}\text{C}$  values of the global vegetation are at present about  $18\%$  lower than  $\delta^{13}\text{CO}_2$  of the atmosphere [*Scholze et al.*, 2003]. For the ocean/atmosphere system, the isotopic fractionation during air/sea gas exchange leads to  $\delta^{13}\text{C}$  values of dissolved inorganic carbon (DIC) ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in the surface waters of  $1.5\%$  to  $2\%$  and to  $\delta^{13}\text{C}$  of atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{CO}_2$ ) which is about  $8\%$  lighter [*Kroopnick*, 1985; *Mook*, 1986; *Gruber et al.*, 1999]. Marine organisms use carbon from the DIC pool to build hard shells (calcification) and organic matter (photosynthesis). While photosynthesis at the ocean surface fractionates  $\delta^{13}\text{C}$  by about  $-10\%$  to  $-20\%$  relative to  $\text{CO}_2$  (aq) [*Goericke and Fry*, 1994], the incorporation of C in carbonate shells increases the  $\delta^{13}\text{C}$  of the shells relative to  $\text{HCO}_3^-$  by about  $2\%$  [*Mook*, 1986]. Both organic carbon as well as carbonate shells are exported to the deep ocean, where most of them are remineralized or dissolved. This so-called biological pump establishes gradients with depth in both DIC and  $\delta^{13}\text{C}_{\text{DIC}}$ , which are counterbalanced by ocean circulation, bringing DIC rich waters, depleted in  $^{13}\text{C}$ , back to the surface.

[4] The atmosphere exchanges carbon with both the land and the ocean, therefore atmospheric  $\delta^{13}\text{CO}_2$  contains valuable information on the dynamics of both the marine and the terrestrial carbon cycle. Furthermore,  $\delta^{13}\text{CO}_2$  can, as the atmospheric  $\text{CO}_2$  concentration itself, in principle be measured directly in Antarctic ice cores. However, precise  $\delta^{13}\text{CO}_2$  measurements on polar ice cores turned out to be one of the largest analytical challenges in paleoclimate research, the resolution and quality of the data sets to date are recently improved but they are still limited to the Holocene and the last G/IG transition [*Leuenberger et al.*, 1992; *Indermühle et al.*, 1999; *Smith et al.*, 1999; *Elsig et al.*, 2009; *Lourantou et al.*, 2010].

[5] Because measuring  $\delta^{13}\text{CO}_2$  in ice core samples is a demanding and time consuming task it would help experimentalists to have an a priori estimate where large fluctuations in the  $\delta^{13}\text{CO}_2$  record can be expected. This might help to constrain the temporal resolution desirable to capture the most important features of an ice core  $\delta^{13}\text{CO}_2$  record. Accordingly we used the well tested BICYCLE model in this study in a similar setting as before [*Köhler and Fischer*, 2006] with the special focus on long-term changes in  $\delta^{13}\text{CO}_2$  over the last 740 kyr. In order to test the model performance we compare the simulations in a first step briefly with atmospheric  $\text{CO}_2$  as before, but more importantly with benthic  $\delta^{13}\text{C}$  reconstructions from sediment cores from the deep Pacific, which are presumably a recorder of past variations on  $\delta^{13}\text{C}_{\text{DIC}}$ . The importance of different physical and biogeochemical processes, such as ocean circulation, marine export production, or terrestrial carbon storage, influencing all three variables (atmospheric  $\text{CO}_2$  and  $\delta^{13}\text{CO}_2$ , deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$ ) and the relationships between all of them will be discussed in detail. In addition, millennial-scale variability of the Dansgaard/Oeschger events and its effect

on both terrestrial carbon storage and the marine carbon cycle are investigated in sensitivity studies.

## 2. Methods

### 2.1. BICYCLE: A Box Model of the Isotopic Carbon Cycle

[6] The box model of the global carbon cycle, BICYCLE, used in this study consists of ten homogeneously mixed ocean boxes distinguishing three vertical layers and three ocean basins (Figure 1), as well as a well mixed atmospheric box and a globally averaged terrestrial biosphere consisting of seven compartments with different photosynthetic pathways and soil turnover times. Prognostic variables are carbon (DIC in the ocean),  $\delta^{13}\text{C}$  and  $\Delta^{14}\text{C}$  in all boxes, and additionally alkalinity,  $\text{PO}_4$  and  $\text{O}_2$  in the ocean boxes. The model is based on former box models of the ocean and the terrestrial biosphere, but was adapted and updated in previous studies concentrating on Termination I. It is fully described by *Köhler and Fischer* [2004] (terrestrial part) and *Köhler et al.* [2005a] (marine part).

[7] In the terrestrial part, the values of six control parameters were derived in a sensitivity analysis to match literature targets of preindustrial and LGM vegetation and soil C contents, the fraction of  $\text{C}_4$  vegetation and global net primary productivity (NPP). Out of about 10000 simulations two sets of parameter values with 12 and 14 ensemble members for the control functions meet our predefined targets. However, they differ in the way, how either  $\text{CO}_2$  fertilization ( $\text{TB}_{\text{CO}_2}$ ) or temperature changes ( $\text{TB}_{\Delta\text{T}}$ ) dominate the dynamics of the terrestrial carbon storage over time. In our standard setup (scenario CTRL) we use a realization in which  $\text{CO}_2$  fertilization is more important than temperature ( $\text{TB}_{\text{CO}_2}$ ), which seems to be more in line with global dynamic vegetation models [e.g., *Joos et al.*, 2004], but the use of the more temperature dominated controls for terrestrial C storage ( $\text{TB}_{\Delta\text{T}}$ ) will be used to analyze the potential impact of fast climate change.

[8] In the ocean, the  $\text{CaCO}_3$ , which enters the deep ocean boxes and can be accumulated in the sediments, was produced with a fixed C ratio between exported organic matter (OM) and hard shells in the surface waters ( $C_{\text{OM}}: C_{\text{CaCO}_3} = 10:1$ ).  $C_{\text{OM}}$  export at 100 m depth is prescribed for present-day to  $10 \text{ PgC}$  [e.g., *Schlitzer*, 2000], but depends locally on available macronutrients, implying a global  $\text{CaCO}_3$  export of  $1 \text{ Pg C yr}^{-1}$  similar to other applications [e.g., *Jin et al.*, 2006]. This is realized with maximum productivity (consumption of all  $\text{PO}_4$ ) in the low-latitude surface boxes. Increased export might occur in the Southern Ocean, if macronutrients are available and the proxy for iron input into the Southern Ocean suggests the stimulation of additional productivity due to iron fertilization.  $\text{CaCO}_3$  and  $C_{\text{OM}}$  are partially (20% and about 70%, respectively) dissolved or remineralized in the intermediate layers. In the deep ocean, carbonate compensation is calculated with a relaxation approach resulting in either sedimentation of  $\text{CaCO}_3$  or dissolution of sediments as a function of offset from initial (present-day)  $\text{CO}_3^{2-}$  concentrations. The timescale of the sedimentary response ( $e$ -folding time  $\tau$  of 1.5 kyr) was chosen to fit the measured relaxations of  $\text{CO}_3^{2-}$  anomalies in

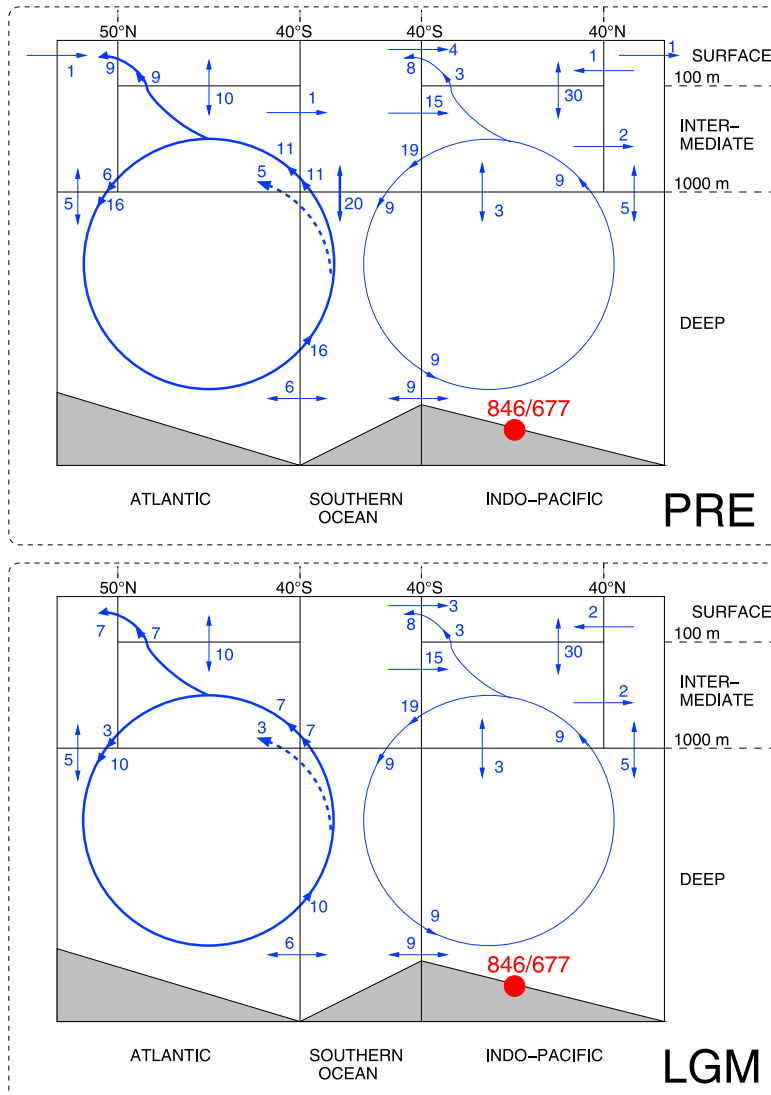
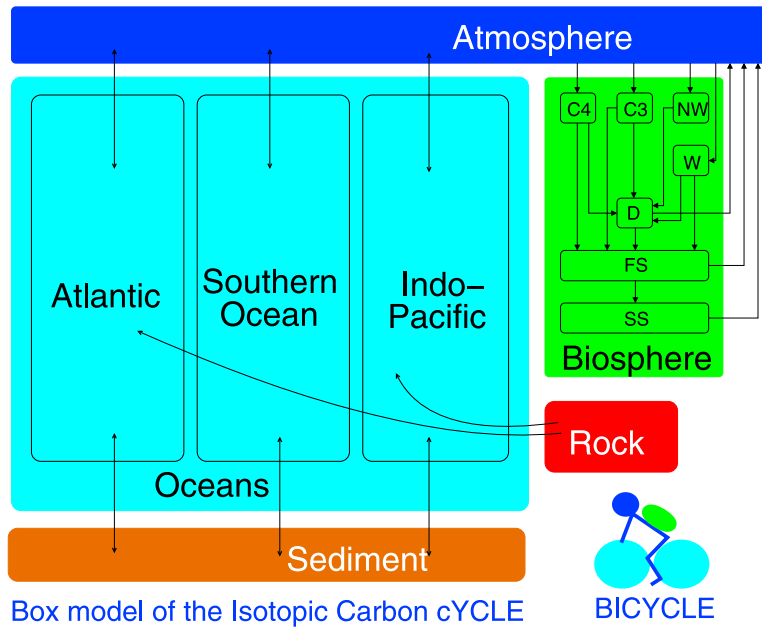


Figure 1

the deep Pacific over the last 25 kyr [Marchitto *et al.*, 2005]. A larger  $\tau$ , as suggested by some modeling studies [Archer *et al.*, 1997, 1998], would lead to longer delays in the carbonate compensation and thus to smaller glacial/interglacial amplitudes in atmospheric  $p\text{CO}_2$  (see Köhler and Fischer [2006] for sensitivity studies on  $\tau$ ), but only to very little effects for the  $^{13}\text{C}$  cycle. During sedimentation and dissolution no isotopic fractionation is assumed:  $\text{CaCO}_3$  which is added to the sediments has the same  $\delta^{13}\text{C}$  as during hard shell production at the water surface, while the dissolved sediments carry the  $\delta^{13}\text{C}$  signal of the sediment box. Organic carbon in the sediments is not considered, thus, all  $\text{C}_{\text{OM}}$  reaching the deep ocean is remineralized. For the analysis of the  $^{13}\text{C}$  cycle, a sediment box containing initially 50,000 Pg of inorganic carbon (as  $\text{CaCO}_3$ ) is introduced in each deep ocean basin (Atlantic, Southern Ocean, Indo-Pacific). The initial  $\delta^{13}\text{C}$  of the sediments (+2.75‰) is similar to the average signature of the  $\text{CaCO}_3$  produced in the surface ocean. Initial values were chosen to minimize temporal drifts in  $\delta^{13}\text{C}$  of the sediments.

[9] The present-day ocean circulation as depicted in Figure 1 was prescribed with results from the World Ocean Circulation Experiment (WOCE) [Ganachaud and Wunsch, 2000]. Assumed temporal changes in ocean circulation over time are (1) a reduced NADW formation (−40% during glacials) and subsequently slower Atlantic meridional overturning circulation (AMOC) [Meissner *et al.*, 2003]; however, we acknowledge that the precise state of the glacial circulation can still not be determined from the available proxy information [Huybers *et al.*, 2007; Lynch-Stieglitz *et al.*, 2007]; (2) a poorly ventilated glacial Southern Ocean (net vertical exchange at the LGM reduced to approximately a fourth of its preindustrial strength) deduced from  $\delta^{13}\text{C}_{\text{DIC}}$  data [Hodell *et al.*, 2003]; and (3) a closure of the Bering Strait during sea level low stands (Figure 1).

[10] Three model improvements were performed since the first publication of BICYCLE: (1) carbonate compensation is now delayed by the  $e$ -folding time  $\tau$  [Köhler and Fischer, 2006], while it was instantaneous before; (2) the introduction of sediment boxes, including  $\delta^{13}\text{C}$  calculations, was necessary for longer simulation studies focusing on the  $^{13}\text{C}$  cycle [Köhler and Bintanja, 2008]; and (3) ocean circulation was slightly revised [Köhler and Bintanja, 2008]. Previously, all of the upwelling water in the Southern Ocean was traveling through the Southern Ocean surface box. Now, 30% of the upwelling flux is immediately relocated to the intermediate box in the equatorial Atlantic (dashed lines in Figure 1). This is reasoned with the short residence time of these waters at the surface which is too short to equilibrate with the atmosphere. The revision has mainly implications

for the simulated  $\delta^{13}\text{C}_{\text{DIC}}$  in the intermediate and deep Atlantic ocean during the LGM (see section 2.3 for details).

[11] For the application presented here, BICYCLE was forced forward in time over the last 740 kyr by the use of various paleodata sets derived from ice and marine sediment cores. These proxy time series are used to prescribe temporal variations of climatic boundary conditions (sea level, sea ice coverage, ocean temperature, ocean circulation, marine export production, global mean temperature (affecting the terrestrial biosphere)). In that way, climate change is not internally calculated in our model, but prescribed externally implying a complete lack of carbon cycle-climate feedbacks in all our applications. A complete description of these data sets is found in the work by Köhler and Fischer [2006], in which the consequences of changing climate conditions on the carbon cycle and especially on atmospheric  $p\text{CO}_2$  were analyzed. Here we use the same forcing data sets, but updated the time series derived from EPICA Dome C ( $\delta\text{D}$ , iron flux) to its new age scale EDC3 [Parrenin *et al.*, 2007].

## 2.2. Simulation Scenarios

[12] Additionally to the control simulation (CTRL) we performed some simulation scenarios to analyze the importance of fast climate changes on atmospheric  $\delta^{13}\text{C}_{\text{CO}_2}$  in more detail (Table 1). These scenarios use atmospheric  $\text{CH}_4$  concentration measured throughout the last 740 kyr in the EPICA Dome C ice core [Loulergue *et al.*, 2008] as crude proxy for Northern Hemispheric temperature change ( $\Delta T_{\text{NH}}^{\text{CH}_4}$ , important for the terrestrial C dynamics). This assumption is based on the synchronicity of fast changes in  $\text{CH}_4$  and temperature proxies in Greenland ice cores throughout the last glacial cycle [North Greenland Ice Core Project members, 2004] and the strong increase in the atmospheric  $\text{CH}_4$  north-south gradient during interstadials [Dällenbach *et al.*, 2000], that points to synchronous climate changes in northern boreal wetland regions. Accordingly, the approach to use  $\text{CH}_4$  for  $\Delta T_{\text{NH}}$  is more concentrating on the timing and abruptness of Dansgaard/Oeschger events while the absolute amplitude of concurrent Northern Hemisphere temperature is probably incorrect (Figure 2a). In the control simulation without rapid climate changes  $\Delta T_{\text{NH}}$  was based on a model-based deconvolution of the LR04 benthic  $\delta^{18}\text{O}$  stack ( $\Delta T_{\text{NH}}^{\text{LR04}}$ ) [Bintanja *et al.*, 2005; Lisiecki and Raymo, 2005] which has a temporal resolution of 1–2 kyr during the time window of interest. Therefore, by switching from LR04- $\delta^{18}\text{O}$  to  $\text{CH}_4$  as forcing data set for  $\Delta T_{\text{NH}}$  we are able to analyze the impact of climate changes faster than 1 kyr on the carbon cycle.

**Figure 1.** The BICYCLE carbon cycle model. (top) Main geometry. The terrestrial biosphere contains seven globally averaged reservoirs representing  $\text{C}_4$  (turn over time  $\tau = 4$  years) and  $\text{C}_3$  ( $\tau = 5$  years) grasses, nonwoody (NW) ( $\tau = 2$  years) and woody (W) ( $\tau = 25$  years) parts of trees, detritus ( $\tau = 5$  years), and fast (FS,  $\tau = 100$  years) and slow (SS,  $\tau = 1000$  years) decomposing soil. (middle and bottom) Geometry and ocean circulation fluxes (in  $\text{Sv} = 10^6 \text{ m}^3 \text{ s}^{-1}$ ) of the oceanic module. PRE, preindustrial situation based on WOCE; LGM, assumed circulation during the LGM. The latitudinal position of the sediment cores (ODP677/846) used for comparison is indicated by the red dot. The conservation of water masses is checked and ensured for every time step. From Köhler and Bintanja [2008].

**Table 1.** Summary of Simulation Scenarios

Scenario	Characteristics	Forcing			
		TB <sup>a</sup>	$\Delta T_{\text{NH}}$ <sup>b</sup>	SST in NATL <sup>c</sup>	NADW <sup>d</sup>
S1.5K	Nearly identical to S1.5K of Köhler and Fischer [2006] <sup>e</sup>	CO <sub>2</sub>	LR04	ODP980	ODP980
CTRL	Identical to S1.5K in all aspects but with revised ocean circulation as plotted in Figure 1	CO <sub>2</sub>	LR04	ODP980	ODP980
TB+	As CTRL, but temperature control of TB is prescribed with atmospheric CH <sub>4</sub> and $\Delta T$ becomes more important for C storage on land than CO <sub>2</sub> fertilization	$\Delta T$	CH <sub>4</sub>	ODP980	ODP980
TB+SST	As TB+, but changes in SST in North Atlantic were forced by CH <sub>4</sub>	$\Delta T$	CH <sub>4</sub>	CH <sub>4</sub>	ODP980
D/O	As TB+SST, but changes in NADW were forced by CH <sub>4</sub>	$\Delta T$	CH <sub>4</sub>	CH <sub>4</sub>	CH <sub>4</sub>

<sup>a</sup>The parameterization of the forcing of the terrestrial biosphere (TB) follows either more CO<sub>2</sub> fertilization (CO<sub>2</sub>) or more temperature changes ( $\Delta T$ ), corresponding to scenarios “case I” or “TB1” and “case I” or “TB2,” respectively, in earlier publications [Köhler and Fischer, 2004; Köhler et al., 2005a].

<sup>b</sup> $\Delta T_{\text{NH}}$  (used to force changes in terrestrial C storage) calculated either out of LR04  $\delta^{18}\text{O}$  [Lisiecki and Raymo, 2005] using an ice sheet–climate model [Bintanja et al., 2005] or out of EPICA Dome C CH<sub>4</sub> [Loulergue et al., 2008].

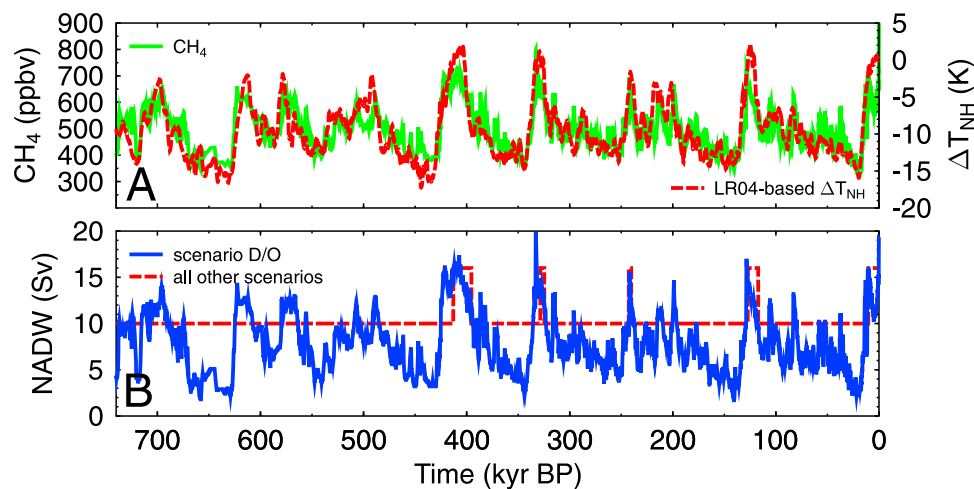
<sup>c</sup>SST in the North Atlantic is prescribed by ODP980 data [McManus et al., 1999; Wright and Flower, 2002] or by the EPICA Dome C CH<sub>4</sub>.

<sup>d</sup>Changes in NADW formation are prescribed by ODP980 data [McManus et al., 1999; Flower et al., 2000] or by the EPICA Dome C CH<sub>4</sub>.

<sup>e</sup>The only change to scenario S1.5K of Köhler and Fischer [2006] is the update of the age model of the EPICA Dome C records.

[13] We proceed in three steps, introducing first CH<sub>4</sub> as proxy for  $\Delta T_{\text{NH}}$  (scenario TB+). In this scenario the set of parameter values forcing the terrestrial part of the C cycle was switched to those depending more on Northern Hemispheric temperature than CO<sub>2</sub> (TB <sub>$\Delta T$</sub> ). This switch in the forcing was performed to constrain the potential range of variability to be recorded in  $\delta^{13}\text{CO}_2$ . In a second step (scenario TB+SST)  $\Delta T_{\text{NH}}^{\text{CH}_4}$  is also taken to force SST changes in the North Atlantic surface box. In the third step (scenario D/O) those temperature changes were also used as prognostic driver of the strength of the NADW formation (Figure 2b). Consequently, the NADW formation is reduced from its interglacial strength (16 Sv) down to 2 Sv in scenario D/O, while it varies only between 10 and 16 Sv in all

other simulations. Switching NADW formation between high interglacial and low glacial states in all but the D/O scenario is based on a threshold in benthic  $\delta^{18}\text{O}$  in ODP980 in the North Atlantic [Köhler and Fischer, 2006]. The proposed strength of the NADW in the scenario D/O should explore the range of potential impacts on  $\delta^{13}\text{CO}_2$  (including nearly complete shutdowns of the AMOC) but should not be understood as a suggestion how ocean circulation changed over time. The latter two scenarios (TB+SST, D/O) are designed to quantify the impact of fast climate changes on the marine carbon cycle. We understand these last scenarios as a zero-order case study, because the assumed changes in the SST and oceanic overturning are completely parameterized. Our approach is limited in various ways. For



**Figure 2.** (a) Atmospheric CH<sub>4</sub> from EPICA Dome C [Loulergue et al., 2008] and Northern Hemispheric temperature change  $\Delta T_{\text{NH}}$  deconvolved from LR04 benthic  $\delta^{18}\text{O}$  by ice sheet modeling [Bintanja et al., 2005]. Both are used alternatively as proxy to force our simulation (see text and Table 1 for details). (b) Assumed changes in NADW formation and subsequent strength of the AMOC.

**Table 2.** Comparison of C Reservoirs and  $\delta^{13}\text{C}$  Signature for Preindustrial and LGM Conditions for the Present Control Run and the Previous Run<sup>a</sup>

	Carbon					$\delta^{13}\text{C}$ (‰)			
	PRE			LGM		PRE		LGM	
	GLODAP	CTRL	GBC05	CTRL	GBC05	CTRL	GBC05	CTRL	GBC05
Ocean <sup>b</sup>									
Surface North Atlantic	2105	2111	2092	2133	2113	1.45	1.56	1.49	1.63
Surface equatorial Atlantic	2011	1987	1971	2065	2101	1.67	1.76	1.63	1.79
Surface Southern Ocean	2163	2152	2140	2188	2257	1.39	1.40	1.78	1.66
Surface equatorial Indo-Pacific	1963	1986	1976	2062	2109	1.38	1.42	1.57	1.56
Surface North Pacific	2252	2178	2167	2288	2339	1.52	1.57	1.51	1.45
Intermediate equatorial Atlantic	2143	2224	2177	2257	2207	0.49	0.76	<b>0.80</b>	<b>1.52</b>
Intermediate equatorial Indo-Pacific	2185	2202	2196	2263	2333	0.41	0.42	0.75	0.66
Deep Atlantic	2189	2233	2211	2347	2095	0.55	0.66	<b>0.18</b>	<b>0.81</b>
Deep Southern Ocean	2253	2250	2234	2549	2586	0.52	0.57	-0.64	-0.50
Deep Indo-Pacific	2317	2343	2332	2550	2603	0.08	0.10	-0.48	-0.44
Mean ocean	2249	2268	2253	2436	2438	0.39	0.44	-0.05	0.08
Atmosphere <sup>c</sup>		263	267	178	179	-6.61	-6.55	-6.60	-6.59

<sup>a</sup>For the preindustrial ocean DIC data from GLODAP (corrected for anthropogenic C) [Key *et al.*, 2004] are also shown. Note that the LGM in CTRL shows values for 21 kyr B.P. (time with  $p\text{CO}_2$  minima), while the LGM in GBC05 shows those for 20 kyr B.P. (as published by Köhler *et al.* [2005a]). Bold numbers in  $\delta^{13}\text{C}$  highlight the main differences and our reason for changing the circulation scheme. PRE, preindustrial; CTRL, present control run; GBC05, previous run [Köhler *et al.*, 2005a].

<sup>b</sup>Carbon as DIC ( $\mu\text{mol kg}^{-1}$ ).

<sup>c</sup>Carbon as  $p\text{CO}_2$  ( $\mu\text{atm}$ ).

example, changes in SST have no influence on the circulation scheme, prescribed changes in ocean circulation are operating instantaneously without time delay and do not change ocean temperature. These details are better captured in general circulation models, which contain the respective physics of the ocean.

### 2.3. Model Validation

[14] We briefly evaluate here, how the model performance was modified as consequence of the three model improvements (Table 2). We therefore compare DIC and  $\delta^{13}\text{C}_{\text{DIC}}$  of all oceanic reservoirs for the CTRL run and our previous application [Köhler *et al.*, 2005a, Tables 1 and 3] (labeled GBC05 hereafter) for preindustrial (PRE) and LGM climates. For the preindustrial ocean, DIC is furthermore compared with recent GLODAP measurements, which were corrected for anthropogenic C input [Key *et al.*, 2004].

[15] For the preindustrial situation, nearly all DIC values of GLODAP and our two simulations differ by less than  $20 \mu\text{mol kg}^{-1}$ . Differences are only larger in the equatorial intermediate Atlantic (box 6,  $\sim 80 \mu\text{mol kg}^{-1}$ ) and deep Atlantic (box 8,  $\sim 50 \mu\text{mol kg}^{-1}$ ), which is probably the consequence of the revised overturning cell in the Atlantic ocean. The differences between CTRL and GBC05 at the LGM are between 20 and  $70 \mu\text{mol kg}^{-1}$  for individual reservoirs, nearly negligible for the mean ocean, but about  $350 \mu\text{mol kg}^{-1}$  in the deep Atlantic. Thus, the shortcut of upwelling waters via the intermediate box to the North Atlantic shifts the storage of C in the deep ocean slightly from the Indo-Pacific to the Atlantic. Even with these variabilities in DIC, atmospheric  $p\text{CO}_2$  in both simulations is very similar for both climates (PRE, 263 versus  $267 \mu\text{atm}$  and LGM, 178 versus  $179 \mu\text{atm}$ ).

[16] Differences in  $\delta^{13}\text{C}_{\text{DIC}}$  are less than 0.1‰ (PRE) and 0.2‰ (LGM) in all boxes apart from the boxes 6 and 8. Here,  $\delta^{13}\text{C}_{\text{DIC}}$  in CTRL is 0.3‰ (PRE) and 0.7‰ (LGM)

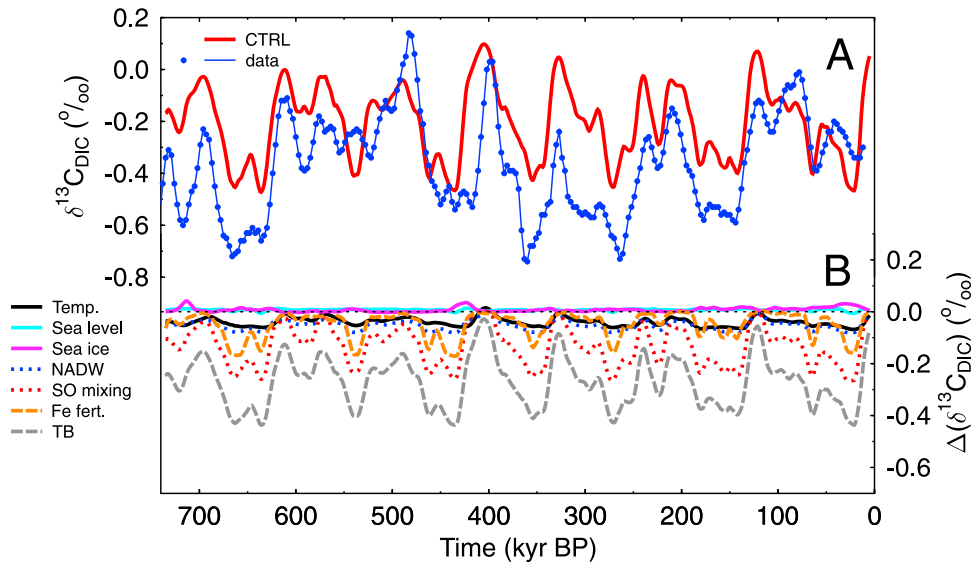
lower in the intermediate Atlantic, and 0.1‰ (PRE) and 0.6‰ (LGM) in the deep Atlantic than in GBC05. These differences, especially in the LGM, were our motivation for the revision of the ocean circulation scheme. The DIC in GBC05 in the intermediate Atlantic has a  $\delta^{13}\text{C}_{\text{DIC}}$  typical for surface, not for intermediate waters ( $\sim 1.5\text{‰}$ ), and with 0.8‰ the deep Atlantic was not in line with LGM reconstructions [Curry and Oppo, 2005]. However, we acknowledge that our box model by definition cannot resolve all major aspect of  $\delta^{13}\text{C}_{\text{DIC}}$ , e.g., vertical gradients within the Atlantic ocean.

[17] In summary, we believe that the refinements of the model performed over the years were necessary improvements to include processes relevant for long-term investigations of the  $^{13}\text{C}$  cycle.

## 3. Results and Discussion

### 3.1. Simulated Deep Pacific $\delta^{13}\text{C}_{\text{DIC}}$ and the Sediment Record

[18] For a validation of our simulation results with paleo-data sets we concentrate first on the well established records of  $\delta^{13}\text{C}$  measured in benthic foraminifera derived from deep sea cores. Some benthic species are known to record a  $\delta^{13}\text{C}$  signal which is offset from that of DIC in the surrounding waters by  $\sim 0.3\text{‰}$ – $0.4\text{‰}$  due to the phytodetritus or Mackensen effect [Mackensen *et al.*, 1993]. For the main paleoreconstructions of  $\delta^{13}\text{C}$  used here the time series can be assumed to be unaffected by the phytodetritus effect (thus  $\delta^{13}\text{C} = \delta^{13}\text{C}_{\text{DIC}}$ ) as discussed in detail elsewhere [Raymo *et al.*, 2004]. We focus only on changes in the deep Pacific Ocean as recorded in the sediment cores ODP677 ( $1^\circ\text{N}$ ,  $84^\circ\text{W}$ , 3461 m water depth [Shackleton *et al.*, 1990; Raymo *et al.*, 1997]) and ODP846 ( $3^\circ\text{S}$ ,  $91^\circ\text{W}$ , 3307 m water depth [Mix *et al.*, 1995a; Raymo *et al.*, 2004]). In the deep eastern Pacific, where our Pacific sites are located, the horizontal and vertical gradients in  $\delta^{13}\text{C}_{\text{DIC}}$  in the modern ocean are



**Figure 3.** (a) Simulated  $\delta^{13}\text{C}_{\text{DIC}}$  for the deep Indo-Pacific Ocean box for scenarios CTRL and data-based reconstruction. (b) Contribution of major processes to variations of deep Indo-Pacific  $\delta^{13}\text{C}_{\text{DIC}}$ : changes in ocean temperature (temp.), sea level, gas exchange through sea ice coverage (sea ice), strength of the NADW formation (NADW), Southern Ocean vertical mixing (SO mixing), iron fertilization in the Southern Ocean (Fe fert.), and carbon storage on land (TB). All simulation results are 9 kyr running means.

very small [Kroopnick, 1985]. A similar uniform distribution of  $\delta^{13}\text{C}_{\text{DIC}}$  exists in large parts of the glacial Pacific [Boyle, 1992] (see also  $\delta^{13}\text{C}_{\text{DIC}}$  data compilation in Figure 5 of Köhler and Bintanja [2008]). Therefore, observed changes are assumed to be representative of basin wide variations, which we can resolve with our coarse box model. The records are presented on the orbital tuned age scale derived for ODP677 by Shackleton *et al.* [1990]. They were interpolated to a uniform 3 kyr spacing and smoothed with a three-point running mean, as performed already in the compilation of Raymo *et al.* [2004]. For the comparison with our basin wide simulation results we will rely on the average of both sediment cores.

[19] Simulated  $\delta^{13}\text{C}_{\text{DIC}}$  is smoothed with 9 kyr running mean to make it comparable with the benthic  $\delta^{13}\text{C}_{\text{DIC}}$  reconstructions. Reconstructed deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  varies between +0.2‰ and -0.8‰. The data range (absolute maximum minus absolute minimum) in CTRL is with 0.7‰ somewhat smaller than the range (1.0‰) spanned by the data set (Figure 3a). This difference in absolute range is caused by the underlying 400 kyr cycle found in  $\delta^{13}\text{C}_{\text{DIC}}$  reconstructions, which is (by definition) missing in the simulations, and which makes a point-to-point comparison of simulations and data impossible [Mix *et al.*, 1995b; Wang *et al.*, 2004; Köhler and Bintanja, 2008]. One hypothesis on its explanation is based on the variability of the hydrological cycle and weathering rates [Wang, 2007], which are both not included in our modeling approach and thus differences in this frequency domain between simulations and paleoreconstructions are expected. The general pattern on time-scales up to 100 kyr (timing of strong changes in  $\delta^{13}\text{C}_{\text{DIC}}$ , G/IG amplitudes) is reproduced reasonably well in our

simulations. The mean G/IG amplitudes in  $\delta^{13}\text{C}_{\text{DIC}}$  over the last 740 kyr in CTRL and the reconstruction agree within their standard derivation (CTRL,  $0.45\text{‰} \pm 0.11\text{‰}$ ; data,  $0.53\text{‰} \pm 0.07\text{‰}$ ).

[20] The processes being mainly responsible for the simulated dynamics in deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  were identified by a factorial analysis (Figure 3b and Table 3). It is based on differences between CTRL and simulations in which the one process in question is shut off. Because  $\text{CaCO}_3$  compensation is active in this factorial analysis the contributions of the individual processes include the partial effect of the sediment/ocean interaction. This factorial analysis is a first-order estimate of individual contributions which neglects nonlinear interacting effects. Terrestrial carbon storage is most important for low glacial deep ocean  $\delta^{13}\text{C}_{\text{DIC}}$ , because terrestrial carbon depleted in  $^{13}\text{C}$  was released into the atmosphere during these times (-0.44‰ at the LGM). This is followed by Southern Ocean processes: (1) reduced vertical mixing (-0.26‰ at the LGM) leads to less glacial upwelling of DIC depleted in  $^{13}\text{C}$  and an accumulation of isotopically light carbon in the abyss and (2) enhanced marine export production through iron fertilization (-0.16‰ at the LGM) brings more isotopically light carbon to the deep ocean. The contributions from sea ice, sea level, temperature and NADW formation strength (AMOC) to changes in deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  are very small ( $\leq \pm 0.1\text{‰}$  each throughout the last 740 kyr).

[21] In our control simulation the mean ocean  $\delta^{13}\text{C}_{\text{DIC}}$  is 0.43‰ lower at the LGM than during preindustrial times (Table 3), which is slightly smaller than changes in the deep Pacific ocean (-0.47‰). This agrees within the uncertainties with data-based estimates of 0.32‰–0.46‰ [Curry *et al.*,

**Table 3.** Summary of the Contribution of Different Processes to the Simulated Changes in Atmospheric  $p\text{CO}_2$  and  $\delta^{13}\text{CO}_2$  and Deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  and Mean Ocean  $\delta^{13}\text{C}_{\text{DIC}}$  During Termination I<sup>a</sup>

Process	Atmosphere $\Delta(\delta^{13}\text{CO}_2)$ (‰)	Atmosphere $\Delta(p\text{CO}_2)$ ( $\mu\text{atm}$ )	Deep Pacific $\Delta(\delta^{13}\text{C}_{\text{DIC}})$ (‰)	Mean Ocean $\Delta(\delta^{13}\text{C}_{\text{DIC}})$ (‰)
Lower ocean temperatures	-0.49	-30	-0.08	-0.07
Smaller terrestrial carbon storage	-0.44	+12	-0.44	-0.44
Lower sea level	+0.06	+14	-0.01	+0.02
Weaker NADW formation	+0.10	-24	-0.08	-0.08
Enhanced marine export production	+0.19	-28	-0.16	-0.10
Larger sea ice cover (gas exchange)	+0.18	+12	+0.03	+0.03
Higher Southern Ocean stratification	+0.31	-46	-0.26	-0.16
Summed-up changes	-0.09	-90	-1.00	-0.80
Simulated changes in CTRL	+0.00	-85	-0.47	-0.43
Nonlinearities <sup>b</sup>	-0.09	+5	+0.53	+0.40

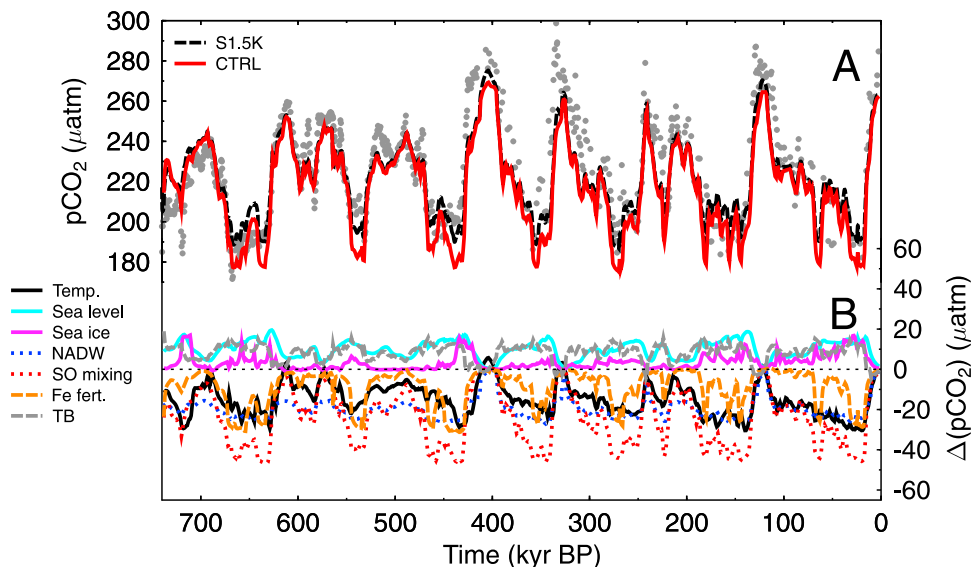
<sup>a</sup>The contributions are calculated by subtracting results with the process in question switch off (all but one) from the control run.

<sup>b</sup>Nonlinearity values are sum minus CTRL.

1988; Duplessy *et al.*, 1988]. Shackleton [1977] was the first who proposed that the change in mean ocean  $\delta^{13}\text{C}_{\text{DIC}}$  was caused by the injection of  $^{13}\text{C}$ -depleted carbon from terrestrial pools and could be used to infer the magnitude of the changes in the land storage. Bird *et al.* [1994] used 0.32‰ as best guess for the rise in mean oceanic  $\delta^{13}\text{C}_{\text{DIC}}$  from the LGM to present and calculated an increase in terrestrial carbon storage over Termination I of 250–650 PgC. To test this hypothesis independently we investigate if and how much other processes contribute to the changes in the mean ocean  $\delta^{13}\text{C}_{\text{DIC}}$  by an additional simulation in which the terrestrial carbon pools were kept constant. Indeed, only about 10% of the G/IG changes in mean ocean  $\delta^{13}\text{C}_{\text{DIC}}$  (0.035‰ in case of Termination I) are not of terrestrial or-

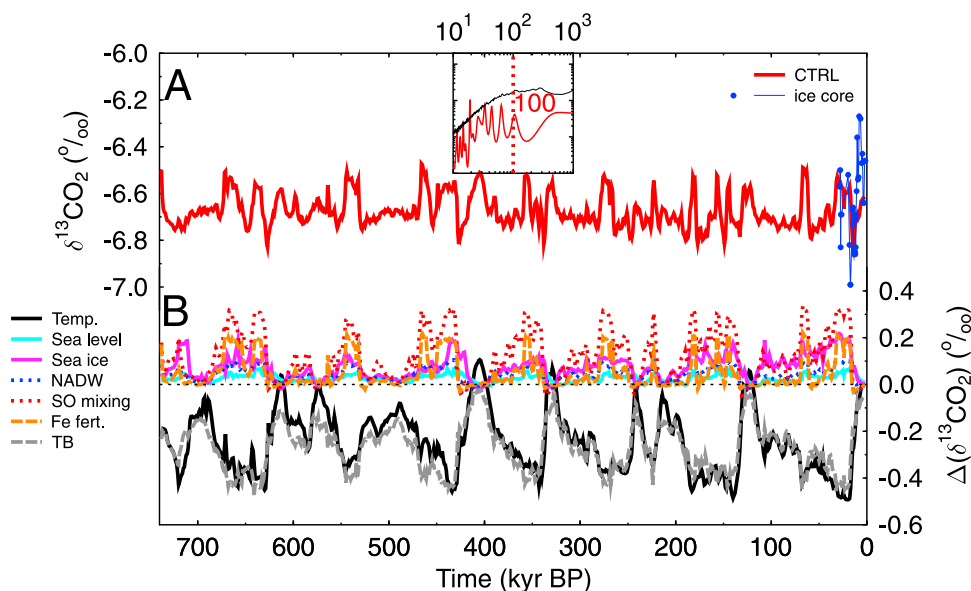
igin, mainly caused by the changing C content of the atmosphere and the ocean.

[22] A comparison of our analysis for  $\delta^{13}\text{C}_{\text{DIC}}$  with other simulation studies is restricted to Brovkin *et al.* [2007]. In all other glacial studies, which are available to us, no results for  $\delta^{13}\text{C}_{\text{DIC}}$  are discussed, e.g., Crucifix [2005] analyzed only the effect of a changed ocean overturning on the distribution of carbon isotopes within the ocean. Brovkin *et al.* [2007] simulate a reduced terrestrial C storage of 540 PgC at the LGM responsible for a drop in mean ocean  $\delta^{13}\text{C}_{\text{DIC}}$  of 0.4‰, in line with our results. In their study enhanced marine export production increases the vertical gradient in  $\delta^{13}\text{C}_{\text{DIC}}$  by up to 0.2‰, while sea level change has no im-



**Figure 4.** Simulated and measured atmospheric carbon dioxide. (a) Recent (CTRL (this study)) and previous (S1.5K [Köhler and Fischer, 2006]) control simulations.  $\text{CO}_2$  data from Vostok [Petit *et al.*, 1999] on the orbitally tuned age scale [Shackleton, 2000] and EPICA Dome C data [Siegenthaler *et al.*, 2005; Lüthi *et al.*, 2008] on the gas age scale of the EDC3 dating [Loulergue *et al.*, 2007; Parrenin *et al.*, 2007]. (b) Contribution of major processes to variations in atmospheric  $p\text{CO}_2$ ; see caption of Figure 3 for details.





**Figure 5.** (a) Simulated atmospheric  $\delta^{13}\text{CO}_2$  for scenarios CTRL and Taylor Dome  $\delta^{13}\text{CO}_2$  ice core data [Smith *et al.*, 1999]. The inset shows maximum entropy spectral analysis (MESA) of  $\delta^{13}\text{CO}_2$  in CTRL with black line showing the 99% confidence level. Labels on top of the plot show the length of the periods in years. (b) Contribution of major processes to variations in atmospheric  $\delta^{13}\text{CO}_2$ ; see caption of Figure 3 for details.

impact on  $\delta^{13}\text{C}_{\text{DIC}}$ , which is again in line with our results (Table 3).

[23] In summary G/IG changes in deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  are reproduced in our model reasonably well, providing important constraints on the representativeness of our long-term terrestrial carbon cycle changes in our model and the uptake of additional carbon in the ocean.

### 3.2. Atmospheric $p\text{CO}_2$ and $\delta^{13}\text{CO}_2$ During the Last 740 kyr

[24] Both  $p\text{CO}_2$  and  $\delta^{13}\text{CO}_2$  time series are closely related to each other and understanding  $\delta^{13}\text{CO}_2$  dynamics is not possible without investigations on  $p\text{CO}_2$ . Accordingly, we start with a short repetition of our simulation results for atmospheric  $p\text{CO}_2$  to illustrate the representativeness of our model results compared to ice core measurements and to provide estimates of the influence of individual processes in the global carbon cycle in the past. An in-depth description of simulated and measured atmospheric carbon dioxide was previously published by Köhler and Fischer [2006].

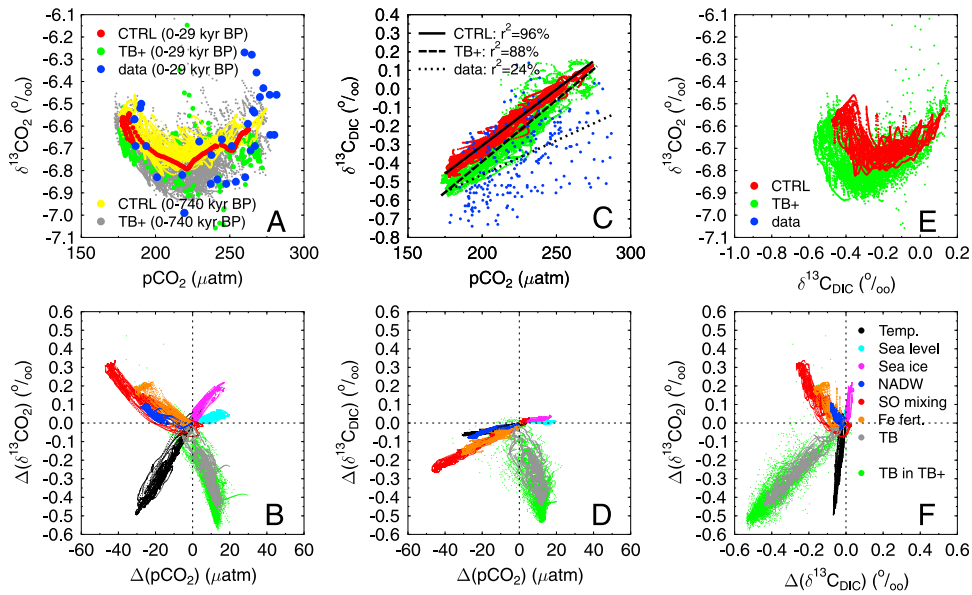
[25] Simulated  $p\text{CO}_2$  in CTRL varies between its glacial values of about 180  $\mu\text{atm}$  and its maximum during interglacial of about 280  $\mu\text{atm}$ . The simulated  $p\text{CO}_2$  in CTRL during peak glacial times are about 10  $\mu\text{atm}$  lower than in our previous model runs (scenario S1.5K of Köhler and Fischer [2006]) leading to 10  $\mu\text{atm}$  larger G/IG amplitudes (Figure 4a), mainly related to the change in the Southern Ocean hydrography in our model. This glacial offset counterbalances the effect of a time delayed carbonate compensation (which reduces G/IG amplitudes in  $p\text{CO}_2$ ). Our results here are therefore for Termination I very similar to those published by Köhler *et al.* [2005a].

[26] In CTRL, atmospheric  $\delta^{13}\text{CO}_2$  is very similar during glacial maxima and the following full interglacial (Figure 5a). However, during the transition from a glacial to an interglacial state  $\delta^{13}\text{CO}_2$  drops by 0.2‰ to 0.3‰ before it regains previous values. These dynamics of minimum  $\delta^{13}\text{CO}_2$  for intermediate  $p\text{CO}_2$  values are clearly illustrated in a scatterplot (Figure 6a) and fit to the general behavior seen in the ice core data from Taylor Dome [Smith *et al.*, 1999], however, the range of  $\delta^{13}\text{CO}_2$  is about twice as large in the measurements than in the simulations for scenario CTRL.

[27] Throughout the last 740 kyr simulated atmospheric  $\delta^{13}\text{CO}_2$  (Figure 5a) fluctuates with subglacial frequency between  $-6.8\text{‰}$  and  $-6.5\text{‰}$  (CTRL). In a spectral analysis (inset in Figure 5a) no significant components with periods around 100 kyr are found, which is remarkable, because this frequency is found in most paleoclimatic records of the late Pleistocene [Hays *et al.*, 1976], including atmospheric  $\text{CO}_2$  (and even deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$ ) and in the records which force BICYCLE forward in time.

[28] A factorial analysis equivalent to that shown for benthic  $\delta^{13}\text{C}_{\text{DIC}}$  above was performed to identify which processes contribute to the changes in atmospheric  $p\text{CO}_2$  and  $\delta^{13}\text{CO}_2$  (Figures 4b and 5b and Table 3) in our model.

[29] 1. The process being most important for lowering glacial atmospheric  $\delta^{13}\text{CO}_2$  is the ocean temperature leading to a reduction at the LGM of  $-0.49\text{‰}$ . Ocean temperature is one process, which influences  $\delta^{13}\text{CO}_2$  and  $p\text{CO}_2$  in a similar manner: reduced temperatures lead to a high oceanic carbon uptake (atmospheric  $p\text{CO}_2$ ,  $-30 \mu\text{atm}$  at the LGM), preferable of the heavier isotope, thus depleting  $\delta^{13}\text{CO}_2$  and reducing  $p\text{CO}_2$  at the same time.



**Figure 6.** (a) Scatterplot of atmospheric  $p\text{CO}_2$  and  $\delta^{13}\text{CO}_2$  of simulations and data from the Taylor Dome ice core data over the last 29 kyr. (b) Contribution of individual processes in a similar scatterplot to Figure 6a over the whole simulation period. (c) Scatterplot of atmospheric  $p\text{CO}_2$  and deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  of simulations and sediment data over the whole simulation period. (d) Contribution of individual processes in a similar scatterplot to Figure 6c. (e) Scatterplot of deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  and atmospheric  $\delta^{13}\text{CO}_2$  of simulations over the whole simulation period. (f) Contribution of individual processes in a similar scatterplot to Figure 6d. See caption of Figure 3 for details on the different processes. The legend in Figure 6e is also valid for Figure 6c, and that in Figure 6f is also valid for Figures 6b and 6d.

[30] 2. Second most important for the dynamic of  $\delta^{13}\text{CO}_2$  is the terrestrial carbon storage. The release of about 500 PgC of  $^{13}\text{C}$ -depleted terrestrial carbon (with  $\delta^{13}\text{C}$  between  $-20\text{‰}$  and  $-25\text{‰}$ ) results in a drop in  $\delta^{13}\text{CO}_2$  by  $0.44\text{‰}$  in the LGM and a rise in  $p\text{CO}_2$  by only  $12 \mu\text{atm}$ .

[31] 3. Changes in sea level are nearly neutral for  $\delta^{13}\text{CO}_2$ . Its small effect of  $+0.06\text{‰}$  for the LGM is connected with the 3% higher salinity, which leads to an outgassing and a rise of  $p\text{CO}_2$  by  $14 \mu\text{atm}$ .

[32] 4. Within BICYCLE an ocean with a weaker AMOC stores more carbon ( $\Delta p\text{CO}_2 = -24 \mu\text{atm}$  at the LGM). This results from the balance of carbon uptake in the region of the NADW formation and carbon release in the Southern Ocean, where the circulation of the AMOC comes back to the surface [Mikaloff-Fletcher *et al.*, 2007]. The effect of the AMOC on  $\delta^{13}\text{CO}_2$  is an increase at the LGM of  $+0.10\text{‰}$  caused by less upwelling of carbon-enriched deep waters (depleted in  $\delta^{13}\text{C}_{\text{DIC}}$ ) in the Southern Ocean.

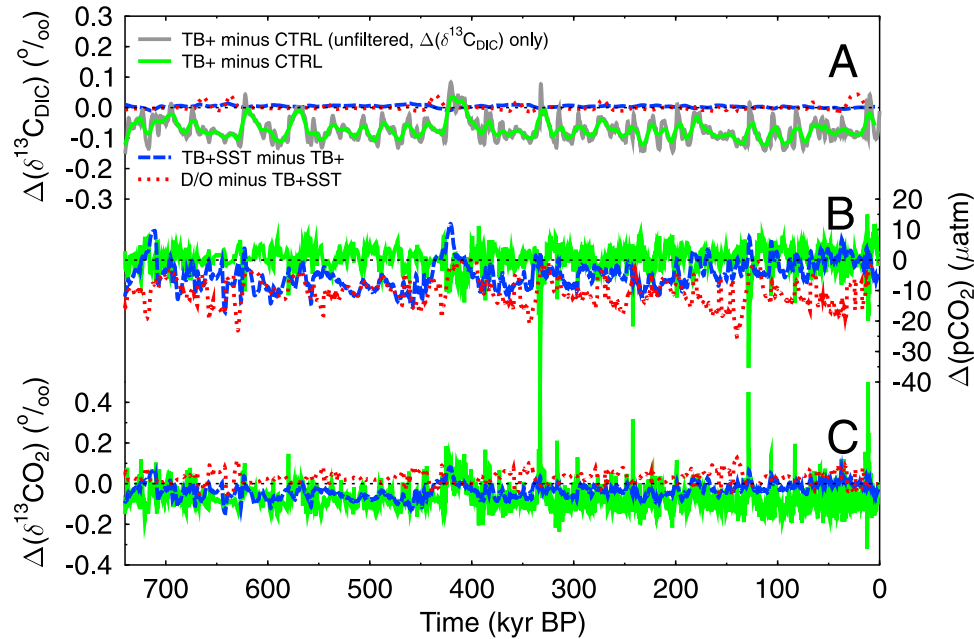
[33] 5. An enhanced glacial marine export production, stimulated by additional aeolian iron input into the Southern Ocean, leads to a rise in  $\delta^{13}\text{CO}_2$  by  $+0.19\text{‰}$  and a drop in  $p\text{CO}_2$  by  $28 \mu\text{atm}$  at the LGM. Export of organic matter rises from present  $10.0 \text{ Pg C yr}^{-1}$  to  $12.5 \text{ Pg C yr}^{-1}$  at the LGM. Organic carbon is depleted in  $^{13}\text{C}$  (e.g.,  $\delta^{13}\text{C}$  between  $-20\text{‰}$  and  $-30\text{‰}$  [Goericke and Fry, 1994]); consequently DIC of the surface waters becomes enriched in  $^{13}\text{C}$  and so  $\text{CO}_2$  of the atmosphere.

[34] 6. A larger sea ice cover at the LGM reduces the gas exchange. It was shown [Köhler and Fischer, 2006] that sea

ice in the north and in the south has opposing effects on atmospheric  $\text{CO}_2$  because they block the gas exchange in either a sink region (north) or a source region (south) for atmospheric  $\text{CO}_2$  [Mikaloff-Fletcher *et al.*, 2007]. It was furthermore analyzed, that in the present model configuration the gas exchange effects of sea ice in the north dominate in our model over that in the south resulting in a  $p\text{CO}_2$  rise of  $12 \mu\text{atm}$  at the LGM. Accordingly, larger glacial sea ice reduces the oceanic carbon uptake. As mentioned earlier, the isotopic fractionation during gas exchange is temperature-dependent with preferential uptake of  $^{13}\text{C}$  during cold temperatures. A reduction of the gas exchange at the cold high latitudes implies less gas exchange during cold conditions and therefore less uptake of  $^{13}\text{C}$ , leading consequently to a rise in  $\delta^{13}\text{CO}_2$  of  $+0.18\text{‰}$  during the LGM.

[35] 7. The process having the largest positive impact on glacial  $\delta^{13}\text{CO}_2$  ( $+0.31\text{‰}$  at the LGM) and at the same time the largest negative impact on  $p\text{CO}_2$  ( $-46 \mu\text{atm}$  at the LGM) is the stratification in the Southern Ocean. The underlying principles are the same as for a reduced AMOC: less vertical exchange during glacials brings less deep waters enriched in DIC and depleted in  $^{13}\text{C}$  to the surface. Consequently, the DIC of the surface waters become progressively enriched in  $^{13}\text{C}$  (i.e., increasing the vertical gradient in  $\delta^{13}\text{C}_{\text{DIC}}$  in the ocean), thus increasing also atmospheric  $\delta^{13}\text{CO}_2$  via gas exchange.

[36] Altogether, the dynamics in the simulated atmospheric  $p\text{CO}_2$  and  $\delta^{13}\text{CO}_2$  can be understood in the context of our modeling exercise. Marine processes, mainly those



**Figure 7.** Additional contributions of fast climate change scenarios. See Table 1 for details. (a) The  $\delta^{13}\text{C}_{\text{DIC}}$  of the deep Indo-Pacific. (b) Atmospheric  $p\text{CO}_2$ . (c) Atmospheric  $\delta^{13}\text{CO}_2$ . All simulation results in Figure 7a (apart from the unfiltered one) are 9 kyr running means; in Figures 7b and 7c unfiltered data are shown.

responsible for the depth gradient in  $\delta^{13}\text{C}_{\text{DIC}}$  in the water column (biological pump and ocean circulation) compensates the effects of temperature and terrestrial light carbon on atmospheric  $\delta^{13}\text{CO}_2$ , consequently leading to a lack in 100 kyr periodicity.

### 3.3. Relationships Between Atmospheric $p\text{CO}_2$ , $\delta^{13}\text{CO}_2$ , and Deep Pacific $\delta^{13}\text{C}_{\text{DIC}}$

[37] If we now analyze in detail, which processes are controlling atmospheric  $p\text{CO}_2$ ,  $\delta^{13}\text{CO}_2$  and deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  at the same time some interesting conclusions can be drawn (Table 3). Apart from sea ice coverage (with sea level being neutral), all processes lead to a lower glacial  $\delta^{13}\text{C}_{\text{DIC}}$  in the deep ocean. Hence, deep ocean  $\delta^{13}\text{C}_{\text{DIC}}$  in effect integrates constructively the process operating over the G/IG cycles. This very much contrasts with the atmosphere, for which  $\delta^{13}\text{CO}_2$  is dominated by four (if one includes sea ice) processes with comparable magnitudes of impact, but differing in sign (two negative, two positive). Thus, no clearly expressed G/IG variations in  $\delta^{13}\text{CO}_2$  are expected. However, any large excursions in  $\delta^{13}\text{CO}_2$  (in either direction) are not only possible, but a priori expected, as any small phase difference between the relative timing of the dominant and oppositely sign processes may create short-lived, transient changes in  $\delta^{13}\text{CO}_2$ . Note that some of these transient changes in Figure 5 may be due to real phase differences in carbon cycle changes, while others may be artifacts caused by an imperfect synchronicity of the time-scales of the individual proxy records used to force BICYCLE forward in time.

[38] Apart from the terrestrial C storage all processes influence in-phase  $p\text{CO}_2$  and  $\delta^{13}\text{C}_{\text{DIC}}$ , meaning they either

increase or decrease both at the same time. If plotted pairwise together in a scatterplot (Figure 6c) deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  and atmospheric  $p\text{CO}_2$  are in the modeling world strongly coupled and linearly related ( $r^2 = 96\%$  for CTRL). Thus, deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  has the potential to be used as a predictor for  $p\text{CO}_2$  for times without ice core measurements. However, in reality (if ice core  $\text{CO}_2$  and benthic  $\delta^{13}\text{C}_{\text{DIC}}$  are plotted against other) their relationship is blurred ( $r^2 = 24\%$ ), mainly because of the underlying 400 kyr cycle in benthic  $\delta^{13}\text{C}_{\text{DIC}}$ , but probably also due to a mismatch of the individual age scales.

### 3.4. Fast Climate Changes

[39] In our model atmospheric  $p\text{CO}_2$  fluctuates on millennial timescales with amplitudes smaller than  $10 \mu\text{atm}$  if fast climate changes and fast changes in terrestrial carbon storage (scenario TB+) are simulated (Figure 7). Only for very few events peak amplitudes in  $p\text{CO}_2$  are up to  $35 \mu\text{atm}$ . Assuming furthermore also fast changes in the marine carbon cycle (scenarios TB+SST and D/O) shifts the simulated  $p\text{CO}_2$  throughout the simulation period to lower values. In scenario D/O this is caused by the on average slower AMOC.

[40] In scenario TB+ the data range in the scatterplot of  $\delta^{13}\text{CO}_2$  and  $p\text{CO}_2$  is extended to values as low as  $-7.1\%$ , similar to the measurements in the Taylor Dome ice core (Figure 6a). A point-to-point comparison of simulated and measured data over Termination I is of limited value, as assumed changes in our scenarios were not chosen to optimize any fit to the Taylor Dome data. We admit that for the present study a poor fit of the simulations and the measurements over Termination I exists, because we did not

implement in our time-dependent forcing all abrupt climate changes in detail, but we were interested in the principle behavior of the system. However, the relative dating of different forcing factors (e.g., warming in the north and the south) is important to be able to compare simulated  $\delta^{13}\text{CO}_2$  with measurements. This misfit is based on the design of our simulations scenarios, was expected and has therefore no consequences for our general conclusions. For more details on Termination I, please see Köhler *et al.* [2005a] and Lourantou *et al.* [2010]. There, it is shown that the w shape pattern of  $\delta^{13}\text{CO}_2$  between 20 and 10 kyr B.P. might have been caused by an initial decrease in  $\delta^{13}\text{CO}_2$  caused by the resumed Southern Ocean ventilation and reduced marine export production, which is followed by variability mainly caused by terrestrial C uptake and release during the Bølling/Allerød–Younger Dryas–Early Holocene climate variability.

[41] Large amplitudes in  $\delta^{13}\text{CO}_2$  on the order of 0.5‰ occur at 333, 129 and 11 kyr B.P. (Figure 7c). A consideration of fast climate changes in the ocean (scenarios TB+SST and D/O) leads only to small additional changes in  $\delta^{13}\text{CO}_2$  (<0.1‰). Furthermore, the effects of both processes nearly compensate each other (Figure 7c).

[42] Simulated deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  is only very weakly (<0.05‰) affected by fast changes in the marine carbon cycle (scenarios TB+SST and D/O) (Figure 7a). However, if the land uptake and release of C is fast (TB+) an additional variability of the order of 0.1‰ is introduced. This additional variability between TB+ and CTRL is due the chosen parameter set in TB+ which favors  $\text{C}_4$  over  $\text{C}_3$  grasses during the LGM and which then leads to a higher  $\delta^{13}\text{C}$  value of the terrestrial biosphere in TB+ than in CTRL and as consequence to lower oceanic  $\delta^{13}\text{C}_{\text{DIC}}$  values.

[43] How can we understand the importance of fast terrestrial C uptake/release on  $\delta^{13}\text{CO}_2$ ? According to the concept of the bipolar seesaw [Stocker and Johnsen, 2003] the AMOC is reorganized during Dansgaard/Oeschger climate fluctuations [Johnsen *et al.*, 1992; EPICA Community Members, 2006]. If the AMOC weakens, temperatures in the North Atlantic region and over large parts of the northern continents drop by 5–20 K [Lang *et al.*, 1999; Knutti *et al.*, 2004]. In a study with the LPJ state-of-the-art vegetation model [Köhler *et al.*, 2005b] the tree line in the northern high latitudes shifts southward during these cold temperatures and isotopically light terrestrial carbon is released to the atmosphere. Furthermore, peak-to-peak amplitudes in atmospheric  $\delta^{13}\text{CO}_2$  caused by land carbon release of up to 150 PgC during AMOC weakening were as big as –0.25‰.

[44] In the results presented here, the contribution of the marine carbon cycle to fast variability in  $\delta^{13}\text{CO}_2$  is rather small. We like to stress that our model may have deficiencies in appropriately simulating the overall response of the marine carbon cycle to fast climate changes because of missing ecological processes and coarse spatial resolution. Other studies with more complex models find much larger changes in the marine export production during millennial-scale climate variability [Schmittner, 2005; Menviel *et al.*, 2008a; Schmittner and Galbraith, 2008]. The most recent study by Menviel *et al.* [2008a], which uses the LOVECLIM model, simulates a 130 PgC release from land during an

AMOC shutdown and the time delayed C uptake of 100 PgC in the ocean resulting in a +20  $\mu\text{atm}$  peak in  $p\text{CO}_2$ . Both findings are in line with our simulation results: more C is stored in the ocean with a slowing of the AMOC, and less C is stored on land. However, the consequences of fast AMOC variability or Dansgaard/Oeschger events for atmospheric  $\delta^{13}\text{CO}_2$  are so far not covered in the other studies and can therefore not be compared here.

[45] A transient simulation with the Bern2.5D model was mimicking the Younger Dryas (YD) cold event by an AMOC shutdown [Marchal *et al.*, 1998]. In that model the AMOC shutdown (with constant terrestrial C storage) led to a rise in  $\delta^{13}\text{C}_{\text{DIC}}$  in North Atlantic surface waters by 1.5‰ (changes in atmospheric  $\delta^{13}\text{CO}_2$  were not shown), partially caused by both reduced overturning and smaller marine export production.

[46] In a model intercomparison study on carbon cycle–climate feedbacks for the 21st century all but one of the eleven models exhibited stronger sensitivities to climate warming for land C storage than for ocean C storage [Friedlingstein *et al.*, 2006]. Under the assumption that future warming is a specific case of fast climate change, these stronger terrestrial sensitivities are in line with our findings.

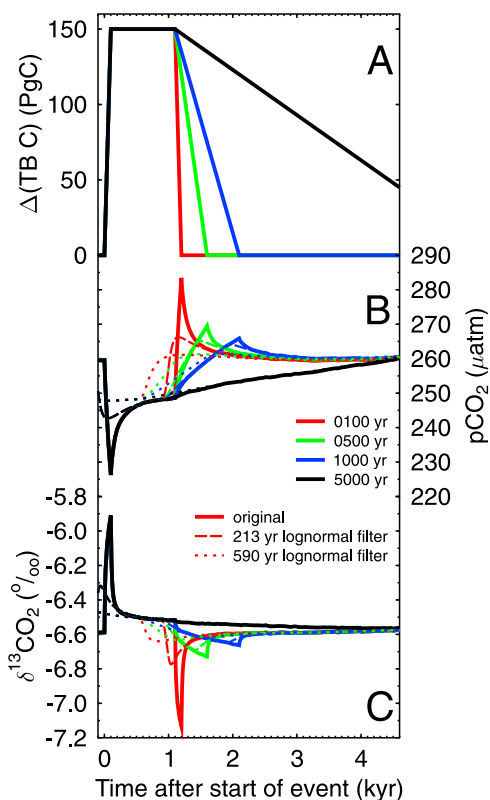
### 3.5. Timescales of Carbon Exchange Processes

[47] With some additional simulations we investigated the influence of the speed of fast climate change (stadials to interstadials and vice versa) on the carbon cycle (Figure 8). Terrestrial carbon uptake of 150 PgC over 100 years is followed by a stable period of 1 kyr and then by a gradual release of 150 PgC over 100 and more (up to 5000) years. The initial  $\delta^{13}\text{CO}_2$  peak of +0.62‰ caused by the terrestrial uptake of isotopically light carbon is reduced to less than a fifth (+0.11‰) after only 200 years. For the following C release the amplitudes vary from –0.62‰ (100 years) over –0.21‰ (500 years) and –0.14‰ (1000 years) to zero (5000 years). The effect is small to nondetectable in slow climate transitions. Attenuation is less important for  $p\text{CO}_2$  than for  $\delta^{13}\text{CO}_2$  because the  $p\text{CO}_2$  amplitudes depend on net ocean uptake which is buffered by the carbonate system (for details see Zeebe and Wolf-Gladrow [2001]), while for  $\delta^{13}\text{CO}_2$  the amplitude is reduced by the much faster air-sea gas exchange with the surface ocean.

[48] In addition to this timescale dependency inherent to the carbon exchange processes between ocean and atmosphere, gas samples in ice cores contain (due to the continuous bubble close-off process in the firn) air with a certain age distribution rather than a single age. This gas age distribution is a function of local conditions at the ice core site and is calculated with firnification models [Schwander *et al.*, 1993; Spahni *et al.*, 2003]. For EPICA Dome C it can be approximated with a lognormal function (Figure 9):

$$y = \frac{1}{x \cdot \sigma \cdot \sqrt{2\pi}} \cdot e^{-0.5 \left( \frac{\ln(x) - \mu}{\sigma} \right)^2}, \quad (1)$$

with gas age  $x$  in years. We chose for simplicity  $\sigma = 1$ , which leads to an expected mean gas age of  $E = e^{\mu-0.5}$ . With  $E_{\text{PRE}} = 213$  years and  $E_{\text{LGM}} = 590$  years given by the model



**Figure 8.** (a) Simulation of terrestrial carbon uptake of 150 PgC in 100 years, followed after 1 kyr by the release of 150 PgC within 100, 500, 1000, and 5000 years and effects on (b) atmospheric  $p\text{CO}_2$  and (c)  $\delta^{13}\text{CO}_2$ . The terrestrial biosphere fractionates  $\delta^{13}\text{C}$  during carbon uptake by 16‰, typical for LGM conditions [Scholze *et al.*, 2003; Köhler and Fischer, 2004]. Solid lines represent original results. Dashed and dotted lines represent after filtering with a lognormal function with mean gas age distribution of 213 years (PRE) and 590 years (LGM), respectively, to mimic amplitude attenuation during gas enclose in the ice core.

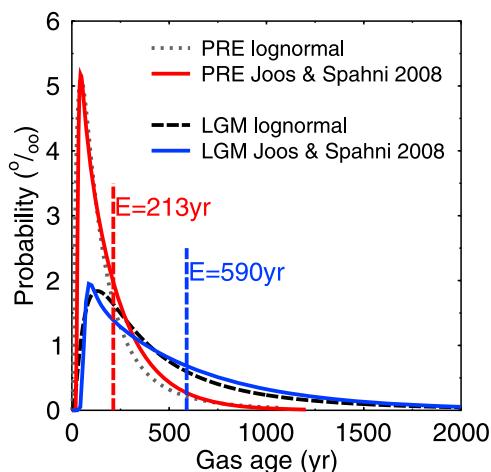
of Joos and Spahni [2008] our analytic function is fully described and can be used as filter to calculate how the original atmospheric signal is attenuated by the firnification processes and which signals might be recorded in an ice core with climatic conditions typical for EPICA Dome C. These gas age distributions for LGM and preindustrial climates can be considered as extremes with the gas distributions for other climate in between.

[49] The filtering of the atmospheric signals by the gas age distribution reduces the original atmospheric amplitude in  $p\text{CO}_2$  for the fastest event (35  $\mu\text{atm}$  in 100 years) to 51% (PRE) and 37% (LGM) in the ice core. The attenuation of the amplitude is even larger for atmospheric  $\delta^{13}\text{CO}_2$ , because of the faster signal dampening via air-sea gas exchange. The 0.62‰ peak during the fast climate transition (100 years) is reduced to 42% (PRE) or 21% (LGM). Furthermore, due to lognormal distribution of the gas age the peak maximum is shifted in time toward earlier years, e.g., up to 350 years in

$\delta^{13}\text{CO}_2$  for LGM climate conditions. This shift in the time of the peak maxima is implicitly included in the gas age scales developed for ice cores.

[50] These two effects on  $\delta^{13}\text{CO}_2$  taken together, signal dilution of slow and attenuation of fast events, poses a conflict of interest for the observer which is difficult to overcome. Fast events produce the largest amplitudes in  $\delta^{13}\text{CO}_2$ , but their original sizes are difficult to determine, while signals of slow events vanish quickly due the gas exchange with the ocean. In order to gain the most information from ice core  $\delta^{13}\text{CO}_2$  records we therefore suggest to first concentrate on fast climate transitions, following several steps: (1) identify climate transitions in  $\text{CH}_4$  which are fast (<one century) at both the onset and the end, (2) use those ice cores for  $\delta^{13}\text{CO}_2$  measurements with highest temporal resolution (thus snow accumulation) available, and (3) to compare carbon cycle modeling results with  $\delta^{13}\text{CO}_2$  measurements one needs to account for the temporal smoothing during the firnification process. This can be achieved by filtering of simulated atmospheric  $\delta^{13}\text{CO}_2$  with an assumed gas age distribution as done here.

[51] For the comparison of simulation results and measurements it is so far not clear how fast the carbon cycle is responding to rapid climate change. Models so far suggest that the carbon cycle responds to an AMOC shutdown within several centuries [Köhler *et al.*, 2005b; Menviel *et al.*, 2008a]. However, these models simulate also temperature anomalies, which are slower than data-based evidences of climate switches within less than a decade [Steffensen *et al.*, 2008]. Recently, one modeling study generated for the first time temperature anomalies over central Greenland on the order and abruptness found in ice core [Smith and Gregory, 2009]. They found, that their model behavior critically depends on the region in which freshwater was put into the North Atlantic in order to generate the climate anomalies. Clement and Peterson [2008] analyzed three different mechanisms potentially causing abrupt climate change



**Figure 9.** Gas age distribution as function of climate state for preindustrial (PRE) and LGM conditions. Calculation by Joos and Spahni [2008], approximated by lognormal functions.

(ocean circulation, sea ice feedbacks, tropical processes) and found that each of these mechanisms has explanatory strengths and weaknesses. If the conclusions of these studies are included in future carbon cycle–climate studies, we can expect to generate fast climate changes, which are in better agreement with the reconstructions.

#### 4. Conclusions

[52] We analyzed the individual contributions of processes changing atmospheric  $p\text{CO}_2$  and  $\delta^{13}\text{CO}_2$  as well as deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  in the carbon cycle box model BI-CYCLE throughout the last 740 kyr. The different dynamics (in terms of response to G/IG changes) in atmospheric  $\delta^{13}\text{CO}_2$  in comparison to both atmospheric  $\text{CO}_2$  and deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  are consistent with our understanding for each of the underlying processes. Only a 400 kyr variability in deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$ , that potentially points to a long-term weathering feedback, is not included in our model runs. Our analyses clearly show that mean ocean and deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  are mainly controlled by the G/IG terrestrial C uptake and release. In contrast,  $p\text{CO}_2$  and  $\delta^{13}\text{CO}_2$  changes represent mainly a mixture of ocean-related processes superimposed on the slow G/IG change in terrestrial carbon storage. Atmospheric  $p\text{CO}_2$  and deep Pacific  $\delta^{13}\text{C}_{\text{DIC}}$  are in principle related to each other and if the latter is high-pass filtered to suppress the  $1/400 \text{ kyr}^{-1}$  frequencies,  $\delta^{13}\text{C}_{\text{DIC}}$  has the potential to predict the variability in atmospheric  $p\text{CO}_2$  in times without ice core measurements.

[53] When changing all individual processes at the same time the different effects on atmospheric  $\delta^{13}\text{CO}_2$  largely compensate each other and cancel all variability with frequencies of  $1/100 \text{ kyr}^{-1}$  in atmospheric  $\delta^{13}\text{CO}_2$ . Large excursions in  $\delta^{13}\text{CO}_2$  on shorter timescales can occur, as any

small phase difference between the relative timing of the dominant and oppositely sign processes might create large changes in  $\delta^{13}\text{CO}_2$ . Amplitudes in  $\delta^{13}\text{CO}_2$  caused by fast terrestrial uptake or release may be imprinted in  $\delta^{13}\text{CO}_2$  but depend not only on the amount of transferred carbon, but also on the speed of these changes. Those, which occur on timescales slower than a millennium are leaving only a subtle imprint in  $\delta^{13}\text{CO}_2$ . The consequence is that typical stadial/interstadial transitions (abrupt warming in the Northern Hemisphere in less than a century) leave a distinct signal in  $\delta^{13}\text{CO}_2$ , while the reverse cooling causes only a subtle reverse trend.

[54] The proposed high-frequency variability in atmospheric  $\delta^{13}\text{CO}_2$  together with signal dilution of slower events and amplitude attenuation of fast events due to the gas age distribution in ice cores calls for both a high temporal resolution and a high precision of atmospheric  $\delta^{13}\text{CO}_2$  in ice core analysis. A filtering of simulated atmospheric  $\delta^{13}\text{CO}_2$  with the assumed gas age distribution as done here is necessary for events faster than one century to correct for the temporal smoothing due to the firnification process before ice core measurements and carbon cycle simulations become comparable. Despite those complications, it is the strength of atmospheric  $\delta^{13}\text{CO}_2$  that it allows us to critically evaluate model results and our general understanding of the global carbon cycle since a large set of processes have to be well captured at the right timing within the models.

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H. Fischer and J. Schmitt, Climate and Environmental Physics, Physics Institute, University of Bern, Sidlerstr. 5, CH-3012 Bern, Switzerland. (hubertus.fischer@climate.unibe.ch; schmitt@climate.unibe.ch)

P. Köhler, Alfred Wegener Institute for Polar and Marine Research, PO Box 120161, D-27515 Bremerhaven, Germany. (peter.koehler@awi.de)