Effects of eustatic sea-level change, ocean dynamics, and nutrient utilization on atmospheric pCO<sub>2</sub> and seawater composition over the last 130,000 years: a model study

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# 13 Abstract

We developed and employed an earth system model to explore the forcings of atmospheric 14 pCO<sub>2</sub> change and the chemical and isotopic evolution of seawater over the last glacial cycle. 15 Concentrations of dissolved phosphorus (DP), reactive nitrogen, molecular oxygen, dissolved 16 inorganic carbon (DIC), total alkalinity (TA), <sup>13</sup>C-DIC and <sup>14</sup>C-DIC were calculated for 24 17 ocean boxes. The bi-directional water fluxes between these model boxes were derived from a 18 3-D circulation field of the modern ocean (Opa 8.2, NEMO) and tuned such that tracer 19 20 distributions calculated by the box model were consistent with observational data from the modern ocean. To model the last 130 kyr, we employed records of past changes in sea-level, 21 22 ocean circulation, and dust deposition. According to the model, about half of the glacial pCO<sub>2</sub> drawdown may be attributed to marine regressions. The glacial sea-level low-stands implied 23 24 steepened ocean margins, a reduced burial of particulate organic carbon, phosphorus, and neritic carbonate at the margin seafloor, a decline in benthic denitrification, and enhanced 25 weathering of emerged shelf sediments. In turn, low-stands led to a distinct rise in the 26 27 standing stocks of DIC, TA, and nutrients in the global ocean, promoted the glacial sequestration of atmospheric CO<sub>2</sub> in the ocean, and added <sup>13</sup>C- and <sup>14</sup>C-depleted DIC to the 28 29 ocean as recorded in benthic foraminifera signals. The other half of the glacial drop in  $pCO_2$ was linked to inferred shoaling of Atlantic meridional overturning circulation and more 30

efficient utilization of nutrients in the Southern Ocean. The diminished ventilation of deep 1 water in the glacial Atlantic and Southern Ocean led to significant <sup>14</sup>C depletions with respect 2 to the atmosphere. According to our model, the deglacial rapid and stepwise rise in 3 atmospheric pCO<sub>2</sub> was induced by upwelling both in the Southern Ocean and subarctic North 4 Pacific and promoted by a drop in nutrient utilization in the Southern Ocean. The deglacial 5 sea-level rise led to a gradual decline in nutrient, DIC, and TA stocks, a slow change due to 6 7 the large size and extended residence times of dissolved chemical species in the ocean. Thus, the rapid deglacial rise in pCO<sub>2</sub> can be explained by fast changes in ocean dynamics and 8 9 nutrient utilization whereas the gradual pCO<sub>2</sub> rise over the Holocene may be linked to the slow drop in nutrient and TA stocks that continued to promote an ongoing CO<sub>2</sub> transfer from 10 11 the ocean into the atmosphere.

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# 13 **1 Introduction**

14 The discussion of mechanisms that might be responsible for the glacial to interglacial change in the atmosphere's CO<sub>2</sub> content is focused on the ocean (Broecker, 1982a). Ever increasing 15 evidence suggests that CO<sub>2</sub> sequestered in the glacial ocean was rapidly released into the 16 17 atmosphere at glacial terminations (Schmitt et al., 2012). The fast decline in dust-bound iron deposition in the Southern Ocean (Martin, 1990; Martinez-Garcia et al., 2014) and upwelling 18 19 pulses in the Southern Ocean (Anderson et al., 2009) and North Pacific (Rae et al., 2014) may have induced the stepwise pCO<sub>2</sub> rise documented in the deglacial ice-core record (Marcott et 20 21 al., 2014). The preceding  $CO_2$  uptake in the glacial ocean may be attributed to enhanced export production, elevated seawater alkalinity, and changes in ocean dynamics. The 22 23 biological pump probably was intensified by iron fertilization (Martin, 1990) and the coeval expansion of nitrate (Deutsch et al., 2004) and phosphate (Broecker, 1982a) stocks in the 24 glacial ocean while seawater alkalinity may have been enhanced by the demise of neritic 25 carbonate formation (Berger, 1982; Opdyke and Walker, 1992; Kleypas, 1997). The 26 sequestration of atmospheric  $pCO_2$  in the glacial ocean may have been further promoted by 27 the glacial shoaling of the Meridional Overturning Circulation (MOC) in the Atlantic 28 29 (Duplessy et al., 1988; Sarnthein et al., 1994), a possible increase in Southern Ocean stratification (Toggweiler, 1999), a prolonged residence time of surface waters in the 30 Southern Ocean providing more time for the biota to draw down nutrients and CO<sub>2</sub> (Watson et 31 al., 2015) and a global decline in MOC intensity and deep ocean ventilation (Sarnthein et al., 32 2013). 33

In part, a glacial rise in nitrate, phosphate, and alkalinity concentrations, which may have 1 contributed significantly to the drawdown of atmospheric pCO<sub>2</sub>, can be explained by eustatic 2 sea-level fall (Wallmann, 2014). It led to a retreat of ocean margins to steeper terrains that 3 reduced the seafloor area located in shallow waters (Fig. 1). The standing stocks of carbon 4 and nutrients in the glacial ocean may have been significantly enhanced by the marine 5 regression and the decrease in shallow margin area since major removal fluxes, that is 6 7 accumulation of neritic carbonate, benthic denitrification, burial of particulate organic carbon (POC) and phosphorus (P), depend on the extent of seafloor located in shallow waters. 8 9 Various authors and earth system models considered the glacial decrease in shelf carbonate burial as a major driver of ocean chemistry and atmospheric pCO<sub>2</sub> change (Berger, 1982; 10 Opdyke and Walker, 1992; Brovkin et al., 2012; Ganopolski et al., 1998), since neritic 11 carbonates contribute  $\geq$ 50 % to the carbonate accumulation at the global seafloor (Milliman 12 13 and Droxler, 1996; Kleypas, 1997; Berelson et al., 2007). However, the effects of sea-level change on POC and nutrient cycling are largely ignored in these state-of-the-art models even 14 15 though >50 % of the global benthic denitrification and burial of marine POC and P occur in shelf and upper slope environments (Berner, 1982; Bohlen et al., 2012; Wallmann, 2010). 16

Against this background, our contribution aims to explore and quantify the effects of sea-level 17 change, ocean dynamics and nutrient utilization on seawater composition and atmospheric 18 pCO<sub>2</sub> over the last glacial cycle. We use a simple earth system box model to simulate both 19 chemical and isotopic changes in seawater composition and employ isotope data ( $\delta^{13}$ C) to 20 constrain changes in ocean dynamics and deep ocean ventilation. Atmospheric pCO<sub>2</sub> and the 21 22 distributions of dissolved oxygen, carbonate, and radiocarbon in the glacial ocean serve as key 23 prognostic model variables. They are compared with independent proxy data to address the following specific questions: What fraction of the glacial pCO<sub>2</sub> draw-down can be ascribed to 24 eustatic sea-level fall (Wallmann, 2014)? To which degree do global <sup>14</sup>C data sets assembled 25 by (Sarnthein et al., 2013; Sarnthein et al., 2015) actually reflect our concepts and ideas on 26 glacial and deglacial ocean circulation and carbon cycling? Do marine <sup>14</sup>C data really form a 27 quantitative proxy of DIC in the glacial deep ocean as proposed by (Sarnthein et al., 2013)? 28 To avoid circular reasoning dissolved oxygen, carbonate, and radiocarbon distributions 29 calculated for the glacial ocean were not used to parameterize our model. These distribution 30 31 patterns and the atmospheric pCO<sub>2</sub> values calculated in the model are non-trivial consequences of interactions between the various model components and thus are employed 32 to validate the model performance. 33

# 1 2 Model set-up

2 The atmospheric partial pressure of  $CO_2$  (p $CO_2$ ) serves as the key prognostic variable of the 3 new multi-box earth system model presented in this paper. It was calculated considering 4 continental weathering and degassing processes and gas exchange with the surface ocean (Wallmann, 2014). The oceans were represented by 24 boxes (Fig. 2). The major ocean 5 basins North Atlantic (NA, 30°- 60°N), Tropical Atlantic (TA, 30°N – 30°S), Southern 6 Ocean (SO, >30°S), Tropical Indo-Pacific (TIP, 30°N – 30°S), North Pacific (NP, 30°- 60°N), 7 8 and Arctic Ocean (AR, >60°N; including the Greenland-Norwegian Sea) each were divided into surface, intermediate, deep and bottom water boxes extending from 0 - 100 m, 100 -9 2000 m, 2000 - 4000 m to >4000 m water depth, respectively. The following tracer 10 concentrations were calculated as prognostic variables for each of the water boxes: Salinity 11 12 (Sal), dissolved phosphorus (DP), dissolved reactive nitrogen (DN), dissolved oxygen (DO), total alkalinity (TA), dissolved inorganic carbon (DIC), dissolved inorganic <sup>13</sup>C (<sup>13</sup>C-DIC), 13 and dissolved inorganic radiocarbon (<sup>14</sup>C-DIC). Details of the model set-up are given in 14 Appendix A. 15

Eustatic sea-level change was applied as major model forcing (Fig. 3). Changes in global 16 ocean volume, salinity, depositional area at continental margins and exposed shelf area were 17 derived from the sea-level record (Stanford et al., 2011; Waelbroeck et al., 2002) and the 18 hypsographic curve (Eakins and Sharman, 2012). The burial rate of neritic carbonates was 19 reduced during marine regressions in proportion to the decrease in seafloor area available for 20 the growth of tropical reefs and carbonate platforms (Appendix B). We tested the degree to 21 which the decrease in seafloor area at 0 - 100 m and 100 - 2000 m water depth during glacial 22 sea-level low-stands affected benthic denitrification and the burial of organic carbon and 23 marine phosphorus on the continental shelf and slope (Appendix B) while we assumed that 24 carbonate, P, and POC weathering were promoted by the exposure of shelf sediments 25 26 (Appendix A).

The comprehensive geological data base on benthic foraminiferal  $\delta^{13}$ C (Oliver et al., 2010; Sarnthein et al., 1994) was employed to constrain water fluxes for the Last Glacial Maximum (LGM). Mean  $\delta^{13}$ C-DIC values were calculated for those ocean boxes where sufficient  $\delta^{13}$ C data were available and compared to model results. Water fluxes were varied until the Holocene-LGM differences in  $\delta^{13}$ C generated by the model were consistent with the differences recorded in foraminifera (Tab. A5). The tuning was done using full transient runs with all forcings applied. The resulting fluxes are shown in Fig. 2. The southward water flux

from the Atlantic into the Southern Ocean was relocated from deep (2000 - 4000 m) to 1 intermediate waters (100 - 2000 m) to mimic the shoaling of the Atlantic Meridional 2 Overturning Circulation (AMOC) which is inferred not only from  $\delta^{13}$ C data but also from 3 various other proxy records (Curry and Oppo, 2005; Piotrowski et al., 2005; Roberts et al., 4 5 2010). Bottom water fluxes from the Southern Ocean into the Atlantic were enhanced during the LGM while the northward flow of surface water was reduced. The overall water exchange 6 7 between Atlantic and Southern Ocean was maintained constant at 15.4 Sv. The bottom and deep water exchange between the Southern Ocean and the Indo-Pacific was reduced by 5 Sv 8 to reproduce the  $\delta^{13}$ C data (Tab. A5). 9

The eustatic sea-level curve (Fig. 3a) was applied to change ocean dynamics continuously 10 over time that is to define water fluxes over the full model period (Fig. 4a-c). Thus we 11 12 assumed that AMOC shoaled gradually during the transition from interglacial to full glacial conditions (130 - 21 ka) while the horizontal exchange flux of intermediate waters between 13 Southern Ocean and Tropical Indo-Pacific was enhanced over the glacial to mimic the 14 15 ventilation of tropical oxygen minimum zones (OMZs) observed in various proxy records (Altabet et al., 1995; Jaccard and Galbraith, 2012). Additional rapid changes were 16 implemented for the deglacial period (Figs. 4a and 4d). NADW formation was strongly 17 reduced during Heinrich Event 1 (H1) and the Younger Dryas (McManus et al., 2004) while 18 upwelling pulses were prescribed in the Southern Ocean during H1 and the Bølling-Allerød 19 (Anderson et al., 2009; Skinner et al., 2010) and in the North Pacific during H1 (Rae et al., 20 2014). Timing and intensity of these deglacial upwelling/ventilation events were varied until 21  $\Delta^{14}$ C-DIC values calculated for deep and surface water boxes were consistent with  $\Delta^{14}$ C 22 values recorded in benthic and pelagic foraminifera (Fig. A2). In addition, the deglacial ice-23 core record of pCO<sub>2</sub> (Marcott et al., 2014) and biogenic opal accumulation rates (Anderson et 24 al., 2009) were employed to constrain the timing and intensity of upwelling pulses in the 25 Southern Ocean. The iron accumulation record from site ODP 1090 was used to constrain 26 changes in nutrient utilization in the Southern Ocean (Martinez-Garcia et al., 2014) assuming 27 that the increase in iron accumulation observed at this site directly translates into an increase 28 in the efficiency of nutrient utilization (Fig. 4e). To calculate realistic marine isotope trends 29 the changing isotopic compositions of atmospheric CO<sub>2</sub> were set to the values documented in 30 the geological record (Fig. 4f-g). Atmospheric  $\delta^{13}$ C-CO<sub>2</sub> was not calculated as a prognostic 31 model variable because a biased vertical  $\delta^{13}$ C-DIC gradient in the Southern Ocean impeded 32 the simulation of <sup>13</sup>C-CO<sub>2</sub> fluxes across the ocean/atmosphere interface (Appendix A, section 33 A8, Fig. A3). 34

The major limitations of our simple box model are i) very low spatial resolution, ii) water
 fluxes between model boxes that are not derived from internal model dynamics, iii) terrestrial
 inventories of POC in vegetation and soil that are kept constant over the model period.

As a consequence of low resolution, OMZs are not resolved by our model since the entire Indo-Pacific intermediate water at 100 - 2000 m water depth is pooled in a single ocean box. In our model, we prescribe a constant rate of pelagic denitrification since we are not able to resolve OMZs. Rates of benthic denitrification and P burial are only moderately affected by the lack of OMZs since the area where OMZs impinge the seafloor only amounts to 1 % of the global seafloor (Bohlen et al., 2012).

The modern water fluxes applied to our box model are based on a dynamically consistent 10 circulation field. As explained in Appendix A, these fluxes were modified to obtain tracer 11 distributions that are consistent with observations in the pre-industrial modern ocean (Fig. 12 A1). Glacial and deglacial changes in ocean circulation were not derived from ocean models 13 but from  $\delta^{13}$ C records (Tab. A5) and additional geochemical observations (Fig. A2). Models 14 with explicit ocean dynamics are superior to any kind of physically unconstrained box model 15 if they generate results that are consistent with observations. However, the physically-16 constrained earth system models that we are aware of are not yet able to reproduce as many 17 18 tracer and proxy data as our box model. Our paper shows that shelf and sea-level effects help to explain a wide range of findings (section 3) and we think that the outputs of physically 19 20 better constrained models may improve in case these effects are included in the model architecture. It is not our intention to promote box modeling per se as the method-of-choice. 21 22 Rather we hope that the concepts and ideas advanced in our paper may stimulate the community and help to further enhance cutting-edge earth system models with explicit ocean 23 dynamics (Tschumi et al., 2011; Menviel et al., 2012; Brovkin et al., 2012; Roth et al., 2014; 24 25 Lambert et al., 2015).

For many decades it was widely assumed that the modern terrestrial carbon pool exceeds the 26 27 glacial pool by hundreds of Gt because of biosphere regrowth after the glacial termination (Köhler and Fischer, 2004). This concept was initially developed to explain reduced  $\delta^{13}$ C 28 29 values in glacial seawater (Shackleton, 1977). However, the latest assessment of terrestrial carbon pools indicates that the sum of the modern stocks does not exceed the LGM stock 30 (Brovkin and Ganopolski, 2015). Moreover, this new view on terrestrial carbon cycling 31 32 suggests a deglacial decline in total carbon stocks since the carbon release from high latitude 33 areas (melting permafrost soils and soils exposed by the retreat of glacial ice sheets) exceeded the carbon uptake by biosphere regrowth and peat accumulation. Our model explains deglacial and Holocene pCO<sub>2</sub> dynamics and the low glacial  $\delta^{13}$ C values by marine processes and sea-level change only. However, we acknowledge that terrestrial processes that are neglected in our model may have played a role especially over the Holocene even though more work needs to be done to constrain the sign and magnitude of terrestrial effects on  $\delta^{13}$ C and pCO<sub>2</sub> dynamics.

7 The major new component included in our earth system model is a comprehensive
8 formulation of shelf processes and sea-level effects. Appendix B explains in detail how sea9 level change affects fluxes at continental margins and how these effects are considered in the
10 model. The full model code is made available by the first author on request.

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# 12 3 Results and Discussion

The model was run over a period of 130 kyr to simulate the behavior of the global system 13 14 over one full glacial cycle. Simulations start at 130 ka with modern (pre-human) tracer distributions applied as initial values. The standard model run (STD) considers all effects 15 16 induced by sea-level change, changes in ocean circulation and nutrient utilization, that is the full model forcing as defined in Figures 3 and 4. Additional simulations were performed to 17 18 better understand the controls on atmospheric pCO<sub>2</sub> and the chemical and isotopic composition of seawater. Simulation STD-CC was run with constant circulation, that is, all 19 water fluxes were maintained at the Holocene level (upper panel of Fig. 2, Tab. A3) over the 20 full model period, whereas simulation STD-CC-CN was performed with the Holocene 21 22 circulation field and constant nutrient utilization.

# 23 3.1 Atmospheric pCO<sub>2</sub>

The pCO<sub>2</sub> trend recorded in ice cores (Monnin et al., 2001; Monnin et al., 2004; Marcott et 24 al., 2014; Petit et al., 1999) was well reproduced by the standard simulation (Fig. 5a and 7a). 25 Over the last interglacial, simulated pCO<sub>2</sub> increased from an initial value of 280 ppmv at 130 26 ka to 285 ppmv at 120 ka (Fig. 5a). This increase was accompanied by a decline in nutrient 27 concentrations (Figs. 5f-g) and export production (Fig. 6d), supported by the high sea-level 28 29 stand promoting burial of phosphorus and benthic denitrification in continental margin sediments. Over the subsequent glacial period, simulated pCO<sub>2</sub> declined due to sea-level fall, 30 enhanced nutrient utilization in the Southern Ocean, and the decline in deep ocean ventilation 31 32 until 21 ka, when a pCO<sub>2</sub> minimum of 190 ppmv was reached (Fig. 7b). The simulated glacial pCO<sub>2</sub> drawdown was discontinuous, marked by several steps and turning points (Fig. 5a). Major minima in atmospheric pCO<sub>2</sub> occurred at 90 ka (220 ppmv) and 65 ka (198 ppmv). Both of them are well documented in the ice-core record (Fig. 5a) and accompanied by maxima in nutrient utilization (Fig. 4e) and minima in sea-level (Fig. 3a). Sea-level fall and nutrient utilization, thus, may have driven most of the glacial pCO<sub>2</sub> decline. Moreover, they may have induced major turning points in the glacial pCO<sub>2</sub> record.

7 At constant ocean circulation and nutrient utilization (simulation STD-CC-CN), simulated 8 pCO<sub>2</sub> declined to a LGM value of 234 ppmv (Fig. 5a). Additional simulations based on the 9 standard simulation STD helped us to specify the driving forces for this decline (Tab. 1). To 10 study their effect on pCO<sub>2</sub> we suppressed the temporal changes of individual variables. A first simulation test was based on the assumption of constant modern sea surface temperatures 11 12 (SSTs). It showed that the glacial decline in global mean SST by ca. 2°C (Schmittner et al., 2011) induced a pCO<sub>2</sub> decline by 16 ppmv since the solubility of CO<sub>2</sub> in surface waters was 13 enhanced under low temperatures (compare rows 1 and 2 in Tab. 1). In a second simulation, 14 salinity was set constant, while the other model parameters varied as defined in the STD 15 simulation. Accordingly, the peak glacial increase in salinity induced a relative atmospheric 16 pCO<sub>2</sub> rise by 5 ppmv by lowering the solubility of CO<sub>2</sub> in surface waters (Tab. 1). In a third 17 test, both salinity and the volume of the ocean boxes were kept constant over time. Changes in 18 19 these parameters induced an LGM pCO<sub>2</sub> rise by 13 ppmv (Tab. 1), illustrating that the contraction of the ocean volume during glacial sea-level low-stands reduced the ocean's 20 capacity to sequester atmospheric  $CO_2$ . In summary, the model runs confirmed previous 21 22 estimates (Broecker, 1982a) showing that the net effect of SST, volume, and salinity changes 23 on glacial pCO<sub>2</sub> is small (decrease by 3 ppmv). Thus, other processes need to be invoked to explain the large glacial drawdown of atmospheric CO<sub>2</sub> simulated by model run STD-CC-CN. 24

25 Changes in the flux of dissolved phosphorus (DP) exert large effects on pCO<sub>2</sub>, since DP is the 26 ultimate limiting nutrient of the model ocean (Menviel et al., 2012). Neglecting the glacial 27 increase in the weathering of P-bearing solids is raising the LGM pCO<sub>2</sub> value by 50 ppmv (Tab. 1, rows 5 vs. 1). Most of the P released during chemical weathering originates from 28 apatite, a mineral equally occurring in all rock types (sedimentary, magmatic and 29 metamorphic). Thus, we assume that the P weathering rate is proportional to the total 30 weathering rate, that is the sum of carbonate, POC and silicate weathering (Wallmann, 2014). 31 During the glacial, total weathering increased due to the weathering of exposed shelf CaCO<sub>3</sub> 32 and POC (Munhoven, 2002; Wallmann, 2014). This rise led to the increase in P weathering 33

simulated in the model. However, a further simulation shows that the overall pCO<sub>2</sub> change 1 induced by chemical weathering of silicate, POC, CaCO<sub>3</sub> and P is small (decrease by 3 ppmv) 2 because the glacial CO<sub>2</sub> draw-down induced by P and CaCO<sub>3</sub> weathering was largely 3 compensated by the CO<sub>2</sub> release induced by POC weathering (Tab. 1, STD run with constant 4 rates of chemical weathering). Applying very high molar C : P ratios for POM in shelf 5 sediments (ca. 200), it was previously calculated that shelf weathering resulted in a net 6 7 increase rather than decrease in atmospheric pCO<sub>2</sub> (Ushie and Matsumoto, 2012). However, most of the phosphorus in shelf sediments and riverine particles is not organic but bound in 8 9 other reactive, inorganic phases such as carbonate-fluoro-apatite (Berner and Rao, 1994) which release DP when exposed to weathering (Ruttenberg, 1992; Ruttenberg and Berner, 10 11 1993). Thus, the global mean atomic ratio of POC over reactive P in shelf sediments is lower than the C : P ratio of marine organic matter (Baturin, 2007; Wallmann, 2010). Hence, the 12 13 glacial weathering of shelf sediments induced a small drop rather than a rise in LGM pCO<sub>2</sub> (Tab. 1). 14

By contrast, a stronger effect results from testing the glacial decrease in depositional areas at 15 continental margins, as revealed by a simulation that ignores the glacial decline in P burial 16 and reveals a glacial pCO<sub>2</sub> rise by 73 ppmv (Tab. 1) with respect to the standard case due to 17 the decline in DP concentration and export production. An additional simulation with constant 18 depositional area for POC burial resulted in a pronounced drawdown of both atmospheric 19 pCO<sub>2</sub> (by 61 ppmv) and DIC since POC burial at continental margins served as major sink for 20 CO<sub>2</sub> and DIC in the model system (Tab. 1). Changes in the burial of neritic carbonates were 21 22 mitigated by carbonate compensation at the deep-sea floor and thus had a less drastic effect on 23 atmospheric pCO<sub>2</sub> (change by 10 ppmv, Tab. 1). Thus the response of the model system to sea-level change was dominated by changes in the burial of P and POC at continental 24 25 margins. The glacial drop in atmospheric  $pCO_2$  that was induced by a decline in P burial, was moderated by a coeval drop in POC burial at continental margins. The overall effect was an 26 27 increase in export production and a transfer of CO<sub>2</sub> from the atmosphere into the ocean via the biological pump. Accordingly, most of the glacial pCO<sub>2</sub> decline in simulation STD-CC-CN 28 was driven by the glacial steepening of ocean margins and the resulting expansion of the DP 29 inventory. This conclusion is consistent with the results of previous experiments conducted 30 31 with more evolved earth system models showing a strong  $pCO_2$  draw-down in response to an increase in the oceanic phosphate inventory (Tschumi et al., 2011; Menviel et al., 2012). 32

The glacial pCO<sub>2</sub> value dropped by 31 ppmv (from 234 ppmv to 203 ppmv) upon enhanced 1 nutrient utilization (difference between simulations STD-CC-CN and STD-CC). This 2 decrease was amplified by the glacial sea-level fall since the nutrient reservoir that was 3 unlocked by the enhanced utilization in the glacial Southern Ocean was enlarged as a result of 4 glacial marine regression. The remaining portion of the interglacial-to-peak glacial  $pCO_2$  drop 5 by 13 ppmv down to the final LGM value of 190 ppmv was induced by ocean dynamics 6 7 (difference between simulation STD and STD-CC). Atmospheric pCO<sub>2</sub> rose by 10 ppmv, when all water fluxes between the Atlantic and the Southern Ocean were maintained at their 8 9 Holocene level over the entire model period (simulation STD with constant AMOC, Tab. 1). The glacial AMOC shoaling (Fig. 4a-b) thus contributed 10 ppmv to the simulated LGM 10 11 decline. This effect can be attributed to enhanced CO<sub>2</sub> storage in the deep Atlantic (>2000 m water depth) which was less ventilated under glacial conditions, since the formation of 12 13 northern deep waters was greatly diminished and replaced by southern-source waters enriched in DIC. Thus additional DIC was stored in the glacial deep ocean (Ganopolski et al., 2010; 14 15 Skinner, 2009; Sarnthein et al., 2013). The glacial decrease in water fluxes between the deep Southern Ocean and Tropical Indo-Pacific applied in the model (Fig. 2) likewise supports 16 17 further sequestration and storage of CO<sub>2</sub> in the deep ocean and the glacial drawdown of atmospheric pCO<sub>2</sub>. The circulation changes employed to simulate LGM conditions (Fig. 2) 18 led to a reduction in the global water exchange across the 2000 m depth horizon from a 19 modern amount of 45 Sv down to 31 Sv at 21 ka. This corresponds to an increase in the 20 average residence time of water in the deep ocean (>2000 m) from 470 years in the modern 21 ocean to 680 years during the LGM where the residence time is calculated as ratio of the deep 22 ocean volume (6.65 x  $10^{17}$  m<sup>3</sup> at >2000m) and the global vertical water fluxes across 2000 m. 23 The glacial increase in residence time by 210 yr may be compared to the 600 yr increase 24 reconstructed from benthic radiocarbon data (Sarnthein et al., 2013). We suggest that the 25 26 difference between these two estimates is related to the elevated production rate of radiocarbon in the glacial atmosphere and changes in carbon cycling affecting the marine 27 28 radiocarbon budget (section 3.4).

A stepwise increase in pCO<sub>2</sub> was simulated over the deglaciation (Fig. 7). The first step occurred from 18.5 to 16.3 ka when the simulated pCO<sub>2</sub> rose rapidly from 193 to 220 ppmv. A second step followed at 15.9 - 14.1 ka with a pCO<sub>2</sub> rise from 222 to 244 ppmv, a third step at 13.0 - 10.8 ka with a strong increase from 243 to 272 ppmv. The first step was driven by the rapid drop in nutrient utilization at the glacial termination (Fig. 4e) and the ventilation of intermediate and deep water masses in the North Pacific during H1 (Figs. 4d and A2). The

second and third steps were driven by the Southern Ocean where CO<sub>2</sub> was released into the 1 atmosphere due to the abrupt decline in stratification and the further decrease in nutrient 2 utilization (Fig. 4d-e). In major parts of the Southern Ocean these steps coincide with maxima 3 in opal accumulation indicating enhanced upwelling (Anderson et al., 2009). The  $pCO_2$ 4 drawdown from 10 to 8 ka reflects a recovery of the ocean system from the antecedent 5 ventilation pulse in the Southern Ocean centered at 11.5 ka (Fig. 4d). According to our model, 6 7 the ventilation pulse removed CO<sub>2</sub> from the ocean interior, enhanced the O<sub>2</sub> content of the deep ocean, and diminished the vertical DIC and O<sub>2</sub> gradients. The subsequent restoration of 8 9 the vertical DIC gradient induced the pCO<sub>2</sub> decline observed in the model from 10 to 8 ka. 10 The biological pump needed about 2 kyr to reestablish the vertical DIC gradient due to the 11 large inventory of DIC in the deep ocean. Sea-level change was not uncovered as major driver for the rapid deglacial  $pCO_2$  rise since the long residence times of DP (13 kyr) and TA (77 12 13 kyr) inhibit fast inventory changes in the global ocean (Menviel et al., 2012; Wallmann, 2014). By contrast, the pCO<sub>2</sub> increase over the Holocene (8 - 0 ka), which is closing the 14 15 glacial cycle, may have been driven by a high sea-level stand inducing a gradual and slow decline in marine DP and TA inventories. 16

In our model about equal portions of the extreme deglacial carbon flux are triggered by changes in circulation and nutrient utilization in the Southern Ocean (Fig. 7). However, this model outcome is not well constrained because the lack of both proxy data and physical process understanding impedes an unequivocal determination of the magnitude of nutrient utilization and stratification change in the Southern Ocean.**3.2 Dissolved nutrients and oxygen** 

The standing stock of DP in the global ocean rose under glacial conditions since P burial was 23 24 diminished by the decrease in depositional area located at shallow water depths (Fig. 6h) 25 while chemical weathering was promoted by the exposure of shelf sediments (Fig. 6g). Most 26 of the glacial DP rise found in our simulations was induced by the glacial steepening of ocean 27 margins reducing the burial of P in margin sediments (Tab. 1, Fig. 1, Appendix B). Vice versa, enhanced utilization in the Southern Ocean induced a strong decrease in glacial DP 28 stocks since more DP was taken up by phytoplankton to be drawn down and finally buried in 29 marine sediments (simulations STD-CC versus STD-CC-CN, Figs. 5f, 6d, 6h), while the 30 glacial DP stock was largely restored by changes in ocean dynamics (simulations STD versus 31 STC-CC, Fig. 5f) separating the large nutrient pool in the deep ocean from the surface layer. 32 The spatial distribution of DP in the global ocean reflects the export of POM by the biological 33

pump and ocean circulation. The overall pattern, that is a strong vertical gradient between 1 2 depleted surface waters and enriched deep water masses and a significant horizontal gradient between the deep North Atlantic and North Pacific, was maintained over the glacial cycle 3 (Fig. 8). However, the vertical DP gradient was amplified over the LGM due to enhanced 4 utilization and the decrease in deep ocean ventilation. Reactive P accumulation rates in 5 marine sediments can be used to validate our model results. A global compilation of these 6 7 data confirmed that P accumulation in shelf sediments decreased drastically under glacial conditions (Tamburini and Föllmi, 2009). The resulting decline in global P burial induced an 8 increase in the glacial DP inventory by 17 - 40 % (Tamburini and Föllmi, 2009) as predicted 9 by our model. Cd/Ca ratios in LGM sediments from the Atlantic Ocean (Boyle and Keigwin, 10 1982) and  $\delta^{13}$ C records (Duplessy et al., 1988; Sarnthein et al., 1994; Oliver et al., 2010) 11 suggest a steepening of the vertical DP gradients broadly consistent with our model results. 12

The dissolved oxygen (DO) content of the global ocean decreased under glacial conditions 13 due to the decline in deep ocean ventilation and increase in export production (Fig. 5h). In 14 contrast, it recovered and peaked over the deglaciation since ocean ventilation was enhanced 15 in the Southern Ocean and the North Pacific. The spatial distribution of DO changed 16 significantly under LGM conditions (Fig. 8). Concentrations declined at >2000 m water depth 17 due to the decrease in ocean ventilation and increase in export production while glacial 18 cooling induced a small DO rise in surface waters. The DO minimum in intermediate waters 19 of the Indo-Pacific expanded and spread into the deep ocean under glacial conditions. The 20 lowest value was calculated for the intermediate water box of the North Pacific where the DO 21 22 concentration declined to 69 µM at 21 ka. The glacial DO decrease in the deep ocean is 23 consistent with a large data set showing that deep waters below 1500 m water depth were significantly depleted in the LGM over all major ocean basins (Jaccard and Galbraith, 2012). 24 25 The glacial oxygen depletion in the intermediate Indo-Pacific (76 µM during the LGM vs. 96 µM in the modern ocean) seems to be at odds with the geological record which shows that 26 27 OMZs located in the tropical ocean were better ventilated under glacial conditions (Altabet et 28 al., 1995). This discrepancy may probably arise from the spatial resolution of the box model that is too coarse to resolve OMZs. Moreover, all sediment cores that have been used to 29 30 reconstruct the oxygen conditions in glacial intermediate waters were taken at continental 31 margins (Jaccard and Galbraith, 2012) while tracer concentrations in the model boxes are basin-wide mean values reflecting open ocean rather than continental margin conditions. 32

The glacial oxygen decline simulated in the model has no significant effect on other model 1 2 parameters since the oxygen level stays above the threshold values for diminished phosphorus burial (20 µM) in all ocean boxes (Wallmann, 2010). It was only benthic denitrification at the 3 deep-sea floor that was enhanced by the glacial oxygen depletion in bottom waters and rising 4 export production (Bohlen et al., 2012). Nevertheless, the global rate of benthic denitrification 5 6 calculated in simulation STD decreased under glacial conditions (Fig. 6j) since ocean margins 7 retreated into steeper terrain such that less nitrate was consumed on the continental shelf. Nitrogen fixation was assumed to increase when the DN/DP ratio in the surface ocean fell 8 9 below the N/P ratio in exported POM (Eq. A8). Nitrogen fixation thus traced the temporal evolution of benthic denitrification (Figs. 6i-j). This negative feedback mechanism (Tyrrell, 10 11 1999; Redfield, 1958) maintained the simulated DN/DP ratio close to its modern value over the entire glacial cycle. The DN inventory peaked during the LGM where it exceeded the 12 modern value by 16 %. A similar increase in the LGM nitrate inventory (10 - 30 %) and 13 glacial decline in denitrification and nitrogen fixation was simulated with a box model 14 constrained by the marine  $\delta^{15}$ N record (Deutsch et al., 2004). 15

# 16 **3.3 Dissolved inorganic carbon, carbonate ion concentrations, and** $\delta^{13}$ C of 17 **dissolved inorganic carbon**

18 In the standard case (STD) the global mean seawater concentrations of dissolved inorganic carbon (DIC) and total alkalinity (TA) decreased over the last interglacial, attained a 19 20 minimum at its end (2267 µM and 2394 µM at 118.5 ka, respectively), increased over the glacial up to a maximum prior to the glacial termination (2467 µM and 2631 µM at 19.5 ka) 21 22 and decreased again over the Holocene (Fig. 5b and 5e). On the basis of our model runs these trends were mainly driven by sea-level change that controlled the burial of neritic carbonate 23 24 (Fig. 3d) and POC (Fig. 6e) and the rates of POC and carbonate weathering by shelf exposure 25 (Figs. 3h and 6c). The glacial DIC and TA rise was mitigated by nutrient utilization enhancing 26 marine export production and carbon burial (compare simulations STD-CC-CN and STD-CC 27 in Figs. 5 and 6). In turn, it was amplified by the glacial decrease in deep ocean ventilation, a reduced turnover rate that also implied a decrease in marine export production, POC burial 28 and pelagic carbonate accumulation (STD-CC versus STD). Considering changes in ocean 29 volume by about 3 % (Fig. 3b), the increase in DIC over the last glacial (118.5 – 19.5 ka) 30 translates into a mean rate of 1.70 Tmol yr<sup>-1</sup>. By comparison, the  $CO_2$  uptake from the 31 32 atmosphere as calculated from the glacial rate of  $pCO_2$  decline amounts to 0.17 Tmol yr<sup>-1</sup>. Thus, only 10 % of the glacial DIC rise was induced by CO<sub>2</sub> uptake from the atmosphere. 33

According to our model, the glacial demise of neritic carbon pools (carbonate and POC) was 1 the major forcing of the DIC rise, while the sequestration of atmospheric CO<sub>2</sub> only was of 2 minor importance for the glacial change in seawater composition. Most of the excess DIC 3 4 accumulating in the glacial ocean originated from exposed shelf carbonate and POC and from 5 riverine DIC which was not buried due to the contraction of depositional areas at ocean margins. The accumulation of TA and DIC in the deep ocean (Fig. 9) was corroborated by a 6 7 change in Atlantic deep water chemistry. As outlined above, this LGM ocean basin was filled with corrosive southern-source waters compromising the preservation of carbonates at the 8 deep-sea floor and diminishing the rate of pelagic carbonate burial (Tab. 1). 9

The global mean concentration of carbonate ions  $(CO_3^{2-})$  in the deep ocean (>2000 m) rose 10 over glacial times in simulation STD due to the decline in neritic carbonate burial and 11 dropped over the deglaciation, at least in part, due to the recovery of neritic carbonate 12 deposition (Fig. 10a). The glacial  $CO_3^{2-}$  rise was mitigated by the decline in deep ocean 13 ventilation and increase in ocean productivity promoting the sequestration of CO<sub>2</sub> in the deep 14 ocean. Interestingly, deep ocean pH and  $CO_3^{2-}$  trends diverged during the transition into the 15 LGM (Figs. 10a-b), that is, pH dropped while  $CO_3^{2-}$  was maintained at a constant level over 16 this period (30 - 20 ka). Due to this divergence, the late glacial pH was lower (that is, more 17 acidic) than the modern value, while the  $CO_3^{2-}$  concentration exceeded the modern 18 concentration in ocean deep waters. This apparent discrepancy may be explained by the fact 19 that alkalinity and DIC were strongly elevated in late glacial seawater (Figs. 5b and 5e) 20 thereby enhancing the concentrations of both  $H^+$  and  $CO_3^{2-}$  ions with respect to the pre-21 industrial modern ocean. The deglacial  $CO_3^{2-}$  minimum is related to ventilation pulses in the 22 Southern Ocean and North Pacific employed in the model. Export production of CaCO<sub>3</sub> and 23 pelagic carbonate burial were enhanced by these upwelling events and removed dissolved 24  $CO_3^{2-}$  from the global ocean. The Holocene was marked by a continuous  $CO_3^{2-}$  decline 25 probably induced by the high sea-level stand promoting neritic carbonate burial. 26

The strong enrichment of dissolved  $CO_3^{2-}$  in glacial surface waters was induced by the decline in atmospheric pCO<sub>2</sub> (Fig. 9). According to our standard simulation, these  $CO_3^{2-}$ concentrations exceeded Holocene values down to water depths of 1000 m, likewise at northern high latitudes where deep-water formation transmitted the signature of glacial surface waters into the ocean's interior. The carbonate ion concentration was almost constant over the entire Indo-Pacific at >1000 m water depth since the strong increase in DIC (Fig. 9) was balanced by a corresponding TA rise. These model results well compare with those of B/Ca ratios in benthic foraminifera which probably record  $CO_3^{2-}$  changes in ambient bottom waters (Yu et al., 2008; Yu et al., 2013). The model is consistent with glacial to interglacial changes in deep-sea  $CO_3^{2-}$  reconstructed from this proxy (Tab. C1 in Appendix C). The only deviation occurs at >4km water depth in the Atlantic where the model predicts elevated LGM values while the data show a glacial  $CO_3^{2-}$  depletion (Tab. C1), possibly the result of a strong east-west gradient in bottom water chemistry not resolved yet by the B/Ca data that accordingly may not be fully representative for the Atlantic at large.

The glacial distribution pattern of  $\delta^{13}$ C-DIC values calculated in the standard simulation (Fig. 8 11) is consistent with observations (Oliver et al., 2010) because glacial  $\delta^{13}$ C-DIC data were 9 employed to define the LGM circulation pattern (section 2, Tab. A5 in Appendix A). In all 10 simulations global mean  $\delta^{13}$ C-DIC values mirror inversely DIC concentrations (Figs. 5b-c) 11 getting depleted with rising DIC concentrations and vice versa. This anti-correlation is linked 12 to the turnover of POC being strongly depleted in <sup>13</sup>C as compared to average seawater. The 13 glacial demise of the sedimentary POC pool, induced by the weathering of exposed shelf 14 sediments and the decline in depositional areas along continental margins, contributed 15 significantly to the glacial DIC rise and affected the isotopic evolution of seawater (Broecker, 16 1982a; Wallmann, 2014). The glacial  $\delta^{13}$ C-DIC depletion was widely ascribed to a glacial 17 loss of terrestrial biomass (Shackleton, 1977; Köhler and Fischer, 2004). However, our model 18 can reproduce almost the entire glacial shift to depleted  $\delta^{13}$ C-DIC values recorded in benthic 19 for a minifera (0.34  $\pm$  0.19  $^{\circ}/_{\circ\circ}$ ; (Peterson et al., 2014)) without invoking any net changes in 20 terrestrial biomass (Tab. A5). This outcome is consistent with results of a new model study 21 22 suggesting that the rise in carbon buried in permafrost and under ice largely compensated for the decline in peat, soil and biomass carbon over the LGM (Brovkin and Ganopolski, 2015). 23

# 24 3.4 Radiocarbon

Atmospheric  $\Delta^{14}$ C-CO<sub>2</sub> was forced to follow the IntCal13 values derived from the geological 25 record by varying the <sup>14</sup>C-production rate in the atmosphere (Appendix A, section A8). The 26 <sup>14</sup>C production rate was calculated for each time step considering the <sup>14</sup>C transfer from 27 atmosphere to oceans and changes in the inventories of atmospheric CO<sub>2</sub> and <sup>14</sup>C-CO<sub>2</sub>. The 28 difference between global mean  $\Delta^{14}$ C-DIC and atmospheric  $\Delta^{14}$ C-CO<sub>2</sub> ( $\Delta\Delta^{14}$ C-DIC =  $\Delta^{14}$ C-29 DIC -  $\Delta^{14}$ C-CO<sub>2</sub>) depended on the radiocarbon content of the atmosphere (Figs. 5d, 4g, and 30 12).  $\Delta^{14}$ C-CO<sub>2</sub> and the model-derived  $\Delta\Delta^{14}$ C-DIC were anti-correlated, since the <sup>14</sup>C uptake 31 from the atmosphere was insufficient to raise the radiocarbon content of the model ocean up 32 to the level of elevated  $\Delta^{14}$ C-CO<sub>2</sub> values attained during periods of strong atmospheric 33

radiocarbon production. This anti-correlation was also observed in an additional simulation 1 (Fig. 12b) where the carbon cycle and ocean circulation were maintained at a steady state 2 representing Holocene boundary conditions, whereas  $\Delta^{14}$ C-CO<sub>2</sub> values were forced to follow 3 the IntCal13 record. In further steady-state simulations the radiocarbon production rate in the 4 5 atmosphere was held constant over time while the carbon cycle operated in a Holocene steady-state mode with a constant  $pCO_2$  value of 280 µatm. These model runs show that the 6 steady-state  $\Delta \Delta^{14}$ C-DIC values attained after about 100 kyr simulation time decreased with 7 increasing production rate (Appendix C, Tab. C2). As previously shown, changing production 8 rates of radiocarbon in the atmosphere may affect the difference between  $\Delta^{14}$ C values in 9 planktonic and benthic foraminifera (Adkins and Boyle, 1997) and the contrast between 10 atmospheric and marine  $\Delta^{14}$ C values (Franke et al., 2008). However, these effects were 11 regarded as transient features induced by a slow <sup>14</sup>C transfer from the atmosphere into the 12 ocean. In contrast, the results of our steady-state model suggest that <sup>14</sup>C depletion of the ocean 13 during periods of elevated atmospheric <sup>14</sup>C production can be a permanent steady-state feature 14 (Tab. C2), a conclusion further substantiated by a simple steady-state model presented in 15 Appendix D. 16

The standard simulation STD yielded a mean ocean  $\Delta\Delta^{14}$ C-DIC of -270 °/<sub>00</sub> for the LGM (21 17 ka) and -152  $^{\circ}/_{\circ\circ}$  at 0 ka corresponding to a glacial  $\Delta\Delta^{14}$ C-DIC decline by 118  $^{\circ}/_{\circ\circ}$ . The 18 simulations depicted in Fig. 12b show that multiple processes contributed to the <sup>14</sup>C glacial 19 depletion of the ocean with respect to the atmosphere. These include the glacial decline in 20 deep ocean ventilation, sea-level fall, nutrient utilization, and rise in atmospheric radiocarbon 21 production. The  $\Delta\Delta^{14}$ C-DIC decline observed upon sea-level fall in part was induced by the 22 glacial decline in sedimentary carbon pools adding fossil carbon to the global ocean. Glacial 23 changes in ocean circulation contributed to the  $\Delta \Delta^{14}$ C-DIC decline since the glacial demise of 24 ventilation across the 2000 m depth horizon isolated the deep ocean from the atmosphere. 25 However, the simulations suggest that changes in ocean ventilation possibly were responsible 26 for less than one third of the glacial rise in the radiocarbon contrast between global ocean and 27 atmosphere. 28

Atmospheric <sup>14</sup>C production rates calculated in the model showed the same trends for all simulations (Fig. 12c). They attained very high values at 25 ka and declined over time. The only significant difference between the model runs occurred during the deglaciation. The standard simulation yielded elevated production rates for this period since the rapid ventilation of the deep ocean considered in simulation STD drew radiocarbon from the atmosphere and released <sup>14</sup>C-depleted CO<sub>2</sub> into the atmosphere such that the production rate was enhanced to maintain atmospheric  $\Delta^{14}$ C-CO<sub>2</sub> at the deglacial level documented by IntCal13 (Fig. 12a). Our model results may support the hypothesis that a significant fraction of the  $\Delta^{14}$ C-CO<sub>2</sub> record is controlled by changes in atmospheric radiocarbon production (Köhler et al., 2006; Broecker et al., 2004).

However, in contrast to our model approach various authors have proposed that most of the 6 7  $\Delta^{14}$ C-CO<sub>2</sub> record can be explained by changes in glacial ocean dynamics and carbon cycling without invoking significantly elevated rates of atmospheric radiocarbon production 8 (Muscheler et al., 2005; Robinson et al., 2005). The Holocene trends calculated in the model 9 are similar to those observed in the <sup>10</sup>Be ice-core record (Muscheler et al., 2005) and derived 10 from Holocene geo-magnetic data (Laj et al., 2002) while the glacial values are closer to the 11 stacked sedimentary <sup>10</sup>Be record (Frank et al., 1997). Various reasons have been evoked to 12 explain the deviations between different records of atmospheric radionuclide production 13 (Köhler et al., 2006). The controversy suggests a clear need to develop a better constrained 14 record of atmospheric <sup>14</sup>C production suitable for model validations (Fig. 12d). 15

The spatial distribution of radiocarbon in the global ocean changed significantly during the 16 LGM (Fig. 11). According to the standard simulation  $\Delta\Delta^{14}$ C-DIC values were strongly 17 depleted over the entire ocean and reached a minimum of -356  $^{\rm o}\!/_{\rm oo}$  in North Pacific deep 18 water. Both, vertical and horizontal gradients were strengthened during the LGM. In the 19 modern ocean, marine  $\Delta^{14}$ C-DIC values are correlated with DIC concentrations at water 20 depths below 2000 m (Sarnthein et al., 2013). If this correlation also holds for the glacial 21 ocean, glacial  $\Delta \Delta^{14}$ C-DIC values may be used as proxy for DIC concentrations in glacial 22 23 seawater (Sarnthein et al., 2013). The model results show that the correlation was indeed maintained in the glacial ocean and the slope of the correlation was similar for all model runs 24 and time slices (Fig. 13). However, the regression line for glacial conditions was shifted to 25 lower DIC and  $\Delta\Delta^{14}$ C-DIC values due to changes in ocean carbon cycling and possibly 26 elevated radiocarbon production rates in the glacial atmosphere. Thus  $\Delta \Delta^{14}$ C-DIC values may 27 serve as new proxy for DIC concentrations in ancient seawater, if suitable methods are found 28 29 to correct for the glacial shift observed in the simulations (Fig. 13). The overall LGM pattern calculated in the standard simulation (Fig. 11) compares well with trends derived from the 30 radiocarbon contents of planktonic and benthic foraminifera even though radiocarbon data 31 indicate strong gradients within ocean basins, which were not resolved by the box model 32 (Appendix C, Tab. C3). A recent review of glacial  $\Delta \Delta^{14}$ C-DIC data (Sarnthein et al., 2013) 33

revealed radiocarbon depletions in the deep Atlantic, Southern Ocean and Indo-Pacific 1 broadly consistent with those calculated by the model. However, the model was not able to 2 reproduce very strong radiocarbon depletions measured at some deep water sites due to its 3 coarse spatial resolution (Tab. C3). Moreover, it predicts significant <sup>14</sup>C-depletions in the 4 Atlantic thermocline which are inconsistent with coral <sup>14</sup>C data (Robinson et al., 2005). <sup>14</sup>C 5 measurements in foraminiferal shells and corals from the glacial ocean feature strong spatial 6 7 and temporal variability (Broecker et al., 2004; Sarnthein et al., 2013). More data will help to resolve this variability and constrain the radiocarbon distribution and dynamics of the glacial 8 9 ocean.

10

# 11 4 Conclusions

For a first time we show model results that are consistent with both the atmospheric  $pCO_2$ 12 record (Figs. 5 and 7) and data on past distribution changes of dissolved oxygen, carbonate, 13 and radiocarbon in the glacial ocean (Figs. 8, 9, 11 and Tabs. C1 and C3). Atmospheric pCO<sub>2</sub> 14 and the glacial distribution of seawater tracers were not prescribed but calculated as 15 prognostic model variables. Only marine  $\delta^{13}C$  data were used to parameterize the glacial 16 circulation model. A comprehensive formulation of shelf processes and sea-level effects is a 17 major new component included in our earth system model. Thus, the conformity between 18 independent proxy data and key model results (atmospheric pCO<sub>2</sub> change over the last 130 19 kyr, distribution of dissolved oxygen, carbonate, and radiocarbon in the LGM ocean) supports 20 our hypothesis that the glacial sea-level drop induced a decline in atmospheric pCO<sub>2</sub> and a 21 rise in the inventories of nutrients, DIC, and alkalinity in the glacial ocean (Wallmann, 2014). 22 23 Also, we first show that the slope of DIC versus radiocarbon observed in the modern deep ocean (Sarnthein et al., 2013) was probably maintained in the glacial ocean (Fig. 13). 24 However, a glacial shift in the intercept now complicates the use of  ${}^{14}C$  as DIC proxy. 25

The shelf hypothesis was originally developed to explain the deglacial rise in atmospheric 26 pCO<sub>2</sub> (Broecker, 1982b). In contrast, our model analysis reveals that shelf and sea-level 27 effects were not responsible for this rapid rise but account for a major portion of the slow 28 glacial decline of atmospheric  $pCO_2$  (Figs. 5 and 7). The deglacial sea-level rise induced a 29 decline in nutrient and carbon stocks in the global ocean. However, these stocks changed only 30 slowly due to their large size (Menviel et al., 2012). The gradual  $pCO_2$  rise over the Holocene 31 may be attributed to the slow relaxation of nutrient and carbon stocks promoting CO<sub>2</sub> transfer 32 from the ocean into the atmosphere. The slow relaxation may also be responsible for the 33

imbalance in phosphate and TA sources and sinks observed in the modern ocean (Wallmann,
2010; Wallmann, 2014). Stocks of these chemical species may decline until today since tens
of thousands of years may be needed to draw down the dissolved P and TA inventories from
their peak values attained over the last glacial maximum.

According to standard Milankovitch theory (Milankovitch, 1941), variations in summer 5 6 insolation at high latitudes (Berger and Loutre, 1991) cause waxing and waning of northern 7 ice sheets (Fig. 14). Most of the global climate change over a glacial cycle is thus believed to 8 be driven by northern summer insolation and ice sheet dynamics (Denton et al., 2010). 9 However, it has always been difficult to explain why atmospheric  $pCO_2$  declined over glacial 10 periods and how this drop was connected to the built-up of large continental ice sheets. The sea-level effects explored in this paper provide the missing link between glacial ice sheet and 11 12  $pCO_2$  dynamics. The sea-level-driven  $pCO_2$  decline was amplified by a decrease in deep ocean ventilation, a decline in sea surface temperature, and enhanced nutrient utilization. 13 These additional changes were driven by a combination of greenhouse gas, albedo, and 14 insolation forcing (Fig. 14). Glacial terminations occurred when summer insolation increased 15 at northern latitudes (Raymo et al., 1997), ice sheets reached a critical size (Denton et al., 16 2010), and carbonate compensation at the deep-sea floor reversed the declining  $pCO_2$  trend 17 (Wallmann, 2014). The deglacial warming was again driven by greenhouse gas, albedo, and 18 19 insolation forcing promoting the retreat of continental ice sheets, sea-level rise, ocean ventilation, and the decline in nutrient utilization in a positive feedback mode. 20

Due to their internal non-linear dynamics, continental ice sheets are able to generate 100-kyr 21 22 cycles with a slow glacial expansion and rapid deglacial contraction of ice volume under Milankovitch forcing even though insolation oscillates on much shorter time scales (Imbrie 23 24 and Imbrie, 1980; Abe-Ouchi et al., 2013; Ganopolski and Calov, 2011; Pollard, 1983). 25 Positive feedbacks embedded in the global carbon cycle are able to generate a 100-kyr cycle 26 without any form of external forcing when surface temperature, ice volume, sea-level and 27 ocean circulation are assumed to be controlled by pCO<sub>2</sub> (Wallmann, 2014). Thus, both, continental ice sheets and the global carbon system have the inherent tendency to generate 28 cycles with a length of 100 kyr. They interact via sea-level and pCO<sub>2</sub> change, respond to 29 insolation forcing, control changes in the climate system (surface temperature, ocean and 30 atmospheric circulation) and may generate the 100-kyr cycle dominating late Quaternary 31 climate change. 32

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#### **1** Appendix A: Model set-up and calibration

## 2 A1 Data and procedures for model calibration

Mean tracer concentrations were calculated for each of the model boxes using the GLODAP 3 data base for total alkalinity, DIC, <sup>13</sup>C-DIC and <sup>14</sup>C-DIC (Key et al., 2004) and the World 4 Ocean Atlas (WOA01) for temperature, salinity, PO<sub>4</sub>, NO<sub>3</sub> and O<sub>2</sub> (Conkright et al., 2002). 5 <sup>14</sup>C-DIC-data were corrected by subtracting the bomb-<sup>14</sup>C signal and DIC data were corrected 6 for the intrusion of anthropogenic CO<sub>2</sub> (Key et al., 2004) whereas  ${}^{13}$ C-DIC data were not 7 corrected and are thus affected by <sup>13</sup>C-depleted anthropogenic CO<sub>2</sub>. The model was run into 8 steady state under pre-anthropogenic boundary conditions and resulting tracer concentrations 9 were compared to data to validate the model output and calibrate the model (Tab. A1 and A2, 10 Fig. A1). The  $pCO_2$  value and global export production of particulate organic carbon were 11 used as additional constraints, i.e. the calculated values had to comply with the corresponding 12 observations (ca. 280 µatm and ca. 700 - 900 Tmol yr<sup>-1</sup>, respectively, (Sarmiento and Gruber, 13 2006). For these initial model runs, the riverine fluxes to the ocean were enhanced to 14 compensate for the removal fluxes observed in the modern ocean. The atmospheric  $pCO_2$ 15 value was calculated applying a constant continental CO<sub>2</sub> uptake rate balancing the CO<sub>2</sub> being 16 produced in the modern ocean by carbonate burial and degassing processes (Wallmann, 17 2014). The isotopic composition of atmospheric  $CO_2$  was maintained at a constant level 18 representative for the pre-human atmosphere ( $\delta^{13}C = -6.5$  °/<sub>00</sub>,  $\Delta^{14}C = 0$  °/<sub>00</sub>). Water fluxes 19 (Tab. A3) and parameter values for key biogeochemical processes (Tab. A4) were varied 20 until pCO<sub>2</sub>, global export production, and the tracer distribution fields generated by the 21 steady-state box model were consistent with data (Tab. A1 and A2, Fig. A1). A good fit was 22 obtained for all tracers except <sup>13</sup>C-DIC. Some of the <sup>13</sup>C mismatch was induced by 23 anthropogenic <sup>13</sup>C which has a strong effect on the observations in the modern ocean but was 24 not considered in the model simulations. 25

#### 26 A2 Ocean circulation and tracer transport

Water fluxes between adjacent boxes were calculated using output of the Opa 8.2 ocean circulation model in the framework of NEMO (Nucleus for European Modeling of the Ocean) to start with a configuration that is dynamically consistent with a 3-D forward ocean model (Madec et al., 1998). NEMO was forced by atmospheric reanalysis data as described in (Aumont and Bopp, 2006). A more detailed analysis of the resulting large-scale circulation pattern is given in (Bordelon-Katrynski and Schneider, 2012). The calculation of water exchange was based on horizontal and vertical velocities on the box model grid. In order to

consider two-way exchange between the boxes, not only the net transports, but fluxes in both 1 2 directions (northward/southward, up/down) were taken into account. Water fluxes at the atmosphere-ocean boundary were calculated as residual fluxes balancing the water exchange 3 for each vertical column. Test runs with the box model revealed, however, that tracer 4 distributions calculated with the NEMO-derived water fluxes were inconsistent with tracer 5 data when the NEMO circulation field was applied in the box model. This mismatch was 6 7 induced by the coarse spatial resolution of the box model and by errors inherent to the NEMO simulations. The NEMO-derived circulation field was, thus, modified to allow for a better fit 8 9 to the independent observations listed in Tab. A1 and Tab. A2 and to bring the circulation field in line with other observations and GCM modeling results. Thus, NEMO features a 10 11 North Atlantic Deep Water (NADW) formation rate of only ca. 10 Sv whereas tracer data (radiocarbon, phosphate, oxygen) constrain this rate at ca. 15 Sv (Broecker et al., 1998). 12 13 Moreover, NEMO predicts that Antarctic Bottom Water (AABW) upwells in the Indo-Pacific all the way to the thermocline and surface ocean. This pattern is consistent with the "great 14 15 ocean conveyer" (Broecker, 1991) but in conflict with other more recent ocean models suggesting that deep water ascent occurs in the Southern Ocean rather than in the Indo-Pacific 16 (Sarmiento and Gruber, 2006). These models show that AABW flowing into the Indo-Pacific 17 returns as deep water to the Southern Ocean where it ascends to form intermediate water 18 masses flowing northwards into the major ocean basins (Imbrie et al., 1993; Gnanadesekian 19 20 and Hallberg, 2002; Marinov et al., 2006). NEMO also predicts an extremely high rate of vertical water exchange in the Southern Ocean across 2000 m water depth of more than 200 21 22 Sv. These strong upward and downward water fluxes are inconsistent with tracer observations showing strong vertical gradients between the deep ocean (>2000 m water depth) and the 23 overlying water masses. The water fluxes derived from NEMO were modified to remove 24 25 these biases and to provide more realistic water fluxes for the box model (Tab. A3). The 26 corresponding best-fit water fluxes are bidirectional, i.e. water flows in both directions between each of the adjacent model boxes (Tab. A3). The net fluxes (Tab. A3) were 27 28 calculated as difference between these opposing fluxes. They represent the meridional overturning circulation (MOC) as implemented in the box model (Fig. 2): NADW is formed 29 30 in the North Atlantic and Arctic basins at an overall rate of ca. 15 Sv. It flows towards the 31 Southern Ocean where Antarctic Bottom Water (AABW) is formed at a rate of ca. 18 Sv. A 32 minor AABW fraction flows northwards into the Atlantic while most of the AABW is filling the deep basins of the Indo-Pacific at a rate of ca. 16 Sv where it upwells and returns into the 33 34 Southern Ocean as deep water. Intermediate water formed by deep water ascent in the Southern Ocean flows into the Indo-Pacific at a rate of ca. 14 Sv where it upwells to form surface water flowing back towards the Southern Ocean. Surface waters flowing northward into the Atlantic and returning as NADW to the Southern Ocean are closing the loop. This overall MOC pattern and the corresponding flow rates are consistent with tracer data and other observations (Sarmiento and Gruber, 2006).

6 The exchange fluxes between adjacent boxes reflect, both, opposing water flows across the 7 box boundaries and eddy diffusive mixing (Tab. A3). The large vertical exchange flux 8 between tropical surface and intermediate waters in the Indo-Pacific is thus supported by 9 intense Ekman driven upwelling and down-welling while wind-driven eddy diffusive mixing 10 explains most of the vertical exchange between surface and intermediate water boxes in the North Atlantic, Southern Ocean and North Pacific. The overall vertical water exchange 11 12 across the 100 m water depth horizon (ca. 297 Sv, Tab. A3) is sufficiently high to ventilate the global thermocline and to support a global rate of new and export production in the order 13 of 700 – 900 Tmol yr<sup>-1</sup>. About 37 % of this vertical exchange flux occurs in the Southern 14 Ocean (>  $30^{\circ}$ S). The global bidirectional water flux across the 2000 m water depth level is 15 much lower (only 45 Sv, 44 % in the Southern Ocean) while the flux across the 4000 m line 16 amounts to ca. 179 Sv with a 74 % contribution by the Southern Ocean. The box model's 17 major internal boundary for vertical exchange is thus located at 2000 m water depth between 18 the thermocline and the underlying deep ocean. 19

In box modeling, water fluxes (F<sub>Wab</sub>) are multiplied by tracer concentrations (C<sub>j</sub>) to calculate
 tracer fluxes (F<sub>Tab</sub>) between adjacent boxes:

$$22 F_{Tab} = C_a \cdot F_{Wab} (A1)$$

where  $F_{Wab}$  and  $F_{Tab}$  are the water and tracer fluxes from box *a* to box *b* while  $C_a$  is the concentration of the considered tracer in box *a*. The back fluxes from box *b* to box *a* are defined correspondingly:

$$26 F_{Tba} = C_b \cdot F_{Wba} (A2)$$

Tracer fluxes arising from the water exchange fluxes listed in Tab. A3 ( $F_{Wex}$ ) are thus proportional to the concentration difference between adjacent boxes:

$$29 F_{Tex} = (C_a - C_b) \cdot F_{Wex} (A3)$$

30 These fluxes can be regarded as diffusion-analog mass transfer processes since their 31 magnitude is proportional to concentration differences rather than concentrations. In contrast, the tracer fluxes arising from the net water fluxes in Tab. A3 are purely advective. Most box models apply unidirectional advective fluxes, only, and ignore diffusive bidirectional fluxes. Tracer distributions observed in the global ocean and simulated with general circulation models are, however, strongly affected by diffusive processes. With the inclusion of bidirectional fluxes in our box model set-up, we aim to better mimic this diffusive behavior.

6 The low spatial resolution of box models is problematic and may induce significant errors. 7 For the box model set-up presented in this paper, the largest errors are associated with the 8 upward fluxes from the thermocline into the surface ocean. Tracer concentrations calculated 9 for the intermediate water boxes represent mean values averaged over the depth range 100 -10 2000 m where strong vertical gradients exist in the natural system. Due to these strong vertical gradients, the mean concentration values are not representative for the thermocline 11 12 waters ascending across the 100 m water depth line. The standard box model approach where tracer fluxes are calculated applying the mean concentration in the source box (s. equations 13 above) was, thus, abandoned for these specific fluxes and tracer fluxes were calculated as: 14

$$15 F_{TIS} = C_{TH} \cdot F_{WIS} (A4)$$

where  $F_{TIS}$  is the tracer flux from the intermediate water box to the overlying surface water box,  $F_{WIS}$  is the corresponding water flux, and  $C_{TH}$  is the tracer concentration in the upwelling thermocline water calculate as:

19 
$$C_{TH} = f_I \cdot C_I + (1 - f_I) \cdot C_S$$
 (A5)

C<sub>I</sub> is the concentration in the intermediate water box, C<sub>S</sub> the concentration in the overlying surface water box and f<sub>I</sub> defines the fraction of C<sub>I</sub> in the ascending two component mixture. The weighing factor f<sub>I</sub> was set to 0.5 for salinity, DIC, and <sup>13</sup>C-DIC. A smaller value was applied for total alkalinity (f<sub>I</sub> = 0.3) to mimic the deeper regeneration of this tracer while larger values were applied for other tracers featuring steeper thermocline gradients (DP and DN: f<sub>I</sub> = 0.55; DO: f<sub>I</sub> = 0.9; <sup>14</sup>C-DIC: 0.7).

# 26 A3 Salinity and surface temperatures

Salinity (Sal) was treated as an inert tracer. The mass balance equations for Sal in each of the
24 ocean boxes were thus simply defined as:

29 
$$\frac{\partial Vol \cdot Sal}{\partial t} = \sum F_{Sal-in} - \sum F_{Sal-out}$$
(A6)

where  $F_{\text{Sal-in}}$  are the salinity fluxes from the neighboring boxes into the considered box while 1 F<sub>Sal-out</sub> gives the corresponding fluxes from the considered box into the adjacent boxes. The 2 volume of the considered box (Vol) was allowed to change over time to mimic the contraction 3 of the ocean volume during glacial sea-level low-stands. Fluxes were calculated as products 4 of water flux and salinity in the source box (Eq. A1 and Eq. A2) with the exception of 5 intermediate to surface water fluxes where thermocline concentrations were applied (Eq. A4 6 7 and A5). Surface water boxes were subject to evaporation and precipitation and received river input from the continents. The fresh water fluxes listed in Tab. A3 represent the overall 8 9 budget of evapotranspiration and river water input. Negative fluxes thus indicate that evaporation exceeds the sum of precipitation and river water input. Freshwater fluxes were 10 11 varied in the initial steady state simulations until the calculated salinity values were consistent with observations. These simulations showed, however, that unrealistically high freshwater 12 13 fluxes were needed to reproduce the low salinity values observed in the Arctic Ocean surface water box. This problem arises since the standard box model procedure demands that water 14 15 masses leaving the Arctic carry a chemical signature corresponding to the mean salinity value integrated over the entire Arctic surface ocean. Observations show, however, that Arctic 16 17 surface waters sinking into the abyss are more salty than mean Arctic surface water. The standard model procedure was, hence, modified to consider this characteristic feature of deep 18 water formation and to avoid unrealistically high freshwater fluxes to the Arctic surface 19 20 ocean, that is an enhanced salinity (+ 0.9 PSU with respect to the mean salinity of Arctic surface water) was employed for the waters sinking into the underlying intermediate water 21 22 box.

23 Over a glacial cycle, surface temperatures are regulated by changes in, both, albedo and the partial pressure of greenhouse gases. In the model it was assumed that 50 % of the 24 25 temperature change is proportional to the prescribed sea-level, that is continental ice sheet formation and albedo change while the remaining 50 % are proportional to the logarithm of 26 27 atmospheric pCO<sub>2</sub> calculated as prognostic model variable. The global mean atmospheric surface temperature was assumed to fall by 3°C during the glacial while the average sea 28 surface temperature (SST) was allowed to drop by ca. 2°C (Schmittner et al., 2011). The SST 29 30 drop was assumed to be twice as high as the global mean at high latitudes and only half as 31 high in the low latitude surface water boxes. Temperatures in intermediate and deep waters were maintained at their modern values, for simplicity. 32

#### 33 A4 Phosphorus

The model includes a comprehensive phosphorus cycle. Rivers transport dissolved phosphorus (DP) into the ocean where it is taken up by phytoplankton, gets exported, degraded, buried in marine sediments, and removed via hydrothermal activity (Wallmann, 2014). Export production (F<sub>EPOP</sub>) of particulate organic P (POP) from the individual surface water boxes across 100 m water depth was calculated applying Liebig's law:

$$6 F_{EPOP} = k_{EXP} \cdot Min \left[ DP_S \cdot \frac{DP_S}{DP_S + K_{DP}}, \frac{DN_S}{r_{NP}} \cdot \frac{DN_S}{DN_S + r_{NP} \cdot K_{DP}} \right] \cdot Vol_S (A7)$$

POP export was thus limited either by dissolved reactive nitrogen (DN) or DP where K<sub>DP</sub> is a 7 Monod constant ( $K_{DP} = 0.01 \ \mu M$ ),  $r_{NP}$  is the atomic N to P ratio in exported particulate 8 organic matter ( $r_{NP} = 17$ ; (Körtzinger et al., 2001)), Vol<sub>s</sub> is the volume of the considered 9 surface water box, and k<sub>EXP</sub> is a site specific kinetic constant defined by fitting the model to 10 DP concentrations observed in the modern surface ocean (Tab. A4). Most of the exported 11 POP was degraded in the water column while a small but significant fraction was permanently 12 13 buried in marine sediments (Appendix B). POP degradation in the water column (incl. the bioturbated surface layer of marine sediments) was distributed between intermediate (93 %), 14 15 deep (6 %) and bottom water boxes (1 %). Export and degradation of particulate organic carbon (POC) and nitrogen (PON) and oxygen respiration were derived from the 16 17 corresponding POP turnover applying constant Redfield ratios (PON/POP = 17, POC/PON = 123/17, O<sub>2</sub>/POC = 1.34 (Körtzinger et al., 2001)). 18

#### 19 A5 Nitrogen

Nitrogen cycling was simulated considering export, degradation and burial of PON, nitrogen fixation, benthic and pelagic denitrification, and riverine fluxes of dissolved reactive nitrogen (DN). Nitrogen fixation in surface water boxes ( $F_{NF}$ ) was calculated as:

23 
$$F_{NF} = k_{NF} \cdot DP_{S} \cdot \frac{DP_{S}}{DP_{S} + K_{DP}} \cdot \frac{r_{NP}}{r_{DNDPS}} \cdot Vol_{S}$$
(A8)

It was controlled by the ambient DP concentration and modulated by the DN/DP ratio in surface water ( $r_{DNDPS}$ ) such that nitrogen fixation decreased when  $r_{DNDPS}$  exceeded the N/P ratio in exported biomass ( $r_{NP}$ ) and vice versa. The biomass of nitrogen-fixing organisms was completely degraded in the surface ocean boxes and the organic nitrogen compounds were transformed into DN. Nitrogen fixation thus enhanced the DN pool in the surface ocean but did not contribute to export production. The kinetic constant for nitrogen fixation ( $k_{NF}$ ) was determined by fitting the model to the nitrate concentrations observed in the modern surface
 ocean (Tab. A1 and Tab. A4).

Denitrification in the water column was limited to the intermediate water box of the Tropical Indo-Pacific where the major oxygen minimum zones (OMZs) are located. It proceeded at a constant rate of 5 Tmol yr<sup>-1</sup> (Deutsch et al., 2001). No attempt was made to simulate the temporal evolution of water column denitrification since the box model did not resolve the dynamics and spatial extent of OMZs. Benthic denitrification was calculated as function of bottom water chemistry (nitrate and oxygen) and the rain rate of particulate organic carbon (POC) to the seafloor (Appendix B) using an empirical transfer function (Bohlen et al., 2012).

# 10 A6 Oxygen

11 Oxygen was produced in the surface ocean via export production and consumed in the 12 ocean's interior by degradation of particulate organic matter. The oxygen exchange between 13 surface ocean and atmosphere was calculated as:

14 
$$F_{DO} = k_W \cdot A_{SUR} \cdot (DO_S - DO_{SEQ})$$
 (A9)

where k<sub>w</sub> is piston velocity, A<sub>SUR</sub> is the ice-free surface area of the considered box (Köhler et 15 al., 2005), DO<sub>S</sub> is the concentration of DO in the considered surface water box while  $DO_{SEO}$  is 16 the temperature-dependent equilibrium concentration of DO in surface water (García and 17 Gordon, 1992). The piston velocity was determined for each surface water box by fitting the 18 model to the observed  $\Delta^{14}$ C values (Tab. A2 and Tab. A4). The deep ocean is ventilated by 19 20 cold and oxygen-enriched surface waters sinking into the ocean's interior at high latitudes with a temperature of ca. -1.5°C. To mimic this process in the box model, the oxygen 21 22 concentration in downward flowing water masses was calculated applying a temperature of -1.5°C rather than the significantly higher mean SSTs of North Atlantic and Southern Ocean 23 24 surface waters.

#### 25 A7 Carbon

POC burial depended on export production and depositional area while neritic carbonate burial was proportional to the shelf area at 0 – 50 m water depths (Appendix B). Export of pelagic PIC (particulate inorganic carbon) was calculated from POC export production and the PIC/POC export ratios which were derived by fitting the TA values in the surface ocean to observations (Tab. A2 and A4). Exported PIC dissolved in intermediate water boxes until the PIC/POC export ratio at 2000 m water depth reached a value of unity as observed in sediment trap studies (Berelson et al., 2007; Honjo et al., 2008). Carbonate compensation was implemented at >2000 m water depth where PIC dissolution was controlled by the carbonate concentrations calculated from TA and DIC values in deep and bottom water boxes (Wallmann, 2014). The remaining PIC was buried in pelagic sediments. The TA mass balance equations considered alkalinity production via denitrification and PON export production and alkalinity consumption via nitrogen fixation and PON degradation. The CO<sub>2</sub> gas flux from the surface ocean into the atmosphere across the seawater/atmosphere boundary layer ( $F_{CO2}$ ) was calculated as (Sarmiento and Gruber, 2006):

8 
$$F_{CO2} = k_{W} \cdot A_{SUR} \cdot (CO_{2S} - CO_{2SEQ})$$
(A10)

where CO<sub>2S</sub> is the concentration of CO<sub>2</sub> in the considered surface water box (as calculated 9 from ambient DIC and TA), while CO<sub>2SEO</sub> is the equilibrium concentration of CO<sub>2</sub> in surface 10 water (as calculated from atmospheric  $pCO_2$ ). The thermodynamic equations included in the 11 box model considered the effects of sea surface temperature (SST) and salinity on CO<sub>2SEQ</sub> and 12 CO<sub>2S</sub> (Zeebe and Wolf-Gladrow, 2001). Constant rates were applied for on-shore volcanic 13 and metamorphic degassing, degassing at mid-ocean ridges, alteration of oceanic crust, and 14 silicate weathering (Wallmann, 2014). The rate of silicate weathering was set to a constant 15 16 value since the weathering of exposed shelf sediments was assumed to compensate for the glacial decrease in silicate weathering in the continental hinterland (Munhoven, 2002). The 17 18 rate of carbonate weathering was assumed to depend on surface temperature, run-off, and the size of the exposed shelf area (Wallmann, 2014). Riverine POC fluxes are ignored in the 19 20 model. However, POC weathering is considered. It has two components: i) weathering of POC in exposed shelf sediments and ii) weathering of fossil POC in continental hinterland 21 (Wallmann, 2014). Both components produce atmospheric  $CO_2$  depleted in <sup>13</sup>C and <sup>14</sup>C. 22

# 23 A8 Carbon isotopes

The model includes <sup>13</sup>C-DIC and <sup>14</sup>C-DIC as tracers in addition to total DIC. Isotope ratios as well as  $\delta^{13}$ C and  $\Delta^{14}$ C values of DIC were calculated from <sup>13</sup>C-DIC/DIC and <sup>14</sup>C-DIC/DIC mole fractions. The gas exchange of <sup>13</sup>C-CO<sub>2</sub> across the seawater/atmosphere boundary layer (F<sub>13CO2</sub>) was calculated as (Schmittner et al., 2013; Zhang et al., 1995):

28 
$$F_{13CO2} = k_{W} \cdot A_{SUR} \cdot \alpha_{aq-g} \cdot \alpha_{k} \cdot \left(\frac{R_{13DIC}}{\alpha_{DIC-g}} \cdot CO_{2S} - R_{13CO2A} \cdot CO_{2SEQ}\right)$$
(A11)

where  $\alpha_{aq-g}$  is the equilibrium fractionation factor for CO<sub>2</sub> gas exchange between seawater and air,  $\alpha_k$  is the corresponding kinetic fractionation factor,  $\alpha_{DIC-g}$  is the equilibrium fractionation factor defining the <sup>13</sup>C fractionation between DIC and gaseous CO<sub>2</sub>, R<sub>13DIC</sub> is the 1  ${}^{13}C/{}^{12}C$  ratio in DIC, and  $R_{13CO2A}$  is the  ${}^{13}C/{}^{12}C$  ratio in atmospheric CO<sub>2</sub>. The isotopic 2 composition of DIC species (CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) was calculated using equilibrium 3 fractionation factors given in (Zeebe and Wolf-Gladrow, 2001). These values were applied to 4 calculate the isotopic composition of exported POC and neritic and pelagic carbonates 5 applying isotopic fractionation factors according to (Ridgewell, 2001) and (Romanek et al., 6 1992), respectively.

Fig. A3 shows the atmospheric  $\delta^{13}$ C-CO<sub>2</sub> record as calculated in our standard simulation. 7 According to this simulation and our previous studies (Sarnthein et al., 2013), the strong 8 negative  $\delta^{13}$ C-excursion observed in the ice-core record was largely caused by deglacial 9 upwelling pulses in the Southern Ocean, though the amplitude of the simulated  $\delta^{13}$ C-CO<sub>2</sub> 10 decline is much larger than that observed in the dataset (Schmitt et al., 2012). The trends of 11 our results and the empiric data are similar. The different extent of shift of the two records is 12 probably related to the poor representation of the <sup>13</sup>C-DIC turnover in the Southern Ocean in 13 our coarse-resolution model. We were not able to reproduce more closely the observed  $\delta^{13}$ C-14 DIC distribution in our model calibration even though a good fit was attained for all other 15 tracers (salinity, DIC, <sup>14</sup>C-DIC, alkalinity, phosphate, nitrate, oxygen, Fig. A1). Hence, we do 16 not conclude that this deviation for  $\delta^{13}$ C-CO<sub>2</sub> implies erroneous model results for all 17 remaining model variables. It rather reflects a specific weakness in the model set-up with 18 respect to the simulation of  $\delta^{13}$ C-DIC in the Southern Ocean. Our model predicts a negative 19 value for intermediate waters in the modern Southern Ocean ( $\delta^{13}$ C-DIC = -0.05  $^{\circ}/_{00}$ ) while 20 observations yield a positive value of  $+0.72^{\circ}/_{\circ\circ}$  for this ocean box (SO<sub>I</sub> in Tab. A2). Due to 21 this deviation the vertical gradient in the model exceeds the observed  $\delta^{13}C$  gradient between 22 surface and intermediate waters by more than a factor of two. The glacial rise and deglacial 23 drop in  $\delta^{13}$ C-CO<sub>2</sub> are amplified by this model artefact. The deglacial intermediate water, 24 overly depleted in <sup>13</sup>C, upwells into the surface ocean where it induces a far too strong 25 atmospheric  $\delta^{13}$ C-CO<sub>2</sub> decline. Since the biased vertical  $\delta^{13}$ C-DIC gradient in the Southern 26 Ocean impedes a meaningful simulation of atmospheric  $\delta^{13}$ C-CO<sub>2</sub>, we tuned the  $^{13}$ C-CO<sub>2</sub> 27 fluxes between the surface ocean and the atmosphere such that the resulting atmospheric 28  $\delta^{13}$ C-CO<sub>2</sub> values were consistent with the ice-core record. By this way we effectively 29 employed the ice-core data to force the  $\delta^{13}$ C-DIC model (Fig. 4f). The  $\delta^{13}$ C values of 30 intermediate, deep and bottom water boxes employed to derive the glacial circulation field 31 (Tab. A5) were not significantly affected by this tuning since the inventory of  ${}^{13}$ C residing in 32 the global ocean exceeds the atmospheric inventory by almost two orders of magnitude. 33

1 The  ${}^{14}C/{}^{12}C$  fractionation between DIC, CO<sub>2</sub>, POC and CaCO<sub>3</sub> was calculated using the 2 squared  ${}^{13}C$  equilibrium fractionation factors since the mass difference between  ${}^{14}C$  and  ${}^{12}C$ 3 exceeds the  ${}^{13}C$  -  ${}^{12}C$  difference by a factor of 2. The gas exchange of  ${}^{14}C$ -CO<sub>2</sub> across the 4 seawater/atmosphere boundary layer (F<sub>14CO2</sub>) was thus calculated as:

5 
$$F_{14CO2} = k_{W} \cdot A_{SUR} \cdot \alpha_{aq-g}^{2} \cdot \alpha_{k} \cdot \left(\frac{R_{14DIC}}{\alpha_{DIC-g}} \cdot CO_{2S} - R_{14CO2A} \cdot CO_{2SEQ}\right)$$
(A12)

6 where  $R_{14DIC}$  is the <sup>14</sup>C/<sup>12</sup>C ratio in DIC of the considered surface water box and  $R_{14CO2A}$  the 7 <sup>14</sup>C/<sup>12</sup>C ratio in atmospheric CO<sub>2</sub>. Moreover, <sup>14</sup>C-DIC was subject to radioactive decay with a 8 decay constant of  $\lambda = 1/8267$  yr<sup>-1</sup>.

9  $\Delta^{14}$ C-DIC values were calculated as:

10 
$$\Delta^{14}C - DIC = \left(\frac{f_N \cdot \Phi_{14DIC}}{\Phi_{abs}} - 1\right) \cdot 1000$$
(A13)

11 where  $\Phi_{14\text{DIC}}$  is the <sup>14</sup>C mole fraction ( $\Phi_{14\text{DIC}} = {}^{14}\text{C}\text{-DIC/DIC}$ ),  $\Phi_{abs}$  is the <sup>14</sup>C mole fraction of 12 the standard (1.175 x 10<sup>-12</sup> (Mook and Plicht, 1999), pre-human atmosphere with a  $\delta^{13}$ C value 13 of -25 °/<sub>00</sub>), f<sub>N</sub> is the normalization factor defined as:

14 
$$f_{N} = \left(\frac{0.975}{\left(1 + \frac{\delta^{13}C}{1000}\right)}\right)^{2}$$
 (A14)

and  $\delta^{13}$ C is the  $\delta^{13}$ C value of DIC in the considered box in  $^{o}/_{oo}$  PDB. The isotopic fractionation experienced by the considered DIC pool was thus taken into account in the calculation of marine  $\Delta^{14}$ C-DIC values by applying the  $\delta^{13}$ C-DIC calculated for the considered ocean box (Stuiver and Polach, 1977).

19 The time-dependent radiocarbon production rate in the atmosphere  $(R_{14})$  was calculated 20 applying the following equation:

21 
$$R_{14} = k_{14} \left( \Delta^{14} \text{C-CO}_2 \text{ (data)} - \Delta^{14} \text{C-CO}_2 \text{ (model)} \right)$$
 (A15)

where  $k_{14}$  is a constant ( $\geq 10^5$  mmol yr<sup>-1</sup> °/<sub>oo</sub><sup>-1</sup>),  $\Delta^{14}$ C-CO<sub>2</sub> (model) is the atmospheric value calculated for each time step of the model, and  $\Delta^{14}$ C-CO<sub>2</sub> (data) is the data trend reconstructed from the geological record (Reimer et al., 2013). R<sub>14</sub> thus increased when  $\Delta^{14}$ C-CO<sub>2</sub> (model) was smaller than  $\Delta^{14}$ C-CO<sub>2</sub> (data) and vice versa. With this approach, the production rate was varied such that the model always complied with the atmospheric <sup>14</sup>C record. The atmospheric radiocarbon model considered production and the decay of radiocarbon in the atmosphere as well as exchange processes with the continents and the surface ocean (Eq. A12). The major output of the atmospheric <sup>14</sup>C model was the timedependent <sup>14</sup>C production rate (Eq. A15).

6

# Appendix B: Impact of sea-level change on benthic processes at continental margins

# 9 B1 Particulate organic carbon (POC) turnover

The overwhelming portion of POC produced in the euphotic zone is degraded in the water 10 column before it can reach the seabed. Hence, in the open ocean, only ca. 1 % of the primary 11 production is deposited at the deep-sea floor (Suess, 1980; Jahnke, 1996; Seiter et al., 2005; 12 Dunne et al., 2007). However, the fraction reaching the seabed increases drastically at 13 14 continental margins where shallow water depths limit the transit time of POC sinking through the water column. Global models and observations thus indicate that ca. 30 % of ambient 15 16 primary production reaches the shallow seafloor at 0-50 m water depth (Dunne et al., 2007). Due to this effect and the high productivity of continental margins, the margin seabed located 17 18 at <2 km water depths receives ca.  $85 \pm 15$  % of the global POC rain rate (Dunne et al., 2007; Burdige, 2007) even though only 16 % of the global seabed is located at <2km water depth 19 (Eakins and Sharman, 2012). Continental margins are even more dominant in terms of POC 20 21 burial because burial is promoted by the deposition of riverine particles (Berner, 1982, 2004) 22 accumulating mostly on the continental shelf during interglacial sea-level high-stands (Burwicz et al., 2011). Thus,  $90 \pm 10$  % of the global POC burial takes place at <2 km water 23 depth (Dunne et al., 2007; Burdige, 2007; Wallmann et al., 2012). 24

POC rain and burial rates at continental margins declined during glacial sea-level low-stands 25 26 since the oceans retreated into steeper terrains. During the LGM when the sea-level was 120 27 m lower than today, the shelf seafloor area at 0 - 100 m contracted by 73 % while the outer shelf and upper slope area located at 100 - 2000 m water depth was reduced by 13 % (Eakins 28 and Sharman, 2012) neglecting isostatic adjustment. Considering the high rain rates at 29 shallow water depths (Dunne et al., 2007), the glacial margin contraction diminished the 30 global POC rain rate by possibly up to 50 %. The burial rate of marine POC may have been 31 reduced by a similar proportion since POC burial is ultimately limited by the amount of POC 32 reaching the seabed. However, there are a number of additional factors that affect the rate of 33

POC burial. These include bulk sedimentation rate (Berner, 1982), surface area of sediment particles (Mayer et al., 2004), oxygen exposure time (Hartnett et al., 1998), and the resuspension and down-slope transport of shelf POC promoting POC burial at the upper slope (Walsh et al., 1981; Dale et al., 2015). These secondary processes control the burial efficiency of POC, that is the ratio between POC burial and POC rain rate.

6 POC burial efficiency is to a large degree controlled by sedimentation processes on the shelf that are strongly affected by sea-level change. At high sea-level most of the riverine particle 7 8 load is deposited on the shelf (Burwicz et al., 2011) while low sea-level stands promote down-9 slope transport (Hay and Southam, 1977). Hence, data on Quaternary shelf and deep-sea fan 10 sedimentation clearly show that the riverine particle flux was discharged over the shelf edge onto deep-sea fans and abyssal plains by turbidity currents over most of the glacial period 11 12 (Hay and Southam, 1977; Hay, 1994; Schlünz et al., 1999). The corresponding increase in sedimentation rate probably led to a rise in burial efficiency and POC burial at >2km water 13 depths (Burwicz et al., 2011; Wallmann, 2014). The efficiency of POC burial at the 14 continental rise and deep-sea floor may have been further amplified by the glacial decline in 15 dissolved oxygen concentrations in the deep ocean (Jaccard and Galbraith, 2012) favoring the 16 preservation of POC in marine sediments (Hartnett et al., 1998; Dale et al., 2015). It is 17 difficult to validate glacial changes in burial efficiency at <2km water depths. Here, POC 18 preservation was possibly reduced by the intense ventilation of the glacial thermocline 19 (Jaccard and Galbraith, 2012) while preservation might have been enhanced if sedimentation 20 21 rates on the outer shelf and upper slope were significantly elevated by the glacial loss of inner 22 shelf regions. Considering the available evidence it can be concluded that the glacial marine 23 regression induced a strong decline in POC burial on the continental shelf while POC burial was enhanced at the continental rise and deep-sea floor. The overall effect was an increase in 24 25 water column degradation and decline in marine POC burial since the focus of POC burial was shifted to >2km water depth where rain and burial rates are limited by the almost 26 27 complete degradation of marine POC in the water column.

# 28 **B2** Nutrient turnover

Continental margins are also major sinks for nitrate and phosphate since >50 % of the global benthic denitrification and burial of marine phosphorus occur in sediments deposited at <2km water depth (Bohlen et al., 2012; Archer et al., 2002; Froelich et al., 1982; Baturin and Savenko, 1997; Wallmann, 2010; Middelburg et al., 1996). These fluxes are driven by the rain of marine POM to the seabed which is focused on shallow water environments (Dunne et al.,

2007). The strong decrease in shallow seafloor area during glacial marine regressions thus 1 2 induced a decline in nitrate and phosphate removal contributing to the expansion of the nutrient inventory in the glacial ocean (Broecker, 1982a; Deutsch et al., 2004; Eugster et al., 3 2013; Wallmann, 2014). A negative feedback was probably established where the expansion 4 of the nutrient inventory induced a rise in export production and rain rate to the seabed which 5 in turn promoted the burial of POC and removal of nutrients from the ocean. The glacial 6 7 decline in POC burial and the glacial rise in the standing stocks of macronutrients may have been mitigated by this negative feedback mechanism (Middelburg et al., 1996). 8

9 Phosphate cycling in marine sediments is affected by oxygen conditions in ambient bottom 10 waters and sediments (Krom and Berner, 1981; Van Cappellen and Ingall, 1994; Wallmann, 2003). Phosphate is released from sediments under suboxic and anoxic conditions due to the 11 12 reduction of iron and manganese oxides and the preferential degradation of P-bearing organic matter (POP). However, a large fraction of the released phosphate is precipitated and retained 13 in the sediment as authigenic carbonate fluorapatite (CFA). Hence, OMZ sediments are 14 depleted in Fe/Mn-bound P, enriched in CFA and characterized by high POC/POP ratios 15 exceeding the Redfield ratio by a factor of 2 - 8 (Schenau and De Lange, 2001; Lomnitz et 16 al., 2015). Ratios between POC and reactive P (P<sub>reac</sub>, sum of POP, CFA and Fe/Mn-bound P) 17 amount to  $POC/P_{reac} = 100 - 300$  in OMZ sediments and 20 - 70 in continental margin 18 19 sediments underlying oxygenated bottom waters (Schenau and De Lange, 2001; Noffke et al., 2012). Hence, the burial efficiency of reactive P and total P is reduced under low oxygen 20 conditions (Ingall and Jahnke, 1994; Schenau and De Lange, 2001) whereas POC is more 21 22 efficiently buried in OMZ sediments covered by oxygen-depleted bottom waters (Dale et al., 23 2015).

## **B3** Equations and parameter values employed to simulate carbon and nutrient turnover

The parameterization of margin processes applied in the model is summarized in Tables B1 25 26 and B2. A very simple approach was chosen to calculate the burial of neritic carbonates. It was assumed that the burial rate is proportional to the seafloor area at 0 - 50 m water depth 27 (A<sub>NM</sub>) which is controlled by sea-level change, only (see Fig. 3). Burial of marine POC and 28 29 phosphorus (P) at continental margins was assumed to be proportional to POC export production ( $F_{EPOC}$ ) and the depositional areas at 0 – 100 m ( $A_S$ ) and 100 – 2000 m ( $A_I$ ) that 30 were controlled by sea-level change (Fig. 3). The decline in seafloor area at 0 - 2000 m water 31 depths was applied to parameterize the rise in POC burial at the deep-sea floor induced by the 32 glacial marine regression. We thus effectively assumed that the burial efficiency of POC 33

remained constant at <2km water depth but increased at >2km during glacial sea-level lowstands.

Phosphorus considered in the model refers to the sum of organic and reactive inorganic P 3 4 phases (CFA and Fe/Mn-bound P). The latter fractions contribute strongly to P burial since 5 most of the marine particulate P deposited at the seafloor is degraded and transformed into inorganic authigenic phases during early diagenesis (Ruttenberg and Berner, 1993). P burial 6 7 decreases when the dissolved oxygen content of ambient bottom waters (DO) falls below a 8 threshold value of about 20 µM (Wallmann, 2010). This effect was taken into account by 9 introducing corresponding Monod terms in the P burial flux definitions (Tab. B2). Moreover, 10 the model formulation ensured that the molar POC/Preac burial ratio did not exceed the maximum value of about 400 observed in Quaternary sediments (Anderson et al., 2001). 11

Benthic denitrification was calculated from the POC rain rate and ambient dissolved oxygen and nitrate concentrations (DN) applying an empirical transfer function calibrated by in-situ benthic flux data (Bohlen et al., 2012). The rain rates needed for this function were derived from POC burial rates using the corresponding burial efficiencies. Marine PON burial was calculated from POC burial applying a molar PON/POC ratio of 17/123 (Körtzinger et al., 2001).

In contrast to previous sediment models (Heinze et al., 1999; Gehlen et al., 2006), our model does not resolve transport processes and reactions within surface sediments. We prefer to employ observational data on POC and P burial and empirical transfer functions to constrain benthic turnover rates (Bohlen et al., 2012; Wallmann, 2010) because most depth-resolving transport-reaction models yield results that are not yet consistent with key data such as benthic oxygen and nitrate fluxes and POC burial rates (Stolpovsky et al., 2015).

24 The applied parameter values were constrained by field data from the modern ocean (Tab. 25 B1). The available POC and P burial data suggest that burial is rather evenly distributed between 0 - 100 m and 100 - 2000 m water depths (Tab. B1) whereas POM rain rates at 0 -26 100 m clearly exceed the corresponding rates at 100 - 2000 m (Dunne et al., 2007). This 27 28 difference is caused by bottom currents transporting marine POM from the inner shelf 29 towards outer shelf and upper slope environments (Walsh et al., 1981). Note that the POC burial rates applied in our model (Tab. B1) are conservative that is lower than most previous 30 estimates (Burdige, 2007; Dunne et al., 2007). The burial efficiency applied in the model is 31 low at shallow water depth since winnowing by bottom currents affects large parts of the 32 shallow seafloor such that about 70 % of the modern shelf sediments are non-accumulating, 33

relict sands with very low POC contents (Burdige, 2007). POM exported laterally from these 1 shallow areas provides POM for slope deposits (Walsh et al., 1981). The highest burial 2 efficiency is applied at 100 - 2000 m water depth where the deposition of fine-grained 3 riverine particles and low oxygen values in ambient bottom waters favor the preservation of 4 marine POC. Parameter values and fluxes listed in Tabs. B1 and B2 refer to global fluxes. 5 These fluxes were distributed among the 6 ocean basins defined in the box model considering 6 7 the respective seafloor areas and export productions. Neritic carbonate burial was distributed between the Tropical Indo-Pacific and Atlantic (Kleypas, 1997). 8

Our model predicts that the global burial rates of POC and P would decline to 7.9 Tmol yr<sup>-1</sup> 9 and 0.14 Tmol yr<sup>-1</sup> during the LGM, respectively, if export production and oxygen 10 concentrations were maintained at their modern value. The export production was, however, 11 12 promoted by the decline in P burial such that the best fit simulation STD produced LGM burial rates of 9.6 Tmol yr<sup>-1</sup> and 0.165 Tmol yr<sup>-1</sup> compared to modern global rates of 11.5 13 Tmol yr<sup>-1</sup> and 0.18 Tmol yr<sup>-1</sup>, respectively (s. Tab. B1). Our standard model run suggests that 14 the shelf (0 - 100 m water depths) trapped a total of 4650 Gt POC over the last glacial cycle 15 (130 - 0 ka) while 7870 Gt POC accumulated on the continental slope (100 - 2000 m water)16 depth). Shelf weathering released a total of 1940 GtC over the last 130 ka in simulation STD 17 that is less than 50 % of the POC accumulating on the shelf over the last glacial cycle. 18 According to the model, the glacial marine regression affected the chemical and isotopic 19 composition of seawater and the CO<sub>2</sub> content of the atmosphere via a chain of interconnected 20 processes: Ocean margins retreated into steeper terrain and shelf areas were exposed by the 21 22 marine regression; the burial of phosphorus and neritic carbonate and benthic denitrification 23 declined due to the steepening of ocean margins; carbonate, POC, and P weathering rates increased due to the exposure of shelf sediments; atmospheric CO<sub>2</sub> was consumed and 24 converted into dissolved alkalinity by enhanced carbonate weathering while isotopically 25 depleted CO<sub>2</sub> was released into the atmosphere by POC weathering; standing stocks of 26 dissolved nutrients and alkalinity in the ocean expanded due to the decrease in burial and 27 denitrification and the increase in weathering; export production rose due to the increase in 28 the dissolved nutrient stocks and CO<sub>2</sub> was transferred from the atmosphere into the ocean 29 interior by the intensified biological pump while CO<sub>2</sub> sequestration was supported by 30 31 enhanced seawater alkalinity.

#### 32 **B4 Model limitations**

Model parameterizations were chosen to the best of our knowledge. It should, however, be 1 noted that key processes such as glacial changes in POC and P burial efficiency are only 2 poorly constrained by available data. Moreover, we assumed that the global mean 3 morphology of continental margins was retained over the glacial cycle and that the average 4 global change in relative sea-level was equal to eustatic sea-level change. This approach 5 neglects the glacial isostatic adjustment, i.e. the glacial subsidence of northern land masses 6 7 loaded by large ice sheets, the uplift in flanking regions, and the numerous far field effects (Daly, 1934; Milne and Mitrovica, 2008). It also neglects changes in margin morphology 8 9 induced by the erosion and down-slope transport of shelf sediments during glacial sea-level 10 low-stands (Hay, 1994) and the deglacial tilting of continental margins (Clark et al., 1978). 11 Moreover, we assumed that during the LGM eustatic sea-level was 120 m lower than today while growing evidence supports the view that LGM sea-level fall was in fact larger than this 12 13 consensus value (Austermann et al., 2013; Lambeck et al., 2014). The changes in the size of depositional and exposed areas at continental margins applied in the model should thus be 14 15 regarded as rough estimates. Clearly, more work needs to be done to improve these estimates. However, there is no doubt that ocean margins retreated into steeper terrain while large shelf 16 areas were exposed during glacial marine regressions and that these changes had a profound 17 effect on glacial seawater composition and atmospheric pCO<sub>2</sub>. 18

Moreover, our model does not consider the growth of land plants and soil formation on 19 emerged shelf regions during glacial sea-level low-stands. Trees and other plants may use 20 sediment nutrients after shelf exposure and accumulate terrestrial POC on the emerged shelf. 21 22 However, we think that the POC accumulation associated with these processes is small compared to the sedimentary POC turnover considered in the model. Modern continental 23 margins (shelf and rise) accumulate sedimentary POC at a rate of about 100 - 200 Gt kyr<sup>-1</sup> 24 (Hedges and Keil, 1995; Burdige, 2007; Wallmann et al., 2012; Dunne et al., 2007). This 25 26 enormous flux is induced by the high marine productivity of the region and the rapid accumulation of sediments facilitating the burial of marine POC. Trees and soils growing on 27 28 the emerged shelf would have to accumulate POC in the order of 10 000 Gt C to maintain this high carbon flux over the glacial period (ca. 80 kyr), an unlikely scenario since the global 29 terrestrial carbon stock is ≤2000 GtC. The standing stock of POC in margin sediments 30 exceeds the global terrestrial stock since POC is buried more efficiently in sediments than in 31 most soils and plants. Sedimentary POC burial and preservation are promoted by high 32 sedimentation rates and the lack of oxygen in these water-saturated deposits. 33

34

#### 1 Appendix C: Model results

2 Key model results are listed in Tabs. C1 to C4 and compared to proxy data where available.

3

# 4 Appendix D: Radiocarbon model

A simple two-box-model helps to explain why the ocean is strongly depleted in radiocarbon with respect to the atmosphere when radiocarbon production rates are high. In this model, radiocarbon is produced in the atmosphere and transferred from the atmosphere to the ocean by a diffusion-analog process. It decays both in the atmosphere and in the ocean. At steady state, this simple system can be represented by the following set of equations:

- 10 Atmosphere mass balance:  $R_{14} \lambda^{14}C_A F_{AO} = 0$  (D1)
- 11 Ocean mass balance:  $F_{AO} \lambda^{14}C_O = 0$  (D2)

12 <sup>14</sup>C flux from atmosphere to ocean:  $F_{AO} = k ({}^{14}C_A - {}^{14}C_O)$  (D3)

where  $R_{14}$  is the radiocarbon production rate,  $\lambda$  is the decay constant,  ${}^{14}C_A$  is the radiocarbon mass in the atmosphere,  ${}^{14}C_O$  is the radiocarbon mass in the ocean, and k is a mass transfer coefficient. Equations C1 – C3 can be combined and solved for the radiocarbon difference between atmosphere and ocean:

17 
$${}^{14}C_A - {}^{14}C_O = \frac{R_{14}}{\lambda + 2 \cdot k}$$
 (D4)

The resulting equation shows that the difference is proportional to the radiocarbon production 18 rate. The steady-state <sup>14</sup>C-depletion of the ocean with respect to the atmosphere, thus, 19 increases under high production rates. The difference would vanish if the mass transport 20 coefficient would be infinitely large. The example of the modern ocean shows, however, that 21 this is not the case and that the ocean is significantly depleted in <sup>14</sup>C with respect to the 22 atmosphere since the transfer of <sup>14</sup>C from the atmosphere into the ocean is too slow to 23 eliminate the <sup>14</sup>C difference. In our simple 2-box model, the radiocarbon flux is assumed to be 24 proportional to the radiocarbon gradient between atmosphere and ocean (Eq. D3). The 25 gradient increases under high production rates such that more  ${}^{14}C$  is transferred from the  ${}^{14}C$ -26 enriched atmosphere into the depleted ocean. The rate of radioactive decay in the ocean ( $\lambda$ 27  $^{14}C_0$  increases since the  $^{14}C$  content of the ocean is raised by the enhanced radiocarbon flux 28 from the atmosphere. Steady state is attained when the decay rate in the ocean and the <sup>14</sup>C 29 flux from the atmosphere are balanced (Eq. D2). The steady-state gradient ( ${}^{14}C_A - {}^{14}C_O$ ), thus, 30
increases in proportion to the atmospheric production rate such that the flux into the ocean 1 compensates for the elevated decay rate in the ocean. The analytical solution for the simple 2 two-box-model (Eq. D4) correctly predicts the steady-state behavior of our more evolved 3 model system where the ocean is represented by 24 boxes and the radiocarbon uptake from 4 the atmosphere is calculated applying Eq. (A12) rather than Eq. (D3). It predicts that  $\Delta\Delta^{14}$ C-5 DIC increases linearly with production rate as observed in the steady state simulations (Tab. 6 7 C2). The real ocean-atmosphere system is obviously more complex than any kind of model. However, the simple 2-box-model captures the basic features of the real system and reveals 8 that the <sup>14</sup>C contrast increases in proportion to the production rate. Since radiocarbon 9 production rates may have changed significantly over the last glacial cycle, this basic system 10 property has to be considered in the interpretation of the marine <sup>14</sup>C-record. 11

12

## 13 Acknowledgements

14 This work was funded by the DFG via the collaborative project SFB 754. The manuscript was

15 greatly improved in the review process thanks to the very helpful comments by the two

16 reviewers (Victor Brovkin and anonymous) and the associated editor (Luke Skinner).

17

## 18 **References**

19 Abe-Ouchi, A., Saito, F., Kawamura, K., Raymo, M. E., Okuno, J., Takahashi, K., and

20 Blatter, H.: Insolation-driven 100,000-year glacial cycles and hysteresis of ice-sheet volume,

21 Nature, 500, 190-193, 10.1038/nature12374, 2013.

Adkins, J. F., and Boyle, E. A.: Changing atmospheric  $\Delta^{14}$ C and the record of deep water paleoventilation ages, Paleoceanography, 12, 337-344, 1997.

Altabet, M. A., Francois, R., Murray, D. W., and Prell, W. L.: Climate-related variations in
 denitrification in the Arabian Sea from sediment <sup>15</sup>N/<sup>14</sup>N ratios, Nature, 373, 506-509, 1995.

26 Anderson, L. D., Delaney, M. L., and Faul, K. L.: Carbon to phosphorus ratios in sediments:

- 27 Implications for nutrient cycling, Global Biogeochemical Cycles, 15, 65-79, 2001.
- 28 Anderson, R. F., Ali, S., Bradtmiller, L. I., Nielsen, S. H. H., Fleisher, M. Q., Anderson, B.

29 E., and Burckle, L. H.: Wind-driven upwelling in the Southern Ocean and the deglacial rise in

30 atmospheric CO<sub>2</sub>, Science, 323, 1443-1448, 2009.

- Archer, D. E., Morford, J. L., and Emerson, S. R.: A model of suboxic sedimentary diagenesis
   suitable for automatic tuning and gridded global domains, Global Biogeochemical Cycles, 16,
   10.1029/2000GB001288, 2002.
- Aumont, O., and Bopp, L.: Globalizing results from ocean in situ iron fertilization studies,
  Global Biogeochem. Cycles, 20, GB2017, doi:10.1029/2005GB002591, 2006.
- Austermann, J., Mitrovica, J. X., Latychev, K., and Milne, G. A.: Barbados-based estimate of
  ice volume at Last Glacial Maximum affected by subducted plate, Nature Geoscience, 6, 553557, 2013.
- 9 Barker, S., Knorr, G., Vautravers, M. J., Diz, P., and Skinner, L. C.: Extreme deepening of the
- 10 Atlantic overturning circulation during deglaciation, Nature Geoscience, 3, 567-571, 2010.
- Baturin, G. N., and Savenko, V. S.: Phosphorus in oceanic sedimentogenesis, Oceanology, 37,
  107-113, 1997.
- Baturin, G. N.: Issue of the relationship between primary productivity of organic carbon in
  ocean and phosphate accumulation (Holocene Late Jurassic), Lithology and Mineral
  Resources, 42, 318-348, 2007.
- Berelson, W. E., Balch, W. M., Najjar, R., Feely, R. A., Sabine, C., and Lee, K.: Relating
  estimates of CaCO<sub>3</sub> production, export, and dissolution in the water column to measurements
  of CaCO<sub>3</sub> rain into sediment traps and dissolution on the sea floor: A revised global carbonate
  budget, Global Biogeochem. Cycles, 21, doi:10.1029/2006GB002803, 2007.
- Berger, A., and Loutre, M. F.: Insolation values for the climate of the last 10 Million years,
  Quaternary Science Reviews, 10, 297-317, 1991.
- Berger, W. H.: Increase of carbon dioxide in the atmosphere during deglaciation: The coral
  reef hypothesis, Naturwissenschaften, 69, 87-88, 1982.
- Berner, R. A.: Burial of organic carbon and pyrite sulfur in the modern ocean: Its geochemical
  and environmental significance, American Journal of Science, 282, 451-473, 1982.
- 26 Berner, R. A., and Rao, J.-J.: Phosphorus in sediments of the Amazon River and estuary:
- 27 Implications for the global flux of phosphorus to the sea, Geochimica et Cosmochimica Acta,
- 28 58, 2333-2339, 1994.

- Berner, R. A.: The Phanerozoic Carbon Cycle: CO<sub>2</sub> and O<sub>2</sub>, Oxford University Press, Oxford,
   150 pp., 2004.
- Bohlen, L., Dale, A., and Wallmann, K.: Simple transfer functions for calculating benthic
  fixed nitrogen losses and C:N:P regeneration ratios in global biogeochemical models, Global
  Biochemical Cycles, 26, 10.1029/2011GB004198, 2012.
- Bordelon-Katrynski, L. A., and Schneider, B.: Modeled CO<sub>2</sub> feedbacks from increased
  phytoplankton DOC exudation, Biogeosciences Discussions, 9, 1-29, 2012.
- Boyle, E. A., and Keigwin, L. D.: Deep circulation of the North Atlantic over the last 200,000
  years: Geochemical evidence, Science, 218, 784-787, 1982.
- Broecker, W. S.: Ocean chemistry during glacial time, Geochimica et Cosmochimica Acta,
  46, 1689-1705, 1982a.
- Broecker, W. S.: Glacial to interglacial changes in ocean chemistry, Prog. Oceanogr., 11, 151197, 1982b.
- 14 Broecker, W. S.: The great ocean conveyor, Oceanography, 4, 79-90, 1991.
- 15 Broecker, W. S., Peacock, S. L., Walker, S., Weiss, R., Fahrbach, E., Schroeder, M.,
- 16 Mikolajewic, U., Heinze, C., Key, R., Peng, T.-H., and Rubin, S.: How much deep water is
- 17 formed in the Southern Ocean?, Journal of Geophysical Research, 103, 15833-15843, 1998.
- 18 Broecker, W. S., Clark, E., Hajdas, I., and Bonani, G.: Glacial ventilation rates for the deep
- 19 Pacific Ocean, Paleoceanography, 19, 10.1029/2003PA000974, 2004.
- Brovkin, V., Ganopolski, A., Archer, D., and Munhoven, G.: Glacial CO<sub>2</sub> cycle as a
  succession of key physical and biogeochemical processes, Clim. Past, 8, 251–264, 2012.
- Brovkin, V., and Ganopolski, A.: The role of the terrestrial biosphere in CLIMBER-2
  simulations of the last 4 glacial CO<sub>2</sub> cycles, Nova Acta Leopoldina NF, 121, 43-47, 2015.
- 24 Bryan, S. P., Marchitto, T. M., and Lehman, S. J.: The release of <sup>14</sup>C-depleted carbon from the
- 25 deep ocean during the last deglaciation: Evidence from the Arabian Sea, Earth and Planetary
- 26 Science Letters, 298, 244-254, 2010.

- Burdige, D. J.: Preservation of organic matter in marine sediments: Controls, mechanisms,
   and an imbalance in sediment organic carbon budgets?, Chem. Rev., 107, 467-485, 2007.
- Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, H. F., and Otto,
  J. B.: Variation of seawater <sup>87</sup>Sr/<sup>86</sup>Sr throughout Phanerozoic time, Geology, 10, 516-519,
  1982.
- Burwicz, E. B., Rüpke, L. H., and Wallmann, K.: Estimation of the global amount of
  submarine gas hydrates formed via microbial methane formation based on numerical reactiontransport modeling and a novel parameterization of Holocene sedimentation, Geochim.
  Cosmochim. Acta, 75, 4562-4576, 2011.
- Clark, J. A., Farrell, W. E., and Peltier, W. R.: Global changes in postglacial sea level: A
  numerical calculation, Quaternary Science Reviews, 9, 265-287, 1978.
- 12 Conkright, M. E., Locarnini, R. A., Garcia, H. E., O'Brien, T. D., Boyer, T. P., Stephens, C.,
- 13 and J. I. Antonov: World Ocean Atlas 2001: Objective Analyses, Data Statistics, and Figures,
- 14 National Oceanographic Data Center, Silver Spring, MD, 17, 2002.
- Curry, W. B., and Oppo, D. W.: Glacial water mass geometry and the distribution of d<sup>13</sup>C of
   SCO<sub>2</sub> in the western Atlantic Ocean, Paleoceanography, 20, 10.1029/2004PA001021, 2005.
- Dale, A. W., Sommer, S., Lomnitz, U., Montes, I., Treude, T., Liebetrau, V., Gier, J., Hensen,
  C., Dengler, M., Stolpovsky, K., Bryant, L. D., and Wallmann, K.: Organic carbon
  production, mineralisation and preservation on the Peruvian margin, Biogeosciences, 12,
  1537-1559, 2015.
- 21 Daly, R. A.: The Changing World of the Ice Age, Yale University Press, New Haven, 1934.
- Denton, G. H., Anderson, R. F., Toggweiler, J. R., Edwards, R. L., Schaefer, J. M., and
  Putnam, A. E.: The Last Glacial Termination, Science, 328, 1652-1656, 2010.
- Deutsch, C., Gruber, N., Key, R. M., and Sarmiento, J. L.: Denitrification and N<sub>2</sub> fixation in
  the Pacific Ocean, Global Biogeochemical Cycles, 15, 483-506, 2001.
- Deutsch, C., Sigman, D. M., Thunell, R. C., Meckler, A. N., and Haug, G. H.: Isotopic
  constraints on glacial/interglacial changes in the oceanic nitrogen budget, Global
  Biogeochem. Cycles, 18, GB4012, doi:10.1029/2003GB002189, 2004.

- Dunne, J. P., Sarmiento, J. L., and Gnanadesikan, A.: A synthesis of global particle export
   from the surface ocean and cycling through the ocean interior and on the seafloor, Global
   Biogeochem. Cycles, 21, doi:10.1029/2006GB002907, 2007.
- 4 Duplessy, J. C., Shackleton, N. J., Fairbanks, R. G., Labeyrie, L., Oppo, D., and Kallel, N.:
  5 Deepwater source variations during the last climatic cycle and their impact on the global
  6 deepwater circulation, Paleoceanography, 3, 343-360, 1988.
- 7 Eakins, B. W., and Sharman, G. F.: Hypsographic curve of Earth's surface from ETOPO1,
  8 NOAA National Geophysical Data Center, Boulder, CO, 2012.
- 9 Eugster, O., Gruber, N., Deutsch, C., Jaccard, S. L., and Payne, M. R.: The dynamics of the
  10 marine nitrogen cycle across the last deglaciation, Paleoceanography, 28, 116-129,
  11 10.1002/palo.20020, 2013.
- Frank, M., Schwarz, B., Baumann, S., Kubik, P. W., Suter, M., and Mangini, A.: A 200 kyr
   record of cosmogenic radionuclide production rate and geomagnetic field intensity from <sup>10</sup>Be
   in globally stacked deep-sea sediments, Earth and Planetary Science Letters, 149, 121-129,
   1997.
- Franke, J., Paul, A., and Schulz, M.: Modeling variations of marine reservoir ages during the
  last 45 000 years, Climate of the Past, 4, 125-136, 2008.
- Froelich, P. N., Bender, M. L., Luedtke, N. A., Heath, G. R., and DeVries, T.: The marine
  phosphorus cycle, American Journal of Science, 282, 474-511, 1982.
- Ganopolski, A., Rahmstorf, S., Petoukhov, V., and Claussen, M.: Simulation of modern and
  glacial climates with a coupled global model of intermediate complexity, Nature, 391, 351356, 1998.
- Ganopolski, A., Calov, R., and Claussen, M.: Simulation of the last glacial cycle with a
  coupled climate ice-sheet model of intermediate complexity, Clim. Past, 6, 229–244, 2010.
- Ganopolski, A., and Calov, R.: The role of orbital forcing, carbon dioxide and regolith in 100
  kyr glacial cycles, Clim. Past, 7, 1415-1425, 2011.
- 27 García, H. E., and Gordon, L. I.: Oxygen solubility in seawater: Better fitting equations,
- 28 Limnol. Oceanogr., 37, 1307-1312, 1992.

- Gebhardt, H., Sarnthein, M., Grootes, P. M., Kiefer, T., Kuehn, H., Schmieder, F., and Röhl,
   U.: Paleonutrient and productivity records from the subarctic North Pacific for Pleistocene
   glacial terminations I to V, Paleoceanography, 23, doi:10.1029/2007PA001513, 2008.
- Gehlen, M., Bopp, L., Emprin, N., Aumont, O., Heinze, C., and Ragueneau, O.: Reconciling
  surface ocean productivity, export fluxes and sediment composition in a global
  biogeochemical ocean model, Biogeosciences, 3, 521-537, 2006.
- Gnanadesekian, A., and Hallberg, R.: Physical oceanography, thermal structure and general
  circulation, in: Encyclopedia of Physical Science and Technology, edited by: Meyers, R. A.,
  Academic Press, San Diego, 189-210, 2002.
- Hartnett, H. E., Keil, R. G., Hedges, J. I., and Devol, A. H.: Influence of oxygen exposure
  time on organic carbon preservation in continental margin sediments, Nature, 391, 572-574,
  1998.
- Hay, W. W., and Southam, J. R.: Modulation of marine sedimentation by the continental
  shelves, in: The Fate of Fossil Fuel CO<sub>2</sub> in the Oceans, edited by: Andersen, N. R., and
  Malahoff, A., Plenum Press, New York, 569-604, 1977.
- Hay, W. W.: Pleistocene-Holocene Fluxes Are Not the Earth's Norm, in: Material Fluxes on
  the Surface of the Earth, edited by: Hay, W. W., and Usselman, T., Studies in Geophysics,
  National Academy Press, Washington, 15-27, 1994.
- Hedges, J. I., and Keil, R. G.: Sedimentary organic matter preservation: an assessment and
  speculative synthesis, Marine Chemistry, 49, 81-115, 1995.
- Heinze, C., Maier-Reimer, E., Winguth, A. M. E., and Archer, D.: A global oceanic sediment
  model for long-term climate studies, Global Biogeochemical Cycles, 13, 221-250, 1999.
- Honjo, S., Manganini, S. J., Krishfield, R. A., and Francois, R.: Particulate organic carbon
  fluxes to the ocean interior and factors controlling the biological pump: A synthesis of global
  sediment trap programs since 1983, Progress In Oceanography, 76, 217-285, doi: DOI:
  10.1016/j.pocean.2007.11.003, 2008.
- Imbrie, J., and Imbrie, J. Z.: Modeling the climatic response to orbital variations, Science,
  207, 943–953, 1980.

- Imbrie, J., Berger, A., E.A., B., Clemens, S. C., Duffy, A., Howard, W. R., Kukja, G.,
   Kutzbach, J., Martinson, D. G., McIntyre, A., Mix, A. C., Molfino, B., Morley, J. J., Peterson,
   L. C., Pjsias, N. G., Prell, W. L., Raymo, M. E., Shackleton, N. J., and Toggweiler, J. R.: On
   the structure and origin of major glaciation cycles. 2. The 100,000-year cycle,
   Paleoceanography, 8, 699–735, 1993.
- Ingall, E. D., and Jahnke, R. A.: Evidence for enhanced phosphorus regeneration from marine
  sediments overlain by oxygen depleted waters, Geochimica et Cosmochimica Acta, 58, 25712575, 1994.
- 9 Jaccard, S. L., and Galbraith, E. D.: Large climate-driven changes of oceanic oxygen
  10 concentrations during the last deglaciation, Nature Geoscience, 5, 151-156, 2012.
- Jahnke, R. A.: The global ocean flux of particulate organic carbon: Areal distribution and
  magnitude, Global Biogeochemical Cycles, 10, 71-88, 1996.
- 13 Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A.,
- Millero, F. J., Mordy, C., and Peng, T.-H.: A global ocean carbon climatology: Results from
  Global Data Analysis Project (GLODAP), Global Biogeochem. Cycles, 18, GB4031,
- 16 doi:10.1029/2004GB002247, 2004.
- 17 Kleypas, J. A.: Modeled estimates of global reef habitat and carbonate production since the18 last glacial maximum, Paleoceanogr., 12, 533-545, 1997.
- Köhler, P., and Fischer, H.: Simulating changes in the terrestrial biosphere during the last
  glacial/interglacial transition, Global and Planetary Change, 43, 33-55, 2004.
- Köhler, P., Fischer, H., Munhoven, G., and Zeebe, R. E.: Quantitative interpretation of
  atmospheric carbon records over the last glacial termination, Global Biochemical Cycles, 19,
  10.1029/2004GB002345, 2005.
- Köhler, P., Muscheler, R., and Schmitt, J.: A model-based interpretation of low-frequency changes in the carbon cycle during the last 120,000 years and its implications for the reconstruction of atmospheric  $\Delta^{14}$ C, Geochemistry, Geophysics, Geosystems, 7, doi:10.1029/2008PA001703, 2006.
- Körtzinger, A., Hedges, J. I., and Quay, P. D.: Redfield ratios revisited: Removing the biasing
  effect of anthropogenic CO<sub>2</sub>, Limnology and Oceanography, 46, 964-970, 2001.

- Krom, M. D., and Berner, R. A.: The diagenesis of phosphorus in a nearshore marine
   sediment, Geochimica et Cosmochimica Acta, 45, 207-216, 1981.
- Laj, C., Kissel, C., Mazaud, A., Michel, E., Muscheler, R., and Beer, J.: Geomagnetic field
  intensity, North Atlantic Deep Water circulation and atmospheric D<sup>14</sup>C during the last 50 kyr,
  Earth and Planetary Science Letters, 200, 177-190, 2002.
- Lambeck, K., Rouby, H., Purcell, A., Sun, Y., and Sambridge, M.: Sea level and global ice
  volumes from the Last Glacial Maximum to the Holocene, PNAS, 111, 15296–15303, 2014.
- 8 Lambert, F., Tagliabue, A., Shaffer, G., Lamy, F., Winckler, G., Farias, L., Gallardo, L., and
- 9 De Pol-Holz, R.: Dust fluxes and iron fertilization in Holocene and Last Glacial Maximum
- 10 climates, Geophysical Research Letters, 42, 6014-6023, 10.1002/2015gl064250, 2015.
- 11 Lomnitz, U., Sommer, S., Dale, A. W., Löscher, C. R., ke, A. N., K. Wallmann, and Hensen,
- 12 C.: Benthic phosphorus cycling in the Peruvian oxygen minimum zone, Biogeosciences
- 13 Discuss., 12, 16755–16801, doi:10.5194/bgd-12-16755-2015, 2015.
- 14 Madec, G., Delecluse, P., Imbard, M., and Levy, C.: OPA8.1 Ocean general circulation model
- reference manual, Notes du pôle de modél. 11, Inst. Pierre-Simon Laplace, Paris, 91, 1998.
- 16 Marcott, S. A., Bauska, T. K., Buizert, C., Steig, E. J., Rosen, J. L., Cuffey, K. M., Fudge, T.
- 17 J., Severinghaus, J. P., Ahn, J., Kalk, M. L., McConnell, J. R., Sowers, T., Taylor, K. C.,
- 18 White, J. W. C., and Brook, E. J.: Centennial-scale changes in the global carbon cycle during
- 19 the last deglaciation, Nature, 514, 616-619, 2014.
- Marinov, I., Gnanadesikan, A., Toggweiler, J. R., and Sarmienton, J. L.: The Southern Ocean
  biogechemical divide, Nature, 441, 964-967, 2006.
- Martin, J. H.: Glacial-interglacial CO<sub>2</sub> change: The iron hypothesis, Paleoceanography, 5, 113, 1990.
- 24 Martinez-Garcia, A., Sigman, D. M., Ren, H., Anderson, R. F., Straub, M., Hodell, D. A.,
- 25 Jaccard, S. L., L.Eglinton, T., and Haug, G. H.: Iron fertilization of the Subantarctic Ocean
- 26 during the last ice age, Science, 343, 1347-1350, 2014.

- Mayer, L. M., Schick, L. L., Hardy, K. R., Wagal, R., and McCarthy, J.: Organic matter in
   small mesopores in sediments and soils, Geochimica et Cosmochimica Acta, 68, 3863-3872,
   2004.
- McManus, J. F., Francois, R., Gherardi, J.-M., Keigwin, L. D., and Brown-Leger, S.: Collapse
  and rapid resumption of Atlantic meridional circulation linked to deglacial climate changes,
  Nature, 428, 834-837, 2004.
- Menviel, L., Joos, F., and Ritz, S. P.: Simulating atmospheric CO2, C-13 and the marine
  carbon cycle during the Last Glacial-Interglacial cycle: possible role for a deepening of the
  mean remineralization depth and an increase in the oceanic nutrient inventory, Quaternary
  Science Reviews, 56, 46-68, 10.1016/j.quascirev.2012.09.012, 2012.
- Middelburg, J. J., Soetaert, K., Herman, P. M. J., and Heip, C. H. R.: Denitrification in marine
  sediments: A model study, Global Biogeochemical Cycles, 10, 661-673, 1996.
- Milankovitch, M.: Kanon der Erdbestrahlung und Seine Anwendung auf das
  Eiszeitenproblem, Royal Serbian Academy Special Publication, Royal Serbian Academy,
  Belgrade, Serbia, 1941.
- Milliman, J. D., and Droxler, A. W.: Neritic and pelagic carbonate sedimentation in the
  marine environment: ignorance is not a bliss, Geol. Rundsch., 85, 496-504, 1996.
- Milne, G. A., and Mitrovica, J. X.: Searching for eustasy in deglacial sea-level histories,
  Quaternary Science Reviews, 27, 2292-2302, 2008.
- Monnin, E., Indermühle, A., Dallenbach, A., Flückiger, J., Stauffer, B., Stocker, T. F.,
  Raynaud, D., and Barnola, J.-M.: Atmospheric CO<sub>2</sub> concentrations over the Last Glacial
  Termination Science, 291, 112-114, 2001.
- Monnin, E., Steig, E. J., Siegenthaler, U., Kawamura, K., Schwander, J., Stauffer, B., Stocker,
  T. F., Morse, D. L., Barnola, J.-M., Bellier, B., Raynaud, D., and Fischer, H.: Evidence for
  substantial accumulation rate variability in Antarctica during the Holocene, through
  synchronization of CO<sub>2</sub> in the Taylor Dome, Dome C and DML ice cores, Earth and Planetary
  Science Letters, 224, 45-54, 2004.
- Mook, W. G., and Plicht, J. v. d.: Reporting C-14 activities and concentrations, Radiocarbon,
  41, 227-239, 1999.

- 1 Munhoven, G.: Glacial-interglacial changes of continental weathering: estimates of the related
- 2  $CO_2$  and  $HCO_3^-$  flux variations and their uncertainties, Global and Planetary Change, 33, 155-
- 3 176, 2002.
- 4 Muscheler, R., Beer, J., Kubik, P. W., and Synal, H.-A.: Geomagnetic field intensity during
- 5 the last 60,000 years based on  ${}^{10}$ Be and  ${}^{36}$ Cl from the Summit ice cores and  ${}^{14}$ C., Quaternary
- 6 Science Reviews, 24, 1849-1860, 2005.
- Noffke, A., Hensen, C., Sommer, S., Scholz, F., Bohlen, L., Mosch, T., Graco, M., and
  Wallmann, K.: Benthic iron and phosphorus fluxes across the Peruvian oxygen minimum
  zone, Limnology and Oceanography, 57, 851-867, 2012.
- 10 Oliver, K. I. C., Hoogakker, B. A. A., Crowhurst, S., Henderson, G. M., Rickaby, R. E. M.,
- 11 Edwards, N. R., and Elderfield, H.: A synthesis of marine sediment core  $\delta^{13}C$  data over the
- 12 last 150 000 years, Clim. Past, 6, 645-673, 2010.
- Opdyke, B. N., and Walker, J. C. G.: Return of the coral reef hypothesis: Basin to shelf
  partitioning of CaCO<sub>3</sub> and its effect on atmospheric CO<sub>2</sub>, Geology, 20, 733-736, 1992.
- Peterson, C. D., Lisiecki, L. E., and Stern, J. V.: Deglacial whole-ocean δ13C change
  estimated from 480 benthic foraminiferal records, Paleoceanography, 29, 549-563,
  doi:10.1002/2013PA002552., 2014.
- Petit, L. R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J.-M., Basile, I., Bender, M.,
  Chappelaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V. M., Legrand, M.,
  Lipenkov, V. Y., Lorius, C., Pépin, L., Ritz, C., Saltzman, E., and Stievenard, M.: Climate
  and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica,
  Nature, 399, 429-436, 1999.
- Piotrowski, A. M., Goldstein, S. L., Hemming, S. R., and Fairbanks, R. G.: Temporal
  relationships of carbon cycling and ocean circulation at glacial boundaries, Science, 307,
  1933-1937, 2005.
- Pollard, D.: Ice-age simulations with a calving ice-sheet model, Quaternary Research, 20, 3048, 1983.

- Rae, J. W. B., Sarnthein, M., Foster, G. L., Ridgwell, A., Grootes, P. M., and Elliott., T.:
   Deep water formation in the North Pacific and deglacial CO<sub>2</sub> rise, Paleoceanography, 29, 645 667, 10.1002/2013PA002570, 2014.
- 4 Raitzsch, M., Hathorne, E. C., Kuhnert, H., Groeneveld, J., and Bickert, T.: Modern and late
  5 Pleistocene B/Ca ratios of the benthic foraminifer *Planulina wuellerstorfi* determined with
  6 laser ablation ICP-MS, Geology, 39, 1039-1042, 2011.
- Raymo, M. E., Oppo, D. W., and Curry, W.: The mid-Pleistocene climate transition: A deep
  sea carbon isotope perspective, Paleoceanogr., 12, 546-559, 1997.
- 9 Redfield, A. C.: The biological control of chemical factors in the environment, American
  10 Scientist, 46, 205-221, 1958.
- 11 Reimer, P. J., Bard, E., Bayliss, A., Beck, J. W., Blackwell, P. G., Ramsey, C. B., Buck, C. E.,
- 12 Cheng, H., Edwards, R. L., Friedrich, M., Grootes, P. M., Guilderson, T. P., Haflidason, H.,
- 13 Hajdas, I., Hatté, C., Heaton, T. J., Hoffmann, D. L., Hogg, A. G., Hughen, K. A., Kaiser, K.
- 14 F., Kromer, B., Manning, S. W., Niu, M., Reimer, R. W., Richards, D. A., Scott, E. M.,
- 15 Southon, J. R., Staff, R. A., Turney, C. S. M., and Plicht, J. v. d.: IntCal13 and marine13
- radiocarbon age calibration curves 0 50,000 years Cal BP, Radiocarbon, 55, 1869-1887,
  2013.
- 18 Ridgewell, A.: Glacial-interglacial perturbations in the global carbon cycle, PhD, University19 of East Anglia, Norwich, UK, 2001.
- Roberts, N. L., Piotrowski, A. M., McManus, J. F., and Keigwin, L. D.: Synchronous
  deglacial overturning and water mass source changes, Science, 327, 75-78, 2010.
- Robinson, L. F., Adkins, J. F., Keigwin, L. D., Southon, J., Fernandez, D. P., Wang, S.-L.,
  and Scheirer, D. S.: Radiocarbon Variability in the Western North Atlantic During the Last
- 24 Deglaciation, Science, 310, 1469-1473, 2005.
- Romanek, C. S., Grossman, E. L., and Morse, J. W.: Carbon isotope fractionation in synthetic
  aragonite and calcite: Effects of temperature and precipitation rate, Geochimica et
  Cosmochimica Acta, 56, 419-430, 1992.

- Roth, R., Ritz, S. P., and Joos, F.: Burial-nutrient feedbacks amplify the sensitivity of
   atmospheric carbon dioxide to changes in organic matter remineralisation, Earth Syst.
   Dynam., 5, 321-343, 2014.
- 4 Ruttenberg, K. C.: Development of a sequential extraction method for different forms of
  5 phosphorus in marine sediments, Limnol. Oceanogr., 37, 1460-1482, 1992.
- Ruttenberg, K. C., and Berner, R. A.: Authigenic apatite formation and burial in sediments
  from non-upwelling, continental margin environments, Geochimica et Cosmochimica Acta,
  57, 991-1007, 1993.
- 9 Sarmiento, J. L., and Gruber, N.: Ocean Biogeochemical Cycles, Princeton University Press,
  10 Princeton, 503 pp., 2006.
- 11 Sarnthein, M., Winn, K., Jung, S. J. A., Duplessy, J.-C., Labeyrie, L., Erlenkeuser, H., and
- 12 Ganssen, G.: Changes in east Atlantic deepwater circulation over the last 30,000 years: Eight
- time slice reconstructions, Paleoceanography, 9, 209-267, 1994.
- Sarnthein, M., Schneider, B., and Grootes, P. M.: Peak glacial <sup>14</sup>C ventilation ages suggest
  major draw-down of carbon into the abyssal ocean, Clim. Past, 9, 2595-2614, 2013.
- Sarnthein, M., Balmer, S., Grootes, P. M., and Mudelsee, M.: Planktic and benthic <sup>14</sup>C
  reservoir ages for three ocean basins, calibrated by a suite of <sup>14</sup>C plateaus in the glacial-todeglacial Suigetsu atmospheric <sup>14</sup>C record, Radiocarbon, in press, 2014.
- Sarnthein, M., Balmer, S., Grootes, P. M., and Mudelsee, M.: Planktic and benthic <sup>14</sup>C
  reservoir ages for three ocean basins, calibrated by a suite of <sup>14</sup>C plateaus in the glacial-todeglacial Suigetsu atmospheric <sup>14</sup>C record, Radiocarbon, 57, 129-151, 2015.
- Schenau, S. J., and De Lange, G. J.: Phosphorus regeneration vs. burial in sediments of the
  Arabian Sea, Marine Chemistry, 75, 201-217, 2001.
- 24 Schlünz, B., Schneider, R. R., Müller, P. J., Swowers, W. J., and Wefer, G.: Terrestrial
- 25 organic carbon accumulation on the Amazon deep sea fan during the glast glacial sea level
- stand, Chemical Geology, 159, 263-281, 1999.

- 1 Schmitt, J., Schneider, R., Elsig, J., Leuenberger, D., Lourantou, A., Chappellaz, J., Köhler,
- 2 P., Joos, F., Stocker, T. F., Leuenberger, M., and Fischer, H.: Carbon isotope constraints on
- 3 the deglacial  $CO_2$  rise from ice cores, Science, 336, 711-714, 2012.
- 4 Schmittner, A., Urban, N. M., Shakun, J. D., Mahowald, N. M., Clark, P. U., Bartlein, P. J.,
- 5 Mix, A. C., and Rosell-Melé, A.: Climate sensitivity estimated from temperature
- 6 reconstructions of the Last Glacial Maximum, Science, 334, 1385-1388, 2011.
- 7 Schmittner, A., Gruber, N., Mix, A. C., Key, R. M., Tagliabue, A., and Westberry, T. K.:
- 8 Biology and air–sea gas exchange controls on the distribution of carbon isotope ratios ( $\delta^{13}$ C)
- 9 in the ocean, Biogeosciences, 10, 5793-5816, 2013.
- Seiter, K., Hensen, C., and Zabel, M.: Benthic carbon mineralization on a global scale, Global
  Biogeochemical Cycles, 19, doi:10.1029/2004GB002225, 2005.
- 12 Shackleton, N. J.: Carbon-13 in Uvigerina: Tropical rainforest history in the equatorial Pacific
- 13 carbonate dissolution cycles, in: The Fate of Fossil Fuel in the Oceans, edited by: Andersen,
- 14 N. R., and Malahoff, A., Plenum, New York, 401-427, 1977.
- Skinner, L. C.: Glacial-interglacial atmospheric CO<sub>2</sub> change: a possible "standing volume"
  effect on deep-ocean carbon sequestration, Climate of the Past, 5, 537–550, 2009.
- Skinner, L. C., Fallon, S., Waelbroeck, C., Michel, E., and Barker, S.: Ventilation of the deep
  Southern Ocean and deglacial CO<sub>2</sub> rise, Science, 328, 1147-1151, 2010.
- Skinner, L. C., Waelbroeck, C., Scrivner, A. E., and Fallon, S. J.: Radiocarbon evidence for
  alternating northern and southern sources of ventilation of the deep Atlantic carbon pool
  during the last deglaciation, PNAS, 111, 5480-5484, 2014.
- Stanford, J. D., Hemingway, R., Rohling, E. J., Challenor, P. G., Medina-Elizalde, M., and
  Lester, A. J.: Sea-level probability for the last deglaciation: A statistical analysis of far-field
  records, Global and Planetary Change, 79, 193-203, 2011.
- Stolpovsky, K., Dale, A. W., and Wallmann, K.: Toward a parameterization of global-scale
  organic carbon mineralization kinetics in surface marine sediments, Global Biogeochemical
  Cycles, 29, 812-829, 10.1002/2015gb005087, 2015.

- Stuiver, M., and Polach, H. A.: Discussion: Reporting of <sup>14</sup>C data, Radiocarbon, 19, 355-363,
   1977.
- Suess, E.: Particulate organic carbon flux in the oceans Surface productivity and oxygen
  utilization, Nature, 288, 260-263, 1980.
- Tamburini, F., and Föllmi, K. B.: Phophorus burial in the ocean over glacial-interglacial time
  scales, Biogeosciences, 6, 501-513, 2009.
- 7 Thornalley, D. J. R., Barker, S., Broecker, W. S., Elderfield, H., and McCave, N.: The
  8 Deglacial Evolution of North Atlantic Deep Convection, Science, 331, 202-205, 2011.
- 9 Toggweiler, J. R.: Variation of atmospheric CO<sub>2</sub> by ventilation of the ocean's deepest water,
  10 Paleoceanography, 14, 571-588, 1999.
- Tschumi, T., Joos, F., Gehlen, M., and Heinze, C.: Deep ocean ventilation, carbon isotopes,
  marine sedimentation and the deglacial CO<sub>2</sub> rise, Climate of the Past, 7, 771800, 10.5194/cp-7-771-2011, 2011.
- Tyrrell, T.: The relative influences of nitrogen and phosphorus on oceanic primaryproduction, Nature, 400, 525-531, 1999.
- Ushie, H., and Matsumoto, K.: The role of shelf nutrients on glacial-interglacial CO<sub>2</sub>: A
  negative feedback, Global Biogeochemical Cycles, 26, doi:10.1029/2011GB004147, 2012.
- Van Cappellen, P., and Ingall, E. D.: Benthic phosphorus regeneration, net primary
  production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of
  carbon and phosphorus, Paleoceanography, 9, 677-692, 1994.
- Waelbroeck, C., Labeyrie, L., Michel, E., Duplessy, J.-C., McManus, J. F., Lambeck, K.,
  Balbon, E., and Labracherie, M.: Sea-level and deep water temperature changes derived from
  benthic foraminifera isotopic records, Quaternary Science Reviews, 21, 295-305, 2002.
- Wallmann, K.: Feedbacks between oceanic redox states and marine productivity: A model
  perspective focused on benthic phosphorus cycling, Global Biogeochemical Cycles, 17, 1084,
  doi: 1010.1029GB001968, 2003.
- Wallmann, K.: Phosphorus imbalance in the global ocean?, Global Biogeochemical Cycles,
  24, doi:10.1029/2009GB003643, 2010.

- Wallmann, K., Burwicz, E., Ruepke, L., Marquardt, M., Pinero, E., Haeckel, M., and Hensen,
   C.: Constraining the global inventory of methane hydrate in marine sediments, Proceedings of
   the 7<sup>th</sup> International Conference on Gas Hydrates, Edinburgh, Edinburgh, Scotland, United
   Kingdom, 2011,
- 5 Wallmann, K., Pinero, E., Burwicz, E., Haeckel, M., Hensen, C., Dale, A., and Ruepke, L.:
  6 The global inventory of methane hydrate in marine sediments: A theoretical approach,
  7 Energies, 5, 2449-2498, 2012.
- 8 Wallmann, K.: Is late Quaternary climate change governed by self-sustained oscillations in
  9 atmospheric CO2?, Geochimica et Cosmochimica Acta, 132, 413-439,
  10.1016/j.gca.2013.10.046, 2014.
- Walsh, J. J., Rowe, G. T., Iverson, R. L., and McRoy, C. P.: Biological export of shelf carbon
  is a sink of the global CO<sub>2</sub> cycle, Nature, 291, 196-201, 1981.
- Watson, A. J., Vallis, G. K., and Nikurashin, M.: Southern Ocean buoyancy forcing of ocean
  ventilation and glacial atmospheric CO<sub>2</sub>, Nature Geoscience, 10.1038/NGEO2538, 2015.
- Yu, J., Elderfield, H., and Piotrowski, A. M.: Seawater carbonate ion-δ13C systematics and
  application to glacial-interglacial North Atlantic ocean circulation, Earth and Planetary
  Science Letters, 271, 209 220, 2008.
- Yu, J., Broecker, W. S., Elderfield, H., Jin, Z., McManus, J., and Zhang, F.: Loss of carbon
  from the deep sea since the Last Glacial Maximum, Science, 330, 1084-1087, 2010.
- Yu, J., Anderson, R. F., Jin, Z., Rae, J. W. B., Opdyke, B. N., and Eggins, S. M.: Responses
  of the deep ocean carbonate system to carbon reorganization during the Last Glacialinterglacial cycle, Quaternary Science Reviews, 76, 39 52, 2013.
- Yu, J., Anderson, R. F., Jin, Z., Menviel, L., Zhang, F., Ryerson, F. J., and Rohling, E. J.:
  Deep South Atlantic carbonate chemistry and increased interocean deep water exchange
  during last deglaciation, Quaternary Science Reviews, 90, 80-89, 2014.
- Zeebe, R., and Wolf-Gladrow, D.: CO<sub>2</sub> in Seawater: Equilibrium, Kinetics and Isotopes,
  Elsevier Oceanography Series, Elsevier, Amsterdam, 346 pp., 2001.

- 1 Zhang, J., Quay, P. D., and Wilbur, D. O.: Carbon-isotope fractionation during gas-water
- 2 exchange and dissolution of  $CO_2$ , Geochimica et Cosmochimica Acta, 59, 107-114, 1995.

- 1 Table 1 Controls on atmospheric  $pCO_2$  and mean dissolved carbon and phosphorus
- 2 concentrations in the global ocean

<u>Circulation</u>					DD ( 01	
Simulation	$pCO_2$ at	pCO <sub>2</sub> at	DIC at	DIC at	DP at 21	DP at 0
	21 ka in	0 ka in	21 ka in	0 ka in	ka in	ka in
	ppmv	ppmv	μM	μM	μM	μM
STD (standard simulation)	190	279	2465	2300	2.44	2.14
STD with constant SST	206	275	2453	2289	2.48	2.15
STD with constant salinity	185	291	2466	2301	2.44	2.14
STD with constant salinity and constant ocean volume	177	281	2409	2310	2.41	2.16
STD with constant riverine DP flux	240	345	2564	2430	2.16	1.98
STD with constant rates of chemical weathering	193	268	2355	2202	2.15	1.98
STD with constant depositional area for P burial	263	367	2599	2478	2.03	1.95
STD with constant depositional area for POC burial	129	180	2132	1925	2.42	2.07
STD with constant burial rate of neritic carbonates	200	277	2437	2291	2.46	2.15
STD-CC-CN	234	255	2400	2273	2.68	2.30
STD with constant AMOC	200	262	2381	2233	2.49	2.12
STD-CC	203	263	2364	2240	2.31	2.14

- 1 Table A1. Salinity (Sal in PSU), dissolved phosphate, nitrate, and oxygen in model boxes (in
- 2  $\mu$ M): Model versus data. Subscripts: S: surface water (0 100m), I: intermediate water (100 –

Box	Sal	Sal	PO <sub>4</sub>	PO <sub>4</sub>	NO <sub>3</sub>	NO <sub>3</sub>	<b>O</b> <sub>2</sub>	O <sub>2</sub>
	Data	Model	Data	Model	Data	Model	Data	Model
AR <sub>s</sub>	32.96	33.01	0.84	0.825	6.58	11.1	340.7	349
NAs	35.55	35.24	0.29	0.325	4.	4.67	257.2	248
TAs	36.22	36.1	0.31	0.335	3.09	4.19	201.6	212
SOs	34.5	34.3	1.05	1.08	13.01	14.2	290.3	284
TIPs	35.03	34.95	0.4	0.447	3.03	4.34	198.9	208
NPs	33.6	33.59	0.84	0.781	8.15	9.88	276.	263
AR <sub>I</sub>	34.83	34.82	0.99	0.961	13.22	13.4	296.7	313
NAI	35.28	35.05	0.87	1.12	16.29	16.8	238.6	234
TAI	34.99	34.93	1.63	1.72	25.1	25.5	181.5	169
SOI	34.58	34.54	1.98	2.05	28.43	29.1	209.7	212
TIP <sub>I</sub>	34.68	34.64	2.37	2.43	32.16	34.1	107.1	93.4
NPI	34.32	34.52	2.75	2.67	38.17	35.7	73.65	90.7
AR <sub>D</sub>	34.94	34.87	1.04	1.07	14.69	15	287.	287
NA <sub>D</sub>	34.95	34.92	1.18	1.19	18.71	16.9	265.1	257
TA <sub>D</sub>	34.92	34.9	1.43	1.54	21.67	21.8	245.5	220
SOD	34.72	34.76	2.2	2.14	31.32	29.2	203.7	211
TIP <sub>D</sub>	34.69	34.75	2.49	2.53	35.5	33.9	145.5	149
NP <sub>D</sub>	34.65	34.69	2.73	2.57	38.63	34.1	116.	134
AR <sub>B</sub>	34.94	34.87	1.05	1.08	14.6	15.2	276.5	285
NA <sub>B</sub>	34.9	34.91	1.33	1.42	20.18	19.3	260.5	237
TA <sub>B</sub>	34.86	34.87	1.56	1.64	23.81	23	242.4	217
SOB	34.7	34.76	2.22	2.16	32.07	29.4	220.2	206
TIP <sub>B</sub>	34.7	34.75	2.34	2.39	33.65	31.8	176.4	173
NP <sub>B</sub>	34.69	34.71	2.51	2.52	36.02	33.4	155.9	144

3 2000m), D: deep water (2000 – 4000m), B: bottom water (>4000m)

1 Table A2. Dissolved inorganic carbon (DIC), total alkalinity (TA),  $\delta^{13}$ C-DIC, and  $\Delta^{14}$ C-DIC

Box	DIC	DIC	TA	TA	$\delta^{13}C$	$\delta^{13}C$	$\Delta^{14}$ C	$\Delta^{14}$ C
	Data*	Model	Data	Model	Data <sup>+</sup>	Model	Data*	Model
ARs	2101	2166	2372.	2357	n. d.	2.11	n. d.	-68.26
NAs	2074	2056	2410.	2410	1.47	2.77	-75.6	-69.02
TA <sub>S</sub>	2061	2032	2444.	2453	1.64	2.77	-67.3	-65.35
SOs	2104	2083	2365.	2340	1.41	1.8	-85.1	-78.38
TIPs	2006	1944	2359.	2347	1.28	2.24	-60.1	-64.04
NPs	2037	2022	2300.	2306	1.3	2.27	-75.7	-72.01
AR <sub>I</sub>	2169	2176	2373.	2375	n. d.	1.79	n. d.	-78.03
NAI	2179	2180	2391.	2392	0.9	1.45	-75.	-90.32
TAI	2225	2259	2386.	2400	0.84	0.625	-101.8	-114
SOI	2254	2257	2392.	2380	0.72	-0.053	-130.4	-126.5
TIPI	2317	2311	2418.	2391	0.32	-0.653	-148.3	-134.7
NPI	2370	2373	2421.	2436	-0.23	-0.875	-179.7	-183.3
AR <sub>D</sub>	2188	2185	2371.	2379	n. d.	1.62	n. d.	-85.97
NA <sub>D</sub>	2216	2195	2388.	2384	0.97	1.44	-87.9	-93.75
TA <sub>D</sub>	2242	2239	2402.	2401	0.96	0.933	-116.6	-122.3
SOD	2315	2314	2431.	2441	0.1	0.119	-166.	-167.1
TIP <sub>D</sub>	2382	2382	2481.	2493	-0.06	-0.272	-199.6	-192.5
NP <sub>D</sub>	2416	2388	2491.	2492	-1.09	-0.432	-217.8	-214.2
AR <sub>B</sub>	2188	2186	2371.	2379	n. d.	1.6	n. d.	-86.2
NA <sub>B</sub>	2241	2221	2403.	2395	0.92	1.17	-118.4	-110.7
TA <sub>B</sub>	2268	2253	2418.	2411	0.77	0.792	-132.1	-132.9
SOB	2318	2319	2434.	2446	0.1	0.102	-162.7	-169.2
TIP <sub>B</sub>	2360	2363	2472.	2488	0.14	-0.111	-184.4	-184.7
NP <sub>B</sub>	2388	2384	2491.	2495	-0.58	-0.352	-206.8	-212.7

2 in model boxes (concentrations in  $\mu$ M, isotope data in  $^{\circ}/_{oo}$ ): Model versus data.

3 \*: corrected for anthropogenic  $CO_2$ ; <sup>+</sup>: not corrected for anthropogenic  $CO_2$ 

1 Table A3. Water fluxes (in Sv) derived from the NEMO model run and fluxes applied in the

Fluxes	NEMO	NEMO	Fluxes	Box	Box model
NEMO	Net	Exchange	Box model	model Net	Exchange
$NA_S \rightarrow AR_S$	1.1	2.64	$NA_S \rightarrow AR_S$	3.	1.74
$NA_S \rightarrow NA_I$	0.43	12.2	$NA_S \rightarrow NA_I$	9.93	42.2
$TA_S \rightarrow NA_S$	1.48	7.26	$TA_S \rightarrow NA_S$	12.83	0.36
$SO_S \rightarrow TA_S$	1.34	4.33	$SO_S \rightarrow TA_S$	12.94	0.43
$SO_S \rightarrow SO_I$	10.43	77.58	$SO_S \rightarrow SO_I$	3.93	106.58
$TIP_S \rightarrow SO_S$	8.16	12.42	$TIP_S \rightarrow SO_S$	15.94	12.42
$NP_S \rightarrow TIP_S$	0.43	10.93	$NP_S \rightarrow TIP_S$	0.31	2.93
$NP_S \rightarrow AR_S$	1.14	0.03	$NP_S \rightarrow AR_S$	1.14	0.03
$AR_S \rightarrow AR_I$	2.37	10.38	$AR_S \rightarrow AR_I$	4.37	45.38
$NA_I \rightarrow AR_I$	2.11	24.51	$NA_I \rightarrow AR_I$	2.11	14.51
$NA_I \rightarrow NA_D$	2.23	23.08	$NA_I \rightarrow NA_D$	8.23	0.08
$TA_I \rightarrow TA_S$	0.58	24.91	$TA_I \rightarrow TA_S$	0.58	0.41
$TA_I \rightarrow NA_I$	3.91	27.73	$TA_I \rightarrow NA_I$	0.41	17.73
$SO_I \rightarrow TA_I$	3.42	24.89	$TA_I \rightarrow SO_I$	0.08	4.87
$SO_I \rightarrow TIP_I$	1.29	88.37	$SO_I \rightarrow TIP_I$	13.79	73.37
$TIP_I \rightarrow TIP_S$	11.39	77.11	$TIP_I \rightarrow TIP_S$	16.39	77.11
$NP_I \rightarrow NP_S$	1.26	16.98	$NP_I \rightarrow NP_S$	1.26	3.98
$NP_I \rightarrow TIP_I$	2.	38.55	$NP_I \rightarrow TIP_I$	2.	3.55
$AR_I \rightarrow AR_D$	4.48	6.87	$AR_I \rightarrow AR_D$	6.48	6.87
$NA_D \rightarrow TA_D$	10.35	3.89	$NA_D \rightarrow TA_D$	15.35	1.19
$TA_D \rightarrow TA_I$	1.07	13.78	$TA_D \rightarrow TA_I$	1.07	8.78
$TA_D \rightarrow SO_D$	9.29	5.68	$TA_D \rightarrow SO_D$	15.29	1.68
$SO_I \rightarrow SO_D$	5.72	224.4	$SO_D \rightarrow SO_I$	9.78	10.12
$SO_D \rightarrow SO_B$	19.65	84.24	$SO_D \rightarrow SO_B$	17.65	114.24
$TIP_D \rightarrow TIP_I$	8.1	18.08	$TIP_D \rightarrow TIP_I$	0.6	3.08
$TIP_D \rightarrow SO_D$	4.64	12.54	$TIP_D \rightarrow SO_D$	12.14	2.54
$NP_D \rightarrow TIP_D$	5.71	10.96	$TIP_D \rightarrow NP_D$	1.29	0.67
$NP_D \rightarrow NP_I$	3.26	2.48	$NP_D \rightarrow NP_I$	3.26	1.48
$AR_D \rightarrow NA_D$	4.48	1.	$AR_D \rightarrow NA_D$	6.48	11.
$NA_B \rightarrow NA_D$	3.64	2.53	$NA_B \rightarrow NA_D$	0.64	2.53
$TA_B \rightarrow TA_D$	0.01	20.75	$TA_B \rightarrow TA_D$	1.01	20.75
$TA_B \rightarrow NA_B$	3.64	2.93	$TA_B \rightarrow NA_B$	0.64	0.43
$SO_B \rightarrow TA_B$	3.65	2.53	$SO_B \rightarrow TA_B$	1.65	2.53
$SO_B \rightarrow TIP_B$	16.	0.72	$SO_B \rightarrow TIP_B$	16.	15.72
$TIP_B \rightarrow TIP_D$	7.03	55.76	$TIP_B \rightarrow TIP_D$	14.03	35.76
$TIP_B \rightarrow NP_B$	8.97	8.65	$TIP_B \rightarrow NP_B$	1.97	0.65
$NP_B \rightarrow NP_D$	8.97	7.32	$NP_B \rightarrow NP_D$	1.97	7.32
$AR_B \rightarrow AR_D$	0	0.19	$AR_B \rightarrow AR_D$	0	1.19
$FRESH \rightarrow NA_S$	0.05		$FRESH \rightarrow NA_S$	0.10	
$FRESH \rightarrow TA_S$	-0.44		$FRESH \rightarrow TA_S$	-0.69	
$FRESH \rightarrow SO_S$	3.61		$FRESH \rightarrow SO_S$	0.93	
$FRESH \rightarrow TIP_S$	-3.66		$FRESH \rightarrow TIP_S$	-0.76	

2 box model to reproduce observed tracer distributions (Tabs. A1 and A2)

$FRESH \rightarrow NP_S$	0.31	$FRESH \rightarrow NP_S$	0.19	
$FRESH \rightarrow AR_S$	0.13	$FRESH \rightarrow AR_S$	0.23	

2 Table A4. Biogeochemical parameter values determined by fitting the model to observations

Parameter	Symbol	Units	AR	NA	ТА	SO	TIP	NP
Kinetic constant for export production	k <sub>EXP</sub>	yr <sup>-1</sup>	0.05	1.5	0.4	0.15	1.1	0.12
Kinetic constant for nitrogen fixation	k <sub>NF</sub>	yr <sup>-1</sup>	0.0	3.0	1.0	0.2	1.0	0.5
PIC/POC export ratio	r <sub>PICPOC</sub>		0.01	0.08	0.20	0.01	0.15	0.07
Piston velocity	k <sub>SA</sub>	cm yr <sup>-1</sup>	0.4	0.1	0.12	0.12	0.24	0.1

3

- 4 Table A5. Difference in  $\delta^{13}$ C-DIC between LGM (21 kyr BP) and Holocene (5 kyr BP) as
- 5 derived from data (Oliver et al., 2010; Sarnthein et al., 1994) and calculated in the standard
- 6 model run

Box	Data	Model
NA <sub>I</sub>	$+0.04 \pm 0.28$	+0.01
NA <sub>D</sub>	$-0.55 \pm 0.16$	-0.60
NA <sub>B</sub>	$-0.70 \pm 0.13$	-0.70
TAI	$+0.15 \pm 0.20$	+0.22
TA <sub>D</sub>	$-0.55 \pm 0.24$	-0.66
TA <sub>B</sub>	$-0.78 \pm 0.21$	-0.73
SOD	$-0.44 \pm 0.26$	-0.52
TIP <sub>D</sub>	$-0.44 \pm 0.20$	-0.36

1 Table B1 Parameter values applied in the simulation of margin processes

Parameter	Symbol	Value	Source
Modern seafloor area at	A <sub>NM</sub>	13.54 x 10 <sup>6</sup> km <sup>2</sup>	(Eakins and Sharman,
0 - 50 m			2012)
Modern seafloor area at	A <sub>SM</sub>	$20.34 \text{ x } 10^6 \text{ km}^2$	(Eakins and Sharman,
0 - 100 m			2012)
Modern seafloor area at	A <sub>IM</sub>	$38.29 \text{ x } 10^6 \text{ km}^2$	(Eakins and Sharman,
100 - 2000 m			2012)
Modern rate of neritic	F <sub>BPICSM</sub>	$10 \text{ Tmol yr}^{-1}$	(Kleypas, 1997)
carbonate burial			
Modern rate of marine POC	<b>F</b> <sub>BPOCSM</sub>	5 Tmol yr <sup>-1</sup>	(Wallmann et al., 2011)
burial at 0 - 100 m			
Modern rate of marine POC	F <sub>BPOCIM</sub>	5 Tmol yr <sup>-1</sup>	(Wallmann et al., 2011)
burial at 100 - 2000 m			
Modern rate of marine POC	<b>F</b> <sub>BPOCDM</sub>	1.3 Tmol yr <sup>-1</sup>	(Wallmann et al., 2011)
burial at 2000 - 4000 m			
Modern rate of marine POC	F <sub>BPOCBM</sub>	0.2 Tmol yr <sup>-1</sup>	(Wallmann et al., 2011)
burial at >4000 m			
Modern POC export production	F <sub>EPOCM</sub>	809 Tmol yr <sup>-1</sup>	(Sarmiento and Gruber, 2006)
Modern rate of marine P burial	<b>F</b> <sub>BPSM</sub>	$0.05 \text{ Tmol yr}^{-1}$	(Wallmann, 2010)
at 0 - 100 m			
Modern rate of marine P burial	F <sub>BPIM</sub>	0.05 Tmol yr <sup>-1</sup>	(Wallmann, 2010)
at 100 - 2000 m			
Modern rate of marine P burial	<b>F</b> <sub>BPDM</sub>	0.06 Tmol yr <sup>-1</sup>	(Wallmann, 2010)
at 2000 - 4000 m			
Modern rate of marine P burial	F <sub>BPBM</sub>	0.02 Tmol yr <sup>-1</sup>	(Wallmann, 2010)
at >4000 m			
Monod constant for P burial	k <sub>P</sub>	20 µM	(Wallmann, 2010)
Burial efficiency of marine	BEs	0.05	This work
POC at 0 - 100 m			
Burial efficiency of marine	BEI	0.2	This work
POC at 100 - 2000 m			
Burial efficiency of marine	BED	0.1	This work
POC at 2000 - 4000 m			
Burial efficiency of marine	BE <sub>B</sub>	0.02	This work
POC at >4000 m			
Maximum POC to P ratio in	r <sub>CPM</sub>	400	(Anderson et al., 2001)
marine sediments			

Process	Equation*
Neritic carbonate burial	$F_{BPICS} = F_{BPICSM} \cdot \frac{A_{N}}{A_{NM}}$
POC burial at 0 - 100 m	$F_{BPOCS} = F_{BPOCSM} \cdot \frac{F_{EPOC}}{F_{EPOCM}} \cdot \frac{A_{S}}{A_{SM}}$
POC burial at 100 - 2000 m	$F_{\text{BPOCI}} = F_{\text{BPOCIM}} \cdot \frac{F_{\text{EPOC}}}{F_{\text{EPOCM}}} \cdot \frac{A_{\text{I}}}{A_{\text{IM}}}$
POC burial at 2000 - 4000 m	$F_{\text{BPOCD}} = F_{\text{BPOCDM}} \cdot \frac{F_{\text{EPOC}}}{F_{\text{EPOCM}}} \cdot \frac{A_{\text{SM}} + A_{\text{IM}}}{A_{\text{S}} + A_{\text{I}}}$
POC burial at > 4000 m	$F_{\text{BPOCB}} = F_{\text{BPOCBM}} \cdot \frac{F_{\text{EPOC}}}{F_{\text{EPOCM}}} \cdot \frac{A_{\text{SM}} + A_{\text{IM}}}{A_{\text{S}} + A_{\text{I}}}$
P burial at 0 - 100 m	$F_{BPS} = Max \left[ F_{BPSM} \cdot \frac{F_{EPOC}}{F_{EPOCM}} \cdot \frac{A_{S}}{A_{SM}} \cdot \frac{DO_{S}}{DO_{S} + k_{P}} \cdot \frac{DO_{SM} + k_{P}}{DO_{SM}}, \frac{F_{BPOCS}}{r_{CPM}} \right]$
P burial at 100 - 2000 m	$F_{BPI} = Max \left[ F_{BPIM} \cdot \frac{F_{EPOC}}{F_{EPOCM}} \cdot \frac{A_{I}}{A_{IM}} \cdot \frac{DO_{I}}{DO_{I} + k_{P}} \cdot \frac{DO_{IM} + k_{P}}{DO_{IM}}, \frac{F_{BPOCI}}{r_{CPM}} \right]$
P burial at 2000 - 4000 m	$F_{BPD} = Max \left[ F_{BPDM} \cdot \frac{F_{EPOC}}{F_{EPOCM}} \cdot \frac{DO_{D}}{DO_{D} + k_{P}} \cdot \frac{DO_{DM} + k_{P}}{DO_{DM}}, \frac{F_{BPOCD}}{r_{CPM}} \right]$
P burial at > 4000 m	$F_{BPB} = Max \left[ F_{BPBM} \cdot \frac{F_{EPOC}}{F_{EPOCM}} \cdot \frac{DO_B}{DO_B + k_P} \cdot \frac{DO_{BM} + k_P}{DO_{BM}}, \frac{F_{BPOCB}}{r_{CPM}} \right]$
Benthic denitrification with i = (S, I, D, B)	$F_{BDENi} = \frac{F_{BPOCi}}{BE_{i}} \cdot (0.06 + 0.19 \cdot 0.99^{(DO_{i} - DN_{i})})$

1 Table B2 Flux parameterizations applied in the simulation of margin processes

2 \*Subscripts indicate modern values (M) and the following environments: shelf (S, 0 - 100 m

3 water depth), outer shelf and slope (I, 100 - 2000 m), continental rise and deep-sea floor (D,

4 2000 – 4000 m), deep-sea floor and abyssal plain (B, >4000 m). The equations define global

5 fluxes. These were distributed among the ocean basins considered their export production and

6 the seafloor areas of individual boxes.

- 1 Table C1. Deep-sea  $CO_3^{2-}$  concentrations (in  $\mu$ mol/kg): Differences between 21 and 5 kyr BP
- 2 (LGM H) calculated in the standard simulation STD are compared to corresponding

3	observational data (derive	d from B/Ca ratios in foraminifer	ra, LGM - Holocene differences).
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Box	Model	Data	Sites/References
AR <sub>D</sub>	36	$24 \pm 10$	60°N, 24°W, 2.4 km (Yu et al., 2008)
NA <sub>D</sub>	23	$18 \pm 9$	55°N, 20°W, 2.0 km (Yu et al., 2008)
		$24 \pm 10$	60°N, 24°W, 2.4 km (Yu et al., 2008)
		$4\pm 6$	55°N, 21°W, 2.8 km (Yu et al., 2008)
		$-18 \pm 8$	51°N, 22°W, 3.5 km (Yu et al., 2008)
		$-19 \pm 9$	52°N, 22°W, 4.0 km (Yu et al., 2008)
NA <sub>B</sub>	15	$-19 \pm 9$	52°N, 22°W, 4.0 km (Yu et al., 2008)
TA <sub>D</sub>	14	$9\pm10$	4°S, 13°W, 2.9 km (Raitzsch et al., 2011)
TA <sub>B</sub>	6	$-17 \pm 12$	4°S, 16°W, 4.7 km (Raitzsch et al., 2011)
SOB	1	$3\pm 2$	41°S, 8°E, 5.0 km (Yu et al., 2014)
TIP <sub>D</sub>	3	$2\pm3$	0°S, 158°E, 2.3 km (Yu et al., 2010)
		$-6 \pm 4$	0°S, 161°E, 3.4 km (Yu et al., 2010)
TIP <sub>B</sub>	2	$1 \pm 4$	1°S, 140°W, 4.3 km (Yu et al., 2013)
		$5\pm3$	10°S, 52°E, 4.1 km (Yu et al., 2010)

5

6 Table C2. Effect of radiocarbon production rate on atmospheric and marine <sup>14</sup>C values under

steady-state conditions.  $R_{14}(0)$  is the pre-human atmospheric production rate applied in the

8 model calibration (1.64 atoms  $\text{cm}^{-2} \text{ s}^{-1} = 437 \text{ mol yr}^{-1}$ ).

Rate	$\Delta^{14}$ C-CO <sub>2</sub> (°/ <sub>00</sub> )	$\Delta^{14}$ C-DIC (°/ <sub>00</sub> )	$\Delta \Delta^{14}$ C-DIC ( $^{0}/_{00}$ )
$R_{14}(0)$	+0	-148	-148
$1.5 \text{ x } \text{R}_{14}(0)$	+500	+278	-222
$2.0 \ge R_{14}(0)$	+1000	+704	-296

9

1 Table C3.  $\Delta\Delta^{14}$ C-DIC for the LGM (19 – 23 kyr BP) calculated in simulation STD and

Box	Model	Data	Reference			
ARs	-196 to	EAST:	GIK 23074 (66°66.67'N, 4°90'E, 1157 m, Norw.			
	-177	-95 to -60	Current), (Sarnthein et al., 2014)			
		WEST:	PS2644 (67°52.02'N, 21°45.92'W, 777 m, East			
		-210 to -240	Greenland Current), (Sarnthein et al., 2013; Sarnthein et			
			al., 2014)			
AR <sub>I</sub>	$ \begin{array}{ccc} R_{I} & -206 \text{ to} & -50 \\ -187 & -220 \text{ to} -270 \end{array} $		PS2644 (67°52.02'N, 21°45.92'W, 777 m, millennial-			
			scale oscillations?), (Sarnthein et al., 2013)			
NAs	$NA_{S}$ -169 to -115 to -40		MD90-917 (41°29.78'N, 17°61.3'E, 1010 m)			
	-153		MD99-2334K (37°48'N, 10°10'W, 3146 m)			
			RAPID-17-5P (61°29'N, 19°32'W, 2303 m)			
			(Thornalley et al., 2011)			
			MD08-3180 (38°N, 31°13.45'W, 3064 m)			
			(Sarnthein et al., 2013)			
$NA_D$	-257 to -	-40 to -60	MD99-2334K (37°48'N, 10°10'W, 3146 m)			
	228		RAPID-17-5P (61°29'N, 19°32'W, 2303 m)			
			(Thornalley et al., 2011)			
		-260 to -275	MD08-3180 (38°N, 31°13.45'W, 3064 m)			
NT A	205.4	220	(Sarnthein et al., 2014)			
NA <sub>B</sub>	-285 to	-330	Extrapolated from Portuguese margin site			
	-253		MD99-2334K (37°48'N, 10°10'W, 3146 m, a site subject			
			to enhanced Coriolis forcing) (Skinner et al., 2014) and			
			assuming a transit time of ~800 yr from TNO57-21 $(41^{\circ}06^{\circ}S, 7^{\circ}48^{\circ}F, 4081, m)$ (Barker et al. 2010)			
TAs	-128 to -	-130 to -95	(41°06'S, 7°48'E, 4981 m) (Barker et al., 2010) ODP 1002 (10°42.37'N, 65°10.18'W, 893 m)			
IAS	108	-130 10 -93	and southward extrapolated from			
	108		MD08-3180 (38°N, 31°13.45'W, 3064 m)			
			(Sarnthein et al., 2014)			
TAI	-241 to	-160 to -185	Dredged coral transects at Gregg, Manning, and Muir Sea			
111	-218	-85	Mt. $33^{\circ}$ – $39^{\circ}$ N, <2300 m, corr. according to (Robinson et			
	210	00	al., 2005)			
SOS	-160 to	-270 to -190	MD07-3076 (44°09'S, 14°13'W, 3770 m)			
~ - 5	-140		(Skinner et al., 2010)			
SOI	-228 to -	-220 to -210	Dredged coral transect Drake Passage, <1800 m			
	201		(Burke et al., 1982), + AWI unpubl. data under review			
SOD	-332 to	-300 to -185	D07-3076 (44°09'S, 14°13'W, 3770 m)			
	-296		ATL. SECTOR: (Skinner et al., 2010)			
		-600 to -500	Sonne core transect off New Zealand			
			PAC. SECTOR: AWI unpubl. records, under review			
SOB	-335 to -	-230 to -130	TNO57-21 (41°06'S, 7°48'E, 4981 m)			
	299		(Barker et al., 2010)			
TIPs	-139 to	-220 to -105	MD01-2378 (13°08.25'S, 121°78.8'E, 1783 m)			
	-120		(Sarnthein et al., 2014)			
TIPI	-238 to	-264 to -61	RC 27-14 (18.3°N, 57.6°E, 596 m)			
1	-211	-205 to -190	RC 27-23 (18.0°N, 57.6°E, 820 m)			
1			(Bryan et al., 2010)			
		-220 to -165	MD01-2378 (13°08.25'S, 121°78.8'E, 1783 m)			

2 derived from radiocarbon measurements in foraminifera (atmosphere – water differences).

			(Sarnthein et al., 2013)
TIP <sub>D</sub>	-363 to	-410 to -320	MD01-2378 (13°08.25'S, 121°78.8'E, 1783 m)
	-324		GIK 17940 (20°07.0'N, 117°23.0'E, 1727 m)
			extrapolated to >2000 m, (Sarnthein et al., 2013)
NPs	-156 to	-190 to -115	MD01-2416 (51°26.8'N, 167°72.5'E, 2317 m)
	-137		MD02-2489 (54°39.07'N, 148°92.13'W, 3640 m)
			(Sarnthein et al., 2013; Sarnthein et al., 2014)
NPD	-378 to	-470	MD01-2416 (51°26.8'N, 167°72.5'E, 2317 m)
	-337		(Sarnthein et al., 2013; Sarnthein et al., 2014)
NP <sub>B</sub>	-375 to	-270	MD02-2489 (54°39.07'N, 148°92.13'W, 3640 m)
	-335		extrapolated to $>4000$ m,
			(Sarnthein et al., 2013; Gebhardt et al., 2008)

- 3 Table C4. LGM tracer concentrations in model boxes at 21 ka in simulation STD (see Tab.
- 4 A1 and A2 for further information)

Box	Sal	PO <sub>4</sub>	NO <sub>3</sub>	<b>O</b> <sub>2</sub>	DIC	ТА	$\delta^{13}C$	$\Delta \Delta^{14} C$
	(PSU)	(µM)	(µM)	(µM)	(µM)	(µM)	(°/ <sub>00</sub> )	(°/ <sub>00</sub> )
AR <sub>s</sub>	33.69	0.93	12.2	369	2244	2562	1.63	-181
NAs	35.84	0.34	4.2	266	2158	2619	2.56	-156
TAs	36.94	0.14	1.7	214	2122	2685	2.90	-119
SOs	35.80	0.42	6.0	306	2184	2588	2.38	-148
TIPs	36.40	0.36	4.1	211	2040	2583	2.51	-128
NPs	34.87	0.79	10.9	282	2131	2521	2.43	-145
AR <sub>I</sub>	35.48	1.07	14.8	330	2268	2579	1.39	-192
NAI	35.69	1.12	16.4	258	2277	2595	1.32	-192
TA <sub>I</sub>	35.72	1.60	23.2	212	2345	2601	0.71	-224
SOI	35.86	2.09	32.3	143	2419	2583	-0.13	-213
TIPI	35.94	2.35	35.5	76	2444	2591	-0.38	-223
NPI	35.72	2.97	42.1	69	2537	2631	-0.96	-300
AR <sub>D</sub>	35.54	1.45	19.4	282	2315	2587	0.96	-221
NA <sub>D</sub>	35.59	1.70	22.5	251	2346	2593	0.69	-239
TA <sub>D</sub>	35.72	2.16	29.2	201	2422	2621	0.11	-281
SOD	35.80	2.81	36.9	179	2518	2649	-0.60	-312
TIP <sub>D</sub>	35.81	3.16	40.4	112	2576	2690	-0.83	-342
NPD	35.79	3.12	40.6	108	2574	2691	-0.86	-356
AR <sub>B</sub>	35.54	1.48	19.7	280	2317	2587	0.94	-222
NA <sub>B</sub>	35.65	2.04	26.4	222	2392	2607	0.32	-266
TA <sub>B</sub>	35.74	2.37	31.5	193	2453	2631	-0.11	-294
SOB	35.80	2.84	37.1	174	2523	2654	-0.61	-315
TIP <sub>B</sub>	35.81	3.06	39.0	135	2565	2694	-0.74	-334
NP <sub>B</sub>	35.79	3.11	40.0	118	2574	2698	-0.81	-353



Figure 1. Morphology of global ocean margin. The black line is the cumulated seafloor area as derived from the high-resolution ETOPE 1 grid (Eakins and Sharman, 2012). The ocean margin at 0 – 100 m water depth is indicated for the modern ocean (red area) and for the LGM when eustatic sea-level was lowered by 120 m (blue area). The global ocean retreated into stepper terrain during the glacial marine regression. The seafloor areas covered by shallow waters were reduced by this steepening of ocean margins.



2 Figure 2. Set-up of the box model: The global ocean is separated into 24 boxes representing surface (0 - 100 m), intermediate (100 - 2000 m), deep (2000 - 4000 m), and bottom (>4000 3 4 m) waters in the Arctic (AR), North Atlantic (NA), Tropical Atlantic (TA), Southern Ocean (SO), Tropical Indo-Pacific (TIP), and North Pacific (NP). Arrows with numbers indicate net 5 water fluxes between boxes in Sv; major fluxes (>5 Sv) are represented by large arrows, 6 minor fluxes (<5 Sv) by small arrows. Arrows crossing the top boundary of the surface water 7 boxes (seawater-atmosphere interface) indicate net freshwater fluxes (precipitation + river 8 water fluxes - evaporation). The upper panel shows the circulation field applied for the 9 modern ocean and the previous interglacial, the lower panel shows the circulation applied 10 over the LGM. 11



Figure 3. Model forcing related to sea-level change. (a) Eustatic sea-level (Waelbroeck et al., 3 4 2002; Stanford et al., 2011); (b) Global ocean volume as calculated from eustatic sea-level and ocean bathymetry data (Eakins and Sharman, 2012); (c) Salinity of global mean seawater 5 6 as calculated from global ocean volume; (d) Global burial rate of neritic carbonate as calculated from seafloor area at 0 - 50 m water depth (Kleypas, 1997; Wallmann, 2014); (e-f) 7 Seafloor area at 0 - 100 m and 100 - 2000 m water depth calculated from sea-level and ocean 8 9 bathymetry data (Eakins and Sharman, 2012); (g) Exposed shelf area calculated from sea-10 level and ocean bathymetry data (Eakins and Sharman, 2012); (h) Global rate of POC weathering calculated from exposed shelf area (Wallmann, 2014). 11



Figure 4. Model forcing applied to define ocean circulation, nutrient utilization in the 2 Southern Ocean, and the isotopic composition of atmospheric CO<sub>2</sub>. (a-b) Net water fluxes 3 between Southern Ocean (SO) and Tropical Atlantic (TA). The horizontal flows are given for 4 5 (from top to bottom) surface water (subscript S), intermediate water (subscript I), deep water (subscript D), and bottom water (subscript B); c) Horizontal exchange flux between Southern 6 7 Ocean and Tropical Indo-Pacific intermediate waters ; d) Vertical water exchange fluxes in the Southern Ocean and North Pacific across 100 m water depth (solid lines) and 2000 m 8 water depth (broken line); (e) Nutrient utilization in the Southern Ocean (Martinez-Garcia et 9 al., 2014); f)  $\delta^{13}$ C value of atmospheric CO<sub>2</sub>. Dots indicate ice-core data (Schmitt et al., 2012) 10 while the solid line defines the values applied in the model. For >24 kyr BP, where data are 11 not available, the  $\delta^{13}$ C-CO<sub>2</sub> value is set to -6.4  $^{\circ}/_{oo}$ ; (g)  $\Delta^{14}$ C value of atmospheric CO<sub>2</sub>, dots 12 indicate values reconstructed from the geological record (Reimer et al., 2013) while the solid 13 14 line defines the values applied in the model. For >50 kyr BP, where data are not available, the atmospheric  $\Delta^{14}$ C-CO<sub>2</sub> is assumed to correspond to the pre-anthropogenic modern value (0 15 °/<sub>00</sub>). 16



Figure 5. Model results for the standard case (simulation STD, black lines), for constant 2 circulation (simulation STD-CC, red lines), and constant circulation and nutrient utilization 3 (simulation STD-CC-CN, blues lines). (a) Atmospheric pCO<sub>2</sub>, dots indicate ice core data 4 (Monnin et al., 2001; Petit et al., 1999; Monnin et al., 2004); (b) - (h) Global mean seawater 5 concentrations and isotopic compositions (b) Dissolved inorganic carbon (DIC); (c)  $\delta^{13}C$  of 6 DIC; (d) Difference between radiocarbon in seawater DIC and atmospheric CO<sub>2</sub> ( $\Delta\Delta^{14}$ C-DIC 7 =  $\Delta^{14}$ C-DIC -  $\Delta^{14}$ C-CO<sub>2</sub>); (e) Total alkalinity (TA); (f) Dissolved phosphorus (DP); (g) 8 Dissolved reactive nitrogen (DN); (h) Dissolved oxygen (DO). 9



Figure 6. Model results for simulations STD (black lines), STD-CC (red lines), and STD-CCCN (blues lines). (a) Global mean atmospheric near-surface temperature (T<sub>atm</sub>); (b) Global
mean sea surface temperature (SST); (c) – (j) Global rates; (c) Carbonate weathering (F<sub>WC</sub>);
(d) Marine export production of POC (F<sub>EPOC</sub>); (e) POC burial (F<sub>BPOC</sub>); (f) Burial of pelagic
carbonate (F<sub>BPICP</sub>); (g) Riverine flux of dissolved phosphorus (F<sub>RDP</sub>); (h) Burial of marine
phosphorus (F<sub>BP</sub>); (i) Nitrogen fixation (F<sub>NF</sub>); (j) Benthic denitrification (F<sub>DENB</sub>).



2 Figure 7. Atmospheric  $pCO_2$  over the last 25 kyr. (a) Model results for simulations STD (black line), STD-CC (red line), and STD-CC-CN (blues line); solid dots indicate ice core 3 data by (Monnin et al., 2004; Monnin et al., 2001) while ice core data reported in (Marcott et 4 al., 2014) are shown as open circles; (b) relative contribution of sea-level change (blue), 5 nutrient utilization (red), and ocean circulation changes (black) to pCO2 model results; the left 6 7 hand column shows contributions to the glacial pCO<sub>2</sub> draw-down (51 % induced by sea-level 8 fall, 34 % by enhanced nutrient utilization, 15 % by changes in ocean circulation); the right 9 hand column indicates the driving forces for the deglacial pCO<sub>2</sub> rise (23 % induced by sealevel rise, 43 % by decrease in nutrient utilization, 34 % by changes in ocean circulation). 10

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Figure 8. Concentrations (in µM) of dissolved phosphorus (DP) and oxygen (DO) in the preanthropogenic modern ocean (PRE, model results for 0 ka, a: DP, c: DO) and during the LGM
(model results for 21 ka, b: DP, d: DO, Tab. C4). The contour plots shown here and in Figures
9 and 11 are based on concentrations calculated in simulation STD for each of the 24 ocean
boxes (indicated as grid points).



Figure 9. Concentrations of dissolved inorganic carbon (DIC in μM) and carbonate ions
(CO<sub>3</sub><sup>2-</sup> in μmol kg<sup>-1</sup>) in the pre-anthropogenic modern ocean (PRE, model results for 0 ka, a:
DIC, c: CO<sub>3</sub><sup>2-</sup>) and during the LGM (model results for 21 ka, b: DIC, d: CO<sub>3</sub><sup>2-</sup>, Tab. C4). See
legend of Fig. 8 for further information.



Figure 10. Global mean carbonate ion concentrations (a) and pH values (b) below 2000 m
water depth for simulations STD (black line), STD-CC (red line), and STD-CC-CN (blues
line).



Figure 11. Isotopic composition of dissolved inorganic carbon (DIC) in the global ocean.  $\delta^{13}C$ of dissolved inorganic carbon ( $\delta^{13}C$ -DIC in  $^{\circ}/_{oo}$ ) and radiocarbon composition of dissolved inorganic carbon ( $\Delta\Delta^{14}C$ -DIC in  $^{\circ}/_{oo}$ ) in the pre-anthropogenic modern ocean (PRE, model results for 0 ka, a:  $\delta^{13}C$ -DIC, c:  $\Delta\Delta^{14}C$ -DIC) and during the LGM (model results for 21 ka, b:  $\delta^{13}C$ -DIC, d:  $\Delta\Delta^{14}C$ -DIC, Tab. C4).  $\Delta\Delta^{14}C$ -DIC values represent the difference between the atmospheric value (0  $^{\circ}/_{oo}$  for the pre- anthropogenic modern atmosphere, +446  $^{\circ}/_{oo}$  for the LGM atmosphere) and seawater  $\Delta^{14}C$ -DIC. See legend of Fig. 8 for further information.



Figure 12. Radiocarbon values and production rates. (a) Atmospheric  $\Delta$  <sup>14</sup>C-CO<sub>2</sub>; dots are 2 IntCal13 data (Reimer et al., 2013) while the black line shows the values applied in the model 3 runs. (b) Marine  $\Delta \Delta^{14}$ C-DIC values calculated as difference between radiocarbon in seawater 4 DIC and atmospheric CO<sub>2</sub>. The results of simulations STD-CC-CN, STD-CC, and STD are 5 indicated as blue, red and black lines, respectively. The green line indicates the results 6 obtained in a steady-state simulation under Holocene boundary conditions where all variables 7 except atmospheric  $\Delta$  <sup>14</sup>C-CO<sub>2</sub> and radiocarbon production rate were kept constant over 8 time.(c) Production rates of radiocarbon in the atmosphere calculated in the model runs and 9 normalized to the pre- anthropogenic modern value (1.64 atoms cm<sup>2</sup> s<sup>-1</sup>); (d) <sup>14</sup>C production 10 rates calculated from the geo-magnetic record (Laj et al., 2002), <sup>10</sup>Be production rate as 11 reconstructed from Greenland ice core data (Muscheler et al., 2005; Reimer et al., 2013),<sup>10</sup>Be 12 production rate as reconstructed from sediment data (Frank et al., 1997); all rates are 13 normalized to their pre- anthropogenic modern values 14



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Figure 13. DIC versus difference between radiocarbon in seawater DIC and atmospheric CO<sub>2</sub> ( $\Delta\Delta^{14}$ C-DIC) at >2000 m water depth. Data are mean values for deep water and bottom water boxes derived from water column measurements. Model results are shown for the standard case (STD), for constant circulation (STD-CC), and constant values for circulation and nutrient utilization (STD-CC-CN). LGM refers to model results at 21 kyr BP.



2 Fig. 14. Key elements of the 100 kyr cycle. Summer insolation at high northern latitudes (June insolation at 60°N, diagram in the upper right corner, (Berger and Loutre, 1991)) affects 3 4 the growth and melting of continental ice sheets and thereby eustatic sea-level change. The glacial draw-down of atmospheric pCO<sub>2</sub> and its deglacial rise are supported by sea-level 5 change. The cycle is closed by atmospheric pCO<sub>2</sub> affecting global climate and thereby the 6 7 volume of continental ice sheets. It is accelerated and further strengthened by additional 8 positive feedbacks: Ice sheets affect the Earth's albedo and climate while changes in ocean and atmosphere circulation support the glacial pCO<sub>2</sub> draw-down and are largely responsible 9 for the rapid deglacial rise in atmospheric  $pCO_2$ . The records of atmospheric  $pCO_2$  and 10 eustatic sea-level change (diagrams in the upper left corner, (Monnin et al., 2001; Petit et al., 11 1999; Monnin et al., 2004; Waelbroeck et al., 2002; Stanford et al., 2011) reflect the internal 12 non-linear dynamics of the Earth system and its response to external insolation forcing. 13

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Fig. A1. Tracer concentrations in ocean boxes: Model versus data. Open circles indicate concentrations applied as initial values at 130 ka (Tab. A1 and A2). Crosses are concentrations obtained at the end of simulation STD at 0 ka after the completion of a full glacial cycle. Lines indicate the 1:1 relationship, e.g. the best fit to the data.  $\delta^{13}$ C data at <2000 m water depth are excluded from the model-data comparison since they are affected by anthropogenic CO<sub>2</sub>.



Fig. A2. Deglacial benthic – pelagic radiocarbon record in the North Pacific: Model (line)
versus data (squares). The Δ<sup>14</sup>C-DIC difference between deep water and surface water boxes
in the North Pacific is compared to data (Δ<sup>14</sup>C difference between benthic and pelagic
foraminifera, B-P Δ<sup>14</sup>C) from core MD02-2489 taken at the Alaskan Margin at 3.6 km water
depth (Rae et al., 2014). The vertical mixing across 100 m and 2000 m water depth was
enhanced by a factor of 10 at 16.5 ka (Fig. 4d) to reproduce the radiocarbon data.



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3 Fig. A3: Stable carbon isotopic composition of atmospheric CO<sub>2</sub>. Model results versus ice-

4 core data (Schmitt et al., 2012). The model results were obtained in the standard simulation

5 STD without any tuning of the  ${}^{13}$ C-CO<sub>2</sub> fluxes across the seawater-atmosphere interface.