Reply to the referee comments by Victor Brovkin

First of all we would like to thank the referee for his very constructive and valid comments. He raises a number of important questions and issues that we address as outlined below:

My main critical remark is about motivation of this study.

To better explain the motivation of our study, we added the following paragraph at the end of the introduction (page 3, lines 25-32):

"Atmospheric pCO₂ and the distributions of dissolved oxygen, carbonate, and radiocarbon in the glacial ocean serve as key prognostic model variables. They are compared with independent proxy data to address the following specific questions: What fraction of the glacial pCO₂ draw-down can be ascribed to eustatic sea-level fall (Wallmann, 2014)? To which degree do global ¹⁴C data sets assembled by (Sarnthein et al., 2013; Sarnthein et al., 2015) actually reflect our concepts and ideas on glacial and deglacial ocean circulation and carbon cycling? Do marine ¹⁴C data really form a quantitative proxy of DIC in the glacial deep ocean as proposed by (Sarnthein et al., 2013)?"

Why to invest huge intellectual effort into making box model more realistic? Since circulation between model boxes is prescribed by hand, it cannot be more realistic that in a model with explicit ocean dynamics. In my view, the usefulness of box models is limited to conceptual studies.

To address this point and to justify our approach, we added the following paragraph at the end of the section on model set-up (pages 6-7, lines 22-4)

"The modern water fluxes applied to our box model are based on a dynamically consistent circulation field. As explained in Appendix A, these fluxes were modified to obtain tracer distributions that are consistent with observations in the pre-industrial modern ocean (Fig. A1). Glacial and deglacial changes in ocean circulation were not derived from ocean models but from δ^{13} C records (Tab. A5) and additional geochemical observations (Fig. A2). Models with explicit ocean dynamics are superior to any kind of physically unconstrained box model if they generate results that are consistent with observations. However, the physically-constrained earth system models that we are aware of are not yet able to reproduce as many 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 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. 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 dynamics (Tschumi et al., 2011a; Menviel et al., 2012; Brovkin et al., 2012; Roth et al., 2014; Lambert et al., 2015)."

We also added two figures to Appendix A (Figs. A1 an A2) to show that we are able to fit a wide range of observations with our box model.

What really new can we learn from the improved model study? The novelty should be more clearly presented in conclusions and in the abstract.

We added the following paragraphs at the start of the conclusion section to highlight the novel results (pages 19-20, lines 17-9)

"For a first time we show model results that are consistent with both the atmospheric pCO₂ record (Figs. 5 and 7) and data on past distribution changes of dissolved oxygen, carbonate, and radiocarbon in the glacial ocean (Figs. 8, 9, 11 and Tabs. C1 and C3). Atmospheric pCO₂ and the glacial distribution of seawater tracers were not prescribed but calculated as prognostic model variables. Only marine δ^{13} C data were used to parameterize the glacial circulation model. A comprehensive formulation of shelf processes and sea-level effects is a major new component included in our earth system model. Thus, the conformity between independent proxy data and key model results (atmospheric pCO₂ change over the last 130 kyr, distribution of dissolved oxygen, carbonate, and radiocarbon in the LGM ocean) supports our hypothesis that the glacial sea-level drop induced a decline in atmospheric pCO₂ and a rise in the inventories of nutrients, DIC, and alkalinity in the glacial ocean (Wallmann, 2014). 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). However, a glacial shift in the intercept now complicates the use of ¹⁴C as DIC proxy.

The shelf hypothesis was originally developed to explain the deglacial rise in atmospheric pCO_2 (Broecker, 1982). In contrast, our model analysis reveals that shelf and sea-level effects were not responsible for this rapid rise but account for a major portion of the slow glacial decline of atmospheric pCO_2 (Figs. 5 and 7). The deglacial sea-level rise induced a decline in nutrient and carbon stocks in the global ocean. However, these stocks changed only slowly due to their large size (Menviel et al., 2012). The gradual pCO_2 rise over the Holocene may be attributed to the slow relaxation of nutrient and carbon stocks promoting CO_2 transfer from

the ocean into the atmosphere. The slow relaxation may also be responsible for the imbalance in phosphate and TA sources and sinks observed in the modern ocean (Wallmann, 2010, 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."

Another problem with discussion of the box model results is that it is difficult to avoid circular logic... The authors should clearly indicate which results are direct implications of their assumptions and which ones are novel, non-trivial consequences of interactions between biogeochemical components.

We added the following paragraph at the end of the introduction to better explain our approach (page 4, lines 3-8):

"To avoid circular reasoning dissolved oxygen, carbonate, and radiocarbon distributions calculated for the glacial ocean were not used to parameterize our model. These distribution patterns and the atmospheric pCO_2 values calculated in the model are non-trivial consequences of interactions between the various model components and thus are employed to validate the model performance."

Regarding the POC hypothesis, there are still a few conceptual questions, which require more detailed discussion in introduction. Firstly, why terrestrial plants cannot utilize sediment nutrients after the shelf exposure? Tree roots could be many meters deep.

We added the following paragraph to appendix B, section B4 to address this issue (page 38, lines 7-21):

"Moreover, our model does not consider the growth of land plants and soil formation on emerged shelf regions during glacial sea-level low-stands. Trees and other plants may use sediment nutrients after shelf exposure and accumulate terrestrial POC on the emerged shelf. 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 margins (shelf and rise) accumulate sedimentary POC at a rate of about 100 - 200 Gt kyr⁻¹ (Hedges and Keil, 1995; Burdige, 2007; Wallmann et al., 2012; Dunne et al., 2007). This 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 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 terrestrial carbon stock is \leq 2000 GtC. The standing stock of POC in margin sediments exceeds the global terrestrial stock since POC is buried more efficiently in sediments than in most soils and plants. Sedimentary POC burial and preservation are promoted by high sedimentation rates and the lack of oxygen in these water-saturated deposits."

Secondly, increased nutrient inventory and utilization reduces the oxygen content. How good is the box model in reproducing oxygen minimum zones at present? Since ocean boxes are huge, do they represent the oxygen limitation in a plausible way?

We added the following paragraphs to address these issues (page 6, lines 16-21):

"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). "

and (page 13, lines 26-28)

"The glacial oxygen decline simulated in the model has no significant effect on other model parameters since the oxygen level stays above the threshold value for diminished phosphorus burial (20 μ M) in all ocean boxes (Wallmann, 2010)."

P 2406, *l*.15-17. Who are "they"? Sea-level changes? Does weathering add depleted 13C or 14C to the ocean? Changes in 14C are rather a signal of overturning and water masses changes than a result of sea-level changes.

"They" refers to glacial sea-level low-stands. Hence, we replaced "they" by "low-stands" (page 1, line 27). Sea-level change affects the rates of carbon burial and weathering and thereby marine ¹⁴C values (see section 3.4, page 17, lines 22-33 and Fig. 12).

I.19: What does "reduced deep ocean dynamics" mean: slower overturning? Do we have a proxy for it? The Atlantic overturning was shoaled, but was it slower? How do we know that "transit time" was longer – in the whole ocean? Is it the model outcome or is it the model assumptions? It is written like it is a fact – but is it a model truth or a

data truth? If it is an artifact of the model setup, should it be highlighted in the abstract?

We replaced "reduced deep ocean dynamics" by "inferred shoaling of Atlantic meridional overturning circulation" and eliminated "increased transit time" in the abstract (page 2, line 1 and line 4). We added the following paragraph to better explain our model approach (page 11, line 3-14):

"The circulation changes employed to simulate LGM conditions (Fig. 2) led to a reduction in the global water exchange across the 2000 m depth horizon from a modern amount of 45 Sv down to 31 Sv at 21 ka. This corresponds to an increase in the average residence time of water in the deep ocean (>2000 m) from 470 years in the modern ocean to 680 years during the LGM where the residence time is calculated as ratio of the deep ocean volume (6.65 x 10^{17} m³ at >2000m) and the global vertical water fluxes across 2000 m. The glacial increase in residence time by 210 yr may be compared to the 600 yr increase reconstructed from benthic radiocarbon data (Sarnthein et al., 2013). We suggest that the 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 radiocarbon budget (section 3.4)."

I. 28: terrestrial biosphere is not accounted for in the study. Can we consider the Holocene dynamics without accounting for the biosphere regrowth and peat accumulation on land? We added the following paragraph to address this issue (page 7, lines 5-18):

"For many decades it was widely assumed that the modern terrestrial carbon pool exceeds the 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 δ^{13} C 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 (Brovkin and Ganopolski, 2015). Moreover, this new view on terrestrial carbon cycling suggests a deglacial decline in total carbon stocks since the carbon release from high latitude 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 pCO₂ dynamics and the low glacial δ^{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 δ^{13} C and pCO₂ dynamics."

P. 2407, *l*.1-110: How could a decline in iron deposition lead to an increase in atmospheric CO2 by 12-13 ppm in few decades? This corresponds to a source of about 30-40 GtC from the ocean. What can cause a sustainable flux of 1-2 GtC/yr from the ocean?

In our model system about equal portions of the extreme carbon flux are triggered by ventilation pulses in the Southern Ocean and North Pacific and changes in nutrient utilization (Fig. 7). As recommended by the editor we replaced the terms "iron fertilization" and "dust deposition" by "nutrient utilization" in the title and throughout the manuscript since new modeling studies show that nutrient utilization was not only affected by iron fertilization but also by glacial/interglacial changes in ocean circulation changing the residence time of nutrients in the euphotic zone of the Southern Ocean (Watson et al., 2015). To further address this issue we added the following paragraph at the end of section 3.1 (page 12, lines 3-12):

"As shown in Fig. 7, about equal portions of the extreme deglacial carbon flux may have been triggered by changes in circulation and nutrient utilization. Nutrients may have been used more efficiently in the glacial Southern Ocean due to the enhanced dust input fertilizing the surface layer (Martinez-Garcia et al., 2014) and because of buoyancy forces prolonging the residence time of nutrients in the euphotic zone (Watson et al., 2015). However, further processes that are not considered in our model such as the deglacial melting of permafrost (Zimov et al., 2006) and volcanic CO_2 degassing (Huybers and Langmuir, 2009) may have also contributed to the p CO_2 rise because the lack of proxy data and physical process understanding impedes an unequivocal determination of the magnitude of nutrient utilization and stratification change in the Southern Ocean."

P2409, I.24-29 constraining glacial water fluxes based on d13C: this process should be explained in more details. Was it optimization of parameters?

We added the following paragraph to better explain our approach (page 5, lines 3-9): "The comprehensive geological data base on benthic foraminiferal δ^{13} C (Oliver et al., 2010; Sarnthein et al., 1994) was employed to constrain water fluxes for the Last Glacial Maximum (LGM). Mean δ^{13} C-DIC values were calculated for those ocean boxes where sufficient δ^{13} C data were available and compared to model results. Water fluxes were varied until the Holocene-LGM differences in δ^{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."

P2413: C:P ratio in POM is roughly 100:1, while it is about 50:1 for soils and 1000:1 for wood biomass. Trees on exposed tropical shelves could store much more C than marine sediments, and the net effect on atmospheric CO_2 would be rather neutral We added a paragraph to address this issue (page 38, lines 7-21).

Figure 2: numbers are not readable

We will ask the production team to display this figure at a size that allows the reader to read the numbers.

Fig. 3h, POC weathering: is river POC flux included? If so, is this POC originated from shelves or from internal continental area? Exposed shelf area goes to 0, but POC flux from exposed area is not 0: please explain

The following paragraph was added to address this question (page 30, lines 19-22): "Riverine POC fluxes are ignored in the 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 (Wallmann, 2014). Both components produce atmospheric CO₂ depleted in ¹³C and ¹⁴C."

Figure 7: What mechanisms are responsible for the pCO_2 drawdown from 10 to 8 ka? A usual interpretation is that this CO_2 drop is an effect of terrestrial carbon uptake.

The following paragraph was added to address this question (page 11, lines 25-30): "The pCO₂ drawdown from 10 to 8 ka reflects a recovery of the ocean system from the antecedent ventilation pulse in the Southern Ocean centered at 11.5 ka (Fig. 4d). According to our model, the ventilation pulse removed CO₂ from the ocean interior, enhanced the O₂ content of the deep ocean, and diminished the vertical DIC and O₂ gradients. The subsequent restoration of the vertical DIC gradient induced the pCO₂ decline observed in the model from 10 to 8 ka."

Figure 10a, black line: the model shows a decrease in carbonate ion concentration

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during deglaciation. This would lead to a $CaCO_3$ dissolution spike during deglaciation, opposite to what was observed.

Indeed, carbonate ion concentrations regulate the dissolution of pelagic carbonates but are likewise controlled by the rates of carbonate dissolution and burial. Moreover, carbonate burial is not only affected by carbonate dissolution but also by the production and export of carbonate via the biological pump. According to our model, export production reached a deglacial maximum at 16.5 ka (Fig. 6d) which was responsible for the peak in global carbonate burial at that time (Fig. 6f) and the deglacial CO_3^{2-} minimum (Fig. 10a). The following paragraph was added to address this question (page 15, lines 24-27): "The deglacial CO_3^{2-} minimum is related to ventilation pulses in the Southern Ocean and North Pacific employed in the model. Export production of $CaCO_3$ and pelagic carbonate burial were enhanced by these up-welling events and removed dissolved CO_3^{2-} from the deep ocean."

Figure 8: Please add a plot of difference LGM to PRE, otherwise it is difficult to see how exactly the P and O2 pools are re-distributed at LGM. Figure 9: Please add a plot of difference LGM to PRE. Figure 11: plot a difference LGM to PRE.

We added a table with all tracer concentrations calculated for the LGM in the standard simulation to Appendix C (Tab. C4, page 65). The LGM numbers listed in this new table and the PRE numbers given in Tabs. A1 and A2 can be employed to calculate the LGM-PRE differences for each tracer and each model box.

Also, add a plot of observations for PRE as averaged on the model resolution from the data.

We added Fig. A1 to Appendix A to show how PRE model results compare to observations (page 80).

Figure 13: please add arrows of shifts from STD to STD LGM. Is there added value of showing CC and CC-CN LGM versions?

We tested whether arrows would improve the plot and found out that this is actually not the case. The CC and CC-CN results confirm that the slope is rather constant irrespectively of the model assumptions.

Figure 14: a nice conceptual plot, but arrows are very selective. Why there is no direct effect of insolation on climate (temperature) and circulation (via SST/precip pattern)? Also, sea level changes have a direct effect on circulation eg through the Bering Straight. The figure is not meant to show all interactions. As indicated in the figure legend (page 79), it tries to illustrate the *key elements* only.

Reply to the comments by the anonymous Referee #2

I miss a discussion with a critical assessment of the model and its results.

We added a comprehensive text on model limitations at the end of the model set-up section (pages 6-7):

"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 circulation field. As explained in Appendix A, these fluxes were modified to obtain tracer distributions that are consistent with observations in the pre-industrial modern ocean (Fig. A1). Glacial and deglacial changes in ocean circulation were not derived from ocean models but from δ^{13} C records (Tab. A5) and additional geochemical observations (Fig. A2). Models with explicit ocean dynamics are superior to any kind of physically unconstrained box model if they generate results that are consistent with observations. However, the physically-constrained earth system models that we are aware of are not yet able to reproduce as many 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 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. 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 dynamics (Tschumi et al., 2011a; Menviel et al., 2012; Brovkin et al., 2012; Roth et al., 2014; Lambert et al., 2015).

For many decades it was widely assumed that the modern terrestrial carbon pool exceeds the 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 δ^{13} C 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 (Brovkin and Ganopolski, 2015). Moreover, this new view on terrestrial carbon cycling suggests a deglacial decline in total carbon stocks since the carbon release from high latitude 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 pCO₂ dynamics and the low glacial δ^{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 δ^{13} C and pCO₂ dynamics."

1a) The authors are asked to perform a simulation where atmospheric d13C is not prescribed but evolves freely for the standard setup and for the setup with constant circulation...

Unfortunately, the coarse resolution of our model does not allow for a meaningful simulation of atmospheric δ^{13} C. We added the following paragraph to address this issue (page 32, lines 1-9):

"The atmospheric records are affected by vertical mixing processes in the Southern Ocean and the distribution of SSTs and vertical δ^{13} C and Δ^{14} C gradients within this region (Schmitt et al., 2012; Tschumi et al., 2011b; Köhler et al., 2005). Sediment records show an anti-phased pattern in export production and vertical mixing between the region south of the Antarctic Polar Front and the Subantarctic Ocean (Anderson et al., 2014) which may have a strong effect on atmospheric isotope values but was not resolved by our model since the entire global surface ocean at >30°S was pooled in a single box (Fig. 2). This lack of resolution

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hindered us to simulate the carbon isotopic composition of atmospheric pCO_2 with our box model."

1a) continued: By prescribing atm. d13C, the ocean d13C signature is also forced through air-sea gas exchange; the comparison of measured and "simulated" d13C-DIC in table A5 appears therefore not very relevant...

To avoid circular reasoning, we indeed excluded surface water δ^{13} C values from our modeldata comparison (Tab. A5) because they are affected by the prescribed atmospheric δ^{13} C values. We added the following paragraph to address this issue (page 32, lines 9-13):

"Sensitivity tests showed that the δ^{13} C values of intermediate, deep and bottom water boxes employed to derive the glacial circulation field (Tab. A5) were not significantly affected by the prescribed atmospheric δ^{13} C values since the inventory of ¹³C residing in the global ocean exceeds the atmospheric inventory by almost two orders of magnitude."

1b) 2409, line 27: LGM water fluxes were tuned to match LGM d13C distribution. It is not clear to me how this tuning was performed...

We added the following paragraph to answer this question (page 5, lines 6-9): "Water fluxes were varied until the Holocene-LGM differences in δ^{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."

2a) ... (i) to which extent this 24-box model can meaningfully simulate oxygen concentrations (ii) to which extent oxygen in the water column is a proxy for oxygen in the sediment layer. Finally it is controversially discussed whether and to which extent such a fractionation between the burial of C and P indeed occurs (Anderson et al., 2001) and it would be worthwhile to mention this.

(i) Our model predicts for the glacial ocean a general oxygen decline at >2000 m water depth (Fig. 8), consistent with analytical data (Jaccard and Galbraith, 2012). However, it does not resolve OMZs.

(ii) We use transfer functions derived from global compilations of in-situ benthic fluxes to define benthic denitrification rates and turnover rates of P in marine sediments (Bohlen et al., 2012; Wallmann, 2010). Analyses of these benthic flux data suggest that rates of benthic

denitrification are influenced by both the rain rate of POC to the seabed and the oxygen content of ambient bottom waters since these parameters affect the oxygen concentration and redox state of surface sediments (Tab. B2). In contrast, benthic P fluxes are only affected by bottom water oxygen if the concentrations fall below the threshold value of 20 μ M (Wallmann, 2010), expressed as a Monod term in our model formulation (Tab. B2). In our model runs the minimum oxygen concentration (69 μ M in North Pacific intermediate water at 21 ka) clearly exceeds this threshold value. Hence, our calculated P burial rates do not reflect any changes in bottom water oxygen.

(iii) We added a paragraph to better explain the effects of oxygen on benthic P cycling (page 34-35, lines 30-11):

"Phosphate cycling in marine sediments is affected by oxygen conditions in ambient bottom 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 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 in the sediment as authigenic carbonate fluorapatite (CFA). Hence, OMZ sediments are depleted in Fe/Mn-bound P, enriched in CFA and characterized by high POC/POP ratios exceeding the Redfield ratio by a factor of 2 - 8 (Schenau and De Lange, 2001; Lomnitz et al., 2015). Ratios between POC and reactive P (P_{reac}, sum of POP, CFA and Fe/Mn-bound P) amount to POC/P_{reac} = 100 - 300 in OMZ sediments and 20 - 70 in continental margin 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 conditions (Ingall and Jahnke, 1994; Schenau and De Lange, 2001) whereas POC is more efficiently buried in OMZ sediments covered by oxygen-depleted bottom waters (Dale et al., 2015)."

The paper by (Anderson et al., 2001) shows that the preferential P release from reducing sediments is limited by CFA precipitation. We updated our model formulation accordingly by introducing a maximum POC/P burial ratio and a maximum condition in our P burial flux definition (Tabs. B1 and B2, pages 61-62). The following sentence serves to explain the approach (page 35, lines 31-33):

"Moreover, the model formulation ensured that the molar POC/P_{reac} burial ratio did not exceed the maximum value of about 400 observed in Quaternary sediments (Anderson et al., 2001)."

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This model update did not affect the model results because the POC/P_{reac} ratios calculated in the model were always <<200.

2b) There are alternative mechanistic formulations to describe the diagenetic processes and sediment models that describe the transport, dissolution and burial of biogenic particles as well as the transport of solutes within the active sediment layers (Heinze et al., 1999;Gehlen et al., 2006) and such models are applied to study ocean sediment interactions on the glacial interglacial time scales, including the possible role of changes in burial, a whole ocean nutrient increase, iron fertilization, or ocean circulation (e.g., (Brovkin et al., 2012;Brovkin et al., 2007;Matsumoto et al., 2014;Menviel et al., 2012;Roth et al., 2014;Tschumi et al., 2011;Lambert et al., 2015) and other). The findings of this study should be compared to the findings of these and similar earlier studies that discussed burial-nutrient-pCO2 feedbacks and glacial-interglacial CO2 variations

We added the following paragraph to compare our approach to previous sediment modeling approaches (page 36, lines 7-12):

"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)." We now refer to the results of previous earth system models in several paragraphs. Page 7, lines 1-4: "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 dynamics (Tschumi et al., 2011a; Menviel et al., 2012; Brovkin et al., 2012;

Roth et al., 2014; Lambert et al., 2015)"

Page 10, lines 16-19: "This conclusion is consistent with the results of previous experiments conducted 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., 2011a; Menviel et al., 2012)."

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Page 20, lines 1-3: "The deglacial sea-level rise induced a decline in nutrient and carbon stocks in the global ocean. However, these stocks changed only slowly due to their large size (Menviel et al., 2012)."

2c) I am confused about the role of POM weathering. On page 2424, line 20 it is stated that POC weathering increases due to expansion of shelves and the increase appears to be displayed in Figure 3h that shows global rate of POC weathering calculated from Figure 3h, I estimate that this additional weathering leads to an input of about 2000 – 3000 GtC and presumably similar amounts of P and N. Is this realistic? This amount corresponds roughly to the carbon stored in today's soils.

We added the following paragraphs to better explain our results:

Page 37, lines 3-7: "Our standard model run suggests that the shelf (0 - 100 m water depths) trapped a total of 4650 Gt POC over the last glacial cycle (130 - 0 ka) while 7870 Gt POC accumulated on the continental slope (100 - 2000 m water depth). Shelf weathering released a total of 1940 GtC over the last 130 ka in simulation STD that is less than 50 % of the POC accumulating on the shelf over the last glacial cycle."

Page 38, lines 18-21: "The standing stock of POC in margin sediments exceeds the global terrestrial stock since POC is buried more efficiently in sediments than in most soils and plants. Sedimentary POC burial and preservation are promoted by high sedimentation rates and the lack of oxygen in these water-saturated deposits."

2c) continued: I note that the model does not account for the growth of plants on exposed shelves that would supply such a flux by photosynthesis. How does an increase in the amount of POC weathering during glacial times compare with land area covered by ice and the generally smaller productivity and carbon pools during glacial times compared to interglacials?

The latest assessment of terrestrial POC stocks concluded that the modern total stock is close to the LGM stock since the storage in permafrost and below ice largely compensated for the glacial decline in plant and soil carbon (Brovkin and Ganopolski, 2015). Thus, the overall change in the terrestrial POC stock is probably small. Changes in terrestrial carbon stocks are probably outpaced by much larger changes in POC weathering (Fig. 3h) and POC burial (Fig. 6e) on the continental shelf.

d) page 2413, line 2 it is stated: "Neglecting the glacial increase in the weathering of P-bearing solids is raising the LGM pCO2 value by 50 ppmv." In other words, about 50 ppm of the glacial-interglacial CO2 difference are attributable to an increase in P weathering. What is the evidence for this increase?

We do **not** attribute 50 ppm of the CO_2 difference to an increase in P weathering. We added the following paragraph to better explain our model results (page 9, lines 9-19): "Most of the P released during chemical weathering originates from apatite, a mineral equally occurring in all rock types (sedimentary, magmatic and metamorphic). Thus, we assume that the P weathering rate is proportional to the total weathering rate, that is the sum of carbonate, POC and silicate weathering (Wallmann, 2014). During the glacial, total weathering increased due to the weathering of exposed shelf CaCO₃ and POC (Munhoven, 2002; Wallmann, 2014). This rise led to the increase in P weathering simulated in the model. However, a further simulation shows that the overall pCO₂ change induced by chemical weathering of silicate, POC, CaCO₃ and P is small (decrease by 3 ppmv) because the glacial CO₂ draw-down induced by P and CaCO₃ weathering was largely compensated by the CO₂ release induced by POC weathering (Tab. 1, STD run with constant rates of chemical weathering)."

3) The burial mechanism applied leads to a large increase in atm. CO2 over the Holocene. How realistic is this given that the model does not include changes in terrestrial carbon storage and implied carbonate compensation and transient changes in the lysocline (Broecker et al., 2001)?

We now acknowledge that the Holocene pCO_2 record may be affected by changes in terrestrial POC pools that are not considered in our model (page 7, lines 15-18): "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 pCO₂ dynamics."

4) It would be useful to clearly outline which data are used for model tuning and which data are used for the a posteriori evaluation of results.

We added the following paragraph to address this question (page 4, lines 3-8): "To avoid circular reasoning dissolved oxygen, carbonate, and radiocarbon distributions calculated for the glacial ocean were not used to parameterize our model. These distribution patterns and the atmospheric pCO₂ values calculated in the model are non-trivial consequences of interactions between the various model components and thus are employed to validate the model performance."

5) Given the cost-efficiency of a 24-box model I miss a comprehensive variation of model parameters to assess how uncertainties in model parameters affect results

The model includes about 100 parameter values. Thus, it is not possible to perform a comprehensive variation of model parameters and systematic sensitivity test. However, we switched on and off a number of key parameters to study the response of the model system (see Tab. 1, page 56).

6) Figure 8, 9, and 11 should be changed. The contouring suggests higher model resolution than provided by a 24 box model and is misleading. It would be more appropriate to show the colors on the model grid given in Figure 2 without any interpolation.

We added grid points to these figures to indicate the underlying coarse resolution.

Moreover, we added Tab. C4 to Appendix C (page 65) listing all LGM tracer concentrations

for all boxes to augment the PRE data listed in Tabs. A1 and A2.

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Effects of eustatic sea-level change, ocean dynamics, and iron fertilizationnutrient utilization on atmospheric pCO₂ and seawater composition over the last 130,000 years

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13

14 Abstract

We developed and employed an earth system model to explore the forcings of atmospheric 15 pCO₂ change and the chemical and isotopic evolution of seawater over the last glacial cycle. 16 Concentrations of dissolved phosphorus (DP), reactive nitrogen, molecular oxygen, dissolved 17 inorganic carbon (DIC), total alkalinity (TA), ¹³C-DIC and ¹⁴C-DIC were calculated for 24 18 ocean boxes. The bi-directional water fluxes between these model boxes were derived from a 19 20 3-D circulation field of the modern ocean (Opa 8.2, NEMO) and tuned such that tracer distributions calculated by the box model were consistent with observational data from the 21 22 modern ocean. To model the last 130 kyr, we employed records of past changes in sea-level, ocean circulation, and dust deposition. According to the model, about half of the glacial pCO₂ 23 24 drawdown may be attributed to marine regressions. The glacial sea-level low-stands implied 25 steepened ocean margins, a reduced burial of particulate organic carbon, phosphorus, and 26 neritic carbonate at the margin seafloor, a decline in benthic denitrification, and enhanced 27 weathering of emerged shelf sediments. In turn, they-low-stands led to a distinct rise in the 28 standing stocks of DIC, TA, and nutrients in the global ocean, promoted the glacial sequestration of atmospheric CO₂ in the ocean, and added 13 C- and 14 C-depleted DIC to the 29 ocean as recorded in benthic foraminifera signals. The other half of the glacial drop in pCO_2 30

was linked to reduced deep ocean dynamics, a inferred shoaling of Atlantic meridional 1 2 overturning circulation, and a-more efficient utilization of nutrients in the Southern Ocean. rise in iron fertilization. The diminished ventilation of deep water in the glacial Atlantic and 3 Southern Ocean The increased transit time of deep waters in the glacial ocean led to 4 significant ¹⁴C depletions with respect to the atmosphere. <u>According to our model, The the</u> 5 deglacial rapid and stepwise rise in atmospheric pCO₂ was induced by upwelling both in the 6 7 Southern Ocean and subarctic North Pacific and promoted by a drop in dust borne iron dischargenutrient utilization to in the Southern Ocean. The deglacial sea-level rise led to a 8 9 gradual decline in nutrient, DIC, and TA stocks, a slow change due to the large size and extended residence times of dissolved chemical species in the ocean. Thus, the rapid deglacial 10 11 rise in pCO₂ can be explained was dominated by fast changes in ocean dynamics and reduced dust deposition <u>nutrient utilization</u> whereas the gradual pCO₂ rise over the Holocene may be 12 13 linked to the slow drop in nutrient and TA stocks that continued to promote an ongoing CO₂ transfer from the ocean into the atmosphere. 14

15

16 **1 Introduction**

17 The discussion of mechanisms that might be responsible for the glacial to interglacial change in the atmosphere's CO₂ content is focused on the ocean (Broecker, 1982a). There is Ever 18 19 increasing evidence suggesting suggests that CO₂ sequestered in the glacial ocean was rapidly released into the atmosphere at glacial terminations (Schmitt et al., 2012). The fast decline in 20 dust-bound iron deposition in the Southern Ocean (Martin, 1990; Martinez-Garcia et al., 21 2014) and upwelling pulses in the Southern Ocean (Anderson et al., 2009) and the North 22 23 Pacific (Rae et al., 2014) may have induced the stepwise pCO₂ rise documented in the deglacial ice-core record (Marcott et al., 2014). The preceding CO₂ uptake in the glacial ocean 24 may be attributed to enhanced export production, elevated seawater alkalinity, and changes in 25 ocean dynamics. The biological pump was probably was intensified by iron fertilization 26 (Martin, 1990) and the coeval expansion of nitrate (Deutsch et al., 2004) and phosphate 27 (Broecker, 1982a) stocks in the glacial ocean while seawater alkalinity may have been 28 29 enhanced by the demise of neritic carbonate formation (Berger, 1982; Opdyke and Walker, 1992; Kleypas, 1997). The sequestration of atmospheric pCO_2 in the glacial ocean may have 30 been further promoted by the glacial shoaling of the Meridional Overturning Circulation 31 (MOC) in the Atlantic (Duplessy et al., 1988; Sarnthein et al., 1994), a possible increase in 32 Southern Ocean stratification (Toggweiler, 1999), a prolonged residence time of surface 33

waters in the Southern Ocean providing more time for the biota to draw down nutrients and
 CO₂ (Watson et al., 2015) and a global decline in MOC intensity and deep ocean ventilation
 (Sarnthein et al., 2013).

4 In part, A a glacial rise in nitrate, phosphate, and alkalinity concentrations, which may have contributed significantly to the drawdown of atmospheric pCO₂, can be explained by eustatic 5 6 sea-level fall (Wallmann, 2014). It led to a retreat of ocean margins to steeper terrains that 7 reduced the seafloor area located in shallow waters (Fig. 1). The standing stocks of carbon 8 and nutrients in the glacial ocean may have been significantly enhanced by the marine 9 regression and the decrease in shallow margin area since major removal fluxes, that is 10 accumulation of neritic carbonate, benthic denitrification, burial of particulate organic carbon (POC) and phosphorus (P), depend on the size extent of seafloor area located in shallow 11 12 waters. Various authors and earth system models considered the glacial decrease in shelf carbonate burial as a major driver of ocean chemistry and atmospheric pCO₂ change (Berger, 13 1982; Opdyke and Walker, 1992; Brovkin et al., 2012; Ganopolski et al., 1998), since neritic 14 carbonates contribute \geq 50 % to the carbonate accumulation at the global seafloor (Milliman 15 16 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 17 though >50 % of the global benthic denitrification and burial of marine POC and P occur in 18 shelf and upper slope environments (Berner, 1982; Bohlen et al., 2012; Wallmann, 2010). 19

Against this background, our contribution aims to explore and quantify the effects of sea-level 20 change, ocean dynamics and dust deposition nutrient utilization on seawater composition and 21 atmospheric pCO₂ over the last glacial cycle. We use a simple earth system box model to 22 simulate consider both chemical and isotopic changes in seawater composition and employ 23 isotope data ($\delta^{13}C_{-}\Delta^{14}C$) to constrain changes in ocean dynamics and deep ocean ventilation. 24 Atmospheric pCO_2 and the distributions of dissolved oxygen, carbonate, and radiocarbon in 25 the glacial ocean serve as key prognostic model variables. They are compared with 26 independent proxy data to address the following specific questions: What fraction of the 27 glacial pCO₂ draw-down can be ascribed to eustatic sea-level fall (Wallmann, 2014)? To 28 which degree do global ¹⁴C data sets assembled by (Sarnthein et al., 2013; Sarnthein et al., 29 2015) actually reflect our concepts and ideas on glacial and deglacial ocean circulation and 30 carbon cycling? Do marine ¹⁴C data really form a quantitative proxy of DIC in the glacial 31 32 deep ocean as proposed by (Sarnthein et al., 2013)? Using a simple earth system model, we show that a significant fraction of the pCO₂ drawdown over the glacial period was possibly 33

induced by the marine regression promoting the expansion of dissolved phosphate, nitrate, 1 and total alkalinity inventories in the glacial ocean whereas the fast deglacial pCO₂ rise was to 2 a large degree driven by rapid changes in ocean dynamics and dust deposition. To avoid 3 circular reasoning dissolved oxygen, carbonate, and radiocarbon distributions calculated for 4 the glacial ocean were not used to parameterize our model. These distribution patterns and the 5 atmospheric pCO₂ values calculated in the model are non-trivial consequences of interactions 6 7 between the various model components and thus are employed to validate the model 8 performance.

9

10 2 Model set-up

The atmospheric partial pressure of CO_2 (p CO_2) serves as the key prognostic variable of the 11 new multi-box earth system model presented in this paper. It was calculated considering 12 continental weathering and degassing processes and gas exchange with the surface ocean 13 (Wallmann, 2014). The oceans were represented by 24 boxes (Fig. 2). The major ocean 14 basins North Atlantic (NA, 30°- 60°N), Tropical Atlantic (TA, 30°N – 30°S), Southern 15 Ocean (SO, >30°S), Tropical Indo-Pacific (TIP, 30°N – 30°S), North Pacific (NP, 30°- 60°N), 16 17 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 -18 2000 m, 2000 - 4000 m to >4000 m water depth, respectively. The following tracer 19 concentrations were calculated as prognostic variables for each of the water boxes: Salinity 20 (Sal), dissolved phosphorus (DP), dissolved reactive nitrogen (DN), dissolved oxygen (DO), 21 total alkalinity (TA), dissolved inorganic carbon (DIC), dissolved inorganic ¹³C (¹³C-DIC), 22 and dissolved inorganic radiocarbon (¹⁴C-DIC). Details of the modelThe set-up-of the model 23 is presented are given in Appendix A. 24

Eustatic sea-level change was applied as major model forcing (Fig. 3). Changes in global 25 ocean volume, salinity, depositional area at continental margins and exposed shelf area were 26 derived from the sea-level record (Stanford et al., 2011; Waelbroeck et al., 2002) and the 27 hypsographic curve (Eakins and Sharman, 2012). The burial rate of neritic carbonates was 28 reduced during marine regressions in proportion to the decrease in seafloor area available for 29 the growth of tropical reefs and carbonate platforms (Appendix B). We tested the degree to 30 which the decrease in seafloor area at 0 - 100 m and 100 - 2000 m water depth during glacial 31 sea-level low-stands affected benthic denitrification and the burial of organic carbon and 32 marine phosphorus on the continental shelf and slope (Appendix B) while we assumed that 33

carbonate, P, and POC weathering were promoted by the exposure of shelf sediments
 (Appendix A).

The comprehensive geological data base on benthic foraminiferal δ^{13} C (Oliver et al., 2010; 3 Sarnthein et al., 1994) was employed to constrain water fluxes for the Last Glacial Maximum 4 (LGM). Mean δ^{13} C-DIC values were calculated for those ocean boxes where sufficient δ^{13} C 5 data were available and compared to model results. Water fluxes were varied until the 6 Holocene-LGM differences in δ^{13} C generated by the model were consistent with the 7 differences recorded in foraminifera (Tab. A5). The tuning was done using full transient runs 8 with all forcings applied. The LGM water fluxes were tuned until the model reproduced the δ 9 ¹³C distribution pattern (Tab. A5). The resulting fluxes are shown in Fig. 2. The southward 10 water flux from the Atlantic into the Southern Ocean was relocated from deep (2000 - 4000 11 12 m) to intermediate waters (100 - 2000 m) to mimic the shoaling of the Atlantic Meridional Overturning Circulation (AMOC) which is well documented inferred not only by from δ^{13} C 13 data but also fromin various other proxy records (Curry and Oppo, 2005; Piotrowski et al., 14 2005; Roberts et al., 2010). Bottom water fluxes from the Southern Ocean into the Atlantic 15 were enhanced during the LGM while the northward flow of surface water was reduced. The 16 overall water exchange between Atlantic and Southern Ocean was maintained constant at 15.4 17 Sv. The bottom and deep water exchange between the Southern Ocean and the Indo-Pacific 18 was reduced by 5 Sv to reproduce the δ^{13} C data (Tab. A5). 19

The eustatic sea-level curve (Fig. 3a) was applied to change ocean dynamics continuously 20 over time, that isi.e. to define water fluxes over the full model period (Fig. 4a-c). Thus we 21 assumed that AMOC shoaled gradually during the transition from interglacial to full glacial 22 conditions (130 - 21 ka) while the horizontal exchange flux of intermediate waters between 23 Southern Ocean and Tropical Indo-Pacific was enhanced over the glacial to mimic the 24 25 ventilation of tropical oxygen minimum zones -(OMZs) observed in various proxy records (Altabet et al., 1995; Jaccard and Galbraith, 2012). Additional rapid changes were 26 implemented for the deglacial period (Figs. 4a and 4d). NADW formation was strongly 27 reduced during Heinrich Event 1 (H1) and the Younger Dryas (McManus et al., 2004) while 28 upwelling pulses were prescribed in the Southern Ocean during H1 and the Bølling-Allerød 29 (Anderson et al., 2009; Skinner et al., 2010) and in the North Pacific during H1 (Rae et al., 30 2014). Timing and intensity of these deglacial upwelling/ventilation events were varied until 31 Δ^{14} C-DIC values calculated for deep and surface water boxes were consistent with The 32 differences between Δ^{14} C values recorded in benthic and pelagic foraminifera in the deglacial 33

Southern Ocean (Skinner et al., 2010) and North Pacific(Fig. A2). (Rae et al., 2014) were 1 compared to differences in Δ^{14} C-DIC between the corresponding deep water and surface 2 water boxes calculated in the model, moreover, the timing and intensity of deglacial mixing 3 events was varied until the model output was consistent with these data (Fig. A3). In addition, 4 the deglacial ice-core record of pCO₂ (Marcott et al., 2014) and biogenic opal accumulation 5 rates (Anderson et al., 2009) were employed to constrain the timing and intensity of upwelling 6 7 pulses in the Southern Ocean. The iron accumulation record from site ODP 1090 was used to constrain changes in nutrient utilization in the Southern Ocean (Martinez-Garcia et al., 2014) 8 9 assuming that the increase in iron accumulation observed at this site directly translates into an increase in the efficiency of nutrient utilization (Fig. 4e). To calculate realistic marine isotope 10 11 trends the changing isotopic compositions of atmospheric CO₂ were set to the values documented in the geological record (Fig. 4f-g). 12

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).
- 22 The modern water fluxes applied to our box model are based on a dynamically consistent 23 circulation field. As explained in Appendix A, these fluxes were modified to obtain tracer distributions that are consistent with observations in the pre-industrial modern ocean (Fig. 24 A1). Glacial and deglacial changes in ocean circulation were not derived from ocean models 25 but from $\delta^{13}C$ records (Tab. A5) and additional geochemical observations (Fig. A2). Models 26 with explicit ocean dynamics are superior to any kind of physically unconstrained box model 27 if they generate results that are consistent with observations. However, the physically-28 29 constrained earth system models that we are aware of are not yet able to reproduce as many tracer and proxy data as our box model. Our paper shows that shelf and sea-level effects help 30 to explain a wide range of findings (section 3) and we think that the outputs of physically 31 better constrained models may improve in case these effects are included in the model 32 architecture. It is not our intention to promote box modeling per se as the method-of-choice. 33

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
dynamics (Tschumi et al., 2011a; Menviel et al., 2012; Brovkin et al., 2012; Roth et al., 2014;
Lambert et al., 2015).

For many decades it was widely assumed that the modern terrestrial carbon pool exceeds the 5 6 glacial pool by hundreds of Gt because of biosphere regrowth after the glacial termination 7 (Köhler and Fischer, 2004). This concept was initially developed to explain reduced $\delta^{13}C$ 8 values in glacial seawater (Shackleton, 1977). However, the latest assessment of terrestrial 9 carbon pools indicates that the sum of the modern stocks does not exceed the LGM stock 10 (Brovkin and Ganopolski, 2015). Moreover, this new view on terrestrial carbon cycling suggests a deglacial decline in total carbon stocks since the carbon release from high latitude 11 12 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 13 deglacial and Holocene pCO₂ dynamics and the low glacial δ^{13} C values by marine processes 14 and sea-level change only. However, we acknowledge that terrestrial processes that are 15 neglected in our model may have played a role especially over the Holocene even though 16 more work needs to be done to constrain the sign and magnitude of terrestrial effects on δ^{13} C 17 and pCO₂ dynamics. 18

The major new component included in our earth system model is a comprehensive
 formulation of shelf processes and sea-level effects. Appendix B explains in detail how sea level change affects fluxes at continental margins and how these effects are considered in the
 model.

23

24 **3 Results and Discussion**

The model was run over a period of 130 kyr to simulate the behavior of the global system 25 26 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 27 induced by sea-level change, changes in ocean circulation, and iron fertilization nutrient 28 29 utilization, that is the full model forcing as defined in Figures 3 and 4. Additional simulations were performed to better understand the controls on atmospheric pCO_2 and the chemical and 30 isotopic composition of seawater. Simulation STD-CC was run with constant circulation, that 31 32 is, all water fluxes were maintained at the Holocene level (upper panel of Fig. 2, Tab. A3) over the full model period, whereas simulation STD-CC-CN was performed with the
 Holocene circulation field and constant nutrient utilization.

3 3.1 Atmospheric pCO₂

4 The pCO₂ trend recorded in ice cores (Monnin et al., 2001; Monnin et al., 2004; Marcott et 5 al., 2014; Petit et al., 1999) was well reproduced by the standard simulation (Fig. 5a and 7a). 6 Over the last interglacial, simulated atmospheric pCO₂ increased from an initial value of 280 7 ppmv at 130 ka to 285 ppmv at 120 ka (Fig. 5a). This increase was accompanied by a decline 8 in nutrient concentrations (Figs. 5f-g) and export production (Fig. 6d), supported by the high sea-level stand promoting burial of phosphorus and benthic denitrification in continental 9 margin sediments. Over the subsequent glacial period, simulated pCO₂ declined due to sea-10 level fall, enhanced nutrient utilization in the Southern Oceaniron fertilization, and the decline 11 in deep ocean ventilation until 21 ka, when a pCO₂ minimum of 190 ppmv was reached (Fig. 12 7b). The simulated glacial pCO₂ drawdown was discontinuous, marked by several steps and 13 turning points (Fig. 5a). Major minima in atmospheric pCO₂ occurred at 90 ka (220 ppmv) 14 and 65 ka (198 ppmv). Both of them are well documented in the ice-core record (Fig. 5a) and 15 accompanied by maxima in nutrient utilizationiron fertilization (Fig. 4e) and minima in sea-16 level (Fig. 3a). Sea-level fall and nutrient utilizationiron fertilization, thus, may have driven 17 most of the glacial pCO₂ decline. Moreover, they may have induced major turning points in 18 the glacial pCO_2 record. 19

20 At constant ocean circulation and nutrient utilization (simulation STD-CC-CN), simulated pCO₂ declined to a LGM value of 234 ppmv (Fig. 5a). Additional simulations based on the 21 22 standard simulation STD helped us to specify the driving forces for this decline (Tab. 1). To 23 study their effect on pCO₂ we suppressed the temporal changes of individual variables. A first simulation test was based on the assumption of constant modern sea surface temperatures 24 (SSTs). It showed that the glacial decline in global mean SST by ca. 2°C (Schmittner et al., 25 2011) induced a pCO₂ decline by 16 ppmv since the solubility of CO₂ in surface waters was 26 enhanced under low temperatures (compare rows 1 and 2 in Tab. 1). In a second simulation, 27 salinity was set constant, while the other model parameters varied as defined in the STD 28 simulation. Accordingly, the peak glacial increase in salinity induced a relative atmospheric 29 pCO₂ rise by 5 ppmv by lowering the solubility of CO₂ in surface waters (Tab. 1). In a third 30 test, both salinity and the volume of the ocean boxes were kept constant over time. Changes in 31 these parameters induced an LGM pCO₂ rise by 13 ppmv (Tab. 1), illustrating that the 32 contraction of the ocean volume during glacial sea-level low-stands reduced the ocean's 33

1 capacity to sequester atmospheric CO₂. In summary, the model runs confirmed previous 2 calculations estimates (Broecker, 1982a) showing that the net effect of SST, volume, and 3 salinity changes on glacial pCO₂ is small (decrease by 3 ppmv). Thus, other processes need to 4 be invoked to explain the large glacial drawdown of atmospheric CO₂ simulated by model run 5 STD-CC-CN.

6 Changes in the flux of dissolved phosphorus (DP) exert large effects on pCO₂, since DP is the 7 ultimate limiting nutrient of the model ocean_(Menviel et al., 2012). Neglecting the glacial 8 increase in the weathering of P-bearing solids is raising the LGM pCO₂ value by 50 ppmv 9 (Tab. 1, rows 5 vs. 1). Most of the P released during chemical weathering originates from apatite, a mineral equally occurring in all rock types (sedimentary, magmatic and 10 metamorphic). Thus, we assume that the P weathering rate is proportional to the total 11 12 weathering rate, that is the sum of carbonate, POC and silicate weathering (Wallmann, 2014). During the glacial, total weathering increased due to the weathering of exposed shelf CaCO₃ 13 and POC (Munhoven, 2002; Wallmann, 2014). This rise led to the increase in P weathering 14 simulated in the model. However, a further simulation shows that the overall pCO₂ change 15 induced by chemical weathering of silicate, POC, CaCO₃ and P is small (decrease by 3 ppmv) 16 because the glacial CO₂ draw-down induced by P and CaCO₃ weathering was largely 17 compensated by the CO₂ release induced by POC weathering (Tab. 1, STD run with constant 18 rates of chemical weathering). In a further simulation we evaluated the overall effect of 19 chemical weathering on atmospheric pCO₂, that is, the weathering rates of P-bearing solids, 20 carbonate, and POC were maintained at their modern values over the entire model period (see 21 22 STD run with constant rates of chemical weathering, Tab. 1). The net effect was an LGM pCO₂ rise that did not exceed 3 ppmv with respect to simulation STD, since the CO₂ release 23 by POC weathering largely compensated for the CO₂ loss induced by carbonate and P 24 weathering. Applying very high molar C : P ratios for POM in shelf sediments (ca. 200), it 25 was previously calculated that shelf weathering resulted in a net increase rather than decrease 26 in atmospheric pCO₂ (Ushie and Matsumoto, 2012). However, most of the phosphorus in 27 shelf sediments and riverine particles is not organic but bound in other reactive, inorganic 28 phases such as carbonate-fluoro-apatite (Berner and Rao, 1994) which release DP when 29 exposed to weathering (Ruttenberg, 1992; Ruttenberg and Berner, 1993). Thus, The-the global 30 31 mean atomic ratio of POC over reactive P in shelf sediments is thus lower than the C : P ratio of marine organic matter (Baturin, 2007; Wallmann, 2010). Hence, the glacial weathering of 32 shelf sediments induced a small drop rather than a rise in LGM pCO_2 (Tab. 1). 33

By contrast, a stronger effect results from testing the glacial decrease in depositional areas at 1 2 continental margins, as revealed by a simulation that ignores the glacial decline in P burial 3 and reveals a glacial pCO_2 rise by 73 ppmv (Tab. 1) with respect to the standard case due to the decline in DP concentration and export production. An additional simulation with constant 4 depositional area for POC burial resulted in a pronounced drawdown of both atmospheric 5 pCO₂ (by 61 ppmv) and DIC since POC burial at continental margins served as major sink for 6 7 CO₂ and DIC in the model system (Tab. 1). Changes in the burial of neritic carbonates were mitigated by carbonate compensation at the deep-sea floor and thus had a less drastic effect on 8 9 atmospheric pCO₂ (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 10 11 margins. However, tThe 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 12 13 effect was a strong n increase in export production and a transfer of CO₂ from the atmosphere into the ocean via the biological pump. Accordingly, most of the glacial pCO₂ decline in 14 15 simulation STD-CC-CN was driven by the glacial steepening of ocean margins and the resulting expansion of the DP inventory-and the glacial steepening of ocean margins. This 16 17 conclusion is consistent with the results of previous experiments conducted with more evolved earth system models showing a strong pCO₂ draw-down in response to an increase in 18 the oceanic phosphate inventory (Tschumi et al., 2011a; Menviel et al., 2012). 19

The glacial pCO₂ value dropped by 31 ppmv (from 234 ppmv to 203 ppmv) in response 20 toupon enhanced iron fertilization nutrient utilization (difference between simulations STD-21 22 CC-CN and STD-CC). This decrease was amplified by the glacial sea-level fall since the 23 nutrient (DP) reservoir that was unlocked by the glacial dust input toenhanced utilization in the glacial Southern Ocean was expanded enlarged as a result of glacial marine regression. 24 25 The remaining portion of the interglacial-to-peak glacial pCO_2 drop by 13 ppmv down to the final LGM value of 190 ppmv was induced by ocean dynamics (difference between 26 27 simulation STD and STD-CC). Atmospheric pCO₂ rose by 10 ppmv, when all water fluxes between the Atlantic and the Southern Ocean were maintained at their Holocene level over 28 the entire model period (simulation STD with constant AMOC, Tab. 1). The glacial AMOC 29 shoaling (Fig. 4a-b) thus contributed 10 ppmv to the simulated LGM decline. This effect can 30 31 be attributed to enhanced CO₂ storage in the deep Atlantic (>2000 m water depth) which was less ventilated under glacial conditions, since the formation of northern deep waters was 32 greatly diminished and replaced by southern-source waters enriched in DIC. Thus additional 33 DIC was stored in the glacial deep ocean (Ganopolski et al., 2010; Skinner, 2009; Sarnthein et 34

al., 2013). The glacial decrease in water fluxes between the deep Southern Ocean and 1 Tropical Indo-Pacific applied in the model (Fig. 2) likewise supports further sequestration and 2 storage of CO_2 in the deep ocean and the glacial drawdown of atmospheric p CO_2 . The 3 circulation changes applied employed to simulate LGM conditions (Fig. 2) led to a reduction 4 in the global water exchange across the 2000 m depth horizon from a modern amount of 45 5 Sv down to 31 Sv near at 21 ka. This corresponds to an increase in the average residence time 6 7 of water in the deep ocean (>2000 m) from 470 years in the modern ocean to 680 years during the LGM where the residence time is calculated as ratio of the deep ocean volume (6.65 x 8 10^{17} m³ at >2000m) and the global ver<u>tical water fluxes across 2000 m.</u> The glacial increase 9 in residence time by 210 yr may be compared to the 600 yr increase reconstructed from 10 benthic radiocarbon data (Sarnthein et al., 2013). We suggest that the difference between 11 these two estimates is related to the elevated production rate of radiocarbon in the glacial 12 atmosphere and changes in carbon cycling affecting the marine radiocarbon budget (section 13 3.4). 14

A stepwise increase in pCO₂ was simulated over the deglaciation (Fig. 7). The first step 15 occurred from 18.5 to 16.3 ka when the simulated pCO_2 rose rapidly from 193 to 220 ppmv. 16 A second step followed at 15.9 - 14.1 ka with a pCO₂ rise from 222 to 244 ppmv, a third step 17 at 13.0 - 10.8 ka with a strong increase from 243 to 272 ppmv. The first step was driven by 18 19 the rapid drop in <u>nutrient utilization dust deposition</u> at the glacial termination (Fig. 4e) and the ventilation of intermediate and deep water masses in the North Pacific during H1 (Figs. 4d 20 and A2). The second and third steps were driven by the Southern Ocean where CO_2 was 21 22 released into the atmosphere due to the abrupt decline in stratification and the further decrease in <u>nutrient utilization</u>dust input (Fig. 4d-e). In major parts of the Southern Ocean these steps 23 coincide with maxima in opal accumulation indicating enhanced upwelling (Anderson et al., 24 25 2009). The pCO₂ drawdown from 10 to 8 ka reflects a recovery of the ocean system from the antecedent ventilation pulse in the Southern Ocean centered at 11.5 ka (Fig. 4d). According to 26 our model, the ventilation pulse removed CO_2 from the ocean interior, enhanced the O_2 27 content of the deep ocean, and diminished the vertical DIC and O₂ gradients. The subsequent 28 restoration of the vertical DIC gradient induced the pCO₂ decline observed in the model from 29 10 to 8 ka. Sea-level change was not uncovered as major driver for the rapid deglacial pCO_2 30 31 rise since the long residence times of DP (13 kyr) and TA (77 kyr) inhibit fast inventory changes in the global ocean (Menviel et al., 2012; Wallmann, 2014). By contrast, the pCO₂ 32 increase over the Holocene ($\frac{10-8}{2}$ – 0 ka), which is closing the glacial cycle, may have been 33

driven by a high sea-level stand inducing a gradual and slow decline in marine DP and TA
inventories.

3 As shown in Fig. 7, about equal portions of the extreme deglacial carbon flux may have been

4 <u>triggered by changes in circulation and nutrient utilization. Nutrients may have been used</u>

5 more efficiently in the glacial Southern Ocean due to the enhanced dust input fertilizing the

6 <u>surface layer (Martinez-Garcia et al., 2014) and because of buoyancy forces prolonging the</u>

7 <u>residence time of nutrients in the euphotic zone (Watson et al., 2015). However, further</u>

- 8 processes that are not considered in our model such as the deglacial melting of permafrost
- 9 (Zimov et al., 2006) and volcanic CO₂ degassing (Huybers and Langmuir, 2009) may have
- 10 also contributed to the pCO₂ rise because the lack of proxy data and physical process
- 11 <u>understanding impedes an unequivocal determination of the magnitude of nutrient utilization</u>
- 12 and stratification change in the Southern Ocean.

13 **3.2 Dissolved nutrients and oxygen**

The standing stock of DP in the global ocean rose under glacial conditions since P burial was 14 diminished by the decrease in depositional area located at shallow water depths (Fig. 6h) 15 while chemical weathering was promoted by the exposure of shelf sediments (Fig. 6g). Most 16 17 of the glacial DP rise found in our simulations was induced by the glacial steepening of ocean margins reducing the burial of P in margin sediments (Tab. 1, Fig. 1, Appendix B). Iron 18 19 fertilization Vice versa, enhanced utilization in the Southern Ocean induced a strong decrease in glacial DP stocks since more DP was taken up by phytoplankton to be drawn down and 20 finally buried in marine sediments (simulations STD-CC versus STD-CC-CN, Figs. 5f, 6d, 21 6h), while the glacial DP stock was largely restored by changes in ocean dynamics 22 23 (simulations STD versus STC-CC, Fig. 5f) separating the large nutrient pool in the deep ocean from the surface layer. The spatial distribution of DP in the global ocean reflects the 24 export of POM by the biological pump and ocean circulation. The overall pattern, that is a 25 strong vertical gradient between depleted surface waters and enriched deep water masses and 26 a significant horizontal gradient between the deep North Atlantic and North Pacific, was 27 maintained over the glacial cycle (Fig. 8). However, the vertical DP gradient was enhanced 28 29 amplified over the LGM due to iron fertilization enhanced utilization and the decrease in deep ocean ventilation. Reactive P accumulation rates in marine sediments can be used to validate 30 our model results. A global compilation of these data confirmed that P accumulation in shelf 31 sediments decreased drastically under glacial conditions (Tamburini and Föllmi, 2009). The 32 resulting decline in global P burial induced an increase in the glacial DP inventory by 17 - 4033

% (Tamburini and Föllmi, 2009) as predicted by our model. Cd/Ca ratios in LGM sediments
 from the Atlantic Ocean (Boyle and Keigwin, 1982) and δ¹³C records (Duplessy et al., 1988;
 Sarnthein et al., 1994; Oliver et al., 2010) suggest a steepening of the vertical DP gradients
 broadly consistent with our model results.

The dissolved oxygen (DO) content of the global ocean decreased under glacial conditions 5 6 due to the decline in deep ocean ventilation and increase in export production (Fig. 5h). In 7 contrast, it recovered and peaked over the deglaciation since ocean ventilation was enhanced 8 in the Southern Ocean and the North Pacific. The spatial distribution of DO changed 9 significantly under LGM conditions (Fig. 8). Concentrations declined at >1500-2000 m water 10 depth due to the decrease in ocean ventilation and increase in export production while glacial cooling induced a small DO rise in surface waters. The DO minimum in intermediate waters 11 12 of the Indo-Pacific expanded and spread into the deep ocean under glacial conditions. The lowest value was calculated for the intermediate water box of the North Pacific where the DO 13 concentration declined to 69 µM at 21 ka. The glacial DO decrease in the deep ocean is 14 consistent with a large data set showing that deep waters below 1500 m water depth were 15 significantly depleted in the LGM over all major ocean basins (Jaccard and Galbraith, 2012). 16 The glacial oxygen depletion in the intermediate Indo-Pacific (76 μ M during the LGM vs. 96 17 µM in the modern ocean) seems to be at odds with the geological record which shows that 18 OMZs oxygen minimum zones (OMZs)-located in the tropical ocean were better ventilated 19 under glacial conditions (Altabet et al., 1995). This discrepancy may probably arise from the 20 spatial resolution of the box model that is too coarse to resolve OMZs. Moreover, all sediment 21 22 cores that have been used to reconstruct the oxygen conditions in glacial intermediate waters 23 were taken at continental margins (Jaccard and Galbraith, 2012) while tracer concentrations in the model boxes are basin-wide mean values reflecting open ocean rather than continental 24 25 margin conditions.

26 The glacial oxygen decline simulated in the model has no significant effect on other model 27 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 28 deep-sea floor that was enhanced by the glacial **DO**-oxygen depletion in bottom waters and 29 rising export production (Bohlen et al., 2012). Nevertheless, the global rate of benthic 30 denitrification rate calculated in simulation STD decreased under glacial conditions (Fig. 6j) 31 since ocean margins retreated into steeper terrain such that less nitrate was consumed on the 32 continental shelf. Pelagic denitrification was not simulated but maintained at its Holocene 33

value since the box model did not capture OMZs. Nitrogen fixation was assumed to increase 1 when the DN/DP ratio in the surface ocean fell below the N/P ratio in exported POM (Eq. 2 A8). Nitrogen fixation thus traced the temporal evolution of benthic denitrification (Figs. 6i-3 j). This negative feedback mechanism (Tyrrell, 1999; Redfield, 1958) maintained 4 the simulated DN/DP ratio close to its modern value over the entire glacial cycle. while tThe DN 5 inventory peaked during the LGM where it exceeded the modern value by 16 %. A similar 6 7 increase in the LGM nitrate inventory (10 - 30 %) and glacial decline in denitrification and nitrogen fixation was simulated with a box model constrained by the marine $\delta^{15}N$ record 8 (Deutsch et al., 2004). 9

10 **3.3 Dissolved inorganic carbon, carbonate ion concentrations, and** δ^{13} C of 11 dissolved inorganic carbon

12 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 13 minimum at its end (2267 µM and 2394 µM at 118.5 ka, respectively), increased over the 14 15 glacial up to reach a maximum prior to the glacial termination (2467 µM and 2631 µM at 19.5 ka) and decreased again over the Holocene (Fig. 5b and 5e). On the basis of our model runs a 16 significant portion of these trends were mainly driven by sea-level change that controlled the 17 burial of neritic carbonate (Fig. 3d) and POC (Fig. 6e) and the rates of POC and carbonate 18 weathering by shelf exposure, in particular during the build-up of glacial ice sheets (Figs. 3h 19 and 6c). The glacial DIC and TA rise was mitigated by iron fertilization nutrient utilization 20 enhancing marine export production and carbon burial (compare simulations STD-CC-CN 21 22 and STD-CC 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, 23 POC burial and pelagic carbonate accumulation (STD-CC versus STD). Considering changes 24 in ocean volume by about 3 % (Fig. 3b), the increase in DIC over the last glacial (118.5 – 19.5 25 ka) translates into a mean $\frac{\text{DIC increase}}{\text{DIC increase}}$ rate of 1.70 Tmol yr⁻¹. By comparison, the CO₂ uptake 26 27 from the atmosphere as calculated from the glacial rate of pCO₂ decline amounts to 0.17 Tmol vr^{-1} . Thus, only 10 % of the glacial DIC rise was induced by CO₂ uptake from the atmosphere. 28 According to our model, The the glacial demise of neritic carbon pools (carbonate and POC) 29 30 thus formed was a the major reason for forcing of the DIC rise, while the sequestration of atmospheric CO₂ only was of minor importance for the glacial change in seawater 31 composition. Most of the excess DIC accumulating in the glacial ocean originated from 32 exposed neritic-shelf carbonates and sedimentary POC released at the exposed shelves and 33

1 from riverine DIC which was not buried due to the contraction of depositional areas at ocean margins. The accumulation of TA and DIC and TA in the deep ocean (Fig. 9) was 2 corroborated by a change in Atlantic deep water chemistry. As outlined above, this LGM 3 ocean basin was filled with corrosive southern-source waters compromising the preservation 4 5 of carbonates at the deep-sea floor and diminishing the rate of pelagic carbonate burial (Tab. 1, compare simulation STD with constant AMOC and STD). However, the DIC distribution 6 7 calculated for the LGM indicates that DIC concentrations increased in all major ocean basins (Fig. 9). In summary, the glacial DIC rise was not limited to single ocean basins but spread 8 over the entire global ocean. 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 12 dropped over the deglaciation, at least in part, due to the recovery of neritic carbonate 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 CO₂ 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 20 that alkalinity and DIC were strongly elevated in late glacial seawater (Figs. 5b and 5e) thereby enhancing the concentrations of both H^+ and CO_3^{2-} ions with respect to the pre-21 industrial modern ocean. The deglacial minimum at 15.5 ka and the subsequent maximum at 22 13 ka were related to coeval changes in the accumulation rate of pelagic carbonate (Fig. 6f) 23 which were induced by upwelling pulses in the Southern Ocean (Fig. 4d). The deglacial CO_3^{2-} 24 minimum is related to ventilation pulses in the Southern Ocean and North Pacific employed in 25 the model. Export production of CaCO₃ and pelagic carbonate burial were enhanced by these 26 up-welling events and removed dissolved CO_3^{2-} from the deep ocean. The Holocene was 27 marked by a continuous CO_3^{2-} decline probably induced by the high sea-level stand promoting 28 neritic carbonate burial. 29

We ascribe t<u>T</u>he strong enrichment of dissolved CO₃²⁻ in glacial surface waters <u>was induced</u>
 by to the decline in atmospheric pCO₂ (Fig. 9). <u>According to our standard simulation</u>, <u>These</u>
 these CO₃²⁻ 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 1 constant over the entire Indo-Pacific at >1000 m water depth since the strong increase in DIC 2 (Fig. 9) was balanced by a corresponding TA rise. These model results well compare well 3 with those of B/Ca ratios in benthic foraminifera which probably record CO_3^{2-} changes in 4 ambient bottom waters (Yu et al., 2008; Yu et al., 2013). The model is consistent with glacial 5 to interglacial changes in deep-sea CO_3^{2-} reconstructed from this proxy (Tab. C1 in Appendix 6 C). The only deviation occurs at >4km water depth in the Atlantic where the model predicts 7 elevated LGM values while the data show a glacial CO_3^{2-} depletion (Tab. C1), possibly the 8 result of a strong east-west gradient in bottom water chemistry not resolved yet by the B/Ca 9 data that accordingly may not be fully representative for the Atlantic at large. 10

The glacial distribution pattern of δ^{13} C-DIC values calculated in the standard simulation (Fig. 11 11) is broadly consistent with observations (Oliver et al., 2010). To avoid circular reasoning, 12 this evidence cannot be used to validate the model results, since because glacial δ^{13} C-DIC 13 data were employed to define the LGM circulation pattern (section 2, Tab. A5 in Appendix 14 A). In all simulations global mean δ^{13} C-DIC values mirror the inversely DIC concentrations 15 (Figs. 5b-c)-and getting depleted with rising DIC concentrations, and vice versa. This anti-16 correlation may be be linked to the turnover of POC being strongly depleted in ${}^{13}C$ as 17 compared to average seawater. The glacial demise of the sedimentary POC pool, induced by 18 the weathering of exposed shelf sediments and the decline in depositional areas at-along 19 20 continental margins, contributed significantly to the glacial DIC rise and determined affected the isotopic evolution of seawater (Broecker, 1982a; Wallmann, 2014). The glacial δ^{13} C-DIC 21 depletion was widely ascribed to a glacial loss of terrestrial biomass (Shackleton, 1977; 22 Köhler and Fischer, 2004). However, our model can reproduce almost the entire glacial shift 23 to depleted δ^{13} C-DIC values recorded in benthic foraminifera (0.34 ± 0.19 %), (Peterson et 24 al., 2014)) without invoking any net changes in terrestrial biomass (Tab. A5). This result 25 outcome is consistent with results of a new modeling study suggesting that the rise in carbon 26 buried in permafrost and under ice largely compensated for the decline in peat, soil and 27 biomass carbon over the LGM (Brovkin and Ganopolski, 2015). 28

29 3.4 Radiocarbon

Atmospheric Δ^{14} C-CO₂ was forced to follow the IntCal13 values derived from the geological record by varying the ¹⁴C-production rate in the atmosphere (Appendix A, section A8). The ¹⁴C production rate was calculated for each time step considering the ¹⁴C transfer from atmosphere to oceans and changes in the inventories of atmospheric CO₂ and ¹⁴C-CO₂. The

difference between global mean Δ^{14} C-DIC and atmospheric Δ^{14} C-CO₂ ($\Delta \Delta^{14}$ C-DIC = Δ^{14} C-1 DIC - Δ^{14} C-CO₂) depended on the radiocarbon content of the atmosphere (Figs. 5d, 4g, and 2 12). Δ^{14} C-CO₂ and the model-derived $\Delta\Delta^{14}$ C-DIC were anti-correlated, since the ¹⁴C uptake 3 from the atmosphere was insufficient to raise the radiocarbon content of the model ocean up 4 to the level of elevated Δ^{14} C-CO₂ values attained during periods of strong atmospheric 5 radiocarbon production. This anti-correlation was also observed in an additional simulation 6 7 (Fig. 12b) where the carbon cycle and ocean circulation were maintained at a steady state representing Holocene boundary conditions, whereas Δ^{14} C-CO₂ values were forced to follow 8 the IntCal13 record. In further steady-state simulations the radiocarbon production rate in the 9 atmosphere was held constant over time while the carbon cycle operated in a Holocene 10 steady-state mode with a constant pCO_2 value of 280 µatm. These model runs show that the 11 steady-state $\Delta \Delta^{14}$ C-DIC values attained after about 100 kyr simulation time decreased with 12 increasing production rate (Appendix C, Tab. C2). As previously shown, changing production 13 rates of radiocarbon in the atmosphere may affect the difference between Δ^{14} C values in 14 planktonic and benthic foraminifera (Adkins and Boyle, 1997) and the contrast between 15 atmospheric and marine Δ^{14} C values (Franke et al., 2008). However, these effects were 16 regarded as transient features induced by a slow ¹⁴C transfer from the atmosphere into the 17 ocean. In contrast, the results of our steady-state model suggest that ¹⁴C depletion of the ocean 18 during periods of elevated atmospheric ¹⁴C production can be a permanent steady-state feature 19 (Tab. C2), a conclusion further substantiated by a simple steady-state model presented in 20 21 Appendix D.

The standard simulation STD yielded a mean ocean $\Delta \Delta^{14}$ C-DIC of -270 °/₀₀ for the LGM (21 22 ka) and -152 $^{\rm o}/_{\rm oo}$ at 0 ka corresponding to a glacial $\Delta\Delta^{14}$ C-DIC decline by 118 $^{\rm o}/_{\rm oo}$. The 23 simulations depicted in Fig. 12b show that multiple processes contributed to the ¹⁴C glacial 24 depletion of the ocean with respect to the atmosphere. These include the glacial decline in 25 deep ocean ventilation, sea-level fall, iron fertilization nutrient utilization, and rise in 26 atmospheric radiocarbon production. The $\Delta \Delta^{14}$ C-DIC decline observed upon sea-level fall in 27 part was induced by the glacial decline in sedimentary carbon pools adding fossil carbon to 28 the global ocean. Glacial changes in ocean circulation contributed to the $\Delta\Delta^{14}$ C-DIC decline 29 since the glacial demise of ventilation across the 2000 m depth horizon isolated the deep 30 31 ocean from the atmosphere. However, the simulations suggest that changes in ocean ventilation possibly were responsible for less than one third of the glacial rise in the 32 radiocarbon contrast between global ocean and atmosphere. 33

Atmospheric ¹⁴C production rates calculated in the model showed the same trends for all 1 simulations (Fig. 12c). They attained very high values at 25 ka and declined over time. The 2 only significant difference between the model runs occurred during the deglaciation. The 3 standard simulation yielded elevated production rates for this period since the rapid 4 5 ventilation of the deep ocean considered in simulation STD drew radiocarbon from the atmosphere and released ${}^{14}C$ -depleted CO₂ into the atmosphere such that the production rate 6 was enhanced to maintain atmospheric Δ^{14} C-CO₂ at the deglacial level documented by 7 IntCal13 (Fig. 12a). Our model results may support the hypothesis that a significant fraction 8 of the Δ^{14} C-CO₂ record is controlled by changes in atmospheric radiocarbon production 9 (Köhler et al., 2006; Broecker et al., 2004). 10

However, in contrast to our model approach various authors have proposed that most of the 11 Δ^{14} C-CO₂ record can be explained by changes in glacial ocean dynamics and carbon cycling 12 without invoking significantly elevated rates of atmospheric radiocarbon production 13 (Muscheler et al., 2005; Robinson et al., 2005). The Holocene trends calculated in the model 14 are similar to those observed in the ¹⁰Be ice-core record (Muscheler et al., 2005) and derived 15 from Holocene geo-magnetic data (Laj et al., 2002) while the glacial values are closer to the 16 stacked sedimentary ¹⁰Be record (Frank et al., 1997). Various reasons have been evoked to 17 explain the deviations between different records of atmospheric radionuclide production 18 (Köhler et al., 2006). The controversy suggests a clear need to develop a better constrained 19 record of atmospheric ¹⁴C production suitable for model validations (Fig. 12d). 20

The spatial distribution of radiocarbon in the global ocean changed significantly during the 21 LGM (Fig. 11). According to the standard simulation $\Delta\Delta^{14}$ C-DIC values were strongly 22 depleted over the entire ocean and reached a minimum of -356 $^{\circ}/_{\circ\circ}$ in North Pacific deep 23 water. Both, vertical and horizontal gradients were strengthened during the LGM. In the 24 modern ocean, marine Δ^{14} C-DIC values are correlated with DIC concentrations at water 25 depths below 2000 m (Sarnthein et al., 2013). If this correlation also holds for the glacial 26 ocean. glacial $\Delta \Delta^{14}$ C-DIC values may be used as proxy for DIC concentrations in glacial 27 28 seawater (Sarnthein et al., 2013). The model results show that the correlation was indeed 29 maintained in the glacial ocean and the slope of the correlation was similar for all model runs and time slices (Fig. 13). However, the regression line for glacial conditions was shifted to 30 lower DIC and $\Delta \Delta^{14}$ C-DIC values due to changes in ocean carbon cycling and possibly 31 elevated radiocarbon production rates in the glacial atmosphere. Thus $\Delta \Delta^{14}$ C-DIC values may 32 serve as new proxy for DIC concentrations in ancient seawater, if suitable methods are found 33
to correct for the glacial shift observed in the simulations (Fig. 13). The overall LGM pattern 1 2 calculated in the standard simulation (Fig. 11) compares well with trends derived from the radiocarbon contents of planktonic and benthic foraminifera even though radiocarbon data 3 indicate strong gradients within ocean basins, which were not resolved by the box model 4 (Appendix C, Tab. C3). A recent review of glacial $\Delta \Delta^{14}$ C-DIC data (Sarnthein et al., 2013) 5 revealed radiocarbon depletions in the deep Atlantic, Southern Ocean and Indo-Pacific 6 7 broadly consistent with those calculated by the model. However, the model was not able to reproduce very strong radiocarbon depletions measured at some deep water sites due to its 8 coarse spatial resolution (Tab. C3). Moreover, it predicts significant ¹⁴C-depletions in the 9 Atlantic thermocline which are inconsistent with coral ¹⁴C data (Robinson et al., 2005). ¹⁴C 10 measurements in foraminiferal shells and corals from the glacial ocean feature strong spatial 11 and temporal variability (Broecker et al., 2004; Sarnthein et al., 2013). More data will help to 12 13 resolve this variability and constrain the radiocarbon distribution and dynamics of the glacial 14 ocean.

15

16 4 Conclusions

For a first time we show model results that are consistent with both the atmospheric pCO₂ 17 record (Figs. 5 and 7) and data on past distribution changes of dissolved oxygen, carbonate, 18 and radiocarbon in the glacial ocean (Figs. 8, 9, 11 and Tabs. C1 and C3). Atmospheric pCO₂ 19 and the glacial distribution of seawater tracers were not prescribed but calculated as 20 prognostic model variables. Only marine $\delta^{13}C$ data were used to parameterize the glacial 21 circulation model. A comprehensive formulation of shelf processes and sea-level effects is a 22 23 major new component included in our earth system model. Thus, the conformity between independent proxy data and key model results (atmospheric pCO₂ change over the last 130 24 kyr, distribution of dissolved oxygen, carbonate, and radiocarbon in the LGM ocean) supports 25 our hypothesis that the glacial sea-level drop induced a decline in atmospheric pCO₂ and a 26 rise in the inventories of nutrients, DIC, and alkalinity in the glacial ocean (Wallmann, 2014). 27 Also, we first show that the slope of DIC versus radiocarbon observed in the modern deep 28 ocean (Sarnthein et al., 2013) was probably maintained in the glacial ocean (Fig. 13). 29 However, a glacial shift in the intercept now complicates the use of ¹⁴C as DIC proxy. 30 The shelf hypothesis was originally developed to explain the deglacial rise in atmospheric 31

32 pCO₂ (Broecker, 1982b). In contrast, our model analysis reveals that shelf and sea-level
 33 effects were not responsible for this rapid rise but account for a major portion of the slow

19

glacial decline of atmospheric pCO₂ (Figs. 5 and 7). The deglacial sea-level rise induced a 1 decline in nutrient and carbon stocks in the global ocean. However, these stocks changed only 2 slowly due to their large size (Menviel et al., 2012). The gradual pCO₂ rise over the Holocene 3 may be attributed to the slow relaxation of nutrient and carbon stocks promoting CO₂ transfer 4 5 from the ocean into the atmosphere. The slow relaxation may also be responsible for the imbalance in phosphate and TA sources and sinks observed in the modern ocean (Wallmann, 6 7 2010, 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 8 9 values attained over the last glacial maximum.

Since many relevant processes are not fully understood outcomes of earth system models
 depend on somewhat subjective choices of model parameterizations. Nevertheless, we are
 confident that the major conclusions drawn from our study are robust, since the structure of
 our model is based on sound geochemical principals and the model results are consistent with
 observations in the modern and glacial ocean.

15 Our model experiments suggest that the glacial sea level fall induced an expansion of nutrient and alkalinity stocks in the global ocean contributing significantly to the drawdown of 16 atmospheric pCO₂. Most of the glacial decline in global mean δ^{13} C-DIC observed in benthic 17 foraminifera can be attributed to the weathering of exposed shelf sediments and the glacial 18 decline in POC burial. Glacial changes in seawater chemistry and atmospheric composition 19 were also affected by iron fertilization and ocean dynamics. Iron fertilization promoted export 20 production in the Southern Ocean and burial of POC, particulate P, and pelagic carbonate at 21 the deep-sea floor. These changes mitigated the expansion of the dissolved nutrient, TA and 22 DIC stocks in the ocean induced by the marine regression. The nutrient and CO₂ 23 concentrations in surface waters of the Southern Ocean were reduced by iron fertilization such 24 25 that more CO₂ could be retained in the ocean interior. The glacial AMOC shoaling and decline in deep ocean ventilation amplified the rise in dissolved nutrient and carbon stocks in 26 27 the glacial ocean since export production and burial were restricted by the enclosure of 28 nutrients in the deep ocean. The glacial isolation of the deep ocean contributed to the pCO2 drawdown since more CO₂ was stored in poorly ventilated deep water masses. 29

The rapid and stepwise rise in atmospheric pCO₂ over the deglaciation was possibly induced
 by the repeated break down of Southern Ocean stratification and the sudden ventilation of
 intermediate and deep water masses in the North Pacific over Heinrich Event 1. The decrease
 in dust and iron delivery to the Southern Ocean contributed strongly to the deglacial pCO₂

increase. The deglacial sea-level rise supported the pCO₂ rise and induced a decline in 1 nutrient and carbon stocks in the global ocean. These stocks changed only slowly due to their 2 large size and the extended residence times of chemical species in the global ocean. The 3 gradual pCO₂ rise over the Holocene can be attributed to the slow relaxation of nutrient and 4 carbon stocks promoting CO2 transfer from the ocean into the atmosphere. The slow 5 relaxation is also responsible for the imbalance in phosphate and TA sources and sinks 6 7 observed in the pre-human modern ocean (Wallmann, 2010, 2014). Stocks of these chemical species are declining until today since tens of thousands of years are needed to draw down the 8 9 dissolved P and TA inventories from their peak values attained over the last glacial maximum. 10 Various earth system models were previously used to study potential controls of past changes in atmospheric pCO₂ over the last glacial cycle. All models show changes that resulted from 11 12 several interacting forcings including ocean dynamics and iron fertilization . The major new component of the present model is linked to the simulation of POM and nutrient cycling at 13 continental margins under eustatic sea level change (as explained in detail in Appendix B). 14 The changing turnover of sedimentary POC, N and P has a strong effect on seawater 15 chemistry and may have contributed significantly to the glacial drawdown and Holocene rise 16 of atmospheric pCO₂. It should, thus, be considered in future earth system models. 17

18 According to standard Milankovitch theory (Milankovitch, 1941), variations in summer insolation at high latitudes (Berger and Loutre, 1991) cause waxing and waning of northern 19 20 ice sheets (Fig. 14). Most of the global climate change over a glacial cycle is thus believed to be driven by northern summer insolation and ice sheet dynamics (Denton et al., 2010). 21 22 However, it has always been difficult to explain why atmospheric pCO₂ declined over glacial periods and how this drop was connected to the built-up of large continental ice sheets. The 23 24 sea-level effects explored in this paper provide the missing link between glacial ice sheet and pCO_2 dynamics. The sea-level-driven pCO_2 decline was amplified by a decrease in deep 25 26 ocean ventilation, a decline in sea surface temperature, and enhanced dust deposition nutrient 27 utilization. These additional changes were driven by a combination of greenhouse gas, albedo, and insolation forcing (Fig. 14). Glacial terminations occurred when summer insolation 28 increased at northern latitudes (Raymo et al., 1997), ice sheets reached a critical size (Denton 29 et al., 2010), and carbonate compensation at the deep-sea floor reversed the declining pCO_2 30 trend (Wallmann, 2014). The deglacial warming was again driven by greenhouse gas, albedo, 31 32 and insolation forcing promoting the retreat of continental ice sheets, sea-level rise, ocean ventilation, and the decline in dust deposition nutrient utilization -in a positive feedback mode. 33

Due to their internal non-linear dynamics, continental ice sheets are able to generate 100-kyr 1 cycles with a slow glacial expansion and rapid deglacial contraction of ice volume under 2 Milankovitch forcing even though insolation oscillates on much shorter time scales (Imbrie 3 and Imbrie, 1980; Abe-Ouchi et al., 2013; Ganopolski and Calov, 2011; Pollard, 1983). 4 Positive feedbacks embedded in the global carbon cycle are able to generate a 100-kyr cycle 5 6 without any form of external forcing when surface temperature, ice volume-and, sea-level and 7 ocean circulation are assumed to be controlled by pCO₂ (Wallmann, 2014). Thus, both, continental ice sheets and the global carbon system have the inherent tendency to generate 8 cycles with a length of 100 kyr. They interact via sea-level and pCO₂ change, respond to 9 insolation forcing, control changes in the climate system (surface temperature, ocean and 10 atmospheric circulation, dust deposition) and may generate the 100-kyr cycle dominating late 11 12 Quaternary climate change.

13

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, ¹³C-DIC and ¹⁴C-DIC (Key et al., 2004) and the World 4 Ocean Atlas (WOA01) for temperature, salinity, PO₄, NO₃ and O₂ (Conkright et al., 2002). 5 ¹⁴C-DIC-data were corrected by subtracting the bomb-¹⁴C signal and DIC data were corrected 6 for the intrusion of anthropogenic CO₂ (Key et al., 2004) whereas ¹³C-DIC data were not 7 corrected and are thus affected by ¹³C-depleted anthropogenic CO₂. 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⁻¹, 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 CO₂ uptake rate balancing the CO₂ being 16 produced in the modern ocean by carbonate burial and degassing processes (Wallmann, 17 2014). The isotopic composition of atmospheric CO₂ was maintained at a constant level 18 representative for the pre-human atmosphere ($\delta^{13}C = -6.5$ °/₀₀, $\Delta^{14}C = 0$ °/₀₀). Water fluxes 19 (Fig. A2 and Tab. A3) and parameter values for key biogeochemical processes (Tab. A4) 20 were varied until pCO₂, global export production, and the tracer distribution fields generated 21 by the steady-state box model were consistent with data (Tab. A1 and A2, Fig. A1). A good 22 fit was obtained for all tracers except ¹³C-DIC (Fig. A1). Most of the ¹³C mismatch was 23 induced by anthropogenic ¹³C which has a strong effect on the observations in the modern 24 ocean but was 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) up-wells in the Indo-Pacific all the way to the thermocline and surface ocean. This pattern is consistent with the 14 15 "great 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 and Hallberg, 2002; Marinov et al., 2006). NEMO also predicts an extremely high rate of 20 21 vertical water exchange in the Southern Ocean across 2000 m water depth of more than 200 Sv-(Fig. A2). These strong upward and downward water fluxes are inconsistent with tracer 22 observations showing strong vertical gradients between the deep ocean (>2000 m water 23 24 depth) and the overlying water masses. The water fluxes derived from NEMO were modified to remove these biases and to provide more realistic water fluxes for the box model (Fig. A2, 25 Tab. A3). The corresponding best-fit water fluxes are bidirectional, i.e. water flows in both 26 directions between each of the adjacent model boxes (Tab. A3). The net fluxes (Tab. A3) 27 28 were 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 Southern Ocean where Antarctic Bottom Water (AABW) is formed at a rate of ca. 18 Sv. A 31 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 up-wells 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 up-wells 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 up-welling 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⁻¹. About 37 % of this vertical exchange flux occurs in the Southern 14 Ocean (> 30°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_{Wab}) are multiplied by tracer concentrations (C_j) to calculate
 tracer fluxes (F_{Tab}) 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_I is the concentration in the intermediate water box, C_S the concentration in the overlying surface water box and f_I defines the fraction of C_I in the ascending two component mixture. The weighing factor f_I was set to 0.5 for salinity, DIC, and ¹³C-DIC. A smaller value was applied for total alkalinity (f_I = 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_I = 0.55; DO: f_I = 0.9; ¹⁴C-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_{Sal-in} are the salinity fluxes from the neighboring boxes into the considered box while 1 F_{sal-out} 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, i.e. that is an enhanced salinity (+ 0.9 PSU) with respect to the mean salinity of Arctic 21 surface water) was ascribed to employed for the waters sinking into the underlying intermediate water box. 22

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 temperature change is proportional to the prescribed sea-level, *i.e.*that is continental ice sheet 25 formation and albedo change while the remaining 50 % are proportional to the logarithm of 26 27 atmospheric pCO₂ 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 drop was assumed to be twice as high as the global mean at high latitudes and only half as 30 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

1 The model includes a comprehensive phosphorus cycle. Rivers transport dissolved 2 phosphorus (DP) into the ocean where it is taken up by phytoplankton, gets exported, 3 degraded, buried in marine sediments, and removed via hydrothermal activity (Wallmann, 4 2014). Export production (F_{EPOP}) of particulate organic P (POP) from the individual surface 5 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_{DP} 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_s is the volume of the considered 9 surface water box, and k_{EXP} 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 corresponding POP turnover applying constant Redfield ratios (PON/POP = 17, POC/PON = 17 123/17, O₂/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⁻¹ (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_W is piston velocity, A_{SUR} is the ice-free surface area of the considered box (Köhler et 15 al., 2005), DO_S 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 Δ^{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 CO₂ 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_{2S} is the concentration of CO₂ in the considered surface water box (as calculated 9 from ambient DIC and TA), while CO_{2SEO} is the equilibrium concentration of CO₂ 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_{2SEQ} and 12 CO_{2S} (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 value since the weathering of exposed shelf sediments was assumed to compensate for the 16 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 ¹³C and ¹⁴C. 22

23 A8 Carbon isotopes

The model includes ¹³C-DIC and ¹⁴C-DIC as tracers in addition to total DIC. Isotope ratios as well as δ^{13} C and Δ^{14} C values of DIC were calculated from ¹³C-DIC/DIC and ¹⁴C-DIC/DIC mole fractions. The gas exchange of ¹³C-CO₂ across the seawater/atmosphere boundary layer (F_{13CO2}) 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 α_{aq-g} is the equilibrium fractionation factor for CO₂ gas exchange between seawater and air, α_k is the corresponding kinetic fractionation factor, α_{DIC-g} is the equilibrium fractionation factor defining the ¹³C fractionation between DIC and gaseous CO₂, R_{13DIC} is the

 $^{13}C/^{12}C$ ratio in DIC, and R_{13CO2A} is the $^{13}C/^{12}C$ ratio in atmospheric CO₂. The isotopic 1 composition of DIC species (CO₂, HCO_3^{-} , CO_3^{2-}) was calculated using equilibrium 2 fractionation factors given in (Zeebe and Wolf-Gladrow, 2001). These values were applied to 3 calculate the isotopic composition of exported POC and neritic and pelagic carbonates 4 applying isotopic fractionation factors according to (Ridgewell, 2001) and (Romanek et al., 5 1992), respectively. The ${}^{14}C/{}^{12}C$ fractionation between DIC, CO₂, POC and CaCO₃ was 6 calculated using the squared ¹³C equilibrium fractionation factors since the mass difference 7 between ${}^{14}C$ and ${}^{12}C$ exceeds the ${}^{13}C$ - ${}^{12}C$ difference by a factor of 2. The gas exchange of 8 14 C-CO₂ across the seawater/atmosphere boundary layer (F_{14CO2}) was thus calculated as: 9

10
$$F_{14CO2} = k_{W} \cdot A_{SUR} \cdot \alpha_{aq-g}^{2} \cdot \alpha_{k} \cdot \left(\frac{R_{14DIC}}{\alpha_{DIC-g}} \cdot CO_{2S} - R_{14CO2A} \cdot CO_{2SEQ}\right)$$
(A12)

where R_{14DIC} is the ¹⁴C/¹²C ratio in DIC of the considered surface water box and R_{14CO2A} the ¹⁴C/¹²C ratio in atmospheric CO₂. Moreover, ¹⁴C-DIC was subject to radioactive decay with a decay constant of $\lambda = 1/8267$ yr⁻¹.

14 Δ^{14} C-DIC values were calculated as:

15
$$\Delta^{14} \mathbf{C} - \mathbf{DIC} = \left(\frac{\mathbf{f}_{N} \cdot \Phi_{14\text{DIC}}}{\Phi_{abs}} - 1\right) \cdot 1000$$
(A13)

where $\Phi_{14\text{DIC}}$ is the ¹⁴C mole fraction ($\Phi_{14\text{DIC}} = {}^{14}\text{C}\text{-DIC/DIC}$), Φ_{abs} is the ¹⁴C mole fraction of the standard (1.175 x 10⁻¹² (Mook and Plicht, 1999), pre-human atmosphere with a δ^{13} C value of -25 °/₀₀), f_N is the normalization factor defined as:

19
$$f_{N} = \left(\frac{0.975}{\left(1 + \frac{\delta^{13}C}{1000}\right)}\right)^{2}$$
 (A14)

and δ^{13} C is the δ^{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 Δ^{14} C-DIC values by applying the δ^{13} C-DIC calculated for the considered ocean box (Stuiver and Polach, 1977).

The isotopic compositions of atmospheric CO_2 were not calculated as prognostic model variables but prescribed using data from the geological record. Ice-core data were applied to define the $\delta^{13}C$ -CO₂ values (Schmitt et al., 2012) while $\Delta^{14}C$ -CO₂ values were forced to

follow the IntCal13 values (Reimer et al., 2013). The atmospheric records are affected by 1 vertical mixing processes in the Southern Ocean and the distribution of SSTs and vertical δ^{13} C 2 and Δ^{14} C gradients within this region (Schmitt et al., 2012; Tschumi et al., 2011b; Köhler et 3 al., 2005). Sediment records show an anti-phased pattern in export production and vertical 4 mixing between the region south of the Antarctic Polar Front and the Subantarctic Ocean 5 (Anderson et al., 2014) which may have a strong effect on atmospheric isotope values but 6 7 wase not resolved by our model since the entire global surface ocean at >30°S was pooled in a single box (Fig. 2). This lack of resolution hindered us to simulate the carbon isotopic 8 <u>composition of atmospheric pCO₂ with our box model.</u> Sensitivity tests showed that the δ^{13} C 9 values of intermediate, deep and bottom water boxes employed to derive the glacial 10 circulation field (Tab. A5) were not significantly affected by the prescribed atmospheric δ^{13} C 11 values since the inventory of ¹³C residing in the global ocean exceeds the atmospheric 12 inventory by almost two orders of magnitude. 13

14 The time-dependent radiocarbon production rate in the atmosphere (R_{14}) was calculated 15 applying the following equation:

16
$$R_{14} = k_{14} \left(\Delta^{14} \text{C-CO}_2 \text{ (data)} - \Delta^{14} \text{C-CO}_2 \text{ (model)} \right)$$
 (A15)

where k_{14} is a constant ($\geq 10^5$ mmol yr⁻¹ °/₀₀⁻¹), Δ^{14} C-CO₂ (model) is the atmospheric value 17 calculated for each time step of the model, and Δ^{14} C-CO₂ (data) is the data trend 18 reconstructed from the geological record (Reimer et al., 2013). R_{14} thus increased when Δ^{14} C-19 CO_2 (model) was smaller than $\Delta^{14}C$ - CO_2 (data) and vice versa. With this approach, the 20 production rate was varied such that the model always complied with the atmospheric ¹⁴C 21 record. The atmospheric radiocarbon model considered production and the decay of 22 radiocarbon in the atmosphere as well as exchange processes with the continents and the 23 surface ocean (Eq. A12). The major output of the atmospheric ¹⁴C model was the time-24 dependent ¹⁴C production rate (Eq. A15). 25

26

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

29 B1 Particulate organic carbon (POC) turnover

The overwhelming portion of POC produced in the euphotic zone is degraded in the water column before it can reach the seabed. Hence, in the open ocean, only ca. 1 % of the primary production reaches the deep-sea floor (Suess, 1980; Jahnke, 1996; Seiter et al., 2005; Dunne

et al., 2007). However, the fraction reaching the seabed increases drastically at continental 1 margins where shallow water depths limit the transit time of POC sinking through the water 2 column. Global models and observations thus indicate that ca. 30 % of ambient primary 3 production reaches the shallow seafloor at 0 - 50 m water depth (Dunne et al., 2007). Due to 4 this effect and the high productivity of continental margins, the margin seabed located at <25 km water depths receives ca. 85 ± 15 % of the global POC rain rate (Dunne et al., 2007; 6 7 Burdige, 2007) even though only 16 % of the global seabed is located at <2km water depth (Eakins and Sharman, 2012). Continental margins are even more dominant in terms of POC 8 9 burial because burial is promoted by the deposition of riverine particles (Berner, 1982, 2004) accumulating mostly on the continental shelf during interglacial sea-level high-stands 10 11 (Burwicz et al., 2011). Thus, 90 ± 10 % of the global POC burial takes place at <2 km water depth (Dunne et al., 2007; Burdige, 2007; Wallmann et al., 2012). 12

13 POC rain and burial rates at continental margins declined during glacial sea-level low-stands since the oceans retreated into steeper terrains. During the LGM when the sea-level was 120 14 m lower than today, the shelf seafloor area at 0 - 100 m contracted by 73 % while the outer 15 shelf and upper slope area located at 100 - 2000 m water depth was reduced by 13 % (Eakins 16 and Sharman, 2012) neglecting isostatic adjustment. Considering the high rain rates at 17 shallow water depths (Dunne et al., 2007), the glacial margin contraction diminished the 18 global POC rain rate by possibly up to 50 %. The burial rate of marine POC may have been 19 reduced by a similar proportion since POC burial is ultimately limited by the amount of POC 20 reaching the seabed. However, there are a number of additional factors that affect the rate of 21 22 POC burial. These include bulk sedimentation rate (Berner, 1982), surface area of sediment 23 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 24 25 (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. 26

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 load is deposited on the shelf (Burwicz et al., 2011) while low sea-level stands promote downslope transport (Hay and Southam, 1977). Hence, data on Quaternary shelf and deep-sea fan 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 (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 1 depths (Burwicz et al., 2011; Wallmann, 2014). The efficiency of POC burial at the 2 continental rise and deep-sea floor may have been further amplified by the glacial decline in 3 dissolved oxygen concentrations in the deep ocean (Jaccard and Galbraith, 2012) favoring the 4 preservation of POC in marine sediments (Hartnett et al., 1998; Dale et al., 2015). It is 5 6 difficult to validate glacial changes in burial efficiency at <2km water depths. Here, POC 7 preservation was possibly reduced by the intense ventilation of the glacial thermocline (Jaccard and Galbraith, 2012) while preservation might have been enhanced if sedimentation 8 9 rates on the outer shelf and upper slope were significantly elevated by the glacial loss of inner 10 shelf regions. Considering the available evidence it can be concluded that the glacial marine 11 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 12 13 water column degradation and decline in marine POC burial since the focus of POC burial 14 was shifted to >2km water depth where rain and burial rates are limited by the almost 15 complete degradation of marine POC in the water column.

16 <u>B2 Nutrient turnover</u>

17 Continental margins are also major sinks for nitrate and phosphate since >50 % of the global 18 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 19 20 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., 21 22 2007). The strong decrease in shallow seafloor area during glacial marine regressions thus induced a decline in nitrate and phosphate removal contributing to the expansion of the 23 24 nutrient inventory in the glacial ocean (Broecker, 1982a; Deutsch et al., 2004; Eugster et al., 25 2013; Wallmann, 2014). A negative feedback was probably established where the expansion 26 of the nutrient inventory induced a rise in export production and rain rate to the seabed which 27 in turn promoted the burial of POC and removal of nutrients from the ocean. The glacial decline in POC burial and the glacial rise in the standing stocks of macronutrients may have 28 29 been mitigated by this negative feedback mechanism (Middelburg et al., 1996).

30 <u>Phosphate cycling in marine sediments is affected by oxygen conditions in ambient bottom</u>
 31 waters and sediments (Krom and Berner, 1981; Van Cappellen and Ingall, 1994; Wallmann,

- 32 2003). Phosphate is released from sediments under suboxic and anoxic conditions due to the
- 33 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 1 2 in the sediment as authigenic carbonate fluorapatite (CFA). Hence, OMZ sediments are depleted in Fe/Mn-bound P, enriched in CFA and characterized by high POC/POP ratios 3 exceeding the Redfield ratio by a factor of 2 - 8 (Schenau and De Lange, 2001; Lomnitz et 4 al., 2015). Ratios between POC and reactive P (Preac, sum of POP, CFA and Fe/Mn-bound P) 5 amount to $POC/P_{reac} = 100 - 300$ in OMZ sediments and 20 - 70 in continental margin 6 7 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 8 9 conditions (Ingall and Jahnke, 1994; Schenau and De Lange, 2001) whereas POC is more efficiently buried in OMZ sediments covered by oxygen-depleted bottom waters (Dale et al., 10 11 2015).

12 **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 13 and B2. A very simple approach was chosen to calculate the burial of neritic carbonates. It 14 was assumed that the burial rate is proportional to the seafloor area at 0 - 50 m water depth 15 (A_{NM}) which is controlled by sea-level change, only (see Fig. 3). Burial of marine POC and 16 phosphorus (P) at continental margins was assumed to be proportional to POC export 17 production (F_{EPOC}) and the depositional areas at 0 - 100 m (A_S) and 100 - 2000 m (A_I) that 18 were controlled by sea-level change (Fig. 3). The decline in seafloor area at 0 - 2000 m water 19 20 depths was applied to parameterize the rise in POC burial at the deep-sea floor induced by the glacial marine regression. We thus effectively assumed that the burial efficiency of POC 21 22 remained constant at <2km water depth but increased at >2km during glacial sea-level lowstands. 23

24 Phosphorus considered in the model refers to the sum of organic and reactive inorganic P 25 phases (CFA and Fe/Mn-bound P). The latter fractions contributes strongly to P burial since most of the marine particulate sedimentary organic-P deposited at the seafloor is degraded and 26 transformed into inorganic authigenic phases during early diagenesis (Ruttenberg and Berner, 27 1993). P burial decreases when the dissolved oxygen content of ambient bottom waters (DO) 28 29 falls below a threshold value of about 20 µM (Wallmann, 2010). This effect was considered taken into account by introducing corresponding Monod terms in the P burial flux definitions 30 (Tab. B2). Moreover, the model formulation ensured that the molar POC/P_{reac} burial ratio did 31 not exceed the maximum value of about 400 observed in Quaternary sediments (Anderson et 32 al., 2001). 33

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).

The applied parameter values were constrained by field data from the modern ocean (Tab. 13 B1). The available POC and P burial data suggest that burial is rather evenly distributed 14 between 0 - 100 m and 100 - 2000 m water depths (Tab. B1) whereas POM rain rates at 0 -15 100 m clearly exceed the corresponding rates at 100 - 2000 m (Dunne et al., 2007). This 16 difference is caused by bottom currents transporting marine POM from the inner shelf 17 18 towards outer shelf and upper slope environments (Walsh et al., 1981). Note that the POC 19 burial rates applied in our model (Tab. B1) are conservative that is lower than most previous estimates (Burdige, 2007; Dunne et al., 2007). The burial efficiency applied in the model is 20 low at shallow water depth since winnowing by bottom currents affects large parts of the 21 22 shallow seafloor such that about 70 % of the modern shelf sediments are non-accumulating, relict sands with very low POC contents (Burdige, 2007). POM exported laterally from these 23 24 shallow areas provides POM for slope deposits (Walsh et al., 1981). The highest burial efficiency is applied at 100 - 2000 m water depth where the deposition of fine-grained 25 26 riverine particles and low oxygen values in ambient bottom waters favor the preservation of 27 marine POC. Parameter values and fluxes listed in Tabs. B1 and B2 refer to global fluxes. These fluxes were distributed among the 6 ocean basins defined in the box model considering 28 the respective seafloor areas and export productions. Neritic carbonate burial was distributed 29 between the Tropical Indo-Pacific and Atlantic (Kleypas, 1997). 30

31 The <u>Our</u> model predicts that the global burial rates of POC and P would decline to 7.9 Tmol 32 yr^{-1} and 0.14 Tmol yr^{-1} during the LGM, respectively, if export production and oxygen 33 concentrations were maintained at their modern value. The export production was, however, promoted by the decline in P burial such that the best fit simulation STD produced LGM
burial rates of 9.6 Tmol yr⁻¹ and 0.165 Tmol yr⁻¹ compared to modern global rates of 11.5
Tmol yr⁻¹ and 0.18 Tmol yr⁻¹, respectively (s. Tab. B1). Our standard model run suggests that
the shelf (0 - 100 m water depths) trapped a total of 4650 Gt POC over the last glacial cycle
(130 - 0 ka) while 7870 Gt POC accumulated on the continental slope (100 - 2000 m water
depth). Shelf weathering released a total of 1940 GtC over the last 130 ka in simulation STD
that is less than 50 % of the POC accumulating on the shelf over the last glacial cycle.

8 According to the model, the glacial marine regression affected the chemical and isotopic 9 composition of seawater and the CO₂ content of the atmosphere via a chain of interconnected 10 processes: Ocean margins retreated into steeper terrain and shelf areas were exposed by the marine regression; the burial of phosphorus and neritic carbonate and benthic denitrification 11 12 declined due to the steepening of ocean margins; carbonate, POC, and P weathering rates increased due to the exposure of shelf sediments; atmospheric CO2 was consumed and 13 converted into dissolved alkalinity by enhanced carbonate weathering while isotopically 14 depleted CO2 was released into the atmosphere by POC weathering; standing stocks of 15 dissolved nutrients and alkalinity in the ocean expanded due to the decrease in burial and 16 denitrification and the increase in weathering; export production rose due to the increase in 17 the dissolved nutrient stocks and CO₂ was transferred from the atmosphere into the ocean 18 interior by the intensified biological pump while CO₂ sequestration was supported by 19 enhanced seawater alkalinity. 20

21 **<u>B4 Model limitations</u>**

22 Model parameterizations were chosen to the best of our knowledge. It should, however, be 23 noted that key processes such as glacial changes in POC and P burial efficiency are only poorly constrained by available data. Moreover, we assumed that the global mean 24 morphology of continental margins was retained over the glacial cycle and that the average 25 global change in relative sea-level was equal to eustatic sea-level change. This approach 26 neglects the glacial isostatic adjustment, i.e. the glacial subsidence of northern land masses 27 loaded by large ice sheets, the uplift in flanking regions, and the numerous far field effects 28 29 (Daly, 1934; Milne and Mitrovica, 2008). It also neglects changes in margin morphology induced by the erosion and down-slope transport of shelf sediments during glacial sea-level 30 low-stands (Hay, 1994) and the deglacial tilting of continental margins (Clark et al., 1978). 31 Moreover, we assumed that during the LGM eustatic sea-level was 120 m lower than today 32 while growing evidence supports the view that LGM sea-level fall was in fact larger than this 33

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
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
areas were exposed during glacial marine regressions and that these changes had a profound
effect on glacial seawater composition and atmospheric pCO₂.

7 Moreover, our model does not consider the growth of land plants and soil formation on emerged shelf regions during glacial sea-level low-stands. Trees and other plants may use 8 9 sediment nutrients after shelf exposure and accumulate terrestrial POC on the emerged shelf. However, we think that the POC accumulation associated with these processes is small 10 compared to the sedimentary POC turnover considered in the model. Modern continental 11 margins (shelf and rise) accumulate sedimentary POC at a rate of about 100 - 200 Gt kyr⁻¹ 12 (Hedges and Keil, 1995; Burdige, 2007; Wallmann et al., 2012; Dunne et al., 2007). This 13 enormous flux is induced by the high marine productivity of the region and the rapid 14 15 accumulation of sediments facilitating the burial of marine POC. Trees and soils growing on the emerged shelf would have to accumulate POC in the order of 10 000 Gt C to maintain this 16 17 high carbon flux over the glacial period (ca. 80 kyr), an unlikely scenario since the global terrestrial carbon stock is ≤ 2000 GtC. The standing stock of POC in margin sediments 18 exceeds the global terrestrial stock since POC is buried more efficiently in sediments than in 19 most soils and plants. Sedimentary POC burial and preservation are promoted by high 20 21 sedimentation rates and the lack of oxygen in these water-saturated deposits.

22

23 Appendix C: Model results

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

25

26 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:

32 Atmosphere mass balance: $R_{14} - \lambda^{14}C_A - F_{AO} = 0$ (D1)

1 Ocean mass balance: $F_{AO} - \lambda^{14}C_O = 0$ (D2) 2 ${}^{14}C$ flux from atmosphere to ocean: $F_{AO} = k ({}^{14}C_A - {}^{14}C_O)$ (D3)

where R_{14} is the radiocarbon production rate, λ 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:

7
$${}^{14}C_{A} - {}^{14}C_{O} = \frac{R_{14}}{\lambda + 2 \cdot k}$$
 (D4)

The resulting equation shows that the difference is proportional to the radiocarbon production 8 rate. The steady-state ¹⁴C-depletion of the ocean with respect to the atmosphere, thus, 9 increases under high production rates. The difference would vanish if the mass transport 10 11 coefficient would be infinitely large. The example of the modern ocean shows, however, that this is not the case and that the ocean is significantly depleted in ¹⁴C with respect to the 12 atmosphere since the transfer of ¹⁴C from the atmosphere into the ocean is too slow to 13 eliminate the ¹⁴C difference. In our simple 2-box model, the radiocarbon flux is assumed to be 14 15 proportional to the radiocarbon gradient between atmosphere and ocean (Eq. D3). The gradient increases under high production rates such that more ¹⁴C is transferred from the ¹⁴C-16 enriched atmosphere into the depleted ocean. The rate of radioactive decay in the ocean (λ 17 $^{14}C_0$ increases since the ^{14}C content of the ocean is raised by the enhanced radiocarbon flux 18 from the atmosphere. Steady state is attained when the decay rate in the ocean and the ¹⁴C 19 flux from the atmosphere are balanced (Eq. D2). The steady-state gradient $({}^{14}C_A - {}^{14}C_O)$, thus, 20 increases in proportion to the atmospheric production rate such that the flux into the ocean 21 22 compensates for the elevated decay rate in the ocean. The analytical solution for the simple two-box-model (Eq. D4) correctly predicts the steady-state behavior of our more evolved 23 24 model system where the ocean is represented by 24 boxes and the radiocarbon uptake from the atmosphere is calculated applying Eq. (A12) rather than Eq. (D3). It predicts that $\Delta\Delta^{14}$ C-25 DIC increases linearly with production rate as observed in the steady state simulations (Tab. 26 C2). The real ocean-atmosphere system is obviously more complex than any kind of model. 27 However, the simple 2-box-model captures the basic features of the real system and reveals 28 that the ¹⁴C contrast increases in proportion to the production rate. Since radiocarbon 29 production rates may have changed significantly over the last glacial cycle, this basic system 30 property has to be considered in the interpretation of the marine ¹⁴C-record. 31

32

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- 5

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

Simulation	pCO ₂ at	pCO ₂ 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	μΜ	μМ	μΜ	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 μ M): Model versus data. Subscripts: S: surface water (0 100m), I: intermediate water (100 –

Box	Sal	Sal	PO ₄	PO ₄	NO ₃	NO ₃	O ₂	O ₂
	Data	Model	Data	Model	Data	Model	Data	Model
AR _S	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
ARI	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 _I	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 _D	34.94	34.87	1.04	1.07	14.69	15	287.	287
NA _D	34.95	34.92	1.18	1.19	18.71	16.9	265.1	257
TA _D	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 _D	34.69	34.75	2.49	2.53	35.5	33.9	145.5	149
NPD	34.65	34.69	2.73	2.57	38.63	34.1	116.	134
AR _B	34.94	34.87	1.05	1.08	14.6	15.2	276.5	285
NA _B	34.9	34.91	1.33	1.42	20.18	19.3	260.5	237
TA _B	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 _B	34.7	34.75	2.34	2.39	33.65	31.8	176.4	173
NP _B	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), δ^{13} C-DIC, and Δ^{14} C-DIC

Box	DIC	DIC	ТА	ТА	$\delta^{13}C$	$\delta^{13}C$	Δ^{14} C	Δ^{14} C
	Data*	Model	Data	Model	Data ⁺	Model	Data*	Model
AR _S	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 _S	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
ARI	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 _D	2188	2185	2371.	2379	n. d.	1.62	n. d.	-85.97
NA _D	2216	2195	2388.	2384	0.97	1.44	-87.9	-93.75
TA _D	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 _D	2382	2382	2481.	2493	-0.06	-0.272	-199.6	-192.5
NPD	2416	2388	2491.	2492	-1.09	-0.432	-217.8	-214.2
AR _B	2188	2186	2371.	2379	n. d.	1.6	n. d.	-86.2
NA _B	2241	2221	2403.	2395	0.92	1.17	-118.4	-110.7
TA _B	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 _B	2360	2363	2472.	2488	0.14	-0.111	-184.4	-184.7
NP _B	2388	2384	2491.	2495	-0.58	-0.352	-206.8	-212.7

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

3 *: corrected for anthropogenic CO_2 ; ⁺: 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	Exchange
				Net	C
$NA_S \rightarrow AR_S$	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
$\overline{\text{FRESH}} \rightarrow \text{NA}_{\text{S}}$	0.05		$FRESH \rightarrow NA_S$	0.10	
$FRESH \rightarrow TA_S$	-0.44		$FRESH \rightarrow TA_S$	-0.69	
$\overline{\text{FRESH}} \rightarrow \text{SO}_{\text{S}}$	3.61		$\overline{\text{FRESH}} \rightarrow \text{SO}_{\text{S}}$	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	TA	SO	TIP	NP
Kinetic constant for	k _{EXP}	yr ⁻¹	0.05	1.5	0.4	0.15	1.1	0.12
export production								
Kinetic constant for	k _{NF}	yr ⁻¹	0.0	3.0	1.0	0.2	1.0	0.5
nitrogen fixation								
PIC/POC export	r _{PICPOC}		0.01	0.08	0.20	0.01	0.15	0.07
ratio								
Piston velocity	k _{SA}	cm yr ⁻¹	0.4	0.1	0.12	0.12	0.24	0.1

3

- 4 Table A5. Difference in δ^{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
NAI	$+0.04\pm0.28$	+0.01
NA _D	-0.55 ± 0.16	-0.60
NA _B	-0.70 ± 0.13	-0.70
TAI	$+0.15 \pm 0.20$	+0.22
TA _D	-0.55 ± 0.24	-0.66
TA _B	-0.78 ± 0.21	-0.73
SOD	-0.44 ± 0.26	-0.52
TIP _D	-0.44 ± 0.20	-0.36

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

Parameter	Symbol	Value	Source
Modern seafloor area at	Ayna	$13.54 \times 10^6 \text{ km}^2$	(Fakins and Sharman
0 - 50 m	T NM	13.34 X 10 Km	(Lakins and Sharman, 2012)
Modern seafloor area at	Asm	$20.34 \text{ x } 10^6 \text{ km}^2$	(Eakins and Sharman,
0 - 100 m	5141		2012)
Modern seafloor area at	A _{IM}	$38.29 \text{ x } 10^6 \text{ km}^2$	(Eakins and Sharman,
100 - 2000 m			2012)
Modern rate of neritic	F _{BPICSM}	10 Tmol yr ⁻¹	(Kleypas, 1997)
carbonate burial			
Modern rate of marine POC	F _{BPOCSM}	5 Tmol yr ⁻¹	(Wallmann et al., 2011)
burial at 0 - 100 m			
Modern rate of marine POC	F _{BPOCIM}	5 Tmol yr ⁻¹	(Wallmann et al., 2011)
burial at 100 - 2000 m			
Modern rate of marine POC	F _{BPOCDM}	1.3 Tmol yr ⁻¹	(Wallmann et al., 2011)
burial at 2000 - 4000 m			
Modern rate of marine POC	F _{BPOCBM}	0.2 Tmol yr^{-1}	(Wallmann et al., 2011)
burial at >4000 m			
Modern POC export production	F _{EPOCM}	809 Tmol yr ⁻¹	(Sarmiento and Gruber, 2006)
Modern rate of marine P burial	F _{BPSM}	0.05 Tmol yr ⁻¹	(Wallmann, 2010)
at 0 - 100 m			
Modern rate of marine P burial	F _{BPIM}	$0.05 \text{ Tmol yr}^{-1}$	(Wallmann, 2010)
at 100 - 2000 m			
Modern rate of marine P burial	F _{BPDM}	$0.06 \text{ Tmol yr}^{-1}$	(Wallmann, 2010)
at 2000 - 4000 m			
Modern rate of marine P burial	F _{BPBM}	$0.02 \text{ Tmol yr}^{-1}$	(Wallmann, 2010)
at >4000 m			
Monod constant for P burial	k _P	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	BE _D	0.1	This work
POC at 2000 - 4000 m			
Burial efficiency of marine	BE _B	0.02	This work
POC at >4000 m			
Maximum POC to P ratio in	<u>r</u> <u>cpm</u>	<u>400</u>	(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)	$F_{\text{BDENi}} = \frac{F_{\text{BPOCi}}}{BE_{i}} \cdot (0.06 + 0.19 \cdot 0.99^{(\text{DO}_{i} - \text{DN}_{i})})$

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 μ 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 (derived from B/Ca ratios in foraminifera, LGM Holocene differences).

Box	Model	Data	Sites/References
AR _D	36	24 ± 10	60°N, 24°W, 2.4 km (Yu et al., 2008)
NA _D	23	18 ± 9	55°N, 20°W, 2.0 km (Yu et al., 2008)
		24 ± 10	60°N, 24°W, 2.4 km (Yu et al., 2008)
		4 ± 6	55°N, 21°W, 2.8 km (Yu et al., 2008)
		-18 ± 8	51°N, 22°W, 3.5 km (Yu et al., 2008)
		-19 ± 9	52°N, 22°W, 4.0 km (Yu et al., 2008)
NA _B	15	-19 ± 9	52°N, 22°W, 4.0 km (Yu et al., 2008)
TA _D	14	9 ± 10	4°S, 13°W, 2.9 km (Raitzsch et al., 2011)
TA _B	6	-17 ± 12	4°S, 16°W, 4.7 km (Raitzsch et al., 2011)
SOB	1	3 ± 2	41°S, 8°E, 5.0 km (Yu et al., 2014)
TIP _D	3	2 ± 3	0°S, 158°E, 2.3 km (Yu et al., 2010)
		-6 ± 4	0°S, 161°E, 3.4 km (Yu et al., 2010)
TIP _B	2	1 ± 4	1°S, 140°W, 4.3 km (Yu et al., 2013)
		5 ± 3	10°S, 52°E, 4.1 km (Yu et al., 2010)

5

- 6 Table C2. Effect of radiocarbon production rate on atmospheric and marine ¹⁴C 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	Δ^{14} C-CO ₂ (°/ ₀₀)	Δ^{14} C-DIC (°/ ₀₀)	$\Delta \Delta^{14}$ C-DIC ($^{0}/_{00}$)
$R_{14}(0)$	+0	-148	-148
$1.5 \ge R_{14}(0)$	+500	+278	-222
$2.0 \times R_{14}(0)$	+1000	+704	-296

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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)			
ARI	-206 to	-50	PS2644 (67°52.02'N, 21°45.92'W, 777 m, millennial-			
	-187	-220 to -270	scale oscillations?), (Sarnthein et al., 2013)			
NAs	-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)			
			(Sarnthein et al., 2014)			
NA_B	-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			
			$(41^{\circ}06^{\circ}S, 7^{\circ}48^{\circ}E, 4981 \text{ m})$ (Barker et al., 2010)			
TA _S	-128 to -	-130 to -95	ODP 1002 (10°42.37'N, 65°10.18'W, 893 m)			
	108		and southward extrapolated from			
			MD08-3180 (38°N, 31°13.45°W, 3064 m)			
	0.11	1.60	(Sarnthein et al., 2014)			
TAI	A_{I} -241 to -160 to -185 D		Dredged coral transects at Gregg, Manning, and Muir Sea			
	-218	-85	Mt. 33°–39°N, <2300 m, corr. according to (Robinson et			
	1.60	070 100	al., 2005)			
SO _S	-160 to	-270 to -190	MD07-3076 (44°09'S, 14°13'W, 3770 m)			
	-140	220 . 210	(Skinner et al., 2010)			
SOI	-228 to -	-220 to -210	Dredged coral transect Drake Passage, <1800 m			
	201	200 . 105	(Burke et al., 1982), + AWI unpubl. data under review			
SO_D	-332 to	-300 to -185	D0/-30/6 (44°09′S, 14°13′W, 37/0 m)			
	-296	500 . 500	ATL. SECTOR: (Skinner et al., 2010)			
		-600 to -500	Sonne core transect off New Zealand			
0.0	225.4	220 / 120	PAC. SECTOR: AWI unpubl. records, under review			
SO_B	-335 to -	-230 to -130	$1NU5/-21 (41^{\circ}U6^{\circ}S, 7^{\circ}48^{\circ}E, 4981 \text{ m})$			
TD	299	220 / 107	(Barker et al., 2010)			
$11P_S$	-139 to	-220 to -105	$[\text{WIDU1-25/8} (15^{\circ}\text{U8.25} \text{ S}, 121^{\circ}/\text{8.8}^{\circ}\text{E}, 1/83 \text{ m})]$			
TD	-120		(Sammein et al., 2014)			
IIP_{I}	-238 to	-264 to -61	$KU 2/-14 (18.5^{\circ}N, 5/.6^{\circ}E, 596 m)$			
	-211	-205 to -190	$ \begin{array}{c} KU \ 2/-25 \ (18.0^{\circ}\mathrm{N}, 5/.0^{\circ}\mathrm{E}, 820 \ \mathrm{m}) \\ (Dervor \ at \ al \ 2010) \end{array} $			
		220 4- 165	(Dryan et al., 2010)			
		-220 to -165	$MD01-25/8$ (15-08.25 S, $121^{\circ}/8.8^{\circ}$ E, $1/85^{\circ}$ m)			

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

			(Sarnthein et al., 2013)			
TIP _D	-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)			
NPB	-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. <u>LGM tracer</u> concentrations in model boxes <u>at 21 ka</u> in simulation STD <u>(see Tab.</u>

Box	Sal	PO_4	NO ₃	\mathbf{O}_2	DIC	TA	$\delta^{13}C$	$\Delta \Delta^{14} C$
	(PSU)	(µM)	(µM)	(µM)	(µM)	(µM)	(°/ ₀₀)	(°/ ₀₀)
AR _S	33.69	0.93	12.2	369	2244	2562	1.63	-181
NA _S	35.84	0.34	4.2	266	2158	2619	2.56	-156
TA _S	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 _I	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 _I	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
TIP _I	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 _D	35.54	1.45	19.4	282	2315	2587	0.96	-221
NA _D	35.59	1.70	22.5	251	2346	2593	0.69	-239
TA _D	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 _D	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 _B	35.54	1.48	19.7	280	2317	2587	0.94	-222
NA _B	35.65	2.04	26.4	222	2392	2607	0.32	-266
TA _B	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 _B	35.81	3.06	39.0	135	2565	2694	-0.74	-334
NP _B	35.79	3.11	40.0	118	2574	2698	-0.81	-353

4 <u>A1 and A2 for further information</u>)



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.



Figure 2. Set-up of the box model: The global ocean is separated into 24 boxes representing 2 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 8 boxes (seawater-atmosphere interface) indicate net freshwater fluxes (precipitation + river 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 sealevel and ocean bathymetry data (Eakins and Sharman, 2012); (h) Global rate of POC 10 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 CO₂. (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) δ^{13} C value of atmospheric CO₂. 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 δ^{13} C-CO₂ value is set to -6.4 $^{\circ}/_{\infty}$; (g) Δ^{14} C value of atmospheric CO₂, 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 Δ^{14} C-CO₂ is assumed to correspond to the pre-anthropogenic modern value (0 15 °/₀₀). 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 pCO₂, 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 CO₂ ($\Delta\Delta^{14}$ C-DIC 7 = Δ^{14} C-DIC - Δ^{14} C-CO₂); (e) Total alkalinity (TA); (f) Dissolved phosphorus (DP); (g) 8 Dissolved reactive nitrogen (DN); (h) Dissolved oxygen (DO). 9



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



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 5 al., 2014) are shown as open circles; (b) relative contribution of sea-level change (blue), nutrient utilization (red), and ocean circulation changes (black) to pCO₂ model results; the left 6 7 hand column shows contributions to the glacial pCO₂ 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 pCO₂ 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 the
following Ffigures 9 and 11 – are based on concentrations calculated in simulation STD for
each of the 24 ocean boxes (indicated as grid points).







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 $^{\circ}/_{00}$) and radiocarbon composition of dissolved inorganic carbon ($\Delta\Delta^{14}C$ -DIC in $^{\circ}/_{00}$) 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 $^{\circ}/_{00}$ for the pre- anthropogenic modern atmosphere, +446 $^{\circ}/_{00}$ 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 Δ ¹⁴C-CO₂; 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 CO₂. 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 Δ ¹⁴C-CO₂ 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 cm² s⁻¹); (d) 14 C production 10 rates calculated from the geo-magnetic record (Laj et al., 2002), ¹⁰Be production rate as 11 reconstructed from Greenland ice core data (Muscheler et al., 2005; Reimer et al., 2013),¹⁰Be 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 CO₂ ($\Delta\Delta^{14}$ 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 pCO₂ and its deglacial rise are supported by sea-level 5 change. The cycle is closed by atmospheric pCO₂ 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 9 and atmosphere circulation and dust deposition support the glacial pCO₂ draw-down and are largely responsible for the rapid deglacial rise in atmospheric pCO₂. The records of 10 atmospheric pCO₂ and eustatic sea-level change (diagrams in the upper left corner, (Monnin 11 et al., 2001; Petit et al., 1999; Monnin et al., 2004; Waelbroeck et al., 2002; Stanford et al., 12 2011) reflect the internal non-linear dynamics of the Earth system and its response to external 13 insolation forcing. 14

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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. δ^{13} C data at <2000 m water depth are excluded from the model-data comparison since they are affected by anthropogenic CO₂.



Fig. A2. Deglacial benthic – pelagic radiocarbon record in the North Pacific: Model (line)
versus data (squares). The Δ¹⁴C-DIC difference between deep water and surface water boxes
in the North Pacific is compared to data (Δ¹⁴C difference between benthic and pelagic
foraminifera, B-P Δ¹⁴C) 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.