Dear Professor Joos, dear referees,

Many thanks for the comments and constructive suggestions to improve this manuscript. We have tried to incorporate them into our revised version. Please, find details about the changes made in the responses below and the marked-up manuscript.

The author's response is presented as follows:

1. **Referee #1**: comments from referee #1 with author's response to each comment and summary of author's changes in the manuscript,
2. **Referee #2**: comments from referee #2 with author's response to each comment and summary of author's changes in the manuscript,
3. **Marked-up manuscript**: Author's changes tracked in the new manuscript

As our manuscript went through major revisions, we could often not list the specific changes in the manuscript in our response. We therefore refer to the new version of the manuscript to read the combined result of all changes we have made.

Sincerely, Anne Morée and co-authors

Referee #1

Comment 1)

Modelling study in the context of paleoproxy data: The motivation behind the study is to better understand variations in oceanic $\delta^{13}C$ as measured in foraminiferas. This is discussed in the context of the two site-specific studies: Charles et al., (2010) and Ziegler et al., (2013), comparing mid-depth (400m and 1500m) to deep $\delta^{13}C$ in the Southern Ocean as well as the global study of Oliver et al., (2010). But all the discussion stays very vague and qualitative with "increased/decreased" vertical gradients over "glacial/interglacial" timescales and mostly "globally averaged" for the numerical experiments. This induces some relatively vague conclusions such as in the abstract L. 17-18, or p12 L. 20-25. This is also true in section 3.4. In addition, in that section results of Charles et al. (2010) and Ziegler et al., (2013) are discussed in a bit more detailed but they are compared to the simulated mean vertical $\delta^{13}C$ gradient, which is defined as $\delta^{13}C$ surface $\delta^{13}C$ deep, where $\delta^{13}C$ surface and $\delta^{13}C$ deep respectively represent mean $\delta^{13}C$ for depths above and below 250m (please note that the "deep" ocean cannot be defined as the area below 250m depth). This is however different to Ziegler et al., who compare ~400m depth to the deep ocean (~3000m), and Charles et al., (2010) who compare cores at ~1200m and ~4600m. In general, wouldn't it make sense to show vertical profiles of globally average or basin average $\Delta\delta^{13}C$ ($\delta^{13}C$ at depth compared to $\delta^{13}C$ averaged over the first 250m)? Such a figure could replace Figure 4 and add a bit more information about the processes at play.

Author response to Comment 1)

Referee #1 kindly made us aware of the too generalized and qualitative discussion throughout the manuscript. We addressed this issue by 1) providing and discussing basin-averaged $\delta^{13}C$ profiles (new Figure 4 and S7), 2) redefining $\Delta\delta^{13}C$ (Section 2) and 3) extending our literature study. These adjustments especially changed section 3.3, 3.4 and 4 – which are now presented on both a global and a basin scale.

Author's changes in the manuscript in response to Comment 1)

- Addition of a new Figure 4 and S7 by basin-mean vertical profiles of $\delta^{13}C$ for the Southern Ocean, North Pacific, South Pacific, North Atlantic, South Atlantic and Indian ocean.
- Redefining $\Delta\delta^{13}C$ and updating the results accordingly (Section 2, and throughout manuscript)
- Updating discussion/abstract/conclusion to be more quantitative and specific and using the revised Figure 4 and S7 to discuss the sensitivity of $\Delta\delta^{13}C$ on a basin scale (throughout manuscript)

Comment 2)

Air sea gas exchange experiments: I find the results quite surprising. A pCO_2 increase and δ^{13}CO2 decrease for fast gas exchange make sense, but a pCO_2 increase for a slow gas exchange is surprising. There are no graphs shown for the slow gas exchange case, so it is hard to judge

Author response to Comment 2)

The authors agree with Referee #1 that the discussion of pCO_2 sensitivity to slow gas exchange rates is not explained enough in the current manuscript. As stated in the manuscript, 'pCO_2^{atm} is governed by the transient change in the net air-sea gas exchange flux Fnet, which occurs until a new equilibrium is established'. In order to explain the slow gas exchange experiment, we added carbon flux figures at 100 years (new Fig. S4), when the transient response determines the new equilibrium atmospheric pCO_2 (new Fig. S5). Here one can see that gas exchange is reduced as compared to the model control run for the 'Gas slow' experiment, and increased relative to the control for the 'Gas fast' experiment. Integrated globally, the net air-sea C flux is into the atmosphere during this transient phase for both experiments. In addition to presenting these new SI figures, we revised section 3.3.1 to better explain our results. Last, effects of slow gas exchange on marine $\delta^{13}C$ is now presented in new Fig. S6.

Author's changes in the manuscript in response to Comment 2)

- New figures on carbon fluxes during the transient phase (Fig. S4), atmospheric development during the experiments (Fig. S5) and effects of slow gas exchange on marine $\delta^{13}C$ (Fig. S6).
- Revised section 3.3.1

Comment 3)

POC sinking rate: P7, L.20-21: As POC sinking rate increases, the decrease in air-sea gas exchange is most likely due to a reduced advection/mixing of carbon rich waters into the mixed layer. P7, L.28 it is stated that marine $\delta^{13}C$ increases overall when POC sinking rates are high. Since $\delta^{13}C^{atm}$ increases under high POC sinking rates, it seems surprising that marine $\delta^{13}C$ would also overall increase. . . In fact, the limited negative $\delta^{13}C$ anomalies shown in Figure 5 are surprising. Is there a strong increase in organic carbon burial? Would it then make sense to show the transient changes? I am not sure about L. 33-34 p7: the difference in between the global change in POC and SO only change in POC export could only be due to difference in the area to which the forcing is applied, but might not be specific to SO. When applied globally, there is a significant impact on global export production as well as marine and atmospheric $\delta^{13}C$. The SO is a relatively small area of the ocean, so changes applied to that region only can be easily compensated. Results could be discussed with respect to previous experiments performed with the Bern3D and looking at the influence of the remineralization depth on atmospheric CO_2 and $\delta^{13}C$ (e.g. Roth et al., 2014 Earth system dynamics and Menviel et al., 2012, Quaternary Science Reviews).

Author response to Comment 3)

We thank Referee #1 for several detailed comments on our analysis of the POC sinking rate experiments. We revised section 3.3.2 to include a better literature review and improved explanation of the original P7, L.20-21, L.28 and L. 33-34 as requested. We also extended the model description in section 2, so that the POC sinking experiment is better described. In specific, for the original P7, L.20-21: The reduced air-sea gas exchange rate in response to high POC sinking rates is due to the almost complete export of surface ocean carbon to depth – thus not permitting escape to the atmosphere. Net upward advection/mixing of carbon and nutrients is thus reduced. For original P7, L.28: Both marine (+0.15 permil) and atmospheric $\delta^{13}C$ (+0.23 permil) increase because there is indeed a relatively higher loss of ^{12}C than ^{13}C (in POC) to the sediments in our experiment. The results presented are thus a transient response (new Fig. S5). We have added an additional 10 000 years to the POC fast experiment to show the effects of a continued experiment (new Fig. S5), but argue not to go beyond that due a.o. extremely long equilibration times (as stated in Roth (2014), $\delta^{13}C$ changes for over 200 000 years). The transient character of the experiment is now more clearly described in section 3.3.2. For original P7, L. 33-34: The relatively minor effect of the SO-only POC experiment is indeed compensated for outside of the SO, thank you for this improved explanation of our results.

Author's changes in the manuscript in response to Comment 3)

- Thorough revision of section 3.3.2 to include more literature and better explain the results
- Clarification of transient character of the POC sinking experiment due to sediment burial
- Extended model description in section 2

Comment 4)

Vmax: It is quite surprising that $\delta^{13}C^{atm}$ decreases when nutrient utilization increases.
P8, L. 27: I doubt the correct reason for the surface negative $\delta^{13}C$ anomaly is put forward. Maps of changes in export production and nutrients could be added to better understand the model response. If the nutrient advection to the surface of regions outside of SO is reduced, then so should be the advection of carbon rich - ^{13}C depleted waters. This is also consistent with the significant atmospheric CO_2 reduction, but the $\delta^{13}CO2$ is more surprising. The change in nutrient utilization in the Southern Ocean should be given, as well as control and perturbed surface nutrient content.

Author response to Comment 4)

While re-analysing the V_{max} experiment, we discovered a programming mistake in the setup of the experiment, which caused the non-SO maximum nutrient uptake rate to change as well. We therefore repeated the experiment, which changed the results. We therefore rewrote section 3.3.3 and adjusted the presented results of the V_{max} experiment throughout the manuscript. The effects on phosphate and oxygen concentrations are included in the text, atmospheric fluxes are presented in a new Figure S7 and the effects on POC export production as compared to the control are presented in new Figure S8.

Author's changes in the manuscript in response to Comment 4)

- New SI Figure S7 (equilibrium air-sea fluxes) and S8 (POC export production)
- Revised the whole of section 3.3.3 after the discovery of a mistake in the experiment setup

Comment 5)

Sea-ice: Legend of Figure S4 needs additional information

Author response to Comment 5)

The caption of the old Figure S4 was indeed incomplete. We added units and additional text on how the figure should be understood: the new Figure is S3.

Author's changes in the manuscript in response to Comment 5)

- Caption of Figure S4 (now Fig. S3) adjusted to 'The *p*CO_2 difference [ppm] between the surface ocean and the atmosphere for the model control run, based on an atmospheric value of 279 ppm. Negative values indicate a potential carbon flux into the ocean.'

Comment 6)

Hasted conclusions: The vertical gradient of $\delta^{13}C$ is stated to vary by no more than 0.5 permil. But it should be noted that this includes the full range of anomalies obtained: from much lower to much higher than the control state. For example, the maximum changes in vertical $\delta^{13}C$ gradient are obtained for Vmax (∼+0.2 permil) and a fast gas exchange (∼-0.25 permil), thus leading to ∼0.5 permil change. It would be more appropriate to say that the maximum variation of each parameter leads to a ∼0.25 permil change in vertical $\delta^{13}C$ gradient, as the pre-industrial control state is an interglacial state.
Section 3.4., p10: very broad statements are made with respect to the impact of changes in ocean circulation on $\delta^{13}C$ L. 17-18 and L. 20-27. These statements do not rely on any quantitative work on the impact of changes in ocean circulation on oceanic $\delta^{13}C$. The authors could for example consider looking at Menviel et al., 2015 (Global Biogeochemical Cycles) to have a better estimate of the impact of ocean circulation changes on $\delta^{13}C$. L. 21 to 23 are particularly unjustified because the rate of change of $\delta^{13}C$ resulting from both biogeochemical changes and oceanic circulation are not studied here.
L. 14-15, p 12: I don't think that the results shown here indicate that the changes in *p*CO_2 and $\delta^{13}C^{atm}$ are dependent on the location of the sea-ice edge, nor that sea-ice has a strong impact on atmospheric or oceanic $\delta^{13}C$.

Author response to Comment 6)

We addressed the issues raised in comment 6 by making the discussion (section 3.3 and 3.4) and conclusions (section 3.4 and 4) region-specific (new Figure 4 and S7) and by doing a more elaborate literature study throughout the manuscript. Note that the new definition of $\Delta\delta^{13}C$ causes all gradients to be stronger than in the previous version of the manuscript.

Author's changes in the manuscript in response to Comment 6)

- Effects of the sensitivity experiments on $\Delta\delta^{13}C$ are now described both globally and on a basin scale (sections 3.3, 3.4 and 4)
- Our literature study is extended to include more specific statements on the effects of ocean circulation on $\delta^{13}C$ and compare the basin-specific results to previous studies.

Comment minor points and typos)

Throughout the text, please write "biogeochemical" without parentheses. P2, L. 3: "Air-sea" P6- L.2, please rephrase P6, L. 29: Please remove "In the ocean," Figure 8: y axis of second plot should read "$p\mathrm{CO}_2$ (ppm)"

Author response to minor points and typos)

Our apologies for these mistakes, and thank you for pointing them out.

Author's changes in the manuscript in response to minor points and typos)

- We replaced (bio)geochemical with biogeochemical throughout the manuscript
- We replaced air-se with air-sea on original P2, L. 3
- We removed P6, L. 29 'In the ocean'
- We replaced the Figure 8 y-axis units with [ppm]

Referee #2

Comment 1 General comments

Anne L. Morée and co-authors use the HAMburg Ocean Carbon Cycle Model in its configuration for long-term simulations, HAMOCC2s (Heinze and Maier-Reimer, 1999). The authors report the results of four sensitivity experiments (actually four plus two, as two out of the four are run in duplicate, once for the global ocean and once for the Southern Ocean) to analyse (1) the effect of variations of the air-sea exchange parameters, (2) the sequestration efficiency of the organic pump via changed particulate organic carbon (POC) sinking rates, (3) the sequestration efficiency of the organic pump via increased nutrient utilisation efficiency, (4) changing sea-ice cover on atmospheric $p\mathrm{CO}_2$, δ^{13}C of atmospheric CO_2 and δ^{13}C in the ocean, and more specifically on the global mean vertical gradient of δ^{13}C in dissolved inorganic carbon (DIC), quantified as the difference between DIC δ^{13}C in the surface and the deep ocean, denoted $\Delta\delta^{13}$C . Upon reading the abstract of this paper I got really excited. Carbon isotopes are a particularly useful tool for studying carbon cycling between the different spheres that make it up. They have been used for a long time for this purpose, but over the past years a wealth of new data have been published and more and more comprehensive global data compilations have become available. The time is thus ready to re-assess the different mechanisms with a model that offers an excellent balance between the comprehensiveness of the processes taken into account and their complexity and execution time, so that meaningful simulation experiments can be carried out for time scales of tens to hundreds of millennia.

The manuscript itself, however, did unfortunately not meet my expectations, far from. The language used, albeit generally fluent, seriously lacks precision and is rather colloquial. As an example, we repeatedly read that δ^{13}C is depleted or enriched. It is of course DIC that is depleted or enriched in ^{13}C. A relative deviation — such as δ^{13}C — cannot be enriched or depleted; it can be high(er), greater or low(er), decreased or increased. The literature review is very poor; the same holds for comparison of the results obtained here to those of previous studies. Many important previous studies that called upon carbon isotopes for the study of glacial-interglacial carbon cycle changes are not cited (see below for details). $\Delta\delta^{13}$C , the proxy that is central to the paper really ought to be introduced with a more solid background. It was probably first used by Broecker (1982), at the very beginning of the "gold rush" time of the glacial-interglacial atmospheric CO_2 problem studies (1980s). It was then used as a proxy for glacial-interglacial pCO_2 variations, later fell out of favour, but has resurfaced over the past few years. One thing that would be important to emphasize here is, that it evolved in time: during those early stages, $\Delta\delta^{13}C$ stood for the difference between $\delta^{13}C$ in the deep and the surface ocean DIC. In the recent studies (e.g., Ziegler et al. (2013)), it now most often stands for the difference between $\delta^{13}C$ of DIC in the deep sea and intermediate-depth (typically 400 m). The model description is incomplete. The processes that are relevant for the study are not described at all, only a reference to a previous paper is given. The experimental design leaves quite a number of questions open: the duration of the simulation experiments is only 2000 years. The separation between surface and deep ocean waters is questionable and as it obviously has an important influence on the results, the side-effects of this choice should have been discussed. Not all of the figures are reader-friendly: on Figure 5, e.g., readers are expected to visually extract $\Delta\delta^{13}C$ from latitude-depth transects of $\delta^{13}C$ by first averaging the topmost 250 m, then the depths below and to subtract both averages from each other. As a consequence, I cannot recommend this manuscript for publication in Biogeosciences at this stage. It should nevertheless be possible to reconsider it after a major revision and I strongly encourage the authors to prepare a version that remedies to all the shortcomings mentioned here. Please provide us with a better description of what is done, how it is done and why it is done that way. The study deals with an interesting and timely subject. The biogeochemical model at hand perfectly fits the needs. Please take full advantage of the possibilities it offers!

Author’s response to Comment 1

Thank you for your detailed and thorough review of our manuscript. We appreciate the effort you have made to improve it: See below for a detailed reply to your comments. Regarding the points you only make in Comment 1, we hope you will see that we improved the precision of the language in general. We also replaced the use of enriched/depleted when referring to $\delta^{13}C$ with increased/decreased or higher/lower throughout the manuscript. We also extended the introduction to include a paragraph on the development of $\Delta\delta^{13}C$ research.

Author’s changes in the manuscript in response to Comment 1

- Adjusted the mention of ‘four sensitivity experiments’ to ‘a set of sensitivity experiments’
- Replaced enriched/depleted when referring to $\delta^{13}C$ with increased/decreased or higher/lower throughout the manuscript.
- Language is improved throughout the manuscript to be more specific and quantitative.
- Add information on the development of $\Delta\delta^{13}C$ research in the introduction, based on a selection of the papers mentioned in Comment 2.1.

Comment 2.1 Literature

Since the $\Delta\delta^{13}C$ proxy has been in usage for more than 35 years, there is a wealth of studies that are available. They range from data-oriented studies to model-based studies, covering very similar approaches as done here. Only very few of them are cited in the manuscript and it is not entirely clear for what reasons they are included and others are excluded. There are more than 20 papers that come to my mind right away in this framework and that have not been considered in the literature review and the discussion of this paper
[... literature list provided by Referee #2 ...]

Please do not get me wrong: I do not expect all of these papers to be cited. However, even this "out-of-the-mind" list is simply so long (and still far from exhaustive) that it is incomprehensible that none of these studies has been cited or taken into account for the purpose of discussing the results.

Author's response to Comment 2.1

We have included most of the references listed by Referee #2, as well as some others, in our revised manuscript (mainly affection Sections 1, 3.3, 3.4, 3.5 and 4). The reference list is updated accordingly at the end of the revised manuscript. We feel that this greatly improved our manuscript as we could now provide the reader with both a better comparison to previous studies and with an improved explanation of our results. We thus thank Referee #2 for pointing us to these studies.

Author's changes in the manuscript in response to Comment 2.1

- Extension of the literature review by about 20 previous studies on this or related topics. These references are mainly included in the discussion of our results (Sections 3.3-3.5).

Comment 2.2.1 Model description is insufficient

The model description given in the paper neither allows to reproduce the results reported here without a lot of guesswork, nor does it allow to fully understand the results. The provided description is in some instances even confusing: on page 3 (lines 13–14), we read that "POC is carried as a tracer as well as transported downwards according to an exponential penetration depth and constant settling velocity, [. . .]". The exponential penetration profile and the constant settling velocity are of course not independent of each other. In the original technical reference to HAMOCC2s (Heinze and MaierReimer, 1999) – not cited in the manuscript – we read that "The vertical flux of biogenic particulate matter is parametrised through exponential redistribution profiles which implicitly include both sinking velocity and re-dissolution rate." This is not the same! It is quite easy to establish that the characteristic length scale in the exponential profile is equal to ω/k, if the (constant) settling velocity is denoted ω and POC respiration is assumed to follow first order kinetics with a rate constant k. Since one of the experiments involves changes of the settling velocity, the adopted parametrisations must be correctly described.

Author's response to Comment 2.2.1

We corrected the model description in Section 2 to include a better explanation of the POC sinking parameterisation, as well as the setup of all sensitivity experiments. Next to the description in the main text, we provide the reader with the model details on POC production and sinking in SI 1A.

Author's changes in the manuscript in response to Comment 2.2.1

- Model description improved in Section 2 as well as details added in SI 1A
- Sensitivity experiment description extended in Section 2

Comment 2.2.2 Model spin-up procedure

The description of the model spin-up procedure lacks important details. We only read that "[. . .] a fixed weathering input is used to tune the ocean inventories to values comparable to the observations." (page 3, line 24). On the basis of what quantitative constraints is this weathering flux determined? Are there separate fluxes

- for nutrients (phosphate)? – which would be necessary if organic matter is buried in the sediment together with the nutrients they lock up
- for DIC and alkalinity? – which would have to be separated if organic matter and carbonate are buried in the sediment
- for dissolved silica? – opal is also included in the model
- for ^{13}C? – what is the δ^{13}C signature of the DIC flux?

A decent model description would have answered half of the questions already. . . To what extent are the mismatches in the deep-ocean δ^{13}C and PO4 concentration resulting from this spin-up? I would expect that they go together with global ^{13}C and PO4 inventory mismatches as well, which, according to the description given here, are constraints.

Author's response to Comment 2.2.2

We improved the model description to include more detail, including the equilibration of the model. As now described in the revised Section 2, the 'best-fit' weathering value for ^{13}C was found by running the model with a restored (to a value of -6.5 ‰) atmospheric δ^{13}C until the burial rate reached equilibrium with weathering (after ~110000 model years). After that, we permitted free development of atmospheric δ^{13}C . In this way, the ocean inventories remained close to observed, while permitting free atmospheric change of δ^{13}C and $p\text{CO}_2^{\text{atm}}$. Weathering fluxes are added homogeneously over the first ocean layer as dissolved matter in a fixed stoichiometric ratio for C, O_2, Alkalinity, $PO^{4}{}_{3-}$ and Si. The ^{13}C/^{12}C ratio in the weathering flux would be equivalent to a δ^{13}C of DIC of 14 ‰.

Author's changes in the manuscript in response to Comment 2.2.2

- We extended the explanation of the spinup procedure in Section 2 regarding burial/weathering to include tracers, stoichiometry, and more details.

Comment 2.2.3 Sensitivity experiment duration

The quality of the spin-up experiment is well quantified (residual drifts etc.). Unfortunately, nothing similar is reported for the sensitivity experiments. Readers are only told that these have been run for 2000 yr with the steady-state control run as initial condition. The strength of the model design for allowing long-term simulation experiments is initially emphasized (page 3, lines 10–11), a 110 000 yr spin-up run is carried out, and then the core experiments for the paper are run over a comparatively short duration of 2000 years only. For some of the perturbations (e.g., POC penetration depth changes. . .), the model carbon cycle is still in the transient phase 2000 years after the onset of the perturbation. The choice of such short simulation experiments is thus rather incomprehensible.

Author's response to Comment 2.2.3

The length of the sensitivity experiments is chosen to be 2000 years, as we observe all experiments except for those on the POC sinking rate to show very little change in atmospheric carbon signature after this time (now also presented to the readers in new Fig. S5): Equilibrium is often already reached within the first ~800 years. We agree that the effects of changing the biological pump (i.e., the POC and Vmax experiments) are still ongoing after 2000 years. To reach full isotopic equilibrium in the ocean however, over 200 000 model years of runtime could be needed (Roth (2014), see adjustments made to Page 7, lines 16-17). In an open system, the sediment loss of nutrients and carbon over time will empty the whole ocean of nutrients, which would not give very meaningful results. Besides that, over 200 000 years other feedback processes would happen as well in reality. To show the continued effect of a change in the biological pump efficiency, we provided the reader with atmospheric development results of an extra 10 000 years for the fast POC sinking rate experiment in new Figure S5. From this, we observe atmospheric development of $\delta^{13}C$ indeed going beyond 12000 years, after which we stopped the experiment (Fig. S5). We summarize this result by stressing in the manuscript that the results of the POC sinking rate experiments are transient results (Sections 2 and 3.3.2).

Author's changes in the manuscript in response to Comment 2.2.3

- Provide the reader with the atmospheric development per sensitivity experiment of pCO_2 and $\delta^{13}C$ in new Fig. S5, with an additional 10000 years for the 'POC fast' experiment
- Clarify in sections 2 and 3.3.2 that there are still ongoing changes in the model

Comment 2.3.1 Up- and downward fluxes, equilibrium $\delta^{13}C$

Up- and downward fluxes, equilibrium $\delta^{13}C$ Analysis of the results involves up- and downward fluxes Fup and Fdown: how are these obtained? To my best knowledge, it is only the net exchange flux Fnet which is proportional to the pCO_2 difference between the surface water and the overlying atmosphere that can be calculated. The equilibrium $\delta^{13}C$ (δ 13Ceq, first mentioned on page 7 at line 1) is not defined and an explanation how this is calculated is missing as well.

Author's response to Comment 2.3.1

In the model, separate fluxes Fup and Fdown are calculated by splitting the gas transfer formulation into two parts. A paragraph on this is added to the SI (Section SI 1B) in order to explain this in detail. For clarification of the use of $\delta^{13}C$ diseq and $\delta^{13}C$ eq, we add definitions in Section 3.3.1. $\delta^{13}C$ diseq = $\delta^{13}C$ - $\delta^{13}C$ eq, where $\delta^{13}C$ eq represents the $\delta^{13}C$ signature a water parcel would have had if it would have fully equilibrated with the atmosphere. Not that $\delta^{13}C$ eq is not calculated, but the Gas Fast experiment provides insight into where the surface ocean is over or undersaturated with respect to $\delta^{13}C^{atm}$. We also included several new references to improve our explanation and reasoning.

Author's changes in the manuscript in response to Comment 2.3.1

- SI 1B describes Fup and Fdown
- Definition provided of $\delta^{13}C$ diseq and $\delta^{13}C$ eq in section 3.3.1

Comment 2.3.2 Separation between surface and deep realms

In this study, the ocean is simply partitioned into a surface part, which encompasses the water masses above a 250 m depth horizon, and a deep part for the rest. No justification or explanation regarding this choice are given. First of all, it is a choice that leads to complications. Information gathered from previous publications based up HAMOCC2s (Heinze et al., 1999, 2016) indicates that the eleven-layer configuration has no layer interface at 250 m depth, but a layer centred on 250 m depth. A more natural separation would be located at layer boundaries. Secondly, this choice is critical as it controls the results of the study to a large extent extent. At 250 m depth, the depth profile of DIC $\delta^{13}C$ is generally rapidly decreasing (see e.g., Kroopnick (1985), but this should also be visible from the model results). Accordingly, the average surface ocean $\delta^{13}C$ will be strongly biased towards lower values and the deep ocean slightly towards higher values. As a consequence, the amplitude of the vertical gradient, $|\Delta\delta^{13}C|$, is thus systematically underestimated. I think that surface ocean $\delta^{13}C$ would more conveniently be taken from the surface layer down to 50 or 112.5 m depth (these are layer boundary depths in the 11-layer HAMOCC2s configuration, or even regionally variable in case information on the local mixed-layer depth would be available), and the deep ocean from the 1500 or the 2500 m depth horizons down to the sea floor. In any case care must be taken in the model-data comparison to make sure that surface-to-deep model gradients are compared to surface-to-deep data gradients and not to intermediate-to-deep data gradients.

Author's response to Comment 2.3.2

We see the potential problem with choosing the surface ocean as above 250 m depth and the deep ocean as below 250 m depth. We adjusted the definitions to better fit the model design and to prevent the strong surface ocean δ^{13}C gradient to influence the averaging too much. In order to do so, we define the model photic layer (top 50 meter) as the 'surface ocean', because this is where biological production and fractionation during air-sea gas will mostly increase δ^{13}C . We define 'the deep ocean' as the lowest model layer above the sea floor (if this over 3 km depth), as this is were benthic foraminifera will dwell and this ocean volume will be least influenced by the strong gradient in the vertical δ^{13}C profiles (which could influence $\Delta\delta^{13}$C). As Referee #2 mentions, this increases our estimate of $\Delta\delta^{13}$C everywhere; however, it did not change our conclusions. We realise that due to the different definitions used for $\Delta\delta^{13}$C over the past decades/in different studies, no definition chosen by us will make direct comparison with a previous study possible. We feel however that by providing basin-averaged vertical gradients of δ^{13}C , the reader could deduce their gradient of interest, or directly use the $\Delta\delta^{13}$C we report.

Author's changes in the manuscript in response to Comment 2.3.2

- Adjust $\Delta\delta^{13}$C definition to include the surface ocean as the ocean above 50 m depth/the photic zone and the deep ocean to be the lowermost wet layer in the ocean, if above 3 km depth.
- All reported $\Delta\delta^{13}$C values changed to fit the new definition of $\Delta\delta^{13}$C

Comment 2.3.3 Regionalization

$\Delta\delta^{13}$C results are only shown in the global mean. The three-dimensional HAMOCC2s should allow for a finer analysis than that. In the text, regional $\Delta\delta^{13}$C outcomes are sometimes mentioned, but it would be useful to have these results reported graphically as well, at least for basins or sub-basins (e.g., North Atlantic, South Atlantic, North Pacific, South Pacific, Southern Ocean). Figure 4 could be easily adapted to show such more regionalized values in a useful and expressive way.

Author's response to Comment 2.3.3

A less generalized and more basin-specific discussion of the results is made throughout the manuscript in response to comment 2.3.3. The main improvement lies in the presentation and discussion of the new Figure 4 and S7, which presents basin-average δ^{13}C gradients in response to the sensitivity experiments. In combination with the extended literature review, this made the whole manuscript more region-specific as also requested in the general comment 1 of Referee #2.

Author's changes in the manuscript in response to Comment 2.3.3

- New Figure 4 and S7 show basin-mean δ^{13}C profiles per sensitivity experiment for the North Atlantic, South Atlantic, North Pacific, South Pacific, Southern Ocean and Indian Ocean, with the value for $\Delta\delta^{13}$C stated besides the profile. Part of this plot is put in the SI (new Figure S9),

in order to not overwhelm the reader and focus on the most significant results. The $\Delta\delta^{13}C$ value reported here is based on the new $\Delta\delta^{13}C$ definition.
- Adjust the results, discussion and conclusion sections to use and describe the new Figure 4 and S7.

Comment 2.4 Discussion shortcomings

Parts of the discussion are rather confusing. Section 3.4 is one of them. On one hand, we read that "The idealised and large perturbations [. . .] show that mean $\Delta\delta^{13}C$ varies no more than 0.5‰" on the other hand that "[the] reconstructed intra-millennial variability in $\Delta\delta^{13}C$ could be driven more by changes in the biogeochemical state than by changes in ocean circulation because (bio)geochemical changes might occur more rapidly than whole-ocean circulation changes." Are large and whole-ocean changes in the biogeochemical state of the ocean really that more realistic on the time scales of a few millennia than circulation changes? At the latest from page 10, lines 29–30 on it is not clear any more which conclusions to draw from this study. Readers that have come this far will have seen the discussion revolve around SO $\Delta\delta^{13}C$ in several instances, to learn now that, except for the North Atlantic, "data are too sparse to get a coherent picture of $\Delta\delta^{13}C$ variations". Previously we have been shown that in the North Atlantic the deep-sea $\delta^{13}C$ is mainly controlled by the air-sea exchange $\delta^{13}C$.

Author's response to Comment 2.4

We clarified the discussion by putting it in a broader context (extended literature study, see comment 2.1) and by discussing results on a basin scale as described in our response to the comments above.

Author's changes in the manuscript in response to Comment 2.4

- Incorporation in the discussion of additional literature (see comment 2.1)
- Discussing the results on a basin scale (new Figure 4 and S7, and Sections 3.3-4)

Comment 3 Technical comments

Page 1, lines 3 and 27–28: "The standardised ^{13}C isotope, δ ^{13}C, [. . .]": I have never seen this denomination in the peer-reviewed literature before. $\delta^{13}C$ expresses the molar $^{13}C/^{12}C$ ratio of a sample in terms of its relative deviation from the ratio in a standard (initially PDB, now VPDB), generally expressed in permille. The references provided for this "standardised ^{13}C isotope" are incomprehensible: Stenström et al. (2011) is a non peer-reviewed internal university report, Stuiver and Polach (1977) deals with radiocarbon. It should be straightforward to find an appropriate textbook reference for δ ^{13}C.

Page 2, line 3: "air-se" should read "air-sea" Page 2, line 6: "10s" should be written out as "tens"

Page 2, line 24: the study by Shackleton and Pisias (1985) absolutely needs to be cited here alongside Charles et al. (2010) and Oliver et al. (2010).

Page 3, line 17: should "HAMOCC2" not read "HAMOCC2s"?

Page 3, line 23: should "HAMOCC2" not read "HAMOCC2s" again?

Page 4, line 23: "Eide (2017)": 2017a or 2017b?

Page 4, line 23: on the basis of the provided mean values, the intercept of the δ ^{13}C:PO4 relationship is 3.27733, which would normally be rounded to 3.3, not to 3.4. Please check the numbers.

Page 5, line 12: "The modelled global POC production is [. . .]": I guess this is the new or the export production – please clarify!

Page 5, lines 26–27: “[. . .] with the exception of the Arctic Ocean where no POC production is modelled due to the sea ice cover [. . .]”: elsewhere in the paper we read that the sea-ice cover also isolates the surface ocean with respect to air-sea exchange. Does the partitioning into δ^{13}C perc bio and δ^{13}C percatm make sense in ice-covered regions?

Page 6, line 4: “change more than” should read “change by more than”

Page 6, line 9: “[. . .] due to the fact that ^{12}C needs to speciate [. . .]”: this does not make sense. ^{12}C can only equilibrate at the same time as ^{13}C – there are only the two of them. ^{12}C should probably be corrected to DIC or CO_2 (aq).

Page 6, line 19: “[. . .] 22% of the global ocean area [. . .]”: does this include the ice-covered parts of the SO? – please specify

Page 6, line 21: “Fu” should read “Fup”

Page 6, line 22: “Fd” should read “Fdown”

Page 6, line 30: “[. . .] lowers the surface ocean δ^{13}C −0.2 to −0.9 ‰ in the lower latitudes [. . .]” should read “[. . .] lowers the surface ocean δ^{13}C by −0.2 to −0.9 ‰ at the lower latitudes [. . .]”

Page 6, line 31: “in high latitudes” should read “at high latitudes”

Page 6, line 31–32: “These results indicate the sign of the thermodynamic δ^{13}C disequilibrium between surface ocean and atmosphere.” – this sentence does not make sense, please reformulate.

Page 7, line 7: please add the ‰ sign to the 0.65 and the 1.00

Page 7, lines 16–17: “A more efficient biological pump [. . .] leads to a loss of carbon to the sediments, which dominates the effects on pCOatm 2 and $\delta^{13}C^{atm}$.”: after 2000 years of simulation these effects have certainly not yet developed to their full strength.

Page 7, lines 24–25: “remineralisation horizon”: a horizon depicts, in my understanding, a surface or a narrow zone, such as the calcite saturation horizon. I am not aware of the existence of a POC remineralisation horizon (and not even a carbonate remineralization horizon). Please rewrite.

Page 7, lines 29–30: “When reducing the biological pump efficiency both remineralisation and POC production are confined to the surface ocean.”: as far as I know HAMOCC2s, the POC production is always confined to the surface and the remineralisation is taking place in subsurface intermediate and greater depths. Would “With a lower POC sinking rate, the remineralisation is confined to shallower depths.” not be more correct?

Page 8, lines 5–9: Figure 5 which is referred to here, depicts δ^{13}C and DIC anomalies with respect to the control run. Having readers derive information about $\Delta\delta^{13}$C from that figure is really asking too much. Why not provide the latitudinal evolution of the $\Delta\delta^{13}$C alongside? This would be a straightforward line plot.

Page 9, section 3.3.4: I would expect that such large ice-cover changes would also lead to circulation changes. A comment on this would be of order, wouldn’t it?

Page 9, line 25: δ^{13}C eq: see above

Page 10, lines 23–24: “Analysis of SO $\Delta\delta^{13}$C reconstructions from sediment cores at 42◦S and 46◦S (Charles et al., 2010) shows that there is a strong correlation between these cores and Northern Hemisphere $\Delta\delta^{13}$C variations.” This is not correct. Charles et al. (2010) show that there is a tight correlation between SO $\Delta\delta^{13}$C and “Northern Hemisphere climate fluctuations”; their paper does not even mention any $\Delta\delta^{13}$C record outside the SO.

Figures: if $\Delta\delta^{13}$C informations are to be read from a figure, this latter should then also show $\Delta\delta^{13}$C.

Page 24, Figure 8b: units for $p\mathrm{CO}_2$ on the vertical axis should be ppm or µatm on the vertical axis, not ‰.

Author response to Comment 3

We apologise for the mistakes/lacking information at the points you have listed. We clarified and correct the manuscript accordingly. Because of the major revision of the paper, some sentences may have been totally rephrased or replaced. See below for details.

Author’s changes in the manuscript in response to Comment 3

Page 1, lines 3 and 27–28: Replaced
‘The vertical marine δ^{13}C gradient is the surface-to-deep difference in δ^{13}C , the standardised ^{13}C isotope (Stenström et al., 2011; Stuiver and Pollack, 1977). ^{13}C is slightly heavier than the ^{12}C isotope, which causes a fractionation effect during air-sea gas exchange and biogenic carbon uptake during photosynthesis (Laws et al., 1997; Mackenzie and Lerman, 2006; Zhang et al., 1995).’
By
‘The vertical marine δ^{13}C gradient ($\Delta\delta^{13}$C) is the surface-to-deep difference in δ^{13}C , the standardised ^{13}C/^{12}C ratio expressed in permil (Eq. 1 and 2) (Zeebe and Wolf-Gladrow, 2001). ^{13}C is slightly heavier than the ^{12}C isotope which causes a fractionation effect during air-sea gas exchange and photosynthesis, thereby changing δ^{13}C and $\Delta\delta^{13}$C (Laws et al., 1997; Mackenzie and Lerman, 2006; Zhang et al., 1995)’

$$\delta^{13}\mathrm{C} = \left(\frac{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{\mathrm{sample}}}{\left(\frac{^{13}\mathrm{C}}{^{12}\mathrm{C}}\right)_{\mathrm{standard}}} - 1 \right) * 1000\ {}^{o}\!/_{oo}$$, (Eq. 1)

where we used the PDB (^{13}C/^{12}C)standard (0.0112372).

Page 2, line 3: Corrected as suggested

Page 2, line 6: Corrected as suggested

Page 2, line 24: Added reference to Shackleton and Pisias (1985)

Page 3, line 17: Corrected to HAMOCC2s

Page 3, line 23: Corrected to HAMOCC2s

Page 4, line 23: This should be 2017b, corrected accordingly

Page 4, line 23: Original lines 18-19 are meant here, this should indeed be 3.3 - corrected

Page 5, line 12: Corrected to “The modelled global export POC production is [. . .]”

Page 5, lines 26–27: Partitioning in air-sea gas exchange and biological components does mean something in ice-covered regions, as the upstream signal will be visible in such regions, and if the water mass transports POC, the biological-remineralisation signal can increase with water mass age under the ice as well.

Page 6, line 4: Corrected as suggested

Page 6, line 9: Corrected as suggested
‘This difference in equilibration time is due to the fact that ^{12}C needs to speciate into all marine carbon species to reach equilibrium (~20x slower than O_2), after which 13 10 C needs to go through full isotopic exchange between all carbon species to reach equilibrium (~10x slower than ^{12}C) (Jones et al., 2014; Galbraith et al., 2015).’
to
‘This difference in equilibration time is due to the fact that DIC needs to speciate into all marine carbon species to reach equilibrium (~20x slower than O_2), while ^{13}C needs to go through full isotopic exchange between all carbon species to reach equilibrium (~10x slower than DIC) (Jones et al., 2014; Galbraith et al., 2015; Broecker and Peng, 1974).’

Page 6, line 19: “[. . .] 22% of the global ocean area [. . .]” corrected to “[. . .] 22% of the global ice-free ocean area [. . .]”

Page 6, line 21: Corrected as suggested

Page 6, line 22: Corrected as suggested
Page 6, line 30: Corrected as suggested
Page 6, line 31: Corrected as suggested
Page 6, line 31–32: “These results indicate the sign of the thermodynamic $\delta^{13}C$ disequilibrium between surface ocean and atmosphere.” adjusted to “These results show whether the thermodynamic $\delta^{13}C$ disequilibrium $\delta^{13}C$ diseq is positive or negative.”
For clarification of the use of $\delta^{13}C$ diseq and $\delta^{13}C$ eq, we added definitions in section 3.3.1.
Page 7, line 7: Corrected as suggested
Page 7, lines 16–17: The authors agree that these effects have not yet developed to their full strength, and adjusted the sentence (first paragraph Section 3.3.2) to ‘A more efficient biological pump (here, a higher POC sinking rate) leads to a loss of carbon to the sediments, which affects $p\mathrm{CO}_2^{\mathrm{atm}}$ and $\delta^{13}C^{\mathrm{atm}}$ long-term. The results presented here are therefore 2000-year transient results because full equilibrium of marine $\delta^{13}C$ could take over 200 000 years (Roth et al. 2014). We observe atmospheric development of $\delta^{13}C$ beyond 12000 years, after which we stopped the experiment (Fig. S5). An even longer experiment duration would no longer be meaningful as the open system loses carbon and nutrients to the ocean sediments and in reality, other processes and feedbacks would occur on such timescales (Tschumi et al., 2011).’
Page 7, lines 24–25: “remineralisation horizon” replaced by ‘POC remineralisation’
Page 7, lines 29–30: We rephrase this sentence to “With a lower POC sinking rate, the remineralisation is confined to the surface ocean.”
Page 8, lines 5–9: We addressed the issue with the visualisation of $\Delta\delta^{13}C$ by presenting basin-specific $\delta^{13}C$ profiles in an new Figure 4 (see also comment 1 to Referee #1), with a basin-average $\Delta\delta^{13}C$ noted next to each profile. Referral to that new figure instead of Figure 5 should provide the reader with enough information to understand the effects of the sensitivity experiment on $\Delta\delta^{13}C$.
Page 9, section 3.3.4: We added a sentence here to state that ‘Ocean circulation changes that could result from a changed sea ice cover are not taken into account, as we want to study the potential isolated effect of sea ice on biological production and air-sea gas exchange.’
Page 9, line 25: See response to Page 6, line 31–32
Page 10, lines 23–24: In discussing our results in view of more literature, we also corrected the comparison and discussion with Charles et al. (2010) their results (major revision of Section 3.4).
Figures: When referring to a figure when discussing or presenting $\Delta\delta^{13}C$, we now refer to the basin-specific $\delta^{13}C$ profiles that are presented in a new Figure 4, and include a value for $\Delta\delta^{13}C$ for each basin. The $\Delta\delta^{13}C$ value is based on the new $\Delta\delta^{13}C$ definition.
Page 24, Figure 8b: Corrected to ppm

Marked-up manuscript

Southern Ocean controls of the vertical marine δ^{13}C gradient – a modelling study

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Abstract. ~~The standardised ^{13}C isotope,~~ δ^{13}C, the standardised ^{13}C/^{12}C ratio expressed in permil,~~,~~ is a widely used ocean tracer to study changes in ocean circulation, water mass ventilation, atmospheric pCO$_2$ and the biological carbon pump on timescales ranging from decades to tens~~10s~~ of millions of years. δ^{13}C data derived from ocean sediment core analysis provide information on δ^{13}C of dissolved inorganic carbon and the vertical δ^{13}C gradient (i.e., $\Delta\delta^{13}$C) in past oceans. In order to correctly interpret δ^{13}C and $\Delta\delta^{13}$C variations, a good understanding is needed of the influence from ocean circulation, air-sea gas exchange and biological productivity on these variations. The Southern Ocean is a key region for these processes, and we show here that ~~global mean~~ $\Delta\delta^{13}$C in all ocean basins is sensitive to changes in the biogeochemical state of the Southern Ocean. We conduct ~~four~~ a set of idealised sensitivity experiments with the ocean biogeochemistry general circulation model HAMOCC2s to explore the effect of biogeochemical state changes of the ~~(~~Southern and Global~~)~~ Ocean~~s~~ on atmospheric δ^{13}C, pCO$_2$, and marine δ^{13}C and $\Delta\delta^{13}$C. The experiments cover changes in air-sea gas exchange rates, particulate organic carbon sinking rates, sea ice cover, and nutrient uptake efficiency - in an unchanged ocean circulation field. We conclude that the maximum variation of mean marine $\Delta\delta^{13}$C in response to ~~(bio)~~biogeochemical change is ~±0.4~~5~~ ‰.~~,~~ However, the amplitude of this sensitivity can be higher at smaller scales, as seen from a maximum sensitivity of ~-0.6 ‰ on ocean basin scale. ~~which is about half of the reconstructed variation in $\Delta\delta^{13}$C over glacial-interglacial timescales~~This local $\Delta\delta^{13}$C sensitivity depends on local prior thermodynamic disequilibrium and the sensitivity of local POC export production to biogeochemical change. ~~. Locally, $\Delta\delta^{13}$C variations can surpass or even mirror the mean effects on $\Delta\delta^{13}$C due to the spatial variation in the sensitivity of δ^{13}C to biogeochemical change. The (bio)geochemical environment of a sediment core thus needs to be well constrained in order to be able to interpret reconstructed $\Delta\delta^{13}$C variations in such a core. The sensitivity of $\Delta\delta^{13}$C varies spatially depending on the contribution of air-sea gas exchange versus biological export productivity to the local δ^{13}C signature.~~ Interestingly, the direction of both glacial (intensification of $\Delta\delta^{13}$C) and interglacial (weakening of $\Delta\delta^{13}$C) $\Delta\delta^{13}$C change matches biogeochemical processes associated with these periods. This supports the idea that biogeochemistry likely explains part of the reconstructed variations in $\Delta\delta^{13}$C, ~~and not only~~in addition to changes in ocean circulation.

1 Introduction

The vertical marine δ^{13}C gradient ($\Delta\delta^{13}$C) is the surface-to-deep difference in δ^{13}C of dissolved inorganic carbon (DIC), where the standardised ^{13}C/^{12}C ratio (δ^{13}C) is expressed in permil (Zeebe and Wolf-Gladrow, 2001):

$$\delta^{13}\mathrm{C} = \left(\frac{^{13}C/^{12}C}{(^{13}C/^{12}C)_{standard}} - 1\right) * 1000\ \text{‰}. \qquad (1)$$

Here, ^{13}C/^{12}C$_{standard}$ is the Pee Dee Belemnite standard (0.0112372). ^{13}C is slightly heavier than the ^{12}C isotope which causes a fractionation effect during air-sea gas exchange and photosynthesis, thereby changing δ^{13}C and $\Delta\delta^{13}$C (Laws et al., 1997; Mackenzie and Lerman, 2006; Zhang et al., 1995)~~The vertical marine δ^{13}C gradient is the surface-to-deep difference in δ^{13}C, the standardised ^{13}C isotope (Stenström et al., 2011; Stuiver and Pollack, 1977). ^{13}C is slightly heavier than the ^{12}C isotope, which causes a fractionation effect during air-sea gas exchange and biogenic carbon uptake during photosynthesis (Laws et al., 1997; Mackenzie and Lerman, 2006; Zhang et al., 1995)~~. Photosynthetic~~This~~ fractionation ~~enriches~~ increases the ^{13}C/^{12}C ratio of surface ocean ~~dissolved inorganic carbon (~~DIC~~) at the ocean surface in δ^{13}C~~ (i.e., a δ^{13}C increase) due to the preferred uptake of the lighter ^{12}C into~~ and it depletes the δ^{13}C in~~ biogenic matter~~organic material~~ ~~(e.g. plankton)~~(which therefore has a low δ^{13}C). The deep sea DIC has a ~~depleted~~ relatively low δ^{13}C signature ~~in DIC~~ as a result of the remineralisation of ~~the~~ low-δ^{13}C~~-depleted~~ biogenic matter~~organic detritus~~ at depth. The~~is~~ resulting vertical δ^{13}C gradient is in addition~~-~~ ~~shaped~~ influenced by ~~the interplay between the biological pump,~~ air-sea gas exchange and circulation (Emerson and Hedges, 2008; Zeebe and Wolf-Gladrow, 2001; Ziegler et al., 2013). ~~The~~ Both deep sea and surface ocean δ^{13}C signatures are archived in the calcareous shells of foraminifera in the sediments. Records of δ^{13}C from planktic~~planktonic~~ and benthic foraminiferal shell material cover tens~~10s~~ of millions of years (Hilting et al., 2008). δ^{13}C and $\Delta\delta^{13}$C~~the vertical δ^{13}C gradient~~ ~~($\Delta\delta^{13}$C)~~ have been used to reconstruct for example atmospheric CO_2 concentration~~ carbon~~, ocean circulation and the strength of the biological pump (Bauska et al., 2016; Broecker, 1982; Broecker and McGee, 2013; Crucifix, 2005; Curry and Oppo, 2005; Hollander and McKenzie, 1991; Hoogakker et al., 2015; Keir, 1991; Lisiecki, 2010; Oppo et al., 1990; Shackleton and Pisias, 1985; Zahn et al., 1986; Ziegler et al., 2013). Note that $\Delta\delta^{13}$C is independent of whole-ocean δ^{13}C shifts (due to terrestrial influences) because such influences would affect δ^{13}C equally everywhere, therefore making it a valuable proxy to study the marine carbon cycle. Contemporary measurements of δ^{13}C of ~~dissolved inorganic carbon (~~DIC~~)~~ support the quantification of anthropogenic carbon uptake by the oceans as well as the study of the effects of biology and ocean circulation on tracer distributions (Eide et al., 2017b; Gruber and Keeling, 2001; Holden et al., 2013; Kroopnick, 1980; Kroopnick, 1985; Quay et al., 2003). However, major uncertainties remain in the interpretation of foraminiferal δ^{13}C records and $\Delta\delta^{13}$C (Broecker and McGee, 2013; Oliver et al., 2010) as well as in the interpretation of the present day δ^{13}C data (Eide et al., 2017b).

This article addresses part of these uncertainties by exploring the pre-industrial sensitivity of δ^{13}C and $\Delta\delta^{13}$C to ~~(bio)~~biogeochemical change in idealised model experiments. By doing so we can investigate a number of ~~(bio)~~biogeochemical mechanisms that could explain (part of) the observed changes in δ^{13}C and $\Delta\delta^{13}$C. We focus on the Southern Ocean (SO), the ocean south of 45° S, because the SO plays an important role in the global carbon cycle by regulating atmospheric CO_2 concentrations and uptake of anthropogenic CO_2 (Broecker and Maier-Reimer, 1992; Heinze, 2002; Marinov et al., 2006) as well as influencing the global efficiency of the biological pump, global primary production and preformed nutrients (Primeau et al., 2013).

Variations in $\Delta\delta^{13}C$ over the past few 100 000 years show that~~-~~ $\Delta\delta^{13}C$ is generally increased during glacial periods~~s and reduced during interglacials~~, due to a higher contrast of deep $\delta^{13}C$ with~~-~~ surface and mid-depth $\delta^{13}C$ (Broecker, 1982; Boyle, 1988; Charles et al., 2010; Oliver et al., 2010; Shackleton and Pisias, 1985). Long-term $\delta^{13}C$ and $\Delta\delta^{13}C$ ~~These~~ variations have been explained by ocean circulation changes (Duplessy et al., 1988; Jansen, 2017; Oppo et al., 1990; Toggweiler, 1999; Menviel et al., 2016)~~associated with sea ice formation due to lower glacial temperatures around Antarctica and consecutive stratification (Jansen, 2017)~~. However, ~~not all tracers support a change in circulation (Charles et al., 2010) and processes other than ocean circulation/stratification are likely needed to explain~~ $\Delta\delta^{13}C$ variability cannot be explained by ocean stratification/circulation changes alone: An interaction between biogeochemical and physical processes must be at play (Boyle, 1988; Charles et al., 2010; Keir, 1991; Mulitza et al., 1998; Schmittner and Somes, 2016; Ziegler et al., 2013). $\Delta\delta^{13}C$ has been used in different ways over time: In earlier studies as the contrast between surface and deep water $\delta^{13}C$, derived from planktic versus benthic foraminifera (Boyle, 1988; Broecker, 1982; Duplessy et al., 1988; Shackleton et al., 1983) and now increasingly as the contrast of deep ocean (benthic) $\delta^{13}C$ with thermocline or intermediate ocean $\delta^{13}C$ (Charles et al., 2010; Lisiecki, 2010; Mulitza et al., 1998).

Here, we explore the sensitivity of $\delta^{13}C$ and $\Delta\delta^{13}C$ to changes in the ~~(bio)~~biogeochemical state of the Global Ocean and Southern Ocean under a constant circulation field, ~~. Our results aim~~ to support the paleo-oceanographic interpretation of $\delta^{13}C$ and $\Delta\delta^{13}C$ as well to improve~~as t~~ the understanding of the ~~dominant~~ SO role in global carbon cycling and its variability and sensitivity. In order to study ~~different (bio)~~biogeochemical mechanisms that could influence $\delta^{13}C$ and $\Delta\delta^{13}C$, a set of sensitivity experiments is ~~designed~~ conducted with~~in~~ the ocean biogeochemistry general circulation model HAMOCC2s (Heinze et al., 2016). We first estimate the contribution of biology versus air-sea gas exchange to marine $\delta^{13}C$ of DIC (Sect. 3.2). The~~The~~ experiments~~s~~ ~~each~~ focus on one or more of the ~~(bio)~~biogeochemical aspects ~~described~~ assumed to be important for $\delta^{13}C$ and $\Delta\delta^{13}C$, e.g. the biological pump efficiency and/or equilibration at the air-sea interface (Sect. 3.3.1-3.3.4). Together these experiments provide a broad spectrum of ~~(bio)~~biogeochemical changes that could influence local and global $\delta^{13}C$ and $\Delta\delta^{13}C$. ~~An approximation is made of the contribution of biology versus air-sea gas exchange to $\delta^{13}C$ (Sect. 3.2).~~ The modelling results of Sect. 3.3.1-3.3.4 are discussed in context of~~and compared with~~ observational data from sediment cores (Sect. 3.4). As $\delta^{13}C$ and $\Delta\delta^{13}C$ are used to study changes in atmospheric pCO_2 (pCO_2^{atm}), a final section will cover the ~~changing~~ relationship between atmospheric $\delta^{13}C$, $\Delta\delta^{13}C$ and pCO_2^{atm} under different marine ~~(bio)~~biogeochemical states (Sect. 3.5).

2 Methods

In this study we employ the ocean biogeochemistry general circulation model HAMOCC2s (Heinze et al., 1999; Heinze et al., 2009; Heinze et al., 2016) which simulates the inorganic and organic carbon cycle in the water column and in the sediments. The horizontal resolution of the model is 3.5° × 3.5° and there are 11 depth layers in the ocean. HAMOCC2s has an annual time step and an annually averaged fixed circulation field, as well as a free box atmosphere for O_2, $^{13}CO_2$ and CO_2. The model is computationally very economic and thus an ideal tool for sensitivity experiments over long integration times. Biogenic particulate matter~~Biological particles~~ in the model is represented as~~are~~ particulate organic carbon (POC), calcium carbonate ($CaCO_3$) and biogenic silica (opal). These biogenic particles are only modelled as export production due to the annual time-step of the model. POC and ~~and~~ opal export ~~opal production~~ production are described ~~using~~ by Michaelis-Menten kinetics for nutrient uptake, limited by phosphate and silicic acid respectively ~~(Heinze et al., 1999)~~. $CaCO_3$ export production depends on the ratio between opal and POC production. POC is carried as a tracer as well as transported downwards according to a set of mass balance equations that describe POC gain through surface layer POC production and POC losses through constant sinking and remineralisation~~–~~ rates (SI 1A)~~an exponential particle penetration profile and a constant sinking velocity, thereby consuming oxygen (i.e. remineralisation of POC with depth)~~. This is done similarly for opal and $CaCO_3$ sinking and dissolution. ~~-~~As the model has an annual time step, sea ice is always present south of ~60° S and north of ~70° N in the control run (Fig. S1). A more detailed model description ~~More details about the model are~~is provided in previous studies using a similar configuration of HAMOCC2s (Heinze, 2002; Heinze et al., 2016), as well as SI 1A.

Fractionation during photosynthesis is set to a constant value of -20 ‰ (Lynch-Stieglitz et al., 1995; Tagliabue and Bopp, 2008) as model results are little influenced by the chosen parameterisation (Jahn et al., 2015; Schmittner et al., 2013). The fractionation during air-sea gas exchange depends on temperature according to $\varepsilon=-9.483*10^3/T\,[°\,C] + 23.89$ ‰ (Mook, 1986), causing stronger fractionation at lower temperatures (i.e. at high latitudes). Fractionation during $CaCO_3$ formation is omitted from the model as done in previous studies (Lynch-Stieglitz et al., 1995; Marchal et al., 1998; Schmittner et al., 2013) as its size is uncertain but likely minor (~1 ‰) and effects on $\delta^{13}C$ and $\Delta\delta^{13}C$ are small (Shackleton and Pisias, 1985). In the version of HAMOCC2s used in this study, a fixed weathering input is used for ^{13}C to tune the ocean inventory to values comparable to observations. The ‘best-fit’ weathering value was found by running the model with a restored ~~(to a value of -6.5 ‰)~~ atmosphere~~ic~~ ($\delta^{13}C= -6.5$ ‰) ~~$\delta^{13}C$~~ until the prognostic burial rate and weathering flux ~~reached~~ equilibrated to a constant value F^{w}_{eq} ~~ium with weathering~~ (~~after~~ ~110000 model years). Consecutively, ~~the~~ atmospheric restoring was removed and the weathering rate for ^{13}C was fixed to value F^{w}_{eq}. ~~to~~ Weathering fluxes are added homogeneously over the first ocean layer as dissolved matter and in a fixed stoichiometric ratio for C, O_2, Alkalinity, PO_4^{3-} and Si. The $^{13}C/^{12}C$ ratio in the weathering flux would be equivalent to a $\delta^{13}C$ of DIC of 14 ‰. This procedure created a free atmosphere model setup with close-to-observed marine and atmospheric $\delta^{13}C$ ($\delta^{13}C^{atm}$) values. This equilibrated model version is referred to as the ‘control run’ in the remainder of this article. We define the vertical $\delta^{13}C$ gradient ($\Delta\delta^{13}C$) as:

$$\Delta\delta^{13}C = \delta^{13}C_{surface} - \delta^{13}C_{deep} \;,$$ (2~~1~~)

where $\delta^{13}C_{surface}$ and $\delta^{13}C_{deep}$ are the volume-weighted mean $\delta^{13}C$ of DIC in the surface ocean (< ~~2~~50 m depth, i.e. the model photic zone) and the deep ocean (~~>250m depth~~lowermost wet layer in the model, if top of layer > 3 km depth), respectively. By doing so, we can compare the $\Delta\delta^{13}C$ summarised as one number between the different sensitivity experiments.

We conducted ~~four~~ a set of sensitivity experiments to explore changes in air-sea gas exchange rate, sea ice extent (influencing both biological production and the air-sea gas exchange of carbon) and the efficiency of the biological pump through the POC sinking rate and nutrient uptake rate (Table 1). ~~This article~~We employ~~s~~ the term 'efficiency of the biological pump' as a measure of the success of phytoplankton to maintain low nutrient concentrations in the surface ocean. All experiments are run for 2000 model years starting from the end of the spinup. These runtimes allowed for atmospheric equilibrium to establish (Fig S4), with an exception for the long-term effects caused by POC sinking rate changes (as studied in more detail by Roth et al., 2014). The gas exchange rate and POC sinking rate experiments are done twice, once changing the respective model parameter for the Global Ocean and once ~~only~~ for the Southern Ocean only (SO-only). The model parameters where changed in a way that marine biogeochemical tracer distributions (e.g. PO_4^{3-}, $\delta^{13}C$) remained reasonable but did provide an estimate of the sensitivity of the respective tracer to ~~(bio)~~biogeochemical change. The model has a constant sea ice cover (Fig. S1), which permits gas and light transfer through the ice depending on ice cover fraction. The maximum and minimum sea ice cover experiments (Ice large and Ice small, Table 1) approximate the Last Glacial Maximum winter extent and the modern summer extent of SO sea ice, respectively (Crosta (2009) and Fig. A22 therein) and assume full inhibition of gas and light transfer through ice for simplicity. The experiment on nutrient drawdown (V_{max}) alters the Michaelis-Menten kinetics of POC production by changing the maximum nutrient (i.e. PO_4^{3-}) uptake rate (V_{max}^{POC} in SI 1A). The gas exchange experiments alter the specific gas exchange rate k_w as described in more detail SI 1B. The POC sinking rate experiments change the sinking velocity constant w_{POC} in the POC mass balance equations (SI 1A).

The contribution of biological processes versus air-sea gas exchange to $\delta^{13}C$ is calculated using the method of Broecker and Maier-Reimer (1992) as done for observations by Eide et al. (2017b) and in a modelling context by Sonnerup and Quay (2012):

$$\delta^{13}C_{bio}[‰] = \frac{\varepsilon_{photo}}{\overline{DIC}} * r_{c:p} * (PO_4 - \overline{PO_4}) + \overline{\delta^{13}C} \;,$$ (3~~2~~)

where $\varepsilon_{photo} = -20$ ‰, $r_{c:p} = 122$ and the following model control run mean values are used: $\overline{DIC} = 2308.793\,\mu mol/kg$, $\overline{PO_4} = 2.399\,\mu mol/kg$ and $\overline{\delta^{13}C} = 0.742$ ‰. These values result in the modelled $\delta^{13}C_{bio}$:PO_4^{3-} relationship $\delta^{13}C_{bio}$=3.3~~4~~-1.1* PO_4^{3-}. The constant 3.~~4~~3 is somewhat higher than estimated for observed $\delta^{13}C$ for which a constant of 2.8 was found by Eide et al. (2017b). This higher constant originates from the over-prediction of the model of mean $\delta^{13}C$ and PO_4^{3-} at depth, as seen in other models (Sonnerup and Quay, 2012). Eq. (3~~2~~) assumes a constant biological fractionation as well as a constant $r_{c:p}$ ratio, and these assumptions will introduce some error in the partition of biological and air-sea gas exchange signatures derived from observed $\delta^{13}C$ to PO_4^{3-} ratios (e.g., Eide et al. 2017b). For the purpose of determining $\delta^{13}C_{bio}$ in our model, these assumptions are unproblematic, since $r_{c:p}$ and ε_{photo} actually are taken to be constant in the model formulation. The air-sea gas signature $\delta^{13}C_{AS}$ is approximated as the residual ($\delta^{13}C_{AS} = \delta^{13}C_{model} - \delta^{13}C_{bio}$). $\delta^{13}C_{AS}$ is 0 ‰ when $\delta^{13}C_{model}=\delta^{13}C_{bio}$, i.e. when the $\delta^{13}C$ can be explained by biology only. To aid interpretation of the results, we express $\delta^{13}C_{bio}$ as a percentage as $\delta^{13}C_{bio}^{perc}$ because the absolute values in ‰ depend strongly on the chosen 'reference' values, i.e. mean DIC, PO_4^{3-}, and $\delta^{13}C$ (compare Schmittner et al., 2013; Sonnerup and Quay, 2012; Broecker and Maier-Reimer, 1992; Lynch-Stieglitz et al., 1995; Eide et al., 2017b). The conversion from $\delta^{13}C_{bio}$ to a percentage is calculated as follows:

$$\delta^{13}C_{bio}^{perc}[\%] = \frac{|\delta^{13}C_{bio}|}{|\delta^{13}C_{bio}|+|\delta^{13}C_{AS}|} * 100\ \%$$ (4~~3~~)

In our analysis, we define the total amount of air-sea carbon exchange as $F_{u+d}=|F_{up}|+|F_{down}|$, with F_{up} as the upward annual carbon flux from the ocean into the atmosphere and F_{down} its downward counterpart (SI 1B and Heinze et al. (1999)). F_{u+d} is relevant for understanding the sensitivity of $\delta^{13}C$. The net carbon exchange is defined as $F_{net}=F_{up}+F_{down}$. The sign of F_{net} indicates whether a region is a source or a sink for carbon and is relevant for understanding changes in ~~atmospheric~~ pCO_2^{atm}.

3 Results and discussion

3.1 Model control run

The model reproduces the main features of observed marine $\delta^{13}C$, as shown in Fig. 1 and Fig. S2. The modelled global mean surface ocean $\delta^{13}C_{surface}$ of DIC is ~~enriched~~ higher (1.96~~6~~ ‰ ~~average above 250 m depth~~) than~~and the~~ deep ocean $\delta^{13}C_{deep}$ ~~is more depleted~~ (0.76 ‰ ~~average below 250 m depth~~), creating a~~. The~~ mean ocean $\Delta\delta^{13}C$ ~~is thus~~of 1.20~~0.9~~ ‰. In the North Atlantic and SO, $\Delta\delta^{13}C$ is least pronounced (0.9 and 0.8 ‰ respectively) due to vertical mixing between surface and deep water during deep water formation and upwelling (Duplessy et al., 1988). $\Delta\delta^{13}C$ increases with water mass age as expected from the increased imprint of remineralisation on $\delta^{13}C$. The mean modelled ocean $\delta^{13}C$ is higher~~over-predicted~~ by 0.2 ‰ relative to observations (Eide et al., 2017b), which is especially pronounced in the oldest water masses (Fig. S2). This is observed in other models as well and attributed to the model's relative contribution of deep water production in the North Atlantic and Southern Ocean (Sonnerup and Quay, 2012). The modelled global export POC production is 9.6 Gt C yr^{-1} of which 18 % is produced in the SO, which is within the uncertainty of observational estimates (MacCready and Quay, 2001; Nevison et al., 2012; Dunne et al., 2007; Lutz et al., 2007; Schlitzer, 2002). The free atmosphere has a modelled equilibrium pCO_2^{atm} of 279 ppm and a $\delta^{13}C^{atm}$ of -6.44 ‰ which developed in the model from the 'best-fit' weathering value F_{eq}^{w} as described above in Sect. 2. Net air-sea gas exchange is close to zero (ventilating ~5×10^{-6} Pg of carbon to the atmosphere annually), indicating that the model is in equilibrium. The resulting drift of the model control over 2000 years is +7×10^{-3} ‰ for both $\delta^{13}C^{atm}$ and mean marine $\delta^{13}C$, and +5×10^{-3} ppm for pCO_2^{atm}.

3.2 Air-sea gas exchange versus biology

The contribution of biology based on equations (2) and (3) to the δ^{13}C distribution is presented in Fig. 2, broadly in~~. Our results~~ agreement with previous studies ~~on the relative role of biology and ocean circulation to the δ^{13}C distribution~~ (Kroopnick, 1985; Schmittner et al., 2013). The contribution of biology to the modelled δ^{13}C distribution is generally below 45 % and has a steep gradient from the surface to the deep ocean. The (thermodynamic) fractionation effect of air-sea gas exchange on δ^{13}C is strongly impeded by the long equilibration time of ^{13}C, which results in room for biological processes to contribute significantly to δ^{13}C and $\Delta\delta^{13}$C (Eide et al., 2017a; Lynch-Stieglitz et al., 1995; Murnane and Sarmiento, 2000; Schmittner et al., 2013). In the ~~deep~~ ocean below 250m, the influence of biology increases to 35-45 % due to the remineralisation of POC, with the exception of the Arctic Ocean where no POC production is modelled due to the sea ice cover (Fig. 2b and Fig. S1). $\delta^{13}C_{bio}^{perc}$ is close to 50 % around 1000m depth in the northern Pacific and Indian oceans, due to the old water masses located there, which have accumulated a large fraction of remineralised DIC. At the surface, air-sea gas exchange dominates the δ^{13}C signature of DIC as visible from the low $\delta^{13}C_{bio}^{perc}$ (Fig. 2a). The only exception at the surface is in upwelling regions, where a relatively high $\delta^{13}C_{bio}^{perc}$ is expected due to high POC production and upwelled remineralised carbon. High $\delta^{13}C_{bio}^{perc}$ generally corresponds to a low-δ^{13}C~~-depleted~~ water mass (compare Fig. 1 and Fig. 2), as expected from the upwelling of ~~δ~~^{13}C-~~-~~depleted DIC and modelled and observed close to the Antarctic continent (Fig. 1a and observations by Eide et al. (2017a)). The results presented in Fig. 2 appear to be quite robust as $\delta^{13}C_{bio}^{perc}$ typically does not change by more than 5-10 % for the wide range of biogeochemical states as explored in the sensitivity experiments presented below.

3.3 Sensitivity of Δδ13C and δ^{13}C

3.3.1 Air-sea gas exchange of carbon

Atmospheric and marine ~~δ^{13}C~~ carbon isotopic ratios are generally in thermodynamic disequilibrium because ^{13}C equilibrates ~200 times slower than inert gases like O_2. This difference in equilibration time is due to the fact that DIC~~^{12}C~~ needs to speciate into all marine carbon species to reach equilibrium (~20x slower than O_2), after which ^{13}C needs to go through full isotopic exchange between all carbon species to reach equilibrium (~10x slower than ^{12}C) (Jones et al., 2014; Galbraith et al., 2015; Broecker and Peng, 1974). ~~The extent of this δ^{13}C disequilibrium archives the ventilation time of that water parcel, thereby making δ^{13}C a good tracer for water mass circulation (Eide et al., 2017b).~~ The surface ocean δ^{13}C signature is dominated by air-sea gas exchange in most ocean regions (Fig. 2). Any change in the gas exchange rate can thus potentially have a large effect on surface ocean δ^{13}C, depending on the prior disequilibrium $\delta^{13}C_{diseq}$ ($\delta^{13}C_{diseq} = \delta^{13}C - \delta^{13}C_{eq}$, where $\delta^{13}C_{eq}$ represents the δ^{13}C value a water parcel would have had if it would have fully equilibrated with the atmosphere, see also Gruber et al. (1999)). Isotopic equilibrium with the atmosphere would result in a $\delta^{13}C_{surface}$ of approximately 2 ‰ (Murnane and Sarmiento, 2000), since $\delta^{13}C^{atm}$ is about -6.5 ‰ and air-sea fractionation about 8.5 ‰ (Mook et al., 1986).~~depending on the prior disequilibrium.~~

~~The~~ Our gas exchange experiments (~~Sect. 2,~~ Table 1) result in ~~profound changes in the $\delta^{13}C$ distribution, the $\Delta\delta^{13}C$ as well as $\delta^{13}C^{atm}$ and pCO_2^{atm}. pCO_2^{atm} is governed by the~~a transient change in the net air-sea gas exchange flux F_{net}, which occurs until a new equilibrium is established. We find an increase of pCO_2^{atm} by 9 ppm (fast gas exchange) and by 4 ppm (slow gas exchange), respectively. If gas exchange is only changed in the SO (i.e. for 22 % of the global ice-free ocean area), an effect of 5 ppm and 1 ppm increase is found (Table 2). The spatially variable prior pCO_2 disequilibrium in the SO (Fig. S3) plays an important role in the pCO_2^{atm}~~atmospheric pCO_2~~ sensitivity: The larger increase of the outgassing flux F_{up} of the SO as compared to the carbon uptake flux F_{down} leads to a reduced SO carbon sink and higher pCO_2^{atm} at increased gas exchange rates~~.~~. The reduction in air-sea C flux for the slow gas exchange experiment causes F_{net} to decrease during the transient phase (Fig. S4 and 5), leading to an increase in pCO_2^{atm} which develops during the first ~600 years. F_{net} is reduced during the transient phase because the slow gas exchange rate decreases Southern Hemispheric net C uptake, while maintaining Northern Hemispheric net C outgassing, also for the global experiment. Interestingly, the $\delta^{13}C^{atm}$ gets decoupled from the pCO_2^{atm} signal as $\delta^{13}C^{atm}$ decreases (to -6.8 ‰) during fast gas exchange and increases (to -6.3 ‰) when the gas exchange rate is reduced. This is explained by the increase in the global amount of air-sea gas exchange F_{u+d} in the fast gas exchange experiment. Such an increase leads to a smaller thermodynamic disequilibrium, which ~~enriches~~ increases the mean marine $\delta^{13}C$ and ~~depletes~~ lowers $\delta^{13}C^{atm}$. ~~The opposite occurs for the s~~Slow gas exchange reduces F_{u+d}, causing less fractionation to occur~~experiment~~ which explains the increase of $\delta^{13}C^{atm}$. Moreover, our SO-only experiments show that these effects on $\delta^{13}C^{atm}$ ~~the atmosphere~~ are more pronounced if gas exchange only changes in the SO. This indicates that the remainder of the ocean offsets part of the atmospheric sensitivity to SO change.

~~In the ocean,~~ $\delta^{13}C$ shows a different response in high latitudes as compared to the lower latitudes in the surface ocean (Fig. 3a and S6): An increased air-sea gas exchange rate lowers the surface ocean $\delta^{13}C$ of DIC by -0.2 to -0.9 ‰ ~~in~~ at the lower latitudes and increases surface ocean $\delta^{13}C$ ~~in~~ at high latitudes by 0.2-0.5 ‰ (Fig. 3 and 4). These results indicate whether $\delta^{13}C_{diseq}$ is positive or negative, since $\delta^{13}C$ is closer to equilibrium at high gas exchange rates.~~These results indicate the sign of the thermodynamic $\delta^{13}C$ disequilibrium between surface ocean and atmosphere.~~ In line with previous studies (Schmittner et al., 2013; Galbraith et al., 2015) the disequilibrium is negative ($\delta^{13}C < \delta^{13}C_{eq}$) at high latitudes and in low latitude upwelling regions, and positive elsewhere. This can be understood from the difference between the natural $\delta^{13}C$ distribution (Fig. 1) and the potential ~2 ‰ $\delta^{13}C_{eq}$, which would require an increase in $\delta^{13}C$ in cool high latitude surface waters and a decrease in warm low latitude surface waters (Murnane and Sarmiento, 2000). ~~-~~The net effect of a slower gas exchange rate on surface ocean $\delta^{13}C$ is less pronounced than the effect of ~~and reversed to the effects discussed for~~ an increased gas exchange rate (~~not shown~~Fig. S6, Fig. 3). The smaller effects seen for slow gas exchange indicate that the control model ocean is a ‘slow ocean’, i.e. closer to (very) slow gas exchange than to thermodynamic equilibrium (fast gas exchange).

The effect of the gas exchange rate on marine $\delta^{13}C$ is mostly established in the top 250~~-~~ to 1000 m of the water column (Fig. 3c, d, Fig. 4). Recording this air-sea gas exchange signal thus strongly depends on the reliability of planktic $\delta^{13}C$-based $\delta^{13}C_{surface}$ reconstructions and knowledge of the living depth represented by the planktic foraminifera. The signal penetrates deepest (to ~2000 m depth) into the North Atlantic (Fig. 4, Fig. S7), where $\delta^{13}C$ is strongly influenced by air-sea gas exchange

(Fig. 2a). However, the interpretation of variations in North Atlantic benthic $\delta^{13}C$ as coming partly from air-sea gas exchange (Lear et al., 2016) is not supported by our experiment. Due to the limited export of the $\delta^{13}C$ signal to depth, ~~T~~the sensitivity of $\Delta\delta^{13}C$ to the gas exchange rate ~~therefore~~ mainly ~~depends~~ comes from~~on~~ surface ocean $\delta^{13}C$. ~~On average~~Globally, the $\Delta\delta^{13}C$ weakens to 0.~~65~~84 ‰ ~~-~~when the thermodynamic disequilibrium is decreased (i.e. 'Gas fast', ~~Fig. 4~~Fig. 5) and $\Delta\delta^{13}C$ strengthens to 1.32~~00~~ ‰ when the thermodynamic disequilibrium is increased ('Gas slow', ~~Fig. 4~~Fig. 5). The extent to which thermodynamic equilibrium can develop is thus an efficient way to change the biologically-~~-~~induced $\Delta\delta^{13}C$ (Murnane and Sarmiento, 2000), however only in lower latitudes where $\delta^{13}C_{diseq}$ is positive. ~~Note that local changes in the $\Delta\delta^{13}C$ can be different from the global mean vertical gradient, and can be more pronounced (subtropical gyres in Fig. 3a). Importantly, in t~~The SO ~~the~~ $\Delta\delta^{13}C$ signal has an opposite sign of the global mean and low latitude regions: ~~The $\Delta\delta^{13}C$ is strengthened south of about 40°S w~~When the thermodynamic disequilibrium is decreases~~d~~ (increases), basin-mean $\Delta\delta^{13}C$ in the SO increases (decreases) and thus intensifies the biologically-induced $\Delta\delta^{13}C$ changes ~~-~~(Fig. ~~3a~~4).

~~Note as well that the SO surface ocean enrichment is compensated in low latitude regions (compare Fig. 3a, b).~~

3.3.2 The biological pump: POC sinking rate

The net effect of a regionally changed biological pump efficiency depends on the sequestration efficiency, which depends on the interplay between the biological pump and ocean circulation (DeVries et al., 2012). A more efficient biological pump (here, a higher POC sinking rate) leads to a loss of carbon to the sediments, which affects pCO_2^{atm} and $\delta^{13}C^{atm}$ on millennial timescales. Here we present results from a 2000-year simulation (as for the other experiments), which is still in a transient phase. To reach a full equilibrium of the system could take as long as 200 000 years (Roth et al. 2014). On these long timescales other processes and feedbacks would occur (Tschumi et al. 2011), which complicates the attribution of changes to a primary trigger. A fast POC sinking rate leads to a pCO_2^{atm} decrease of ~~leads to a loss of carbon to the sediments, which dominates the effects on pCO_2^{atm} and $\delta^{13}C^{atm}$. The sediment burial causes efficient long-term removal of carbon from the active carbon cycle which leads to a~~ 28 ppm ~~reduction of pCO_2^{atm}~~ and ~~relatively~~ higher (-6.2 ‰) atmospheric $\delta^{13}C$ ~~(Table 2)~~ after 2000 years (Table 2, Fig. S5) as well as a shift of the mean ocean $\delta^{13}C$ by ~0.15 ‰, caused by the sediment burial of low-$\delta^{13}C$ POC. The imbalance between weathering and burial fluxes can thus cause profound changes in both marine and atmospheric $\delta^{13}C$, and moreover provides an important feedback for the long-term marine carbon cycle (Roth et al., 2014; Tschumi et al., 2011). In our experiment, ~~Besides that, a~~an efficient biological pump leads to a global ~10 % decrease in the amount of air-sea gas exchange F_{u+d} because ~~of~~ of efficient export of carbon to depth, thereby ~~reduced~~lowering the net upward advection of carbon~~POC production as surface waters are depleted of nutrients~~. A mirrored but weaker response is modelled for a decrease in biological pump efficiency:~~.~~ Halving the POC sinking rate leads to a 13 ppm increase in pCO_2^{atm} (of which 28 % can be explained by the SO) and a more negative atmospheric $\delta^{13}C$ (-6.7 ‰) and increased F_{u+d} (Table 2, Fig. S5).

Surface ocean $\delta^{13}C$ is mostly influenced by the changes in productivity and the vertical displacement of the POC remineralisation depth. The deepening of the remineralisation depth has been extensively discussed in the literature (Boyle, 1988; Keir, 1991; Mulitza et al., 1998; Roth et al., 2014), and likely explains lowered mid-depth glacial $\delta^{13}C$ together with changes in ocean circulation (for example, Toggweiler, 1999) ~~horizon~~. POC sinking removes nutrients and preferentially light ^{12}C carbon from the surface ocean, while exporting them to the deep ocean. If POC sinking rates are high, ~~T~~this ~~leaves the~~increases the surface ocean ~~more enriched in δ^{13}C~~δ^{13}C (contributing to the $\delta^{13}C^{atm}$ increase) and lowers~~the~~ deep ocean δ^{13}C ~~more depleted if POC sinking rates are high-~~ ~~,~~despite the overall increase in marine δ^{13}C which occurs due to sediment burial (Fig. 6) ~~(Fig. 5a)~~. Therefore, even though the absolute export production is reduced in all productive regions (-26 %), the biological pump is more efficient as any new nutrients in the surface ocean will immediately be used and exported. ~~-~~With a lower POC sinking rate, the remineralisation is more confined to the surface ocean.~~When reducing the biological pump efficiency both remineralisation and POC production are confined to the surface ocean.~~ The net effect is that the surface ocean ~~becomes more depleted in~~ δ^{13}C becomes lower, ~~as~~ because the fractionation effect during photosynthesis is counteracted by the remineralisation of POC (which would normally have occurred at depth). The SO plays a relatively minor role in these changes (Fig. 6~~5~~b). ~~This suggests that the POC export production of the SO is less determined by the local POC sinking rate than elsewhere.~~ Changes in deep ocean δ^{13}C depend on the water mass age (Fig. 6~~5~~c). Old water (North Pacific) has a larger remineralisation signal when the biological pump is efficient. Independent of the biological pump efficiency, the relatively young waters of the deep North Atlantic ~~seem to~~ generally adopt about the same δ^{13}C signal as the surface ocean δ^{13}C, which is set by air-sea gas exchange. This is in agreement with a relatively low $\delta^{13}C_{bio}^{perc}$ estimate for the deep North Atlantic (~30 %).

~~From Fig. 5 we observe that t~~The sensitivity of ~~the~~ $\Delta\delta^{13}$C to changes in POC sinking rate ~~strongly~~ depends strongly on location (Fig. 4 and 6). In general, the $\Delta\delta^{13}$C strengthens for an increased biological pump efficiency (Fig. 5), and this effect is stronger with water mass age (Fig. 6~~5~~c, Fig. 4). The downward shift of the remineralisation depth of low-δ^{13}C POC drives this increase in $\Delta\delta^{13}$C, a mechanism discussed among others by Boyle (1988) and Mulitza et al. (1998) to understand glacial $\Delta\delta^{13}$C~~-~~ increase. Our results show that the vertical displacement of the δ^{13}C profile is most pronounced in the North and South Pacific for both faster and slower POC sinking rates (Fig. 4 and Fig. S7). The North Atlantic $\Delta\delta^{13}$C is much less affected as these waters are mostly influenced by air-sea gas exchange. Instead, the entire North Atlantic profile is shifted more than in the other ocean basins (Fig. S7). $\Delta\delta^{13}$C weakens~~The opposite happens~~ for a reduced biological pump efficiency ~~, which weakens the $\Delta\delta^{13}$C~~ (Fig. 4 and ~~5~~5), especially in older water where $\delta^{13}C_{bio}^{perc}$ is higher (Fig. 2a). It is worth noting, however, that the changes in $\Delta\delta^{13}$C in the SO are comparably small because the vertical mixing in the SO of the low-δ^{13}C deep water mostly causes shifts in the entire δ^{13}C profile, not a change in the gradient (Fig. 4). ~~In the North Pacific, where the changes in the $\Delta\delta^{13}$C are most pronounced, this is mostly due to the surface ocean sensitivity because the deep ocean changes are small compared to the surface ocean changes.~~

3.3.3 The biological pump: SO nutrient depletion

Consistent with previous studies (Primeau et al., 2013; Marinov et al., 2006; Sarmiento et al., 2004), we find a large atmospheric impact ~~in~~ of our SO nutrient depletion experiment. The high SO nutrient uptake efficiency (i.e. an efficient biological pump) ~~maintains~~ causes a ~~28~~51 ppm reduction in $p\mathrm{CO}_2^{atm}$ after 2000 years ~~as seen similarly for the efficient~~

~~biological pump experiment with a high POC sinking rate (Sect. 3.3.2)~~. The V_{max} experiment largely equilibrates after 800 years, as seen from the time evolution of pCO_2^{atm} and $\delta^{13}C^{atm}$ (Fig. S5). $\delta^{13}C^{atm}$ increases to -6.0 ‰ due to the increased surface ocean $\delta^{13}C$ (Fig. 7a). This 0.5 ‰ increase is high compared to the results of Menviel et al. (2015), who found a $\delta^{13}C^{atm}$ sensitivity of 0.1-0.2 ‰ in response to changes in SO nutrient utilization. The different development time as compared to the fast POC sinking rate experiment is explained by the absence of long-term loss of carbon to the sediments in the V_{max} experiment, probably because transport and water-column remineralisation within the SO limits an increase in POC burial there. ~~However, $\delta^{13}C^{atm}$ behaves differently in the V_{max} experiment than in the efficient biological pump experiment based on POC sinking rates: An increased POC sinking rate leads to a $\delta^{13}C^{atm}$ increase of ~0.2 ‰ due to export of light organic carbon to the sediments (Sect. 3.3.2). In contrast, in the V_{max} experiment $\delta^{13}C^{atm}$ reduces by ~0.2 ‰ to -6.6 ‰.~~ In the SO,~~,~~ net carbon ~~outgassing~~ uptake~~to the atmosphere~~ ($F_{\cancel{u}net\cancel{p}}$) increases fivefold (Fig. S8) ~~is reduced by nearly 40 %~~ because the high nutrient and carbon consumption transport C into the ocean interior and do not permit CO_2 to escape to the atmosphere from the deep ocean~~. This plays a key role in the globally 10 % reduced air-sea exchange, both because of its magnitude and because of stronger thermodynamic fractionation in high latitudes.~~.

~~The global~~ E~~e~~xport production of POC ~~becomes confined~~is increased in ~~to~~ the SO (Fig. S9) by a factor 2.5, causing global POC export production to increase by 17 % albeit reducing lower-latitude productivity by 11 %~~due to the high nutrient uptake rate and the local 5-fold increase in POC production~~. This relocation of global POC export production in response to SO increased nutrient uptake efficiency is in agreement with earlier studies (Primeau et al., 2013; Marinov et al., 2006).

The increased surface ocean $\delta^{13}C$ signature everywhere north of the SO sea ice edge (Fig. 7a) is attributed to increased POC export production counteracted by a decreased F_{u+d} in the SO (which would reduce $\delta^{13}C_{surface}$ in the SO because of the negative $\delta^{13}C_{diseq}$, Fig. 3 and S6). In lower latitudes, the decreased F_{u+d} (which increases $\delta^{13}C_{surface}$ in lower latitudes because of the positive $\delta^{13}C_{diseq}$, Fig. 3 and S6) dominates the effect of the 11 % lower POC export production on $\delta^{13}C_{surface}$. At depth and under the sea ice in the Antarctic where deep water upwells, the imprint of additional POC reminneralisation at depth decreases $\delta^{13}C$ of DIC (Fig. 7). This decrease in $\delta^{13}C$ is only visible in water masses downstream of the SO (Fig.7b and c) and most pronounced in the deep North Pacific (Fig. 7c). The increased nutrient uptake rate in the SO strongly increases mean $\Delta\delta^{13}C$ (Fig. 5) and $\Delta\delta^{13}C$ in all ocean basins (Fig. 4), as seen for the fast POC sinking rate experiment. Besides effects on the $\delta^{13}C$ distribution (Fig. 7), the O_2 and PO_4^{3-} distributions change as well: The O_2 distribution is reorganised such that surface ocean O_2 is increased (up to 10 µmol kg^{-1}, with largest changes in the SO), while deep ocean O_2 is reduced downstream of the SO (up to 40 µmol kg^{-1}). Surface ocean PO_4^{3-} is reduced mostly in the SO (up to -0.8 µmol kg^{-1}). This signal is however too small to significantly increase mean deep ocean PO_4^{3-}. This implies a reduction in global preformed phosphate governed by the efficient nutrient uptake in the SO, see also Primeau et al., (2013). SO nutrient drawdown can thus cause negligible deep ocean PO_4^{3-} changes despite causing large changes in $\delta^{13}C$ and $\Delta\delta^{13}C$. This is interesting in light of glacial proxy interpretation, as deviations from the $\delta^{13}C:PO_4^{3-}$ relationship (Sect. 2) are usually interpreted as the influence of air-sea gas exchange on $\delta^{13}C$ (Eide et al., 2017b; Lear et al., 2016), but could thus also come from changes in nutrient uptake efficiency. As for a changed POC sinking rate, $\Delta\delta^{13}C$ is affected more in older waters (Fig. 4).

~~causes a range of effects on the distribution of $\delta^{13}C$. First, the high POC export in the SO leaves the SO surface ocean enriched in $\delta^{13}C$ and depletes the deep ocean due to remineralisation. This deep SO remineralisation signal is then carried northward with Antarctic Bottom Water into all ocean basins (Fig. 6b, c) and under the sea ice at the surface of the SO (Fig. 6a). Furthermore, the efficient export of carbon to the deep ocean causes the SO to become a much stronger sink for atmospheric carbon (~11x stronger, Fig. S3). Parts of this excess carbon is ventilated back to the atmosphere at lower latitudes (Fig. S3). Productivity and thus POC export and remineralisation are strongly reduced outside of the SO (~10 % global decrease in POC export production). The reduced productivity and export is consistent with previous studies (Primeau et al., 2013; Marinov et al., 2006; Sarmiento et al., 2004), which causes surface ocean $\delta^{13}C$ to become relatively depleted and deep ocean $\delta^{13}C$ to become relatively enriched as compared to the control (Fig. 6b, c). This relatively enriched deep ocean signal surfaces in upwelling regions around the equator and in the Arctic (Fig. 6a). As for the $\delta^{13}C^{atm}$, the mean marine $\delta^{13}C$ is reduced in the V_{max} experiment because the SO, Pacific and Indian deep oceans are filled with a stronger remineralisation signature (Fig. 6b, c). $\Delta\delta^{13}C$ is thus strongly increased in the SO between 60 and 40°S, but decreased or unchanged in the North Atlantic. In the Pacific, there is a pattern with an increase in intermediate water masses, and a decrease at the surface and at depth.~~

3.3.4 Southern Ocean sea ice cover

The sea ice cover of the SO changes considerably over glacial-interglacial cycles, as well as on seasonal timescales (Crosta (2009) and Fig. A22 therein). In general, a sea ice cover will inhibit light penetration into the surface ocean as well as air-sea gas exchange. Here we assume complete inhibition of both light and air-sea carbon exchange by sea ice. In this section we thus explore the effect of both biological production and air-sea gas exchange in two extreme cases, i) the largest realistic sea ice cover based on the glacial maximum winter extreme (50° S) and ii) the smallest sea ice cover based on the contemporary summer minimum sea ice extent (70° S). Note that there is a constant sea ice cover about north of 70°N and south of 60° S in the control run of the model. Therefore, the strongest marine $\delta^{13}C$ change is expected south of 60° S for a decreased sea ice cover and between 50-60° S for an increased sea ice cover, as this is the area where ice cover is altered relative to the control run. Ocean circulation changes that could result from a changed sea ice cover are not taken into account, as we want to study the potential isolated effect of sea ice on $\delta^{13}C$ through biological and air-sea gas exchange changes.

Both local and global air-sea carbon fluxes are influenced by a change of the SO sea ice cover, which results in changes in pCO_2^{atm} and $\delta^{13}C^{atm}$. In our experiment, pCO_2^{atm} increases by 5 ppm for an increased sea ice cover and decreases by 5 ppm for a decreased sea ice cover (Table 2, Fig. S5). As noted in Sect. 3.3.1, a change in pCO_2^{atm} is governed by a transient change in the net air-sea gas exchange flux F_{net} until a new equilibrium is established.~~ Initially, a~~ An extended ice cover causes more CO_2 to remain in the atmosphere because the additional ice covers a part of the SO that is a sink for CO_2 in the control run (Fig. S3~~4~~). As the net global air-sea gas exchange F_{net} approaches equilibrium, the non-SO ocean therefore becomes a smaller source for carbon. This reduces the net gas exchange F_{net} inside and outside of the SO by about one third. Our results show that the effects of a changed~~n extended~~ sea ice cover on pCO_2^{atm} ~~strongly depends on the location of the sea ice edge~~are yet to be fully understood: Stephens and Keeling (2000) for example modelled a strong decrease of pCO_2^{atm} in response to an increased sea ice cover south of the Antarctic Polar Front, because they mostly cover a part of the SO that is a course of C to the atmosphere.

In our study, ~~T~~the reduction in pCO_2^{atm} by 5 ppm due to a reduced sea ice cover is ~~fully~~ attributable to the POC production in the earlier ice-covered area between ~60° S and 70° S. In a sensitivity experiment where the ice cover ~~f the ice would just~~ influences air-sea gas exchange only, the sea ice retreat ~~would~~ leads to an increase in pCO_2^{atm} because the region below the ice is strongly supersaturated in C with respect to the atmosphere. ~~(Fig. S4).~~ The increased sea ice cover leads to a complete suppression of air-sea gas exchange south of 50° S. Since this region is in negative carbon isotopic disequilibrium with the atmosphere ($\delta^{13}C < \delta^{13}C_{eq}$, ~~compare~~ Fig. S6~~2~~), the ice cover inhibits a $\delta^{13}C$ flux into the ocean. As a result, $\delta^{13}C^{atm}$ increases to -6.14 ‰, and the opposite happens for a reduced sea ice cover, leading to a lowered $\delta^{13}C^{atm}$ (-6.~~57~~6 ‰).

The increased sea ice cover over the SO results in a surface ocean $\delta^{13}C$ ~~depletion~~ reduction relative to the control of -0.5 ‰ to -0.1 ‰ in the SO, while $\delta^{13}C$ is ~~enriched~~ increased outside of the SO with 0-0.2 ‰ (Fig. 8~~7~~a). The ~~depletion~~ reduction is especially pronounced between 40-60° S. The ~40 % reduced POC export production in the SO due to light inhibition by the sea ice cover causes a major part of the SO surface $\delta^{13}C$ ~~depletion~~reduction, as the absence of photosynthesis will ~~leave~~ cause lower~~the~~ surface ocean ~~less enriched in~~ $\delta^{13}C$. Next to that~~less enrichment from biological production~~, the reduced air-sea gas exchange F_{u+d} in the SO also leads to a ~~more depleted~~lowered surface ocean $\delta^{13}C$ signature. About the opposite happens when we simulate a strongly decreased sea ice cover (only ice south of 70° S): A small ~~depletion~~ reduction of $\delta^{13}C$ is modelled outside the SO, but the SO $\delta^{13}C_{surface}$ locally becomes up to ~0.8 ‰ ~~enriched~~ higher relative to the control (Fig. 8~~7~~b) as the increased amount of air-sea gas exchange F_{u+d} decreases the carbon isotopic disequilibrium and increases POC production in the newly exposed area, both acting to increase ~~leaves the surface ocean enriched in~~ $\delta^{13}C$ of DIC~~during fractionation~~.

The effect of a changed ice cover on deep ocean $\delta^{13}C$ is less than ~0.1 ‰ (Fig. 8~~7~~c~~a~~, d~~b~~) as the surface signal is diluted while it follows the general ocean circulation. -As for air-sea gas exchange (Sect. 3.3.1), no pronounced deep ocean $\delta^{13}C$ signal is found outside of the SO due to sea ice cover changes (this opposed to interpretations by Lear et al., 2016). Global mean $\Delta\delta^{13}C$ is ~~therefore~~ not significantly affected by changes in the SO sea ice cover (~~Fig. 4~~Fig. 5) because the low and high latitude effects on $\delta^{13}C_{surface}$ cancel each other out. ~~Locally in the SO, however, t~~The SO $\Delta\delta^{13}C$ however weakens considerably to 0.4 ‰ when the 50-60° S region becomes covered with sea ice and strengthens ~~considerably~~ to 1 ‰ ~~between 60-70° S~~ if the sea ice is removed between 60-70° S (Fig. S10). The presence or absence of a sea ice cover should thus be clearly visible in especially planktic SO $\delta^{13}C$ sediment records. The effects on $\Delta\delta^{13}C$ advance downstream of the SO, where $\Delta\delta^{13}C$ is increased up to 0.2 ‰ throughout the Pacific and Indian oceans for an increased SO sea ice cover (Fig. S10).

3.4 Modelled versus observed $\Delta\delta^{13}C$ variations

The variations in $\Delta\delta^{13}C$ on glacial-interglacial timescales provide researchers with a tracer to study the biogeochemical state of the past global ocean, under the condition that we can interpret (variations in) $\Delta\delta^{13}C$. ~~This study shows that the sensitivity of $\Delta\delta^{13}C$ depends on location, which is in agreement with the often incoherent patterns of ocean basin planktonic and benthic foraminiferal $\delta^{13}C$ (Oliver et al., 2010).~~ The idealised ~~and large~~ perturbations made to the ~~biogeochemical state of the~~

(Southern) Ocean in this study show that global mean $\Delta\delta^{13}C$ is particularly sensitive to an increased gas exchange rate and changes in the efficiency of the biological pump. Global mean $\Delta\delta^{13}C$ varies up to~~no more than~~ ~±0.4~~5~~ ‰ around the pre-industrial model reference in response to biogeochemical change (~~Fig. 4~~Fig. 5) - under the assumption of a constant ocean circulation. However, the sensitivity of $\Delta\delta^{13}C$ to biogeochemical changes depends strongly on location for all sensitivity experiments (Fig. 4), possibly explaining part of the incoherency of reconstructed planktic and benthic foraminiferal $\delta^{13}C$ from sediment cores (Oliver et al., 2010). In general, such ~~Locally however, larger variations in $\Delta\delta^{13}C$ can occur.~~ $\Delta\delta^{13}C$ reconstructions ~~based on sediment core $\delta^{13}C$ data~~ show $\Delta\delta^{13}C$ variations of ~1 ‰ over the past 350 000 years (Boyle, 1988; Shackleton et al., 1983; Shackleton and Pisias, 1985; Ziegler et al., 2013; Charles et al., 2010; Oliver et al., 2010). Ocean circulation changes explain at least part of these variations in $\Delta\delta^{13}C$ (Charles et al., 2010; Heinze et al., 1991; Jansen, 2017; Heinze and Hasselmann, 1993; Oppo et al., 1990; Toggweiler 1999). However, the changes in the biogeochemical state of the ocean imposed in our experiments show that ~~reconstructed~~ variations in $\Delta\delta^{13}C$ ~~may~~ could be strongly influenced by (SO) ~~(bio)~~biogeochemistry as well.~~cal change.~~ $\Delta\delta^{13}C$ is increased during glacials and reduced during interglacials across a large set of sediment cores (Boyle, 1988; Charles et al., 2010; Oliver et al., 2010; Ziegler et al., 2013). Rapid and large changes have been documented for SO $\Delta\delta^{13}C$ records (Ziegler et al., 2013), and here we show that biogeochemical changes in the SO affect $\Delta\delta^{13}C$ globally. Our results show that an increase in mean $\Delta\delta^{13}C$ could biogeochemically result from slower gas exchange, increased POC sinking rates, or an increased nutrient uptake rate in the SO (Fig. 5). Such biogeochemical changes have been associated with glacial periods (for example, Ziegler et al. (2013)) and are potential candidates to explain part of the $\Delta\delta^{13}C$ increase in interplay with stronger ocean stratification. Sediment-core reconstructions of $\Delta\delta^{13}C$ show that an increased $\Delta\delta^{13}C$ can originate from a downward shift of the metabolic imprint of low-$\delta^{13}C$ POC which would increase shallow $\delta^{13}C$ (Boyle, 1988; Charles et al., 2010; Mulitza et al., 1998; Toggweiler, 1999), and/or a deep ocean $\delta^{13}C$ decrease (Broecker, 1982; Boyle, 1988; Oliver et al., 2010) with little variation recorded for surface ocean $\delta^{13}C$. The absence of a clear surface $\delta^{13}C$ signal could in the SO be the net effect of an increased sea ice cover (locally decreasing $\delta^{13}C$, Fig. 4 and 8a) and an increased biological pump efficiency (locally increasing $\delta^{13}C_{surface}$, Fig. 6a and b, Fig. 7a) or increased SO thermodynamic equilibrium (Fig. 3a and b) – if these opposing signals get mixed. A pronounced deep ocean $\delta^{13}C$ decrease is associated with an efficient biological pump and older water masses in our study (Fig. 4). Interestingly, large changes in deep ocean $\delta^{13}C$ and $\Delta\delta^{13}C$ do not necessarily imply changes in deep ocean PO_4^{3-} (Sect. 3.3.3). The absence of a pronounced PO_4^{3-} change despite $\Delta\delta^{13}C$ changes shows that changed ocean circulation (Toggweiler, 1999) is not the only candidate for explaining the reconstructed deepening of low-$\delta^{13}C$ water and small deep ocean glacial-interglacial PO_4^{3-} variation.

The local character of the $\Delta\delta^{13}C$ sensitivity (Fig. 4) implies that correlations between sediment core $\Delta\delta^{13}C/\delta^{13}C$ variations and global parameters (e.g. pCO_2) are not easily extrapolated to other sediment cores over large distances. Analysis of SO $\Delta\delta^{13}C$ reconstructions from sediment cores at 42° S and 46° S (Charles et al., 2010) for example shows that there is a strong correlation between these cores and Northern Hemisphere climate fluctuations. We expect that this strong correlation does not exist for cores further south in the SO because our results indicate that the SO south of ~50-60° S often has a different $\Delta\delta^{13}C$ response to biogeochemical change than the rest of the ocean.

~~Rapid changes of a large magnitude are expected in the SO carbon cycle from the $p\mathrm{CO}_2$ and $\Delta\delta^{13}C$ records (Ziegler et al., 2013). We propose that this reconstructed intra-millennial variability in $\Delta\delta^{13}C$ could be driven more by changes in the biogeochemical state than by changes in ocean circulation because (bio)geochemical changes might occur more rapidly than whole-ocean circulation changes. Analysis of SO $\Delta\delta^{13}C$ reconstructions from sediment cores at 42° S and 46° S (Charles et al., 2010) shows that there is a strong correlation between these cores and Northern Hemisphere $\Delta\delta^{13}C$ variations. Based on the local character of the $\Delta\delta^{13}C$ sensitivity, we expect that this strong correlation does not exist for cores further south in the SO: The SO south of ~50-60° S often has a different $\Delta\delta^{13}C$ response to (bio)geochemical change than the rest of the oceans (this study). This difference may be attributed to the existence of the biogeochemical divide (Marinov et al., 2006).~~

~~In general, the reconstructed $\Delta\delta^{13}C$ is increased during glacials and reduced during interglacials (Charles et al., 2010; Oliver et al., 2010; Ziegler et al., 2013). This variation is best supported by data for the North Atlantic, as data are too sparse in other basins to get a coherent picture of $\Delta\delta^{13}C$ variations (Oliver et al., 2010). The results of this study show that fast gas exchange or an inefficient biological pump are candidates to contribute to the reduction of mean $\Delta\delta^{13}C$ (Fig. 4), but the reduction is found for low latitudes only. In the SO, $\Delta\delta^{13}C$ is not very sensitive (POC sinking) or even reversed (fast gas exchange).~~ Interglacial periods ~~, when $\Delta\delta^{13}C$ is reduced,~~ are generally thought to be associated with a decrease in the efficiency of the biological pump and increased deep-ocean ventilation via southern-sourced water masses (Gottschalk et al., 2016). Increased deep-ocean ventilation might be driven by increased winds (Tschumi et al., 2011), which would (apart from changing the SO circulation pattern) also~~we can associate with~~ increase~~d~~ gas exchange rates. Each of these processes indeed reduces $\Delta\delta^{13}C$ in the mean in our experiments (~~Fig. 4~~Fig. 5), although less pronounced in the SO (Fig. 4 and Fig. S7). However, the interglacial reduction of $\Delta\delta^{13}C$ seems to originate from a deep ~~sea~~ ocean $\delta^{13}C$ ~~enrichment~~ increase as compared to the glacial deep ocean $\delta^{13}C$ (Broecker, 1982; Charles et al., 2010; Oliver et al., 2010). Our results show that neither an inefficient biological pump nor fast gas exchange can be associated with a pronounced deep sea $\delta^{13}C$ increase as their effects are restricted to the surface ocean. On the other hand, the interglacial decrease of $\Delta\delta^{13}C$ is a decrease as compared to the glacial state: If glacial SO nutrient uptake was higher (V_{max}), a return to the 'normal' state (i.e. the model control run) would result in a major decrease of $\Delta\delta^{13}C$ (Fig. 4 and 5). ~~Besides that, $\Delta\delta^{13}C$ is only increased in lower latitudes for fast gas exchange rates and the effects of a reduced efficiency of the biological pump on $\Delta\delta^{13}C$ is both vertically and horizontally variable.~~

~~Regarding glacials, our results show that an increase in mean $\Delta\delta^{13}C$ could (bio)geochemically come from slow gas exchange, high POC sinking rates, or efficient nutrient consumption in the SO (Fig. 4). Such biogeochemical changes have been associated with glacial periods (for example, Ziegler et al. (2013)) and are, therefore, potential candidates to explain part of the $\Delta\delta^{13}C$ increase in interplay with stronger ocean stratification. Sediment-core reconstructions of $\Delta\delta^{13}C$ show that an increased $\Delta\delta^{13}C$ can originate either from a mid-depth (1200 m, at 42° S and 46° S) increase in $\delta^{13}C$ (Charles et al., 2010) or a general deep ocean $\delta^{13}C$ decrease (Oliver et al., 2010). A deep sea $\delta^{13}C$ decrease is associated with North-Pacific waters of an efficient biological pump (V_{max} and high POC sinking rate experiments). The effects on $\delta^{13}C$ of slow gas exchange are limited to the surface ocean and $\Delta\delta^{13}C$ is only increased in lower latitudes.~~

3.5 The ~~changing~~ relationship between $\Delta\delta^{13}C$, $\delta^{13}C^{atm}$ and pCO_2^{atm}

One would expect variations of ~~surface water~~ $\delta^{13}C^{atm}$ as well as $\Delta\delta^{13}C$ to correlate with variations in pCO_2^{atm}, because similar processes (biology and air-sea gas exchange) steer their distribution/concentrations (Shackleton and Pisias, 1985; this article). $\Delta\delta^{13}C$ is considered a promising proxy for reconstructions of pCO_2^{atm} for times predating ice-core records (Lisiecki, 2010). Here we show that a ~~rough~~ positive linear relationship between $\delta^{13}C^{atm}$ and global mean $\Delta\delta^{13}C$ (Fig. 9a) and a negative linear relationship between pCO_2^{atm} and global mean $\Delta\delta^{13}C$ (Fig. 9b) hold~~s~~ over a wide range of ~~(bio)~~biogeochemical states~~,~~ as simulated in the sensitivity experiments. This result supports previous studies that show both local correlation between $\Delta\delta^{13}C$ and pCO_2^{atm} (such as found by for example Dickson et al. (2008)) and correlation of modified $\Delta\delta^{13}C$ between ocean basins with pCO_2^{atm} (Lisiecki, 2010). The effects of ocean circulation on glacial-interglacial $\delta^{13}C^{atm}$ changes, not studied here, are most pronounced in response to Antarctic Bottom Water formation rate variations and are of the order of 0-0.15 ‰ (Menviel et al., 2015). Our results show that $\delta^{13}C^{atm}$ varies up to ~±0.5 ‰ in response to biogeochemical changes (Table 2). Figure 9~~8~~a shows that changes in the POC sinking rate lie approximately along a line in $\delta^{13}C^{atm}$:$\Delta\delta^{13}C$ space, suggesting that changes in the biological pump efficiency is important for the $\delta^{13}C^{atm}$:$\Delta\delta^{13}C$ relationship. Likewise, the relationship between pCO_2^{atm} and $\Delta\delta^{13}C$ is mostly coming from the biological pump, as air-sea gas exchange affects $\Delta\delta^{13}C$ much more than pCO_2^{atm} (Fig. 9b). ~~In contrast to that, c~~Changes in air-sea gas exchange (as simulated in the gas exchange and sea ice cover experiments) affect $\delta^{13}C^{atm}$ more than $\Delta\delta^{13}C$. This confirms the idea that $\Delta\delta^{13}C$ is governed by biological processes and will also set $\delta^{13}C^{atm}$, unless air-sea gas exchange gets the chance to dominate $\delta^{13}C^{atm}$. ~~The air-sea gas exchange effect depends on the interplay between thermodynamic disequilibrium and gas exchange rates, see Sect. 3.3.1 and Fig. 3.~~The high potential of SO air-sea gas exchange to steer $\delta^{13}C^{atm}$ (Table 2: Sea ice and gas exchange rate experiments) complements recent studies showing that increased SO ventilation of deep ocean carbon is a likely candidate for glacial-interglacial $\delta^{13}C^{atm}$ excursions – which are of the order of 0.5 ‰ (Bauska et al., 2016; Eggleston et al., 2016; Lourantou et al., 2010; Menviel et al., 2015).

~~A statistically significant relationship was also found across the sensitivity experiments between~~ ~~pCO_2^{atm}~~ ~~and global mean~~ ~~$\Delta\delta^{13}C$~~ ~~(Fig. 8b). A local correlation between~~ ~~$\Delta\delta^{13}C$~~ ~~and~~ ~~pCO_2^{atm}~~ ~~(such as found by for example Dickson et al. (2008)) can thus both be attributed to changes in the (bio)geochemical state and ocean stratification.~~

4 Summary and conclusions

This study addresse~~d~~s the ~~governing processes and~~ sensitivity of modelled marine and atmospheric $\delta^{13}C$ and $\Delta\delta^{13}C$ to changes in the biogeochemical parameters under constant ocean circulation, focusing on the contribution of the SO (the ocean south of 45° S, 22 % of the global ice-free ocean area). Variations of $\Delta\delta^{13}C$ recorded in sediment records are sensitive to ocean circulation changes as shown in previous studies, but here we show that the biogeochemical state of the (Southern) Ocean also can have large effects on $\Delta\delta^{13}C$ across all ocean basins. Using the ocean biogeochemistry general circulation model HAMOCC2s, a set of ~~four~~ sensitivity experiments was carried out, which focuses on the biogeochemical aspects known to be important for $\delta^{13}C$ and $\Delta\delta^{13}C$. Specifically, the experiments explore changes in air-sea gas exchange rate, sea ice extent (influencing both biological production and the air-sea gas exchange of carbon) and the efficiency of the biological pump through the POC sinking rate and nutrient uptake rate. ~~gave insight in the effects of (bio)geochemical change on $\delta^{13}C$ and $\Delta\delta^{13}C$.~~

The results show the important role of the SO in determining global $\delta^{13}C$ and ~~the~~ $\Delta\delta^{13}C$ sensitivities, as well as the strong spatial differences in these ~~sensitivity~~. A new equilibrium state developed mostly within the first 100-800 years of the sensitivity experiments, except for the POC sinking experiment where an imbalance between weathering and burial causes a long-term drift. The $\delta^{13}C$ signature is governed by different processes depending on location:~~.~~ Air-sea gas exchange sets surface ocean $\delta^{13}C$ in all ocean basins, contributing 60-100 % to the $\delta^{13}C$ signature. At depth and with increasing water mass age, the influence of biology increases to 50 % in the oldest water masses (North Pacific) due to POC remineralisation. This spatial ~~diversity of the processes~~pattern behind the $\delta^{13}C$ signature of a water parcel results in a non-uniform sensitivity of $\delta^{13}C$ to ~~(bio)~~biogeochemical change. Global mean $\Delta\delta^{13}C$ varies up to ~±0.4 ‰ due to biogeochemical state changes in our experiments (at a constant ocean circulation) (Fig. 5). This amplitude is almost half of the reconstructed variation in $\Delta\delta^{13}C$ on glacial-interglacial timescales (1 ‰), and could thus contribute to variations in $\Delta\delta^{13}C$ together with ocean circulation changes. However, $\Delta\delta^{13}C$ can have a different response on a basin scale: The ocean's oldest water (North Pacific) responds most to biological changes, the young deep water (North Atlantic) responds strongly to air-sea gas exchange changes, and the vertically well-mixed water (SO) has a low or even reversed $\Delta\delta^{13}C$ sensitivity as compared to the other basins. The amplitude of the $\Delta\delta^{13}C$ sensitivity can be higher at decreasing scale, as seen from a maximum sensitivity of ~-0.6 ‰ on ocean basin scale (Fig. 4). Interestingly, the direction of both glacial (intensification of $\Delta\delta^{13}C$) and interglacial (weakening of $\Delta\delta^{13}C$) $\Delta\delta^{13}C$ change matches changes in biogeochemical processes thought to be associated with these periods. This supports the idea that biogeochemistry explains part of the reconstructed variations in $\Delta\delta^{13}C$, in addition to changes in ocean circulation.~~The variations in $\Delta\delta^{13}C$ are caused by both biology and gas exchange processes in the surface ocean but mostly by biological processes in the deep ocean.~~

An increased gas exchange rate has the potential to reduce the biologically-induced $\Delta\delta^{13}C$ through the reduction of surface ocean and atmospheric $\delta^{13}C$. Increased gas exchange however only reduces $\Delta\delta^{13}C$ in the low latitudes: In high latitudes, increased gas exchange will increase $\Delta\delta^{13}C$ (by increasing $\delta^{13}C_{surface}$) because of the negative disequilibrium $\delta^{13}C_{diseq}$ (i.e. $\delta^{13}C < \delta^{13}C_{eq}$) in this region, and thus a potential to increase $\delta^{13}C_{surface}$ (section 3.3.1).

~~Both $\delta^{13}C^{atm}$ and surface ocean $\delta^{13}C$ are strongly influenced by changes in the amount of air-sea gas exchange F_{u+d}, since this sets the $\delta^{13}C$ atmosphere ocean disequilibrium, whereas pCO_2^{atm} is influenced by net outgassing or uptake of carbon F_{net}. There generally is a stronger thermodynamic disequilibrium between the surface ocean and the atmosphere for $\delta^{13}C$ than for pCO_2. Regional differences in the thermodynamic disequilibrium of $\delta^{13}C$ and pCO_2 are therefore found to cause decoupling of the $\delta^{13}C^{atm}$ and pCO_2^{atm} sensitivity response. A significant relationship was however found across the sensitivity experiments between pCO_2^{atm} and $\Delta\delta^{13}C$. This result shows that paleo-reconstructions of pCO_2^{atm} based on $\Delta\delta^{13}C$ could be valid for a wide range of (bio)geochemical states. Locally however, $\Delta\delta^{13}C$ can respond differently to (bio)geochemical processes, as shown in~~

~~this study.~~ $p\mathrm{CO}_2^{\mathrm{atm}}$, $\delta^{13}\mathrm{C}^{\mathrm{atm}}$ and marine δ^{13}C are shown to be disproportionally sensitive to SO gas exchange rate changes: The SO-only experiment results in a $p\mathrm{CO}_2^{\mathrm{atm}}$ and mean $\Delta\delta^{13}$C change as high as ~50 % of the Global experiment (for 'Gas fast')~~, with lower latitudes offsetting part of this sensitivity~~.

Changes in the efficiency of the biological pump also have a major potential to alter $\Delta\delta^{13}$C as well as $p\mathrm{CO}_2^{\mathrm{atm}}$ and $\delta^{13}\mathrm{C}^{\mathrm{atm}}$. The globally increased POC sinking rate experiment shows that $\Delta\delta^{13}$C strengthens in low latitudes (and more so in older waters) by deepening the low-δ^{13}C signature of remineralised POC, while SO $\Delta\delta^{13}$C is not very sensitive to POC sinking rates. The SO effects are comparably small because the vertical mixing in the SO of the low-δ^{13}C deep water only causes shifts in the entire δ^{13}C profile, not a change in the gradient (Fig. 4). Increased POC sinking causes a long-term imbalance between weathering and sediment burial which leads to an increase in mean δ^{13}C and $\delta^{13}\mathrm{C}^{\mathrm{atm}}$ (of about +0.2 ‰). Increased nutrient uptake in the SO (V_{max} experiment) results in a ~11 % lower POC export production outside of the SO, in agreement with previous studies on the role of the SO biological pump in lower latitude productivity. Interestingly, the increase of $\Delta\delta^{13}$C in all ocean basins occurs without significantly changing deep ocean PO_4^{3-}, which advocates for increased SO nutrient uptake to explain (part of) glacial-interglacial $\Delta\delta^{13}$C variations.~~ The effect of the sea ice cover on $p\mathrm{CO}_2^{\mathrm{atm}}$ and $\delta^{13}\mathrm{C}^{\mathrm{atm}}$ as well as marine δ^{13}C depends strongly on the location of the sea ice edge, but has strong potential to change any of them.~~

~~The experiments on POC sinking rate and SO nutrient uptake show that their effect on $p\mathrm{CO}_2^{\mathrm{atm}}$ is different from the effect on $\delta^{13}\mathrm{C}^{\mathrm{atm}}$. $\delta^{13}\mathrm{C}^{\mathrm{atm}}$ is dominated by the loss of light carbon in the POC sinking rate experiment, while the reduction of SO carbon outgassing dominates the sensitivity to the V_{max} experiment. In the V_{max} experiment $\Delta\delta^{13}$C strengthens in the SO but not in other regions, while in the global increased POC sinking rate experiment $\Delta\delta^{13}$C is not very sensitive in the SO but strengthens in low latitudes.~~

~~Mean $\Delta\delta^{13}$C in our experiments (assuming a constant ocean circulation) varies no more than 0.5 ‰ due to (bio)geochemical state changes (Fig. 4). This amplitude is about half of the reconstructed variation in $\Delta\delta^{13}$C on glacial-interglacial timescales, and could thus contribute to variation in $\Delta\delta^{13}$C together with water column stratification. Locally, $\Delta\delta^{13}$C variations can surpass or mirror the 0.5 ‰ constraint however, due to the spatial variation in the sensitivity of δ^{13}C to biogeochemical change. This emphasises the importance of constraining the (bio)geochemical environment before interpreting $\Delta\delta^{13}$C from sediment cores.~~

~~The variations in $\Delta\delta^{13}$C are caused by both biology and gas exchange processes in the surface ocean but mostly by biological processes in the deep ocean. The role of the SO in $\Delta\delta^{13}$C variations is likely to be disproportionally large, as based on the sensitivity of the global δ^{13}C distribution and mean $\Delta\delta^{13}$C to SO-only (bio)geochemical change (i.e. SO-only experiment for gas exchange, the V_{max} experiment and the sea ice experiments).~~

A significant linear relationship was found across the sensitivity experiments between $p\mathrm{CO}_2^{\mathrm{atm}}$ and $\Delta\delta^{13}$C as well as $\delta^{13}\mathrm{C}^{\mathrm{atm}}$ and $\Delta\delta^{13}$C. This result shows that paleo-reconstructions of $p\mathrm{CO}_2^{\mathrm{atm}}$ based on $\Delta\delta^{13}$C could be valid for a wide range of biogeochemical states. Such a wide applicability of a $p\mathrm{CO}_2^{\mathrm{atm}}$:$\Delta\delta^{13}$C relationship agrees with previous studies that find $p\mathrm{CO}_2^{\mathrm{atm}}$:$\Delta\delta^{13}$C correlation for sediment cores around the globe. The maximum response of $\delta^{13}\mathrm{C}^{\mathrm{atm}}$ to the biogeochemical changes imposed in our experiments (up to 0.5 ‰) is larger than the idealised maximum effect of ocean circulation changes on $\delta^{13}\mathrm{C}^{\mathrm{atm}}$ (0-0.15 ‰ (Menviel et al., 2015)), which underlines the potential importance of biogeochemical processes for variations in $\delta^{13}C^{atm}$. The high potential of SO air-sea gas exchange to steer $\delta^{13}C^{atm}$ (Table 2: Sea ice and gas exchange rate experiments) complements recent studies showing that increased SO ventilation of deep ocean carbon is a likely candidate for glacial-interglacial $\delta^{13}C^{atm}$ excursions.

As an outlook, the use of a more complex model with ~~more ecosystem variables (i.e. more trophic levels),~~ a higher horizontal and vertical resolution and a shorter time-step (resolving seasonal variations) could provide valuable additional information. For example, the role of different regions within the SO on the global $\delta^{13}C$ distribution could be better studied with a more complex model. Sediment core-based reconstructions of the global carbon cycle could possibly be aided by a more complex model with a finer grid and higher time resolution, by providing more detailed information on the contribution of ~~(bio)~~biogeochemical processes to local ocean tracers. Next to that, exploring the effect on $\Delta\delta^{13}C$ of a glacial model circulation field could provide a way to quantify the maximum combined effect of circulation and ~~(bio)~~biogeochemical change on $\Delta\delta^{13}C$.

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Experiment	Experiment setup
Gas fast	CO_2 gas exchange rate * 4
Gas slow	CO_2 gas exchange rate / 4
Efficient biological pump	POC sinking rate doubled to 6m/d
Inefficient biological pump	POC sinking rate halved to 1.5m/d
V_{max}	High nutrient uptake rate (control*5) in the Southern Ocean
Ice large	Southern Ocean sea ice cover south of 50° S
Ice small	Southern Ocean sea ice cover south of 70° S

Table 1 Description of the sensitivity experiments. The sensitivity experiments on the CO_2 gas exchange rate and the biological pump have been done twice, once for the Global Ocean and once only making changes in the Southern Ocean (south of 45° S).

	Global experiments		**SO-only experiments**	
	pCO_2^{atm}	$\delta^{13}C^{atm}$	pCO_2^{atm}	$\delta^{13}C^{atm}$
Control	279	-6,4	-	
Gas exchange				
Fast	288	-6,8	284	-6,9
Slow	284	-6,3	281	-6,1
Biological pump				
POC: Efficient	252	-6,2	275	-6,4
POC: Inefficient	293	-6,7	283	-6,5
V_{max}	-		229	-6,0
Ice				
Large	-		284	-6,1
Small	-		274	-6,6

Table 2 Results of pCO_2^{atm} [ppm] and $\delta^{13}C^{atm}$ [‰] for all sensitivity experiments.

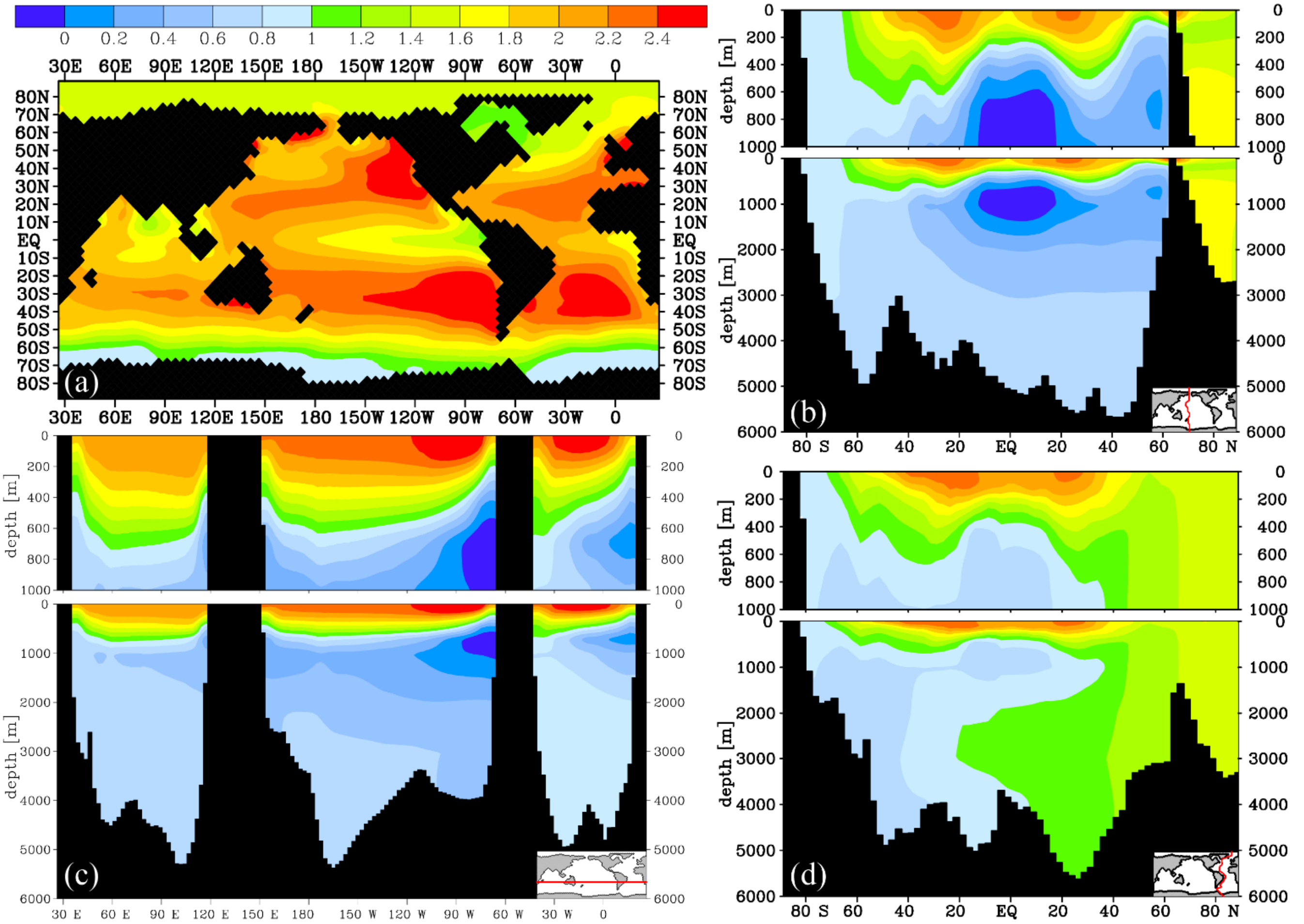

Figure 1 Modelled δ^{13}C of DIC [‰] distribution for the model control run: (a) δ^{13}C at 25 m depth, (b) Pacific transect of δ^{13}C, (c) Zonal transect of δ^{13}C at 26° S, and (d) Atlantic transect of δ^{13}C.

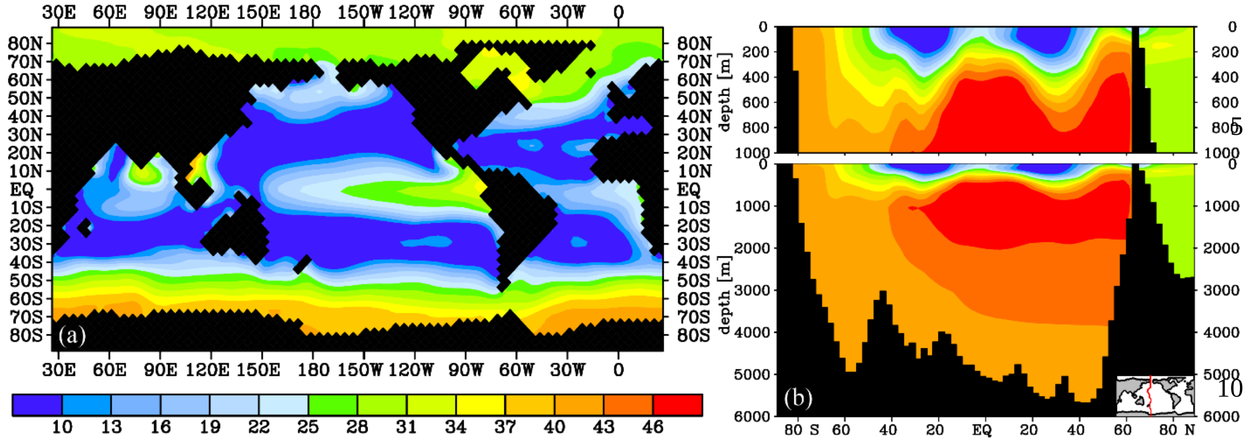

Figure 2 $\delta^{13}C_{bio}^{perc}$, the contribution of biology to the local δ^{13}C signal [%], as calculated using Eq. (4) at (a) 25 m depth and (b) a Pacific transect. The remainder of 100 % is attributed to air-sea gas exchange. The δ^{13}Cbio and δ^{13}C$_{AS}$ values in ‰ are very similar to the values found by Schmittner et al. (2013).

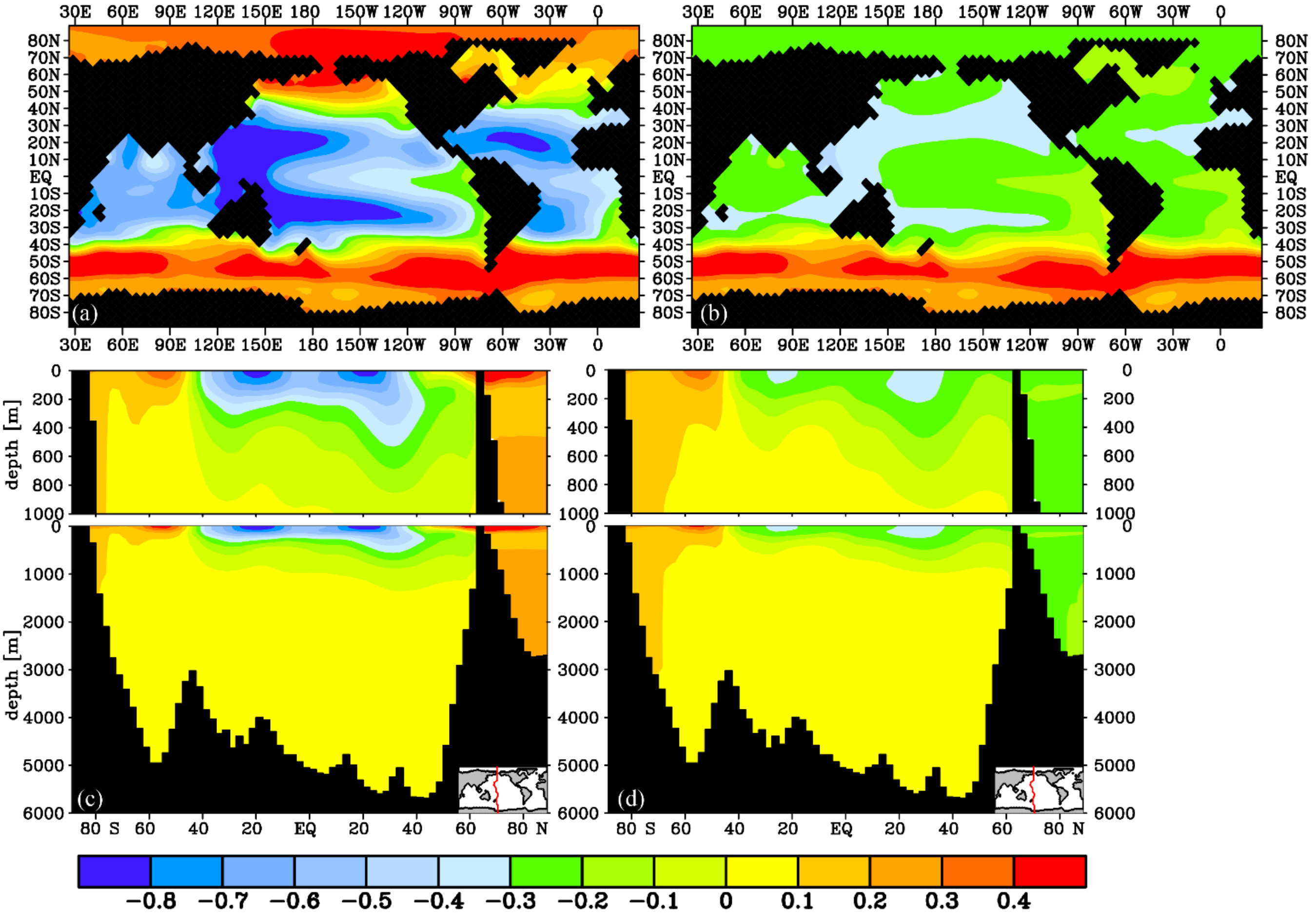

Figure 3 Modelled fast gas exchange sensitivity experiment δ^{13}C of DIC [‰] difference with the model control run: global experiments (a) and (c) and SO-only experiments (b) and (d), at 25 m depth (a) and (b) and as a Pacific transect of δ^{13}C difference (c) and (d).

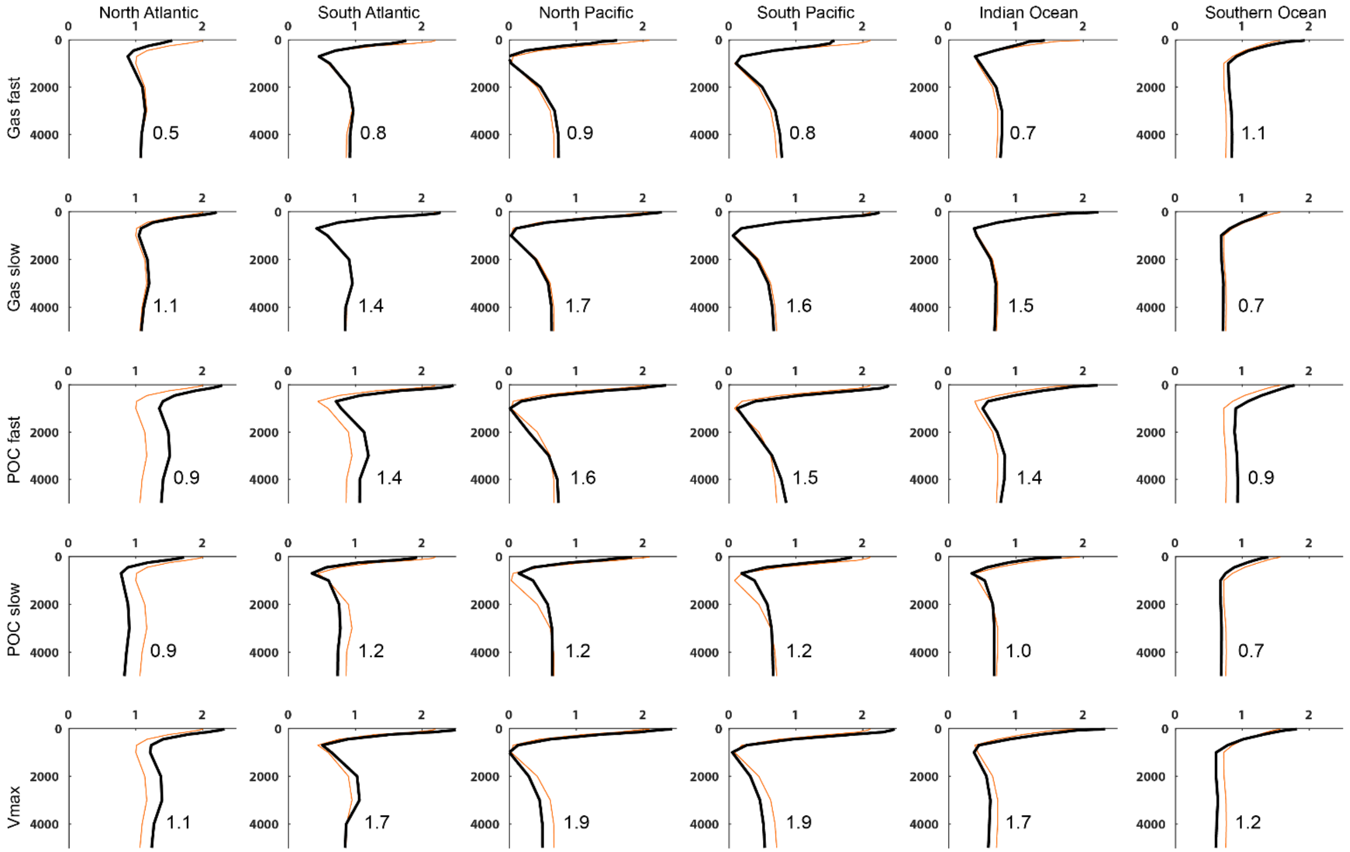

Figure 4 Volume-weighted basin mean profiles of $\delta^{13}C$, with $\Delta\delta^{13}C$ denoted per profile for the sensitivity experiments (thick black lines, Global for gas exchange and POC sinking experiments). Basin extent is visualised in Fig. S11. The thin orange line represents the control model run, which has a $\Delta\delta^{13}C$ of 0.9 (North Atlantic), 1.3 (South Atlantic), 1.4 (North Pacific), 1.4 (South Pacific), 1.2 (Indian Ocean) and 0.8 (Southern Ocean). See Fig. S7 for the resulting anomaly profiles for each experiment.

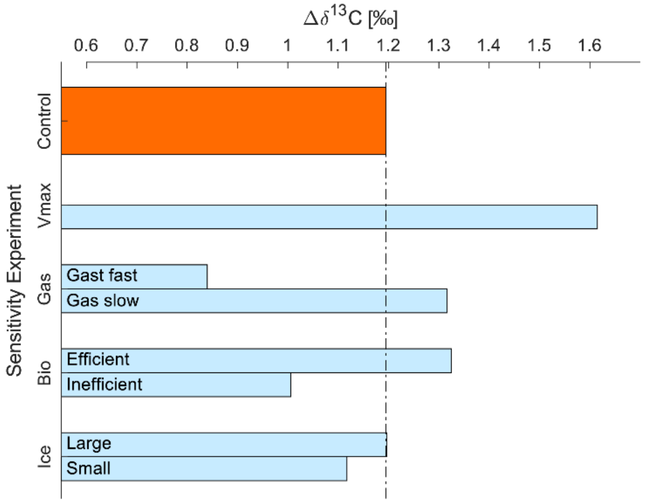

Figure 5 Global mean $\Delta\delta^{13}C$ for the different sensitivity experiments (Table 1). 'Bio Efficient' represents the high POC sinking rate experiment, 'Bio Inefficient' the slow POC sinking rate experiment. The results for the Southern Ocean only experiments (Sect. 2) are described in the text.

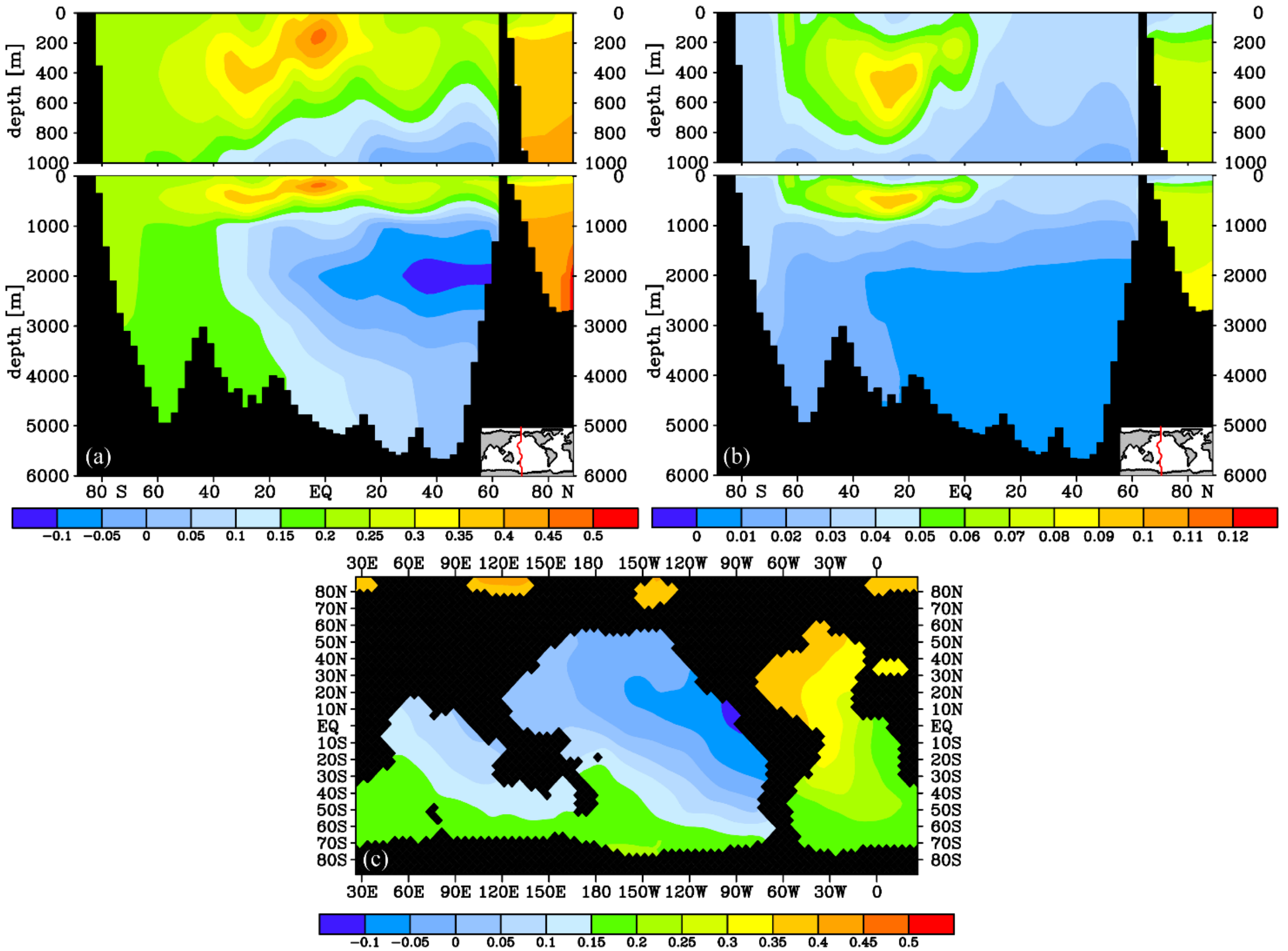

Figure 6 δ^{13}C of DIC difference between model control run and (a) the global efficient biological pump (high POC sinking rate) experiment for a Pacific transect and (b) the SO-only efficient biological pump (high POC sinking rate) experiment for a Pacific transect and (c) at 3000m depth for the global efficient biological pump experiment. Note the different scales.

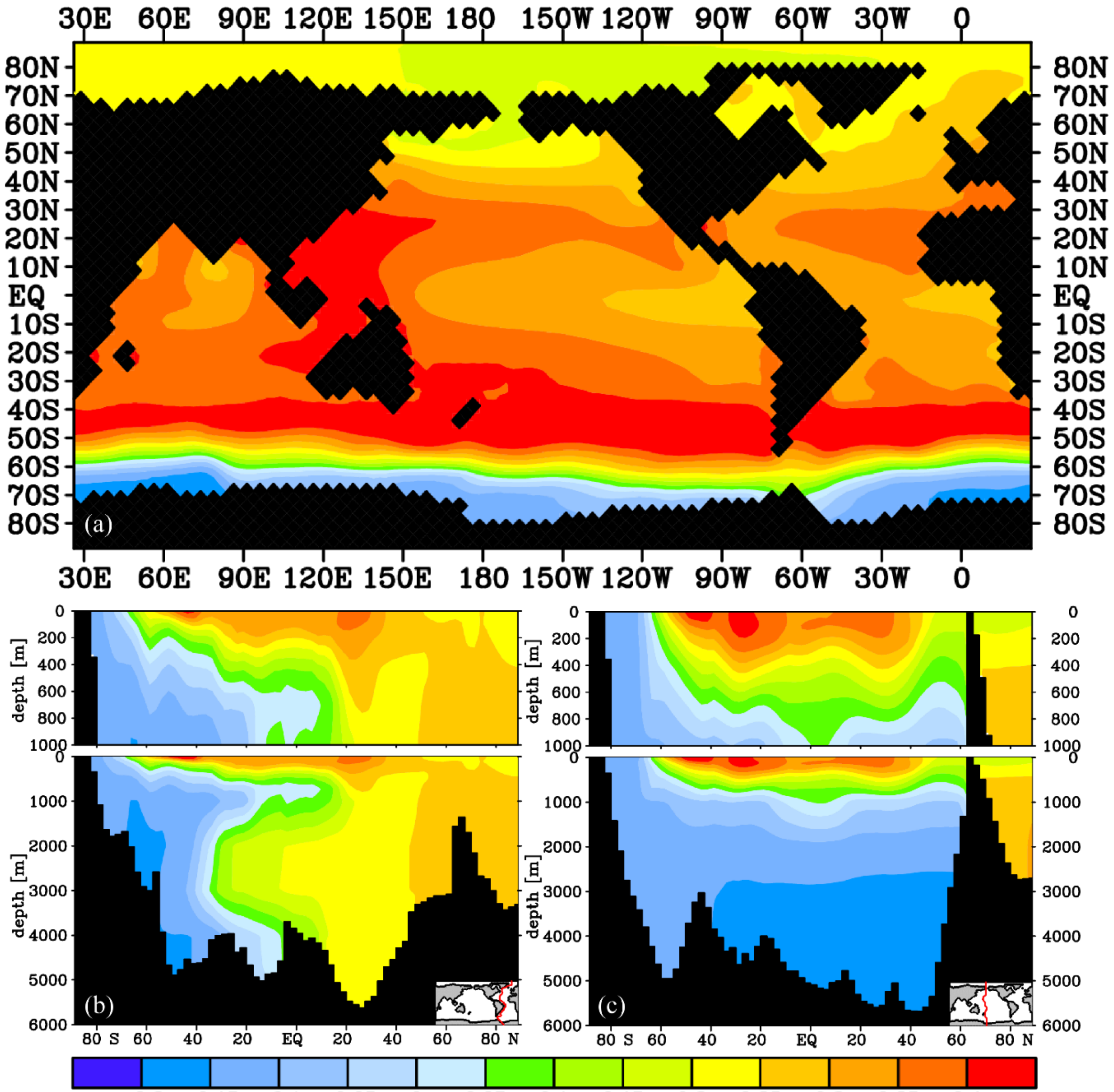

Figure 7 Difference plots between the model control run and the Vmax nutrient depletion experiment at (a) 25m depth and for (b) an Atlantic transect and (c) a Pacific transect.

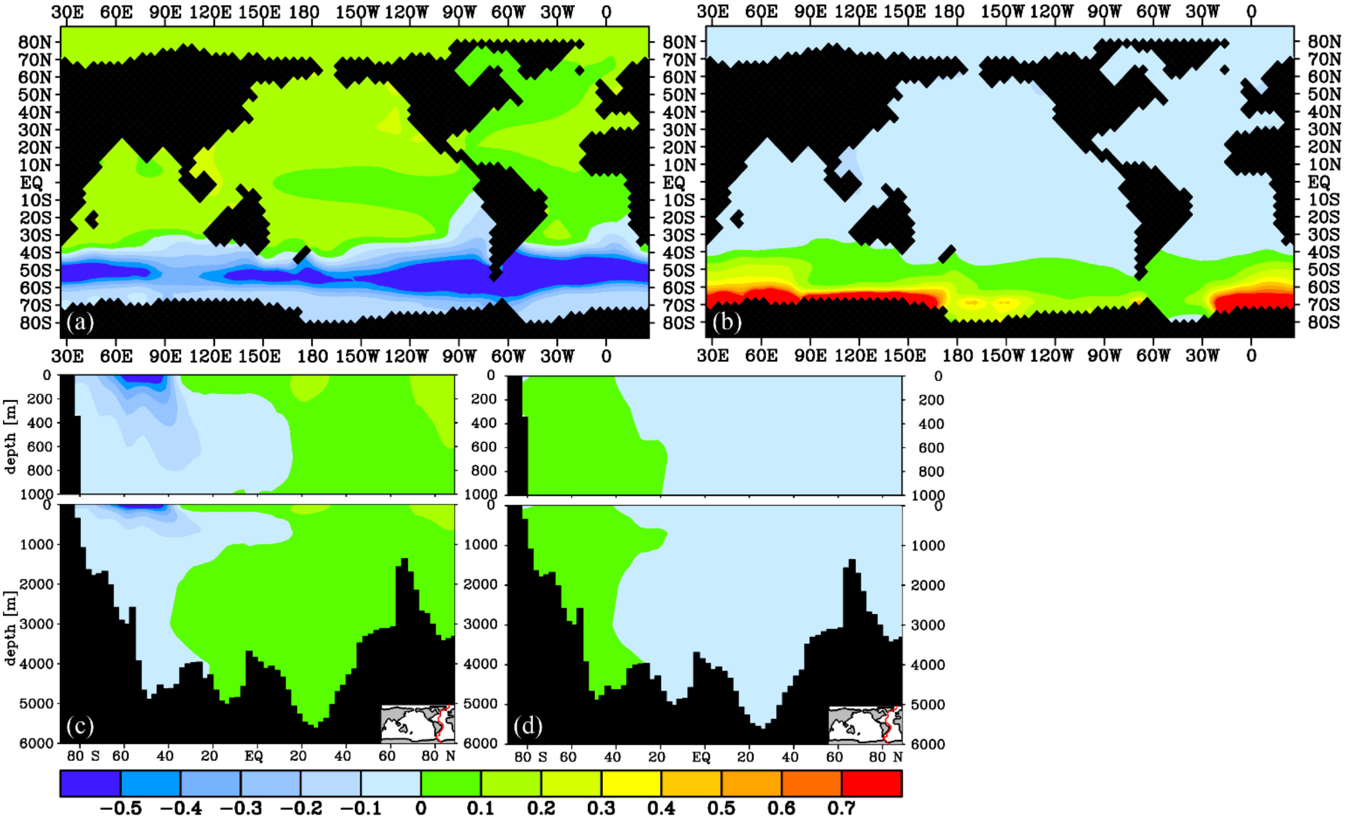

Figure 8 The effect of a large (a, c) and small (b, d) Antarctic sea ice cover on δ^{13}C as compared to the control for 25 m depth (a, b) and an Atlantic transect (c, d).

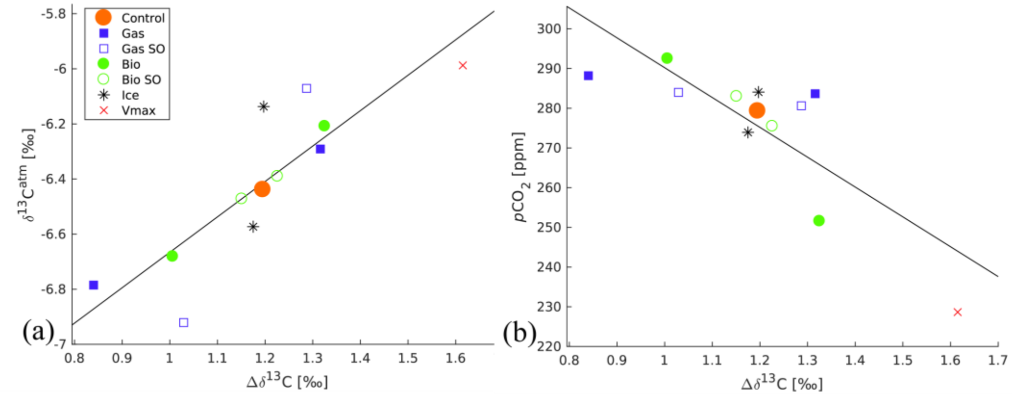

Figure 9 Scatter plot of the global mean $\Delta\delta^{13}C$ and (a) $\delta^{13}C^{atm}$ of the different sensitivity experiments. R-squared of the best-fit line is 0.73 (p-value 0.0004), and the line is described by y=1.3x-7.95 (b) pCO_2^{atm} of the different sensitivity experiments. R-squared of the best-fit line is 0.655 (p-value 0.00143), and the line is described by y=-75x+365.