ALFRED-WEGENER-INSTITUT
HELMHOLTZ-ZENTRUM FÜR POLAR-
UND MEERESFORSCHUNG

Alfred-Wegener-Institut, Postfach 12 01 61, 27515 Bremerhaven

To
Luc Beaufort
Editor-in-charge of the journal
Climate of the Past

Dr. Peter Köhler

Telefon +49 471 4831-1687
Email: peter.koehler@awi.de

Alfred-Wegener-Institut
Helmholtz-Zentrum für
Polar- und Meeresforschung

BREMERHAVEN

Am Handelshafen 12
27570 Bremerhaven
Telefon 0471 4831-0
Telefax 0471 4831-1149
www.awi.de

14.02.2024

Resubmission of a manuscript

Dear Luc,

Please find attached a revised version our draft

No detectable influence of the carbonate ion effect on changes in stable carbon isotope ratios ($\delta^{13}C$) of shallow dwelling planktic foraminifera over the past 160 kyr submitted to Climate of the Past by Peter Köhler and Stefan Mulitza.

The rest of this response letter contains our reasonings for applied changes and (again as already available online) the reply to the comments of the reviewers.

In detail, you find our response to main comments of reviewer 1 (pages 2-7) and to comments of reviewer 2 (pages 14-16) are identical to the uploaded replies in the online discussion. However, this letter additionally includes our detailed responses to the comments made by reviewer 1 in the PDF of our article (pages 8-13) and reasons and content of some further modifications in our revised manuscript (page 17).

A track-changed version of our draft is also included, but note, that since this has been constructed with “latexdiff” for the word processing software LaTeX, it is in detail not correct, when the numbering of sub-sections has been changed.

Hopefully you will find the recent version acceptable for publication.

With Kind Regards

Final and complete authors response to

No detectable influence of the carbonate ion effect on changes in stable carbon isotope ratios (δ13C) of shallow dwelling planktic foraminifera over the past 160 kyr. Under discussion in Climate of the Past, https://doi.org/10.5194/cp-2023-84

Authors: Peter Köhler and Stefan Mulitza

Format: Black / normal font: reviewer #1. *Blue / italics: our response*

Response to comments of reviewer 1

The ms addresses an interesting question, if changes in ocean pH will affect the oxygen and carbon isotope composition of marine organisms. If yes, our interpretation of the isotope composition of fossil shells will be biased due to past changes in ocean chemistry and atmospheric pCO2. Koehler and Mulitza (K&M) present a compilation of glacial/interglacial stable isotope data for G. ruber and G. sacculifer and compare the data to the output from a carbon cycle model, to determine if the isotope data are affected by glacial changes in ocean pH.

The data presented in the ms are probably of fair to good quality and relevant; the conclusions are probably valid and supported by the data. However, the text is badly organised and it is often difficult/impossible to understand what exactly the authors are trying to say. The phrase "probably" is used because the poor presentation leaves room for misinterpretation.

We thank the reviewer for the efforts and comments. We partly agree and will revise significant parts of the manuscript accordingly. Reviewer 1 provided valuable structural comments in an annotated PDF which we will consider in the revised version of the manuscript.

Carbon isotope data - foraminifera. Spero et al (1999) use equations for the relation between d13C and [CO3=] in G. ruber and G. sacculifer to suggest that the offset between the two species in glacial sediments can be used to trace changes in oceanic pH. K&M seem to take these equations as an established fact, only to find that the predicted response cannot be reproduced based on a much larger suite of data. This negative outcome is mentioned immediately at the end of the data section (section 2.3 (not the right place)), which implies that actually there is no real purpose to continue with the modelling part of the study. This is poor salesmanship. I suggest to rewrite the text, emphasising that Spero et al (1999) presented a reconstruction based on a single core, the validity of which can be tested with the current much larger data set.

We agree with the reviewer and will move the section with our findings based on our new $\delta^{13}C$ stacks to Results and Discussion Section. We furthermore will take up the suggestion of using our multi-core $\delta^{13}C$ stacks data to test the findings based on a single core in Spero et al

(1999). While the hypothesis that G. ruber and G. sacculifer have different CIEs can be rejected based on the data alone, we need the model in order to quantify and assess the potential effect of CIE on carbon and oxygen isotope ratios of tropical planktic foraminifera.

However, there are some points to keeps in mind:

1. K&M are focussed mainly on only two papers, Spero et al (1997) and Spero et al (1999). Spero et al (1997) present the famous experiment in which Orbulina and G. bulloides were grown under a wide range of [CO3=] concentrations, after which the d18O and d13C of the test was measured. Spero et al (1999) is not as well documented: the paper is based on "published" experimental results for G. ruber and G. sacculifer, the two species used by K&M. However, the only citation for the actual experiment is a conference abstract, the data are not available as far as I'm aware.

We were mainly interested in results for G. ruber and T. sacculifer because they are among the most abundant and most used species in the non-polar regions, which is the main reason for our focus on the two cited papers. We are aware of the missing documentation of the underlying experiments from which the carbonate ion effect in both species has been proposed. However, the hypothesis that G. ruber and T. sacculifer have different CIEs has been formulated and published in spite of the unavailable data and our paper aims to test this hypothesis.

2. Bijma et al (1999) presented a re-evaluation of data in Spero et al (1997), focussing on pH instead of [CO3=]. They showed that within the range of normal, open-ocean pH there is actually very little variation in isotope composition of Orbulina and G. bulloides. This may well be true for G. ruber and G. sacculifer as well, but this cannot be checked.

Thanks for mentioning Bijma et al. (1999), which we did not consider, since data from G. ruber or T. sacculifer are not included there. This paper makes the case that it cannot be determined if pH or [CO_3^{2-}] is causing the observed fractionations. In addition to the suggestion that there might be little variations in the $\delta^{13}C$ of G. ruber and T. sacculifer in the [CO_3^{2-}] range of interest (which would be ~250-320 μmol/kg), Bijma et al. (1999) proposed alternative processes related to the incorporation of respired CO_2 (depleted in $\delta^{13}C$) during shell formation which might affect foraminiferal isotope data. We will discuss these processes in a revised version of our manuscripts.

3. The range of variation in d13C observed by Spero et al (1997) is too large to explain as a chemical equilibrium reaction (Zeebe, 1999); vital effects related to symbiont activity can explain part of the trend but not the entire magnitude (Zeebe et al., 1999). So something mysterious is going on, if this is relevant for glacial oceanography remains to be seen.

Thanks for these details, which we might have missed so far. We will extend our discussion in that direction.

references (if not cited in K&M)

Bijma, J., Spero, H. J., & Lea, D. W. (1999). Reassessing foraminiferal stable isotope geochemistry: Impact of the oceanic carbonate system (experimental results). In G. Fischer & G. Wefer (Eds.), Use of Proxies in Paleoceanography: Examples from the South Atlantic (pp. 489–512). New York: Springer-Verlag.

Zeebe, R. E. (1999). An explanation of the effect of seawater carbonate concentration on foraminiferal oxygen isotopes. Geochimica et Cosmochimica Acta, 63(13-14), 2001-2007. doi:10.1016/S0016-7037(99)00091-5

Carbon isotope data/model - atmosphere.

The authors write (lines 350-351; my emphasis in bold): "... More interesting is how **simulated changes in atmospheric d13CO2** compares to simulated changes in various marine d13CDIC time series (Figure 7)." However, model version C1 is forced with measured d13C-CO2atm; which means it is input, not output. This raises the question what the modelling contributes - please address this explicitly. The measured isotope data in Figure 3 all show similar trends (with some lead/lags). The modelled d13C-DIC in figure 7 shows, after forcing with atmospheric d13C-CO2, pretty much the same trend, i.e., non-polar d13C-DIC is in equilibrium with the atmosphere. Is this new?

Figure 7 contains two set of simulations. A) one scenario (SEi) in which atmospheric $\delta^{13}CO_2$ is internally simulated plotted in Figs 7a,b. and B) two scenarios (C1, C1CO2) in which atmospheric $\delta^{13}CO_2$ is forced by reconstructions (Figs. 7c,d). The sentence in lines 350-351 is referring to scenario SEi, so to be more precise, we should have indeed only referred to Figs. 7a,b.

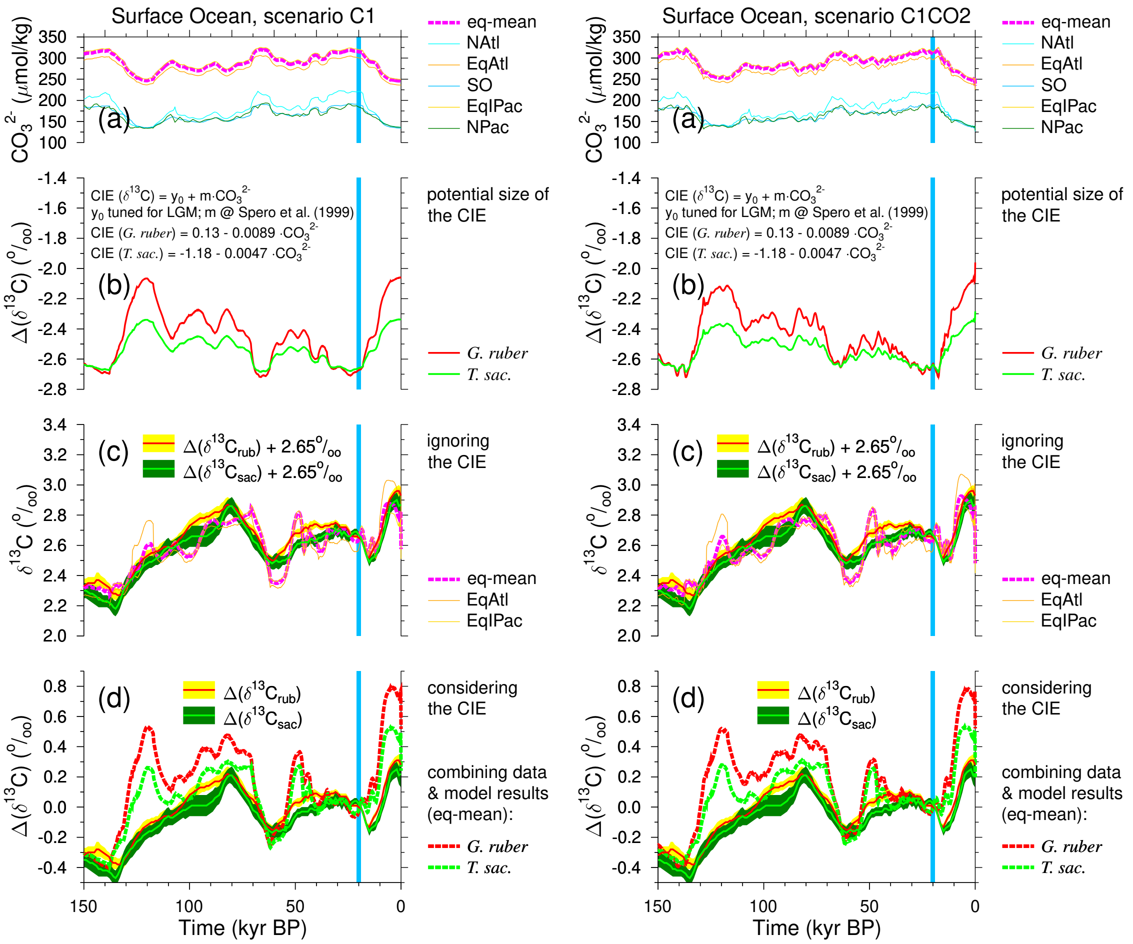
The finding that non-polar $\delta^{13}C_{DIC}$ is in long-term equilibrium with $\delta^{13}CO_2$ in the atmosphere has indeed to some extend been discussed before (e. g. Lynch-Stieglitz et al., 2019; Shao et al., 2021; Pinho et al., 2023, full citations are found in our manuscript). However, since no reliable surface ocean $\delta^{13}C_{DIC}$ time series existed so far, we are for the first time able to compare model results and data in more detail. Furthermore, the modelling helps to understand the relation between atmospheric $\delta^{13}CO_2$ and $\delta^{13}C_{DIC}$ in the global mean ocean surface or in the wider tropical ocean on glacial/interglacial timescales, i. e. that atmospheric $\delta^{13}CO_2$ is more in agreement with the surface ocean $\delta^{13}C_{DIC}$ in the tropics, and how and when the $\delta^{13}C_{DIC}$ in the surface ocean of polar regions differs from that.

More in general, there is a lot of description of the variables/parameters taken into account, but it is not clear which time-series the model is forced with explicitly. There is a reference to a previous version of BICYCLE, but please repeat this information.

When applying an already published model there is always the question how much of the detailed model description should be repeated or not. Following the request of reviewer 1 we will include a figure of forcing time series in the SI.

Lastly, the authors choose model version C1CO2 as their final version, even though this version "violates mass conservation" (line 335). As far as I can see there is little difference between C1 (forced with measured d13C-CO2) and C1CO2 (both CO2 and d13C-CO2 prescribed) - why not stick with C1 as the version with fewer assumptions?

We choose to finally use C1CO2 since this experiment should provide simulated surface ocean [CO_3^{2-}] closest to the reconstructions and therefore should give the most reliable estimate of the CIE (Fig. 8). This motivation was stated in line 411-412. However, the use of scenario C1 (see comparison of scenarios C1 and C1CO2 for the CIE on $\delta^{13}C$ below) would only introduce minor differences and would not affect our main conclusions. This will be mentioned in the revision.



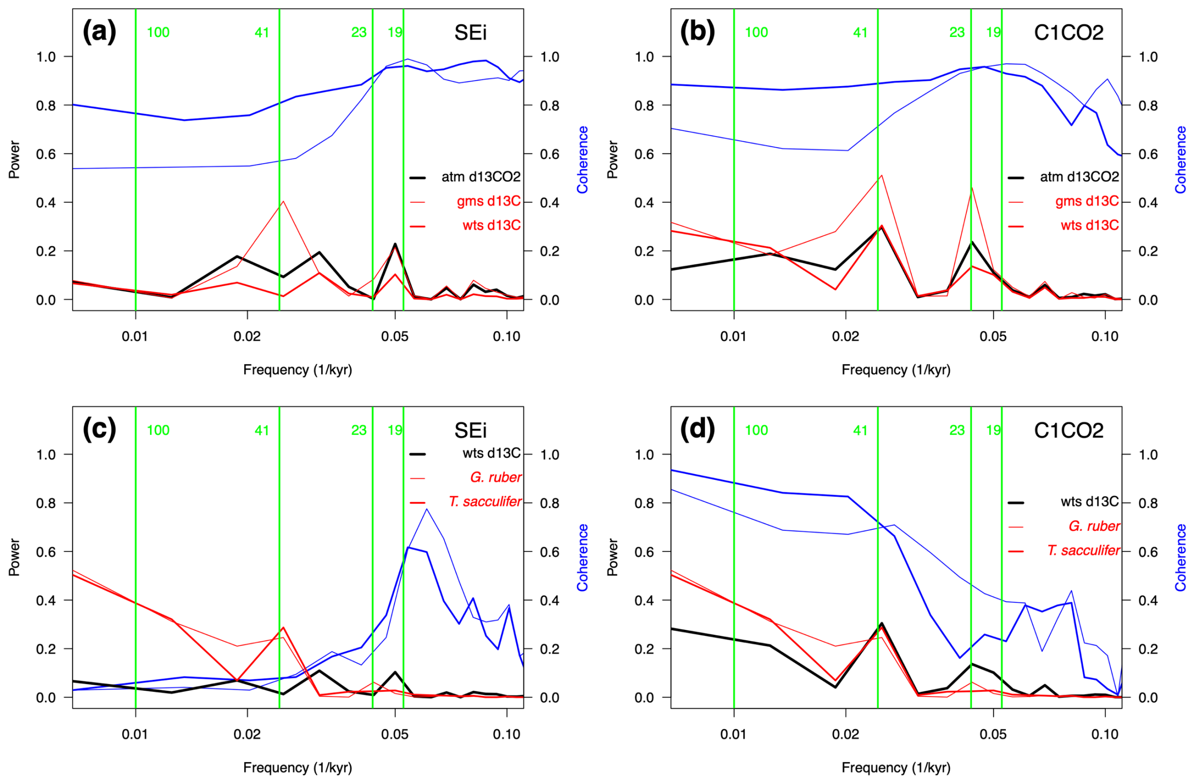
Correlation coefficients. Linear correlation coefficients are not well suited to determine if two time series are correlated. A significant correlation (table 2) means that the time series show similar long-term cycles, i.e., the 100 kyr. That this is the case can be seen visually by inspecting figures 3 and 7. However, the presence/absence of shorter cycles (20 kyr, 40 kyr) cannot be addressed with linear correlation coefficients; neither can leads/lags.

The more appropriate way to test for similarity between time series is to use Fourier Analysis or related methods. I suggest that the authors calculate coherence spectra, to test if the 20 kyr and 40 kyr cycles are present in the isotope data and model input and output. At the very least, Table 2 should go the supplement - it takes up a lot of space, and the essential message (similar long term trends in d13C in the atmosphere, surface ocean, and deep ocean) can be seen in figure 3.

The distinction between 20/40 kyr and 100 kyr cycles is important for the evaluation of Fig. 7. In the basic version of the model (SEi) the modelled d13C shows rapid fluctuations which closely follow those in the atmospheric pCO2 records, at least visually. Only when the model is forced with observed d13C-CO2 does it reproduce the long-term trend (100kyr). It needs coherence spectra to determine what happens with the shorter fluctuations.

We like to emphasize that the long-term (100 kyr) correlation is indeed our main interest. Therefore, we still think the calculated correlation coefficients are of some use and keep them in the draft. We agree that Table 2 is maybe too large in the main text. However, since all details on the regressions are already contained in the figures in the SI (and Table 2 was only meant to be a summary these SI-figures) we thus completely delete Table 2 from our draft. Additionally, we added the root-mean-square-error to our analysis.

Thanks for the suggestions on coherence spectra, which we now calculated together with a frequency analysis of some of the ^{13}C time series plotted in Figure 7. As you see in the resulting new figure below (panels a,b), the coherence between atmospheric $\delta^{13}CO_2$ and wider tropical surface ocean $\delta^{13}C$ (previously called non-polar surface $\delta^{13}C$) is higher than between atmospheric $\delta^{13}CO_2$ and global mean surface $\delta^{13}C$, giving further support for our claim that $\delta^{13}C$ in atmosphere and wider tropical surface are closely connected. Furthermore, the coherence between the simulated wider tropical surface $\delta^{13}C$ and our new $\delta^{13}C$ stack based on either G. ruber or T. sacculifer (panels c,d) is increasing from 0.1 to >0.7 in the 41-100 kyr frequencies, when switching from scenario SEi to scenario C1CO2. This is supporting our approach that when forcing the model with atmospheric $\delta^{13}CO_2$ our simulated wider tropical surface $\delta^{13}C$ is in good long-term agreement with our new $\delta^{13}C$ stack, if the CIE is ignored. We will add details on these findings based on coherence to our discussion.



New figure for the SI with the following caption:
Frequency and coherence analysis of $\delta^{13}C$ time series from our new data stack (c,d) and simulation scenarios (a,c) SEi and (b,d) C1CO2. Power in frequencies is calculated (a,b) for atmospheric (atm) $\delta^{13}CO_2$, global mean surface (gms) $\delta^{13}C$ and wider tropical surface (wts) $\delta^{13}C$, or (c,d) for wts $\delta^{13}C$ and our new $\delta^{13}C$ stacks based on either G. ruber ($\Delta(\delta^{13}C_{rub})$) or T. sacculifer ($\Delta(\delta^{13}C_{sac})$). The coherence (blue lines, right y-axis) is calculated (a,b) between atm $\delta^{13}CO_2$ and either gms $\delta^{13}C$ (thin line) or wts $\delta^{13}C$ (thick line), or (c,d) between wts $\delta^{13}C$ and either $\Delta(\delta^{13}C_{rub})$ (thin line) or $\Delta(\delta^{13}C_{sac})$ (thick line). Main orbital frequencies of 100, 41, 23 and 19-kyr are marked by vertical lines.

Further comments. - see also attached .pdf:

- words like "interesting" and "surprising" should not be used in a scientific manuscript;

We will revise the draft accordingly and avoid these words.

- K&M use the label "non-polar" to describe their isotope data (e.g., fig. 3), however all marine cores in the data set are located between 40°N - 40°S; this leaves a very wide zone (40-66°) unaccounted for in both hemispheres.

We understand the difficulties in calling the latitudinal region of 40°N - 40°S as "non-polar". The wording was adapted from Heaton et al (2020) on the calculation of the Marine20 ^{14}C calibration curve. To be more precise we decided to revise the label from "non-polar" to "wider tropics", since then mentioned area covers the tropics (latitudes: 0°-23°) and most of the sub-tropics (latitudes: 23°-45°).

- The first part of section 3.1 has been copied literally from Koehler and Munhoven 2020; this counts as plagiarism. Please check the rest of the text and modify where necessary.

*According to Climate of the Past's publication ethics, Copernicus "…subscribes to the principles of, the Committee on Publication Ethics (COPE)". In COPE guidelines for text recycling (https://publicationethics.org/sites/default/files/Web_A29298_COPE_Text_Recycling.pdf) it is stated that "**Use of similar or identical phrases in methods sections where there are limited ways to describe a method is not unusual; in fact text recycling may be unavoidable when using a technique that the author has described before and it may actually be of value when a technique that is common to a number of papers is described.**" The first author has published a multitude of papers (most of which are cited) using the same model and hence with very similar model descriptions in the methods sections of those papers. It is therefore not surprising that our paper contains similar or identical sentences when the same model is described as part of the applied methods. We will clarify where the model has been previously described, but see no need to rewrite the model description. We stress that the paper passed the similarity check of the editorial office at a low similarity rate of 3% and find the use of the term "plagiarism" inappropriate in this context.*

Comments made by reviewer 1 in PDF:

Line 5: from the planktic foraminifera Globigerinoides ruber and Trilobatus sacculifer (full genus name first time a species is mentioned; the use of either-or is not correct in this context)
Ok, changed accordingly.

line 26: please start with a brief paragraph explaining what the carbonate ion effect is and why it is relevant for palaeoclimate studies
Ok, included accordingly. A protoype of such a paragraph reads as:
"For a reconstruction of past changes in the ocean and the carbon cycle various variables are measured on fossil specimens obtained from marine sediment cores. Here, classical, nowadays routinely performed measurements are collecting the stable carbon and oxygen isotopes, $\delta^{13}C$ and $\delta^{18}O$, in hard shells of planktic and benthic foraminifera. Since the initial publication of stable isotopes (Emiliani, 1955) a fast number of measurements have been undertaken which led to the most recent data compilation entitled World Atlas of late Quaternary Foraminiferal Oxygen and Carbon Isotope Ratios (Mulitza et al., 2022). One of the not yet completely resolved problems is, how these measurements can be related to past environmental conditions. In other words, how and why was a signal altered on its way from the sea water to the recorder, which here is the hard shell of living foraminifera. Are there vital and other effects necessary to be considered when interpreting the paleo records (e.g. Bijma et al., 1999; Zeebe et al., 2008; Kimoto, 2015)?"

line 55: not the right spot for abbreviations, move to first time delta values are mentioned: e.g., the d13C of G. ruber (d13Crub) and T. sacculifer (d13Csac)
In the next sentence (in line 56) the just mentioned abbreviations are used for the first time, so in our view this is the right place to introduce them here. However, we now also start here (as in the abstract, see comment on line 5) with the full name of the species.

line 56: "from"; or "based on"
Changed to "based on"

line 60: very wordy paragraph; plus, most of this should go to "methods", "results", or "discussion"
This is the last paragraph of the introduction which briefly explains how the manuscript is structured. Naturally, it briefly touches on methods, results, and discussion. We cannot see that splitting this up and moving parts to other sections will help the reader. However, we tried to streamline the paragraph for clarity.

Caption Fig 2: caption does not describe what is actually in the figure; do not use "left" and "right" but sick to a-h
Caption improved as suggested.

line 86: WITH the isotope stacks USING the software (prepositions the wrong way round)
Changed accordingly.

line 97: this is not data - move to the discussion
This is now part of section 4.1, where we discuss what we know from data on the ^{13}C cycle.

line 105: G ruber and T sacculifer
Changed accordingly.

line 106: labels do not match the actual figure
We cannot follow this comment. Here, we refer to Figure 2a,b, which should show the final mono-specific stack of $\delta^{18}O$ and $\delta^{13}C$ anomalies, and this is what is indeed found in this figure.

line 113: "stationary" is a term with a strict statistical meaning, shouldn't be use loosely
Changed to "consistency".

line 122: delete „us“
Done.

line 124: this entire section is a very wordy mixture of methods, results, discussion, and redundant filler-sentences; please split out and be concise
This section is moved into the Results/Discussion and is now section 4.1.

line 139: "surprising" (and other value-judgements) should not be used in a scientific paper
Deleted.

Caption Fig 3, line 4: redundant
Text deleted accordingly.

Line 162: repetition from lines 151-154
Both parts have been revised to minimize repetition. However, we do not simply deleted lines 162-166 as suggested here, since then the PGM-to-LGM changes in the marine data have never been explicitly mentioned in the text.

Line 182: please modify the 1st part of this section, it has been copied literally from Koehler and Munhoven 2020 (=plagiarism)
See above for our response to this comment on the model description (last comment in the main review).

Line 190: Where?
Changed to "In the model"

Line 191: represent
Changed.

Line 198: Explain acronym
The acronym AOBM consists of A=atmosphere, O=ocean, B=terrestrial biosphere and M=sedimentary mixed layer. All four acronyms have been explained during the model description. However, for clarity we repeat the meaning of AOBM here.

Line 216: fractionation
Included as suggested.

Line 217: please check the correction formulation; delta and epsilons are derived from the fractionation factor, not the other way round as implied here

We agree that epsilon is derived from alpha, so we rearranged Eq 1 accordingly. We furthermore changed the wording before Eq 2 from "defined" into "related".

Line 222: replace "2" with e.g., "/", if a distintiction between reservoirs and chemical compounds is needed; "2" is "two", not "to"

We replaced "2" in "a2o" etc. with an arrow to the right.

Line 236: there are lots of mechanisms that contribute to higher productivity during glacial times; there is no need to be specific in the context of this paper

Yes, but iron fertilization is mentioned here because this is the process which in the model drives increased glacial export production. We revised the sentence for clarity saying that this is the process included in the model. These details will become clearer now with a figure showing temporal changes in the forcing (new Figure S1).

Line 242: model scenarios has not been introduced yet

We deleted the mentioning of scenarios in section 3.2, since they are introduced in section 3.3.

Line 248: spread

„breath" changed into "spread" as suggested.

Line 255: which numbers?

This has been specified to "values derived in the previous paragraph from Verwega et al., (2021)".

Line 265: Please don't imply that CIE is the only thing important. There is a lot of literature showing that 13C of planktonic foraminifera is dependent on a lot of things (position in the water column, presence/absence symbionts, temperature). Spero et al 1997 did a very extreme experiment in which they varied pH way beyond what can be expected under natural conditions. I agree that eps(cal-DIC)=0‰ is a reasonable choice,

We changed the text here accordingly. We are pleased that the reviewer finds that our assumption of $\varepsilon_{(cal\text{-}DIC)}$ *= 0‰ is a reasonable choice.*

Line 277: undefined acronym

The acronym has now been defined, see previous comment to line 198.

Line 279: but note that the uncertainty is ±3‰ (

Changed as suggested.

Line 291: this paragraph is mostly redundant. It should not be necessary to have a summary in the middle of a paper.

Ok, the paragraph has been deleted.

Table 1: not referred to in the main text

The caption to Fig. 6 contains a reference to Table 1. However, we add another one in the section in which the scenarios are described.

Table 1, SEi0: without
Changed as suggested

Table 1, C1: is
Corrected as suggested.

Line 308: replace with "AMOC", acronym has already been introduced
Done.

Line 312: delete: repetition from the previous sentence
Done.

Caption Fig 6: it is not clear what this means,
The caption to Fig. 6 has been revised for clarity.

Fig 6: the yellow line is almost invisible, please replace with a different colour; "data spline" - which data??
We changed color and style of line and added the references for the data splines.

Line 330: discussion, not data description
This section described the model (not the data). We think this paragraph motivates our choices made for scenarios C1 and C1CO2 and is well placed here.

Line 339: move down into section 4.1
Done.

Line 354: not visible in figure 7
We think the message is visible in the figure 7. For clarity the color-coded lines are now mentioned in the text, which now reads:
"During glacial times and the onset of deglaciations the dynamics in global mean surface $\delta^{13}C_{DIC}$ (cyan line in Figure 7a) are in close agreement with $\delta^{13}CO_2$ in the atmosphere (black broken line in Figure 7a), while for the later part of the deglaciations and the interglacials the dynamics in non-polar surface $\delta^{13}C_{DIC}$ (magenta line in Figure 7a) fits better to $\delta^{13}CO_2$ in the atmosphere."

Line 353: "than" changed to "as"
Done.

Line 363: incomprehensible sentence
The sentence has been split in two and revised for clarity.

Line 376: is not included
Changed as suggested.

Line 379: incomprehensible

This paragraph touches on details not important for the main message of this draft. We therefore decided to (a) add the notion that 100-kyr periodicities are missing in $\delta^{13}C$ in the model (citing Köhler et al., 2010) to a sentence at the beginning of section 4.1. where Köhler et al (2010) was already cited; (b) delete this whole paragraph here in order to streamline the draft for clarity.

Table 2: linear correlation coefficient are not suitable to determine the relation between time series; use power/coherence spectra
Table 2 is now deleted, see our reply on correlation coefficients and coherence spectra above.

Table 2, line 2 of caption: where
Table 2 is now deleted.

Line 384: Where?
We refined our wording for clarity.

Line 385: where is this shown? if you mean Figure 7a - I don't see much resemblance between measured and modelled d13C surface ocean. you should calculate a coherence spectrum, I would be surprised if there is any correlation at any frequency
This question refers to a sentence where we address simulated vs reconstructed atmospheric CO2 (shown in Fig 6a), not $\delta^{13}C$. We included the reference to Fig 6a for clarity.

Line 387: replace with a less loaded phrase
The word "truth" has been changed to "real world changes".

Line 392: see comment line 386. linear correlation coefficients are not suitable for time series. The long term trend in the modelled d13C-surface looks like the observed records only when you force the model with observed d13C-CO2atm; the higher frequency components are not present in the measured time series.
See our general reply to the issue correlation vs coherence above.

Section 4.2: please provide a critical assessment of Spero et al, 1999 (underlying d13C data never published - abstract only, analysed only a single core)
Spero et al., 1999 is now mentioned with its limitations in the introduction and the final discussion. We do not think these details need to be repeated here in this section.

Line 446: same as d13C (line 386), linear correlation coefficients are not suitable for time-series
See our general reply to the issue correlation vs coherence above.

Line 451: Why go back to discussing d13C suddenly?????
We shifted the details on $\delta^{13}C$ to section 4.2.

Code availability (line 490): should go to the methods section; please address the availability of BICYCLE
PaleoDataView is already mentioned in the data section, but is repeated here. The data analysis tools are now also mentioned in a new subsection in the methods. The code of the BICYCLE model is not available, therefore it is not mentioned here.

Data availability (line 499): not appropriate to list published data here, such papers should be referenced in the text
The cited references here point to PANGAEA data sets (not the related papers, they are cited in the main text) and our reading of the guides to authors is, that they should appear here exactly as has been done.

Line 501: designed the study
Changed as suggested.

Line 501: change "let" in "led"
Corrected.

Response to comments of reviewer 2 (Andreas Schmittner)

The authors present a study of the cycling of carbon-13 over the past glacial cycle. They compile sediment data from two species of planktonic foraminifera and compare the results with box model simulations focusing on the Carbonate Ion Effect (CIE), which has been observed in the lab and proposed to affect paleorecords. However, the authors do not find evidence that the CIE affects paleorecords. To the contrary, the similarity of the two different species records and comparisons with model simulations suggest minimal or no CIE.

I think the paper is well written, nicely illustrated and comes to a conclusion backed up by the evidence provided. I don't have major issues and recommend publication with minor revisions. Below I list two specific points that could be addressed in a revision.

We thank Andreas Schmittner for his efforts in reviewing our study and for his constructive and supportive evaluation.

1. In the abstract (line 13) the authors claim that the model results agree with sediment-data-based reconstructions of d13C_DIC. I don't agree. Fig. 7 shows that the model overestimates the variations in d13C_DIC. However, the comparison does not include the CIE. I suggest to estimate the CIE based on deep ocean model simulated CO3 and include it in the model-data comparison. Does it make a difference?

The comment of the reviewer points to our claimed agreement between $\delta^{13}C$ in model and data in the deep ocean. We agree with the reviewer that on millennial-scale our model shows more variability than the data and that the model has on glacial/interglacial timescales higher amplitudes than the data. The first (overestimate of high frequency changes) is also found in an additional frequency and coherence analysis we did in response to comments of reviewer 1, which showed that when forcing with atmospheric data (scenario C1CO2) the coherence between simulated and reconstructed surface ocean $\delta^{13}C$ is high in 41-100 kyr frequencies, but not in ~20-kyr and higher frequencies. We will revise this sentence in the abstract accordingly.

Furthermore, the reviewer suggests to calculate the CIE for deep ocean data and see if this effort decreases the model/data misfit. We generally agree with the reviewer that the benthic CIE needs to be assessed. Considering a CIE of $(-2.6 \pm 0.4) \times 10^{-3}$‰/(µmol kg-1) for epi-benthic foraminifera (Schmittner et al., 2017) our simulated variations in the carbonate ion concentration would translate to a comparably small reduction of up to 0.05 permil for the glacial deep Pacific which is close to the measurement error of benthic $\delta^{13}C$ (usually about 0.05 ‰). We will add this information to the revised version of the paper, but feel that a more thorough assessment of the benthic CIE would require the comprehensive compilation of benthic $\delta^{13}C$ data, which is beyond the scope of this paper.

2. The authors suggest a temperature dependence of fractionation during photosynthesis, based on observed trends in d13C or organic matter. However, previous formulations of fractionation during photosynthesis proposed it depends on pCO2 (Popp et al.,1989; Rau et al.,1996). Couldn't this also explain the observed trend?

Popp, B. N., Takigiku, R., Hayes, J. M., Louda, J. W., and Baker, E. W.: The post-paleozoic chronology and mechanism of 13C depletion in primary marine organic-matter, Am. J. Sci., 289, 436–454, 1989.

Rau, G. H., Riebesell, U., and Wolf-Gladrow, D.: A model of photosynthetic 13C fractionation by marine phytoplankton based on diffusive molecular CO2 uptake, Mar. Ecol.-Prog. Ser., 133, 275–285, 1996.

This comment refers to our model setup, for which we employed the findings from Verwega et al. (2021) to parameterize the dependency of the isotopic fractionation during marine photosynthesis. As we already wrote in the methods sections the evidence for a dependency of this fractionation on pCO_2 is rather weak in more recent studies than the ones suggested by the reviewer. In detail, we wrote (line 237ff in the submitted version):

"Existing data on fractionation during marine organic matter production (marine photosynthesis) are rather weak in determining if and how it depends on CO_2 (Young et al., 2013; Brandenburg et al., 2022; Liu et al., 2022). Furthermore, as discussed in Brandenburg et al. (2022) some species might contain so-called carbon concentrating mechanisms and use not CO_2, but HCO_3^- as source of their carbon, in which case a completely different isotopic fractionation during marine photosynthesis $\varepsilon(C_{org}$-DIC)) would follow."

We believe this paragraph already completely addresses the concern raised by the reviewer.

Technical comments:

- Line 49 "these" should be "this". *Changed as suggested.*
- 3: For T1 there is a higher resolution record from Bauska et al. (2016; www.pnas.org/cgi/doi/10.1073/pnas.1513868113) available. *This refers to atmospheric $\delta^{13}CO_2$ data. We are aware of these higher resolved data. However, since our approach of forcing the model with atmospheric $\delta^{13}CO_2$ data is increasing the coherence only for time scales of 41-100 kyr (see response to reviewer #1) we do not think higher resolved $\delta^{13}CO_2$ data for Termination 1 will help here. Furthermore, there are also higher resolved $\delta^{13}CO_2$ data in MIS 3 available (Bauska et al 2018, doi: 10.1029/2018GL077881) and we already mentioned that the higher resolved $\delta^{13}CO_2$ data around 70 kyr BP (Menking et al 2022) are of little use here due to our chosen approach and therefore have been ignored here. We will mention both these higher resolved data sets in the revision and plot them in some figures, but will not use them as forcing data.*
- Line 82: replace "ten boxes large ocean" with "ocean with 10 boxes". *We assume that line182 was meant here and revised accordingly.*
- Line 198: explain acronym AOBM. *Done (also raised by rev #1).*
- Line 253: replace "In" with "At". *Done.*
- Lines 255-258: see point (2) above. This also applies to the meridional gradient (e.g. Fig. 8 in biogeosciences.net/10/5793/2013/). *As we wrote in response to point 2 above recent studies do not give supporting evidence for or against CO_2 as main driver for the isotopic fractionation during marine photosynthesis.*

- Line 296-297: how? *This comment refers to a sentence ("The size of this temperature-dependency $\varepsilon(C_{org}$-DIC) was tuned to dynamics in atmospheric $\delta^{13}CO_2$ during the last 20 ka") in the summary section of the methods, which describe the ^{13}C cycle of the model. Actually, this sentence is a leftover from a previous version, where some additional tuning was indeed done. However, since such a tuning was not done here anymore, this sentence should be deleted. Following comments of reviewer #1 this whole paragraph (lines 291-303) will actually be deleted since it contains no new information.*
- Line 300: typo replace "uncertainties" with "uncertain". *Following comments of reviewer #1 this whole paragraph (lines 291-303) will actually be deleted since it contains no new information.*
- Line 387: "not too far away from the truth" It is unclear if the different processes are correct. E.g. you assume large changes in SO ventilation with a big effect on CO2, whereas Khatiwala et al. (2019; doi: 10.1126/sciadv.aaw4981) suggest small effect of ocean circulation. *We were already very careful in writing that "the assumed carbon cycle changes in our approach might be one possible realisation that is not too far away from the truth". We will add Khatiwala et al (2019) to the modelling studies which are cited at the beginning of the subsection "Overview on ^{13}C cycle changes over the last 160 kyr" which would then read (changes in BOLD): "Reconstructed changes in the late Quaternary carbon cycle are still not completely understood. The ice cores give us a precise picture of atmospheric CO_2 (Bereiter et al., 2015; Köhler et al., 2017a) (Fig. 3a), which in the meantime has also been met reasonably well with various different carbon cycle models (e.g. Menviel et al., 2012; Ganopolski and Brovkin, 2017;* ***Khatiwala et al., 2019;*** *Köhler and Munhoven, 2020). These findings suggest, that the main processes responsible for the observed changes on orbital timescales might indeed have been identified, although* ***results are to some extent model-dependent and*** *improvements in details are certainly necessary.*
- 481-482: related to point (2) above, what is the effect of this assumption on the simulated surface d13C_DIC in the case of prescribed atmospheric d13C_CO2? *To answer this question we performed another simulation in which the temperature-dependency in $\varepsilon(C_{org}$-DIC) is switched off (as in scenario SEi0) and atmospheric $\delta^{13}CO_2$ is prescribed from data (as in scenario C1). We find that the simulated non-polar surface ocean $\delta^{13}C_{DIC}$ differs most of the time by less than 0.05 permil, during some time windows by up to 0.13 permil, from the those in scenario C1. This information will be added to the relevant section of the revised draft.*

Additional further implemented changes not directly related to the comments of the reviewers:

- We found an error in Figure 5 (sketch of ^{13}C cycle in BICYCLE-SE). In detail $\varepsilon_{(ara\text{-}DIC)}$ is given in the Figure 5 as +0.3permil, while it is in the model (as stated in the text) 0permil. The figure has therefore been revised accordingly including a change from $\varepsilon_{(ara\text{-}DIC)}$ to $\varepsilon_{(CaCO3\text{-}DIC)}$ as $\varepsilon_{(ara\text{-}DIC)}$ and $\varepsilon_{(cal\text{-}DIC)}$ agree and can be summarized into $\varepsilon_{(CaCO3\text{-}DIC)}$. This revision of Figure 5 includes the change from "ε_{A2O}" to "$\varepsilon_{A\rightarrow O}$" and "$\varepsilon_{O2A}$" to "$\varepsilon_{O\rightarrow A}$", and from "A2S" into "A-S" and "A2O" into "A-O".
- We now also cite Curry and Crowley (1987) in the introduction who calculated a planktic $\delta^{13}C$ stack based on five equatorial cores from the Atlantic.
- We repeated all regression analysis in MATLAB, which led to the same results as before, apart from previous Figure S2a,b (new Fig. S3a,b), where r^2 was 0.0 before, when calculated with GLE, but is slightly better now based on a differed regression line with r^2 of 0.02 and 0.01.
- Some single words or sentences have been modified for streamlining. Especially, the word "compile" was sometimes used in a misleading way, which has been replaced a few times with alternatives (e.g. "construct").
- We refined the sentence citing Oliver et al. (2010) in the introduction for clarity.
- Some repetition related to the source of the data in introduction and methods have been reduced and some too vague specifications have been revised. For example, while the dominant amount of records have indeed been taken from the World Atlas of late Quaternary Foraminiferal Oxygen and Carbon Isotope Ratios (cited as Mulitza et al., 2022), the additional records we use here, but which are not yet included in Mulitza et al (2022), are also in the mean time not yet included in the "World Atlas of late Quaternary Foraminiferal Oxygen and Carbon Isotope Ratios". This was due to a misunderstanding between the two authors not correctly written up in the version initially submitted.