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

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<div align="center">

Response to comments of reviewer 1

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

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?
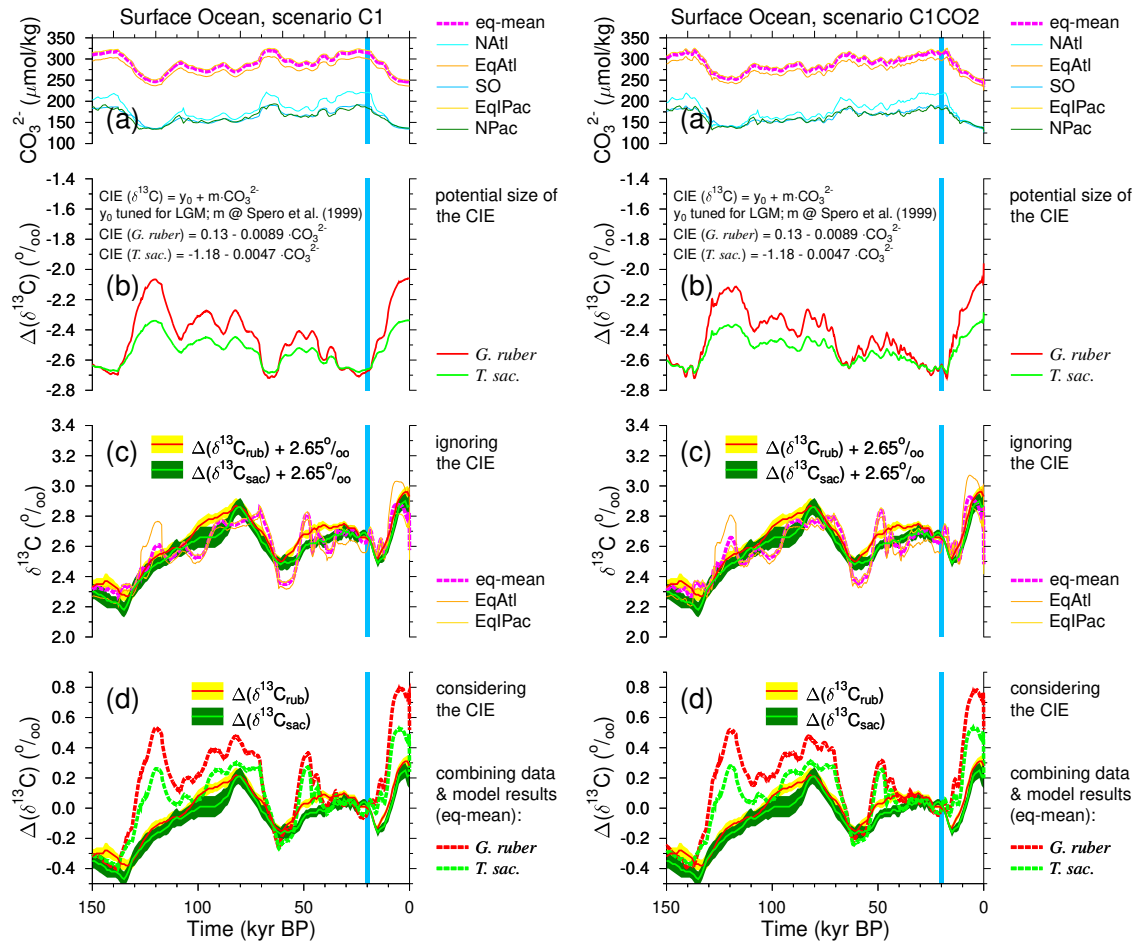
Correlation coefficients. Linear correlation coefficients are not well suited to determine if two time series are correlated. A significant correlation (table 2) means that the time series show similar long-term cycles, i.e., the 100 kyr. That this is the case can be seen visually by inspecting figures 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.
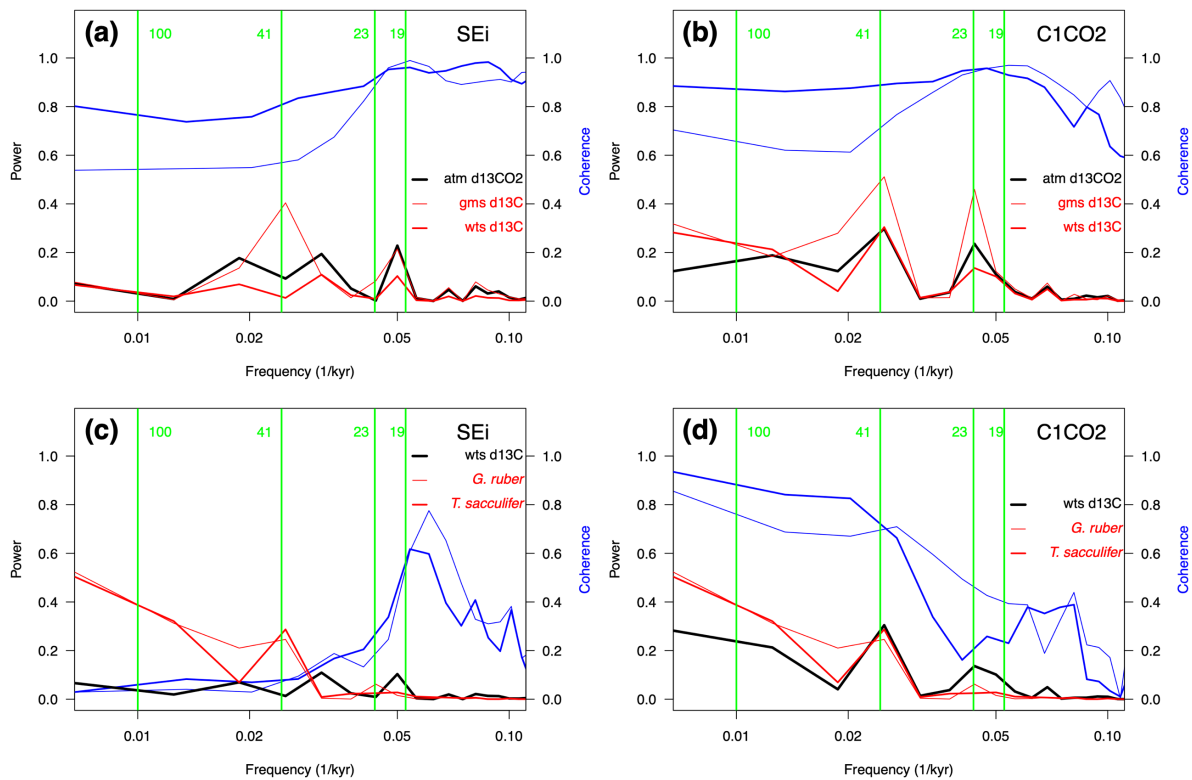
New figure for the SI with the following caption:
Frequency and coherence analysis of $\delta^{13}C$ time series from our new data stack (c,d) and simulation scenarios (a,c) SEi and (b,d) C1CO2. Power in frequencies is calculated (a,b) for

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 <u>be of value</u> 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.*