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. Under discussion in Climate of the Past, https://doi.org/10.5194/cp-2023-84

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Response to comments of reviewer 2 (Andreas Schmittner)

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

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 ± 0.4) × 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 $\varepsilon(C_{org}\text{-}DIC)$ 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 $\varepsilon(C_{org}\text{-}DIC)$ 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.*