An earlier incomplete version of the review response was uploaded on 24/11. Please refer to the final response below. Reviewer comments are in black text and our response in blue. We do not include a tracked changes version of the manuscript or a revised manuscript at this point as the editor request is to respond to the comments only and not to prepare a revised manuscript. We do provide in the response below edits that we would include in a revised manuscript.

RC1

This manuscript presents a null hypothesis prediction for CO$_2$ across the MPT based on generalized least squares regression between Late Pleistocene CO$_2$ records from Antarctic ice and the LR04 global benthic δ$^{18}$O stack, a proxy for changes in global ice volume and deep water temperature. The regression-based predictions are then compared with sparse MPT CO$_2$ estimates from blue ice (Higgins et al, 2015) and boron isotopes (Chalk et al, 2017) with respect to mean value and glacial-interglacial range and compared to trend in CO$_2$ from an intermediate complexity model run across the MPT (Willeit et al, 2019). The authors argue that misfit between pre-MPT CO$_2$ values and the regression-based predictions would be evidence for a change in climate-carbon cycle-cryosphere dynamics across the MPT.

R1 Comment: The analysis appears to be performed well, and I have only a few concerns about the interpretation of the results. However, my main concern is that the work is too simple. I would encourage the authors to add more intellectual substance to the paper by exploring perhaps nonlinear regression between benthic δ$^{18}$O and CO$_2$...

Response: We appreciate the positive comments about the analysis and acknowledge the simplicity of the generalised least squares (GLS) model. In our view the simplicity of the model is a strength – our objective with this manuscript was to generate the simplest reasonable model to predict CO$_2$ from the δ$^{18}$O benthic stack and to test the predictions against available observations. In response to this review and comments from other reviews we have substantially expanded the work in three main areas to add more substance:

1. We bring in substantial additional data to evaluate our predicted record CO$_2$ record, specifically: Allan Hills Blue Ice CO$_2$ data from Yan et al., (2019) at 1.5 Mya; CO$_2$ proxy reconstructions from leaf wax from Yamamoto et al., (2022); δ11B reconstructions by Dyez et al., (2018), and Guillermic et al., (2022) and a high resolution CO$_2$ reconstruction by van de Wal et al. (2011).
2. We add discussion of underlying mechanisms relating benthic δ$^{18}$O and CO$_2$.
3. In light of the additional comparisons with blue and proxy CO$_2$ records from (1.) we find that our regression-based prediction of pre-MPT CO$_2$ is not rejected by the existing data and we discuss the implications.

More on each of these points is provided in the responses to follow. Regarding the specific point about exploring non-linear regression plan to add new text to the manuscript to justify the GLS approach as follows:

“Our objective with this manuscript was to generate the simplest reasonable model to predict CO$_2$ from the δ$^{18}$O benthic stack and to test the predictions against available observations. It is possible that the fit could be further improved using a non-linear approach, however we deliberately refrain from that for several key reasons. First, a scatter plot of the LR04 δ$^{18}$O benthic stack versus observed ice core CO$_2$ over the past 800 kyr yields a Pearson’s correlation coefficient (r) of -0.82 (see Figure R1-1), indicating that ~68% of the variance in observed CO$_2$ is shared with the benthic stack. There is no evidence in this
scatter plot for departure from the linear relationship at high or low CO$_2$ or benthic $\delta^{18}$O levels. Second, following the approach of Chalk et al., 2017 and interpreting the upper 25$^{\text{th}}$ percentile of CO$_2$ data as representing mean interglacial stage CO$_2$ and the lower 25$^{\text{th}}$ percentile of CO$_2$ data as representing mean glacial stages CO$_2$ levels, we see that our predicted interglacial mean value for the past 800 kyr (253.1 ± 2.3 ppm) closely overlaps with the observed interglacial mean value (253.9 ± 4.1 ppm) and similarly, the predicted glacial stage mean (199.7 ± 1.7 ppm) closely overlaps with the observed (202.0 ± 3.2 ppm). Furthermore, the predictions are remarkably insensitive to bootstrap analysis in which 50% of that data are omitted with each iteration of the GLS model (Fig 1). Such insensitivity to the bootstrap analysis and accurate prediction of glacial and interglacial state CO$_2$ values would be unlikely in the case of major non-linear dependencies between the LR04 predictor and CO$_2$ response variables. Third, non-linear approaches would risk generating an improved fit due to statistical artefacts that do not meaningfully relate to any dependence between benthic $\delta^{18}$O and CO$_2$. Finally, the specific causes and sources and sinks involved in glacial to interglacial and millennial-scale CO$_2$ variations still remain poorly constrained (e.g. Archer et al., 2000; Sigman et al., 2010; Gottschalk et al., 2019), and given that process-uncertainty, the GLS model fits our criteria of the simplest reasonable model.”

Figure R1-1: Observed continuous ice core CO$_2$ versus the LR04 benthic $\delta^{18}$O stack over the past 800,000 years. Pearson’s correlation coefficient $r = -0.82$. CO$_2$ data from Bereiter et al., (2015), LR04 benthic stack from Lisiecki & Raymo, (2005).
R1 Comment: “...discussing in more depth the underlying mechanisms relating benthic δ¹⁸O and CO₂ to say more about the implications of potential misfit between CO₂ and the regression-based estimate.”

This is a good suggestion and in response we would revise the manuscript (nominally around lines 58-59) to give more detail on potential underlying mechanisms (while also acknowledging that there is no consensus on these):

“The δ¹⁸O of fossil benthic foraminifera calcite is governed by ocean temperature and global ice volume at the time the foraminifera lived, with higher values indicating both increased ice sheet volume and a colder climate. The first order rationale in using the LR04 δ¹⁸O benthic stack as an input parameter to predict CO₂ is based on the known relationship of ocean temperature with CO₂ solubility (e.g. Millero, 1995). The solubility of CO₂ in the ocean increases with falling sea surface temperatures, particularly in high-latitude deep-water formation regions, where colder ocean temperature drive increased uptake of CO₂ by the ocean, reducing the atmospheric CO₂ concentration (Berends et al., 2021). However, we note that the magnitude of glacial cooling can only account for a portion of observed glacial CO₂ drawdown (Archer et al., 2000) and multiple other dependencies between CO₂ and ocean temperature and/or ice volume are also likely at play in explaining the observed shared variance. These may include (not exhaustively), direct radiative forcing of ice volume changes by CO₂ (e.g. Shackleton et al., 1985), second order effects on atmospheric CO₂ from changing ice volume, including the impact of ice volume/sea level on atmospheric CO₂ via ocean productivity and carbonate chemistry changes (e.g. Broecker et al., 1982; Archer et al., 2004; Ushie and Matsumoto 2012), CO₂ drawdown during periods of high ice volume by increased iron fertilization (e.g. Rothlisberger et al., 2004; Martinez-Garcia et al., 2014) and enhanced sea ice extent during periods of high ice volume capping the ventilation of CO₂ from the ocean interior at high latitudes (Stephens and Keeling, 2000).”

Figure 1 (from manuscript): A) Comparison of our PRED-CO₂ (ppm) record to the current continuous composite record; CO₂ estimates from boron isotope analysis of benthic foraminifera shells (BOR-CO₂) (Chalk, et al., 2017), and direct CO₂ measurements from Allan Hills blue ice core data (BI-CO₂) (Higgins et al., 2015). Indicators for age uncertainty boundaries (± 89 ky) of the blue ice represented by dashed boundaries. Blue shading around the PRED-CO₂ curve represents 95% confidence intervals generated from the bootstrap analysis (Methods).
R1 Additional Specific Concerns

R1 Comment: Abstract, line 18: I think the authors meant benthic foraminiferal stable isotope (δ18O). The δ18O data used is from foraminiferal calcite, not “water.”

Thank you. Corrected to “the existing benthic foraminiferal calcite δ18O record from marine sediment cores.”

R1 Comment: Line 118: It is not clear what the authors mean by “This trend is seen in our predicted record, and in the filtered BI-CO2 and BOR-CO2 data (Fig. 1C).” The previous sentence describes glacial stage CO2 draw-down and the absence of an interglacial draw-down. In Fig. 1C, it appears that this description holds for the predicted CO2 record (i.e., glacial draw-down but steady interglacial values). However, the BI-CO2 and BOR-CO2 data show a change in BOTH glacial and interglacial CO2 compared to the post-MPT average. The text should be revised to make clear which trends are similar between the predictions and observations and which are different.

We take the opportunity to clarify and expand on this section. We would include a comparison to the Yan et al., 2019 BI-CO2 data from 1.5 Mya and draw back on quantitative comparison to BOR-CO2 data on account of its larger uncertainties than BI-CO2 data. Nominal revised text around Line 118 as follows:

“Previous studies conclude that glacial stage draw-down of CO2 occurred across the MPT in the absence of interglacial draw-down; i.e. glacial stage atmospheric CO2 concentrations decline with time across the MPT, whereas interglacial stage CO2 concentrations remain comparatively stable (e.g., Chalk et al., 2017; Hönisch et al., 2009). This trend is also seen in our predicted record (Fig 1A & 1C). For example, our predicted glacial CO2 concentration ca. 1Myr is 217.6 ± 2.3 ppm (central lower blue bar Fig 1C), which is significantly higher than the predicted mean of 199.7 ± 1.7 ppm for glacial stages of the past 800 kyr (lower left blue bar Fig 1C). Comparing this to the observed Higgins et al., (2015) BI-CO2 data (and hereafter interpreting the lowest 25th percentile of the BI-CO2 as representing glacial stage atmospheric CO2, after Chalk et al., (2017)), the BI-CO2 data suggest a concentration of 226.2 ± 4.0 ppm for glacial stages ca. 1Myr (lower black bar Fig 1C), which is significantly higher than the mean observed glacial atmospheric CO2 concentration over the past 800 kyr of 202.0 ± 3.2 ppm (left orange bar Fig 1C). Turning to the interglacials, our GLS model predicts CO2 concentration during the interglacial stages at ca. 1Mya of 256.3 ± 3.8 ppm (central upper blue bar Fig 1C), which is not significantly different to our predicted mean of 253.1 ± 2.3 ppm for the upper 25th percentile (hereafter interglacial) stages of the past 800 kyr (upper left blue bar Fig 1C). In comparison, the interglacial BI-CO2 data from ca. 1Myr suggest a concentration of 271.3 ± 4.5 ppm, which although higher than the observed mean over the past 800 kyr of (253.9 ± 4.1 ppm, orange bar top left of Fig. 1C), is within the range of the observed interglacial CO2 concentration during interglacials 5, 9 and 11 and is less than the glacial stage draw down suggested by the blue ice data.”

“The Higgins et al., (2015) BI-CO2 data indicate greater glacial stage draw down than our predicted record. However, old ice from blue ice areas may be subject to diffusional smoothing of CO2 [e.g. Yan et al., 2019], which would act in the direction of elevating the minimum (lower 25th percentile and assumed glacial) values found in the blue ice above the glacial atmospheric values. Diffusion does not offer an explanation for the blue ice maxima inCO2at 1Mya (upper 25th percentile and assumed interglacial) also being higher than our prediction, so here it may be that our model is under-predicting interglacial CO2 values prior to the MPT. But under predication cannot be confirmed given the caveat that blue ice
samples, which are generally drawn from ice which has passed close to the base of the ice sheet, have risk of artificially elevated concentrations due in-situ respiration of detrital matter. Although respiration effects are screened for by measurements of δ13C of CO₂, it is difficult to demonstrate that all samples are unaffected (Yan et al., 2019). A further argument against rejecting our model predictions is comparison to the Yan et al., (2019) Allan Hills Bl-CO₂ data from 1.5 ± 0.21 Mya; here we see our predicted interglacial and glacial CO₂ levels closely overlapping with the upper and lower 25th percentiles of the Bl data (Figure R1-2).

The BOR-CO₂ data from Chalk et al., (2017) - like our prediction - also does not indicate any significant drawdown during interglacial stages. This is demonstrated by the upper 25 percentile mean for the early MPT BOR-CO₂ data (274.2 ± 13.4 ppm, green bar top right of Fig 1C), being not significantly different to the post MPT upper 25 percentile of 280.9 ± 14.8 ppm. Also like our predictions, the BOR-CO₂ data support significant glacial stage drawdown, as demonstrated by the lower 25 percentile mean for the early MPT data (238.7 ± 22.1 ppm, green bar bottom right Fig 1C), which is significantly higher than the post MPT lower 25 percentile mean (198.9 ± 10.4 ppm). We note that the post MPT interglacial BOR-CO₂ data exceed the observed concentration in the ice core record by ca. 26 ppm (Figure R1-3*) and that the early-MPT interglacial BOR-CO₂ exceed our predictions by a similar amount (Fig 1 C.). Therefore we conclude that the Chalk et al., BOR-CO₂ data also do not provide cause to reject our model predictions.

These changes would necessitate corresponding revisions to other parts of the manuscript, which we would undertake for resubmission.

Figure R1-2: Predicted CO₂ (this work) and the Yan et al. (2019) blue ice CO₂ record from the Allan Hills. Black crosses represent the mean blue ice measurements at 1.5 ± 0.21 Mya filtered into the upper and lower 25th percentiles (with 2σ errors) to represent interglacial and glacial stages respectively and averaged over their age uncertainty range (210kyr). (*n.b. for a revised manuscript we would include this Yan et al. data in Fig 1.)
Figure R1-3: The Bereiter et al., (2015) observed 800 kyr CO$_2$ record (orange) and the Chalk et al. (2017) boron-isotope based CO$_2$ reconstruction (green) filtered into glacial and interglacial values via the upper and lower 25th percentile and averaged over the total time period of each record. This is compared to the predicted CO$_2$ from this study (blue curve) (*n.b. for a revised manuscript we would consider including the Chalk et al., post MPT BOR-CO$_2$ data in revised Fig 2.).

Line 185-186: The authors need to explain why out-of-phase responses in northern and southern ice before the MPT (as proposed by Raymo et al., 2006) would lead them to expect “large discrepancies” between their regression-based CO$_2$ prediction and the realized data. This inference seems to rely on the assumption of a certain relationship between CO$_2$ and northern or southern ice sheets, but I’m not sure what relationship the authors are assuming. Section 4.2 overall is quite short and would benefit from a more in-depth, process-based discussion of implications of the anti-phased hemisphere hypothesis for pre-MPT CO$_2$ variability.

Thank you, this is a good suggestion and we now also have the opportunity to further develop this section with reference to new work presented by Yan et al., 2022 on the phasing of northern and southern ice volume pre and post-MPT. We would further develop Section 4.2 with nominal text as follows:

“Previous work has shown that across the glacial–interglacial cycles captured in the Vostok and EPICA Dome C ice core records there is more than 80% common variance between observed atmospheric CO$_2$ and ice core water stable isotope-based reconstructions of Antarctic temperature [Cuffey and Vimeux, 2001; Wolff et al., 2005; Luthi et al., 2008)]. This observed correlation has contributed to a prevalent view that climate conditions in the circum-Antarctic Southern Ocean (which are assumed to be captured or at least correlate with the Antarctic temperature reconstruction) play a dominant role in modulating glacial-interglacial atmospheric CO$_2$ variations (see Fischer et al., 2010 for a review). The links between Southern Ocean conditions and atmospheric CO$_2$ remain contested, but are proposed to include climate-driven physical changes in CO$_2$ ventilation from the Southern Ocean associated with surface buoyancy (e.g. Watson and Garabato, 2006), sea ice variability as a cap to exchange (Stephens and Keeling, 2000), changes in wind-driven upwelling (e.g. Toggweiler et al., 2006) and temperature sensitivity of solubility (Millero 1995). In addition, there is much literature on direct and indirect modulation of biological carbon fluxes by the effects of SO climate conditions, including on SO export production of
organic material and carbonate compensation feedbacks in the deep ocean (Broecker and Peng, 1987; Fischer et al., 2010) and iron fertilisation (Martinez-Garcia et al., 2014). The assumption inherent in our predicted CO$_2$ record is that processes linking SO climate conditions, global ice volume and carbon cycle changes during the past 800 kyr can be extrapolated across the MPT. This assumption would be violated, and we would expect the model to fail, in the case that the phase locking hypothesis suggested by Raymo et al., (2006) holds. Some discussion of the basis of the phase locking hypothesis is required to understand why.

The phase locking hypothesis offers an explanation for the absence of precession-related (23kyr) periods in the LR04 benthic stack prior to the MPT (see Appendix Fig C), despite the strong precession cycle in insolation (Raymo et al., 2006, Morée et al., 2021). The key concept is that prior to the MPT the Northern Hemisphere and Antarctic ice sheets were responsive (in ice volume) to insolation changes in the precession band, but because precession forcing is out of phase between the hemispheres, the ice volume changes were opposing between the hemispheres and therefore cancelled in the benthic stack. This cancellation of the precession signal left insolation forcing in the 40 kyr obliquity band to dominate globally integrated ice volume changes expressed in the benthic stack. A transition from a smaller and more dynamic terrestrial terminating Antarctic ice sheet to a larger and more stable marine terminating ice sheet with cooling climate across the MPT (e.g. Elderfield et al., 2012) is then proposed to remove sensitivity of Antarctic ice volume to precession forcing and to suppress ice sheet sensitivity to the obliquity band in favour of quasi-100kyr ice volume changes that are in phase between the hemispheres (Raymo et al., 2006).

Recently presented data from Yan et al., support the phase locking hypothesis, specifically with evidence that pre-MPT Antarctic temperature (and by extension ice volume) is positively correlated with a local precession-band insolation proxy that is based on the oxygen-to-nitrogen ratio of trapped air (Yan et al., 2022). Whereas the correlation becomes negative in the blue ice and continuous ice core data post MPT.

To now extend the argument to potential impacts on CO$_2$ exchange, if the phase locking hypothesis holds, then prior to the MPT the Antarctic and Southern Ocean climate conditions and by extension the Southern Ocean mechanisms of CO$_2$ exchange described earlier, would also be expected to fall out of phase with the benthic stack. Since our regression model assumes continuation of the in-phase relationship between the benthic stack and Antarctic and Southern Ocean climate conditions (as inherited from the post-MPT training data) we would expect to see disagreement between our pre-MPT CO$_2$ predictions and a realised oldest ice continuous ice core CO$_2$ record.”

References (added in revisions)


