

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.

RC2

An earlier incomplete version of the review response was uploaded on 24/11. Please refer to the final response below and the responses to the other reviews of our manuscript by R1 and Peter Kohler. 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.

RC2 Overall assessment

The paper by Martin et al. represents a very simple, statistical (further on loosely called regression) model to estimate past atmospheric CO₂ from the LR05 stack of benthic δ¹⁸O. As LR05 is a combined record of deep ocean temperature and ocean volume (not of CO₂) the regression of CO₂ with LR05 is only statistical in nature and does not include a direct causal connection. Accordingly, a good predictive skill of LR05 to calculate CO₂ beyond its calibration period (the last 800 kyr) cannot be expected. Not surprisingly, the predicted CO₂ does not closely reflect the limited data we already have about CO₂ in the MPT from blue ice snap shots and CO₂ reconstructions based on δ¹¹B in foraminifera.

Based on this disagreement, the authors conclude that the null hypothesis of "a common global climate - carbon cycle - cryosphere feedback across the MPT" must be rejected. This is correct in a purely statistical sense, however, without laying out what exactly the causal relationship is between the three Earth System components and why these could be imprinted in the LR05/CO₂ regression, the null hypothesis appears to be not well justified. Accordingly, I think the minimum the author have to do to their manuscript is to discuss this connection and to bolster the justification of the null hypothesis. Another point of criticism could be raised that also the existing CO₂ from blue ice and δ¹¹B may contribute to the difference between observed and predicted CO₂. For example, the very old ice from the bottom of blue ice areas may be subject to diffusional smoothing of CO₂. This could explain that the minimum (glacial?) values found in the blue ice are higher than the true atmospheric values, however, it would not be in line with the (interglacial?) blue ice maxima in CO₂ being also higher than the prediction. Also the limits of the δ¹¹B reconstructions have to be better laid out as they are strongly dependent on the input parameters that are used to calculate CO₂ from δ¹¹B and also from the CO₂ saturation state at the marine drilling site in the past, as also illustrated by the relatively large uncertainty of the δ¹¹B reconstructions compared to ice core records.

In summary, while the study by Martin et al represents an interesting exercise (as was the initial EPICA challenge published in a non-peer reviewed journal), the question remains, whether this contribution in its present form provides sufficient new insight to justify publication in CP.

Thank you for the constructive critique. We believe the manuscript has been strengthened by addressing it. We make a number of changes to address the key concerns, summarised immediately below and more detail can be found further on in the response to specific comments.

Regarding the comment “..Not surprisingly, the predicted CO₂ does not closely reflect the limited data we already have about CO₂ in the MPT from blue ice snap shots and CO₂ reconstructions based on δ¹¹B in foraminifera.” In response, we bring in substantial additional data to evaluate our predicted record CO₂ record, specifically: Allan Hills Blue Ice CO₂ data at from Yan *et al.*, (2019) at 1.5 Mya; CO₂ proxy reconstructions from leaf wax Yamamoto *et al.*, (2022); δ¹¹B reconstructions by Dyez *et al.*, (2018), and Guillermic *et al.*, (2022) and a high resolution CO₂ reconstruction by van de Wal *et al.* (2011). The comparison is shown in a revised Fig 2, below. In the revised figure we see that our predicted CO₂ sits around the middle of the field compared to other estimates and is consistent with the Yan et al (2019) data. Accordingly, we now consider that the null hypothesis cannot yet be rejected by the existing data. Detailed quantitative comparisons between our predicted CO₂ and the existing data are provided in response to comments further below and in the response to R1.

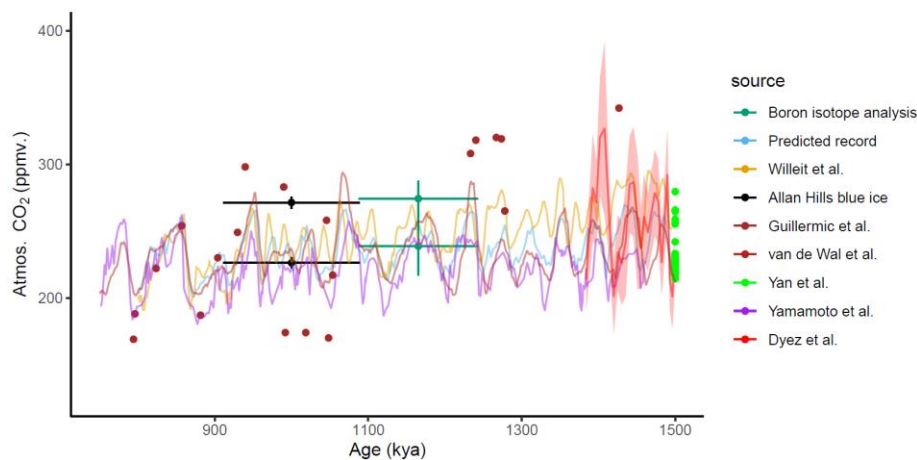


Figure 2 (revised): Predicted CO₂ (this work) and observed, proxy and modelled CO₂ from a range of other sources: δ¹¹B-based pCO₂ reconstructions and measurements by Dyez *et al.* (2018), Guillermic *et al.* (2022) & Chalk *et al.* (2017); model simulation under a regolith removal hypothesis by Willeit *et al.* (2019); blue ice CO₂ measurements by Yan *et al.* (2019) & Higgins *et al.* (2015); δ¹³C leaf wax proxy reconstructions by Yamamoto *et al.* (2022); high resolution CO₂ reconstruction by van de Wal *et al.* (2011)

Regarding the comment “Accordingly, I think the minimum the author have to do to their manuscript is to discuss this (benthic stack to CO₂) connection and to bolster the justification of the null hypothesis.” In response, we propose to add sections in the introduction and discussion discussing potential direct and indirect physical and/or biogeochemical links between LR04 global ice volume and temperature proxy and atmospheric CO₂. The proposed new text is provided further below in the response to specific comments.

We also propose to add discussion of the caveats associated with blue ice and marine sediment boron-isotope based CO₂ reconstructions, again given in full further below.

Fully updating the manuscript to capture all the flow on changes is beyond the scope of what is requested by the editor at this stage, but we hope the responses below now better demonstrate the potential value and suitability of the work for a revised submission to CP.

R2 Specific comments:

R2 Comment line 16: "is to make"

Accepted.

R2 Comment: line 17 and throughout the manuscript: Myr instead of myr

Accepted.

R2 Comment: line 25: the authors state that the null hypothesis should be rejected, however, without laying out the causal relationship between the regression parameters and potential reasons why the regression may not hold back in time, this statement is not entirely satisfying.

We make substantial revisions in three main areas to address this comment.

First, we add more detail on potential mechanisms linking the regression parameters, with nominal new text added around Lines 58-59 as below:

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 $\delta^{18}\text{O}$ 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 $\delta^{18}\text{O}$ benthic stack as an input parameter to predict CO_2 is based on the known relationship of ocean temperature with CO_2 solubility (e.g. Millero, 1995). The solubility of CO_2 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 CO_2 by the ocean, reducing the atmospheric CO_2 concentration (Berends et al., 2021). However, we note that the magnitude of glacial cooling can only account for a portion of observed glacial CO_2 drawdown (Archer et al., 2000) and multiple other dependencies between CO_2 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 CO_2 (e.g. Shackleton et al., 1985), second order effects on atmospheric CO_2 from changing ice volume, including the impact of ice volume/sea level on atmospheric CO_2 via ocean productivity and carbonate chemistry changes (e.g. Broecker et al., 1982; Archer et al., 2004; Ushie and Matsumoto 2012), CO_2 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 CO_2 from the ocean interior at high latitudes (Stephens and Keeling, 2000)."

And we would add corresponding text to the discussion around Lines 177, nominally:

"The range of physical and biogeochemical processes involved in glacial to interglacial CO_2 changes are still contested and glacial to interglacial CO_2 source and sink changes are still not quantitatively constrained (Sigman et al., 2010; Fischer et al., 2010). Given the fundamental uncertainties we cannot quantitatively set out and apportion physical processes responsible for the observed regression. Nevertheless, our analysis shows that 68% of the variance in observed CO_2 over the past 800 kyr is common with the LR04 stack and that strength of this relationship is remarkably insensitive to our bootstrap tests that remove 50% of the data (Methods)."

In addition we develop the discussion around potential reasons why our regression model may not hold prior to the MPT. As an example, we would expand the discussion on the phase locking hypothesis (which was recently bolstered by the new data from Yan et al., 2022). Nominal additions to Section 4.2 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 CO₂ 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 CO₂ variations (see Fischer et al., 2010 for a review). The links between Southern Ocean conditions and atmospheric CO₂ remain contested, but are proposed to include climate-driven physical changes in CO₂ 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 CO₂ 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 suppress too 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 (any 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 CO₂ 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 CO₂ 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 CO₂ predictions and a realised oldest ice continuous ice core CO₂ record.”

R2 Comment: line 58-59: $\delta^{18}\text{O}$ is not just a sea level proxy but also influenced by deep ocean temperature. A process-based discussion of why LR05 is a viable input parameter to predict CO₂ is required.

Addressed within the response to the earlier R2 comment on the physical basis of the regression.

R2 Comment: Line 66: please include also the record by Dyez et al., *Paleoceanography* 2018:

Thanks for the suggestion. This comment refers to the Dyez et al. (2018) $\delta^{11}\text{B}$ -based pCO₂ proxy data spanning 1.38–1.54 Ma. We will add it to the description of records around Line 66, as follows:

“To test the null hypothesis, we compare our predicted CO₂ record to several existing sets of CO₂ or CO₂ proxy data that exist within the predicted range: 1) CO₂ estimates from the analysis of boron isotope ratios in benthic sediment cores which present a proxy for ocean pH to which a transfer function is applied to reconstruct atmospheric CO₂ (hereafter referred to as BOR-CO₂) (Chalk, et al., 2017; Henehan et al., 2013; Dyez et al., 2018).”

This record plotted is plotted below in Figure R2-1 for comparison with our predicted CO₂ record.

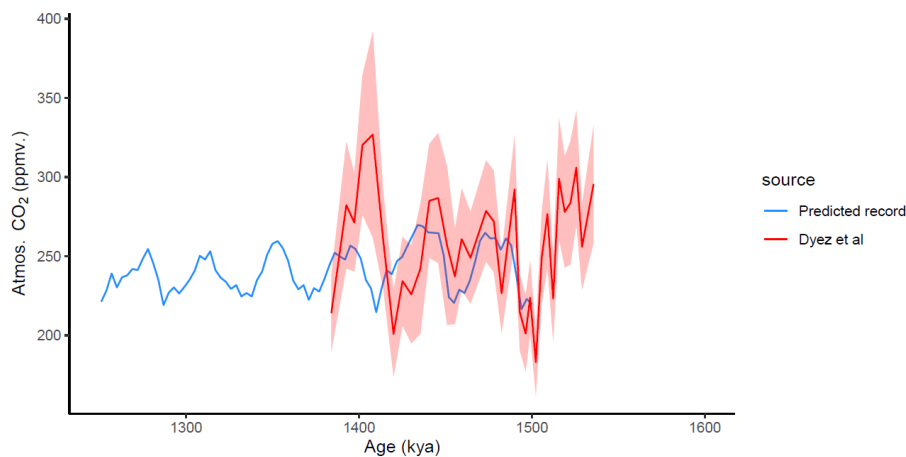


Figure R2-1: Predicted CO₂ (this work) and the Dyez et al. (2018) $\delta^{11}\text{B}$ -based pCO₂ reconstruction.

We would include new text in the discussion along lines:

“For the period of overlap with our predicted record, 1.38–1.5 Mya, the Dyez et al. (2018) $\delta^{11}\text{B}$ -based pCO₂ data appears higher during interglacial periods by 20 to 50 ppm. However the significance of this difference is questionable given the ca. ± 33 ppm uncertainty in the

$\delta^{11}\text{B}$ -based data. What is clearer, is that there is no significant difference between our predicted record and the Dyez et al., data during glacial stages.”

We will also revise Figure 2 in the main manuscript to include the Dyez et al., data (see the revised Fig 2 in our response to the general comments). Including comparisons to this and a number of other records suggested in this and other reviews leads us to revisit our earlier conclusion that our predicted CO_2 record increasingly under predicts CO_2 concentrations indicated by other archives. Rather, our predicted record sits around the central range of other predictions over the 0.8 to 1.5Mya interval.

R2 Comment, line 68: *The very old ice at Allan Hills is not really from the surface but from a shallow ice drilling of more than 100 m depth.*

Good point. Text adjusted as follows:

“..glacial ice that has been brought to the near surface of an ice sheet by ice flow processes, where it is can be accessed by cutting trenches or by shallow drilling of up to several hundred meters (e.g. Higgins et al., 2015).”

R2 Comment: Methods: *the uncertainty in the regression connected to the independent age scales should be discussed*

Good point. We would add some discussion in the revised Methods:

“Limitations in the regression may exist due to uncertainties in the independent age scales of both the LR04 stack and the compiled CO_2 record, even after binning to the 3 kyr grid. The LR04 stack graphically correlates 57 globally distributed $\delta^{18}\text{O}$ sediment cores through common climate signals with an independently developed age model constructed from the average sedimentation rates of each core, assuming global sedimentation rates have remained relatively stable, and tuned to a simple ice model. The authors estimate uncertainty of 6 kyr from 1.5 – 1.0 Mya, and 4 kyr from 1 – 0 Mya due to the tuning technique neglecting higher frequency changes over global climate reorganisations and glacial cycles (Lisiecki & Raymo, 2005). The composite observed CO_2 ice core record (Bereiter et al., 2015) uses six independent dating methods for various core locations both spatially across Antarctica, and stratigraphically for different sections of the same core (firn, ice etc.). The age uncertainty in the gas timescale has a median over the 0–800kyr interval of 2 kyr, but individual uncertainties can reach up to 5 kyr (Veres et al 2013; Bazin et al., 2013). The relative age uncertainties between these input variables may diminish the regression or in some instances lead to spurious correlation. However, we expect any such effects are minor on the basis that our predictions show little sensitivity (Fig 1A) to the bootstrap analysis with 1000 iterations of recomputing the regression after removing 50% of data (Methods). If the model was sensitive to relative timescale uncertainties we would expect larger bootstrap confidence intervals.”

R2 Comment: line 85: *not clear what $r(226)$ means, please explain. Did you allow for lag correlation? (see also comment on age scales above)*

We were referring here to the correlation coefficient between our predicted record of CO_2 and the observed composite ice core record. ‘226’ refers to the degrees of freedom of the test. We change

this to simply report the Pearson correlation coefficient, in this case $r = -0.82$ ($p = \ll 0.01$). Our generalised least square model accounted for autocorrelation/lag between the predictor ($\delta^{18}\text{O}$) and CO_2 using an AR(1) correlation factor.

R2 Comment: line 89: the limitations of blue ice CO_2 reconstructions and $\delta^{11}\text{B}$ reconstructions of CO_2 should be discussed as well.

We plan to add further detail including around line 130 on blue ice and $\delta^{11}\text{B}$ limitations in the opening of the discussion:

“ CO_2 measurements from blue ice, and proxy-reconstructions from boron isotopes have a number of caveats. Old ice from blue ice areas may be subject to diffusional smoothing of CO_2 (Yan et al., 2019) and deformation (Higgins et al., 2015), which would act in the direction of elevating the minimum (lower 25th percentile and assumed glacial) values found in the blue ice higher above the glacial atmospheric values. A caveat that is difficult to entirely eliminate with blue ice samples (which are generally drawn from ice which has passed close to the base of the ice sheet) is the potential for elevated CO_2 levels due to contamination by in-situ respiration of detrital matter. Although respiration effects are screened for by measurements of $\delta^{13}\text{C}$ of CO_2 , it is difficult to demonstrate that all samples are unaffected (Yan et al., 2019)...

... Further, $\delta^{11}\text{B}$ is strongly dependent on the input parameters that are used to calculate CO_2 from $\delta^{11}\text{B}$, i.e., reconstruction of past, local marine carbon chemistry for which additional components of the carbonate system must be known or assumed (Hönisch et al., 2009). $\delta^{11}\text{B}$ is also dependent on the CO_2 saturation state at the marine drilling site in the past, contributing to the relatively large uncertainty (10s of ppm) of the $\delta^{11}\text{B}$ reconstructions compared to continuous ice core records (several ppm)). However, despite the large uncertainties, atmospheric CO_2 reconstructions from boron isotopes by Chalk et al. (2017) from ~0 - 250 kyr displays consistency with the observed ice core record in glacial stages over the last 800 kyr when filtered by the lower 25th percentile of the respective $\delta^{18}\text{O}$ values and averaged over their common time intervals (198.9 ± 10.4 and 202.0 ± 3.2 ppm respectively). However, interglacial stage CO_2 over this time is not consistent between the boron based estimates and the observed 800 kyr record (280.9 ± 14.8 and 253.9 ± 4.1 ppm, respectively) indicating that the boron based estimates are recording artificially elevated CO_2 , at least for the interglacial stages.

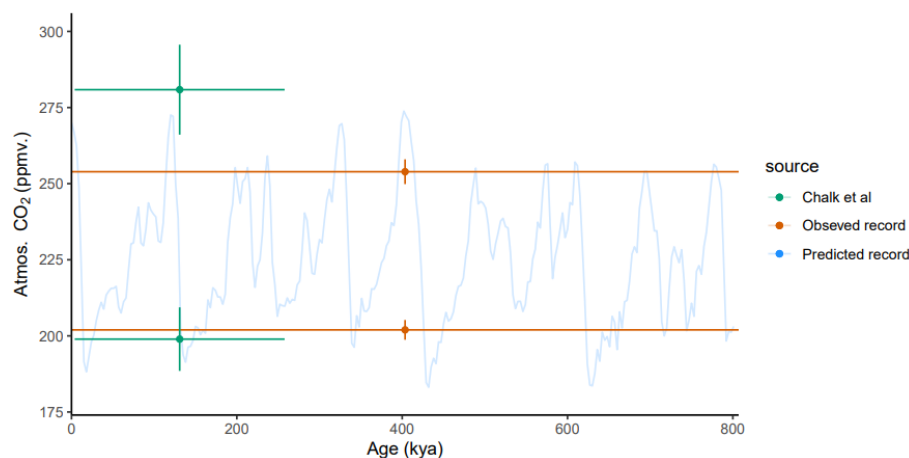


Figure R2-3: Predicted CO₂ (this work, blue curve) compared with the Bereiter et al., (2015) observed 800 kyr CO₂ record filtered into glacial and interglacial values via the upper and lower 25th percentile and averaged over the total time and the boron-isotope based CO₂ reconstruction from Chalk et al., (2017), filtered into glacial and interglacial values via the upper and lower 25th percentile and averaged over the total time period. (*n.b. for a revised manuscript we would consider including the Chalk et al., post MPT BOR-CO₂ data in revised Fig 2.).

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