1 Predicting trends in atmospheric CO₂ across the Mid-

Pleistocene Transition using existing climate archives

- 3 Jordan R.W. Martin¹, Joel Pedro^{2,3}, Tessa R. Vance³
- ¹Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, 7004, Australia
- ²Australian Antarctic Division, Kingston, 7050, Australia
- ³Australian Antarctic Program Partnership, Institute for Marine and Antarctic Studies, University of
- 7 Tasmania, Hobart, 7004, Australia

8 9

Correspondence to: Jordan R.W. Martin (jrmartin@utas.edu.au)

1011

Abstract

- During the Mid-Pleistocene Transition (MPT), ca. 1200–800 thousand years ago (kya), the Earth's glacial cycles
- changed from 41 kyr to 100 kyr periodicity. The emergence of this longer ice-age periodicity was accompanied
- by higher global ice volume in glacial periods and lower global ice volume in interglacial periods. Since there is
- 15 no known change in external orbital forcing across the MPT, it is generally agreed that the cause of this
- transition is internal to the earth system. Resolving the climate, —carbon cycle and —cryosphere dynamics
- 17 processes responsible for the MPT remains a major challenge in earth and palaeoclimate science. To address
- this challenge, the international ice core community has prioritised prioritized recovery of an ice core record
- spanning the MPT interval. The data from such 'oldest ice' projects are still several years away.
- Here we present results from a simple generalised generalized least squares model that predicts atmospheric CO₂
- out to 1.5 Myr. Our prediction utilises existing records of atmospheric carbon dioxide (CO₂) from Antarctic ice
- cores spanning the past 800 kyr along with the existing LR04 benthic δ^{18} O_{calcite} stack (Lisiecki & Raymo, 2005;
- 23 hereafter 'benthic δ18O stack') from marine sediment cores. Our predictions assume that the relationship
- between CO_2 and benthic $\delta^{18}O_{\text{calcite}}$ over the past 800 thousand years can be extended over the last one and a half
- 25 million years. The implicit null hypothesis is that there has been no fundamental change in feedbacks between
- atmospheric CO_2 and the climate parameters represented by benthic $\delta^{18}O_{\text{ealcite}}$, global ice volume and ocean
- 27 temperature.
- 28 We test the GLS-model predicted CO₂ concentrations against observed blue ice CO₂ concentrations, δ¹¹B-based
- 29 CO₂ reconstructions from marine sediment cores and δ^{13} C of leaf-wax based CO₂ reconstructions (Higgins *et al.*,
- 30 Yan et al., 2019 and Yamamoto et al., 2022). We show that there is not clear evidence from the existing blue ice
- or proxy CO₂ data to reject our predictions nor our associated null-hypothesis. A definitive test and/or rejection
- 32 of the null hypothesis may be provided following recovery and analysis of continuous oldest ice core records
- 33 from Antarctica, which is still several years away. The record presented here should provide a useful
- 34 comparison for the oldest ice core records and opportunity to provide further constraints on the processes
- involved in the MPT.

36

1 Introduction

- 41 Ice core records from Antarctica provide comprehensive and continuous records of many climate parameters
- over the last 800 thousand years, e.g. from the Vostok (Petit et al., 1999) and European Project for Ice Coring in
- 43 Antarctica's Dome-C (EDC) ice cores (Jouzel et al., 2007). One of the major challenges in climate science lies
- 44 beyond the current threshold of the ice core record. The Mid-Pleistocene Transition (MPT) spans from ca.
- 45 1200–800 thousand years ago (kya) (Chalk et al., 2017) and is characterised by a change from regularly paced
- 46 40 thousand year (kyr) glacial cycles with thinner glacial ice sheets to quasi-periodic 100 kyr glacial cycles in
- 47 which ice sheets are more persistent and thicker (Clark et al., 2006, Chalk et al., 2017). To resolve the forcings
- and feedbacks involved in this transition, multiple nations are targeting recovery of continuous ice cores
- 49 spanning the MPT under the framework of the International Partnerships in Ice Core Science (IPICS) oldest ice
- 50 core challenge (IPICS, 2020).

51

- The purpose of the current study is to make a simple prediction of atmospheric CO₂ across the MPT. Cross-
- comparison of our and other predicted CO₂ records against observed MPT CO₂ data will aid in testing
- 54 competing hypotheses on the cause of the transition, in particular the role of carbon cycle changes.

55

64

66

67

68 69

70

71

- The MPT occurred in the absence of any changes to orbital insolation forcing, therefore, the mechanisms behind
- 57 the MPT must be internal to the earth system (Raymo, 1997; Ruddiman et al., 1989). Multiple hypotheses have
- been put forward to explain the transition. A common element in many of these, is internal climate/earth system
- 59 changes which allow for the development of thicker, more extensive ice sheets that could endure insolation
- 60 peaks corresponding to the 23 kyr precession and 41 kyr obliquity cycles, i.e., an increase in the threshold for
- deglaciation and altered sensitivity to orbital forcings (Tzedakis et al., 2017; McClymont et al., 2013, Tzedakis
- 62 <u>et al., 2017;</u>). <u>Indeed, the skipped obliquity cycle hypothesis, proposes that 100 kyr signal seen in spectral</u>
- analysis of the post-MPT benthic δ^{18} O stack (e.g. Fig 1A) may be comprised of alternating 80 and 120-kyr
 - signals, i.e. in which the intervening obliquity cycles are skipped. Among the prominent hypotheses to explain
- an increased threshold for deglaciation are the following three.
 - 1) A long_-term decrease in radiative forcing due to a secular reduction in atmospheric CO₂ across the transition (e.g. Berger *et al.*, Hönisch *et al.*, 2009; 1999, Raymo *et al.*, 1988). According to this view,
 - reduced radiative forcing drives the formation of larger and more stable ice sheets.

 2) Progressive removal of sub-glacial regolith during the 41 kyr glacial cycles. Clark & Pollard (1998)
 - proposed that ice sheet basal sliding prior to the MPT was enhanced by the presence of a low-friction sedimentary regolith layer between the Laurentide ice sheet and the crystalline bedrock. According to
 - this view, progressive removal of this sedimentary layer then favoured the development of larger and
- 73 more persistent post-MPT ice sheets.
- 74 3) Phase-locking of the Northern and Southern Hemisphere ice sheets. In frequency spectra of the global
- marine benthic δ^{18} O record (Fig. 1) there is no evidence of the precession (23 kyr) component of
- 76 northern hemisphere insolation prior to the MPT; the spectra is dominated by the obliquity (41 kyr)
- 77 component (Fig. 1C). Emergence of significant precession and 100 kyr eccentricity signals occurs
- 78 across the MPT (Fig. 1B), and all three components are clearly present after the MPT (Fig. 1A). Raymo

et al. (2006) suggested that precession-paced changes in northern and southern hemisphere ice volumes may have occurred prior to the MPT, but are cancelled due to out-of-phase ice volume changes between the two hemispheres (Raymo & Huybers, 2008). According to this view, during the MPT the precession-paced changes to fall into phase between the two hemispheres, such that the precession signal emerges (Raymo et al., 2006). In this view the global synchronise ation of ice volume drives the formation of larger and more stable ice sheets.

These hypotheses are not mutually exclusive. For a recent review on the cause of the MPT see Berends *et al.* (2021a).

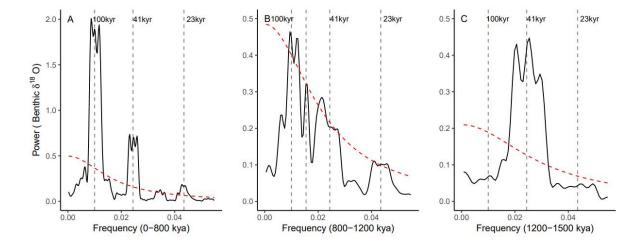


Figure 1: Thomson Multi-taper Method (MTM) spectral analysis representing relative power of signal periodicity for: A) Benthic δ^{18} O stack after (0–800 kya) the Mid-Pleistocene Transition (MPT); B) Benthic δ^{18} O across the MPT (800–1200 kya); C) Benthic δ^{18} O prior to the onset of the MPT (1200 kya–1500 kya). Each with a robust AR (1) 95 % Confidence interval (red dashed line). Benthic δ^{18} O stack data from Lisiecki and Raymo (2005).

For a long-term decrease in radiative forcing by atmospheric CO₂ to be the cause of the MPT, the reduction in CO₂ would be expected in both glacial and interglacial stages (Chalk *et al.*, 2017). However, low resolution boron-isotope-based CO₂ reconstructions by Hönisch *et al.*, (2009), and Chalk *et al.*, (2017) suggest that glacial-stage CO₂ drawdown occurred over the MPT in the absence of interglacial CO₂ drawdown. Glacial-stage CO₂ draw-down across the MPT may be a positive climate—carbon cycle feedback to changes in ice sheet dynamics, including CO₂ drawdown by enhanced iron fertilisation of the Southern Ocean in response to exposed continental shelves due to lower sea level, as well as planetary drying associated with colder climate conditions (Chalk *et al.*, 2017). Colder glacial temperatures that enhance the solubility of CO₂ in the oceans, and reduced abyssal ocean ventilation has also been implicated in enhanced glacial-stage ocean storage of CO₂ (McClymont *et al.*, 2013; Hasenfratz *et al.*, 2019).

Testing of hypotheses on the cause of the MPT is currently limited by the lack of a continuous ice core that spans its duration. The International Partnership in Ice Core Sciences (IPICS) has nominated recovery of such a record as a key priority in ice core research (IPICS, 2020). Multiple national and international projects have

110 commenced, or are soon to commence, drilling for 'oldest ice' (see e.g. Shugi, 2022). In this project, we take inspiration from the "EPICA Challenge" in which the paleoclimate and modeling community was challenged to 111 112 predict the global atmospheric carbon dioxide and methane concentrations from 800-400 kya based on the existing 400 kyr Vostok ice core record (Wolff et al., 2004). Here, we use a generalised least squares (GLS) 113 114 model trained on continuous climate archives to predict a CO₂ record out to 1.5 Mya. We utilise two primary 115 data sets for the GLS model: the existing 800 kyr ice core composite record of atmospheric CO₂ (Bereiter et al., 2015) and the LR04 benthic stack of 52 globally-distributed records of the ¹⁸O to ¹⁶O ratio of fossil benthic 116 117 foraminifera calcite (hereafter referred to as the LR04 δ^{18} O benthic stack). The δ^{18} O ratios in the LR04 benthic 118 stack are governed primarily by deep ocean temperature and global ice volume at the time the foraminifera 119 lived, with higher values indicating both increased ice volume and a colder climate. The relationship between the ice volume and ocean temperature components contributing to the δ^{18} O benthic stack are not linear. 120 Separating the two signals remains challenging and has been attempted elsewhere using a range of approaches 121 from comparison with paired deep ocean temperature proxies (Elderfield et al., 2012), inverse modelling 122 (Berends et al., 2021b) and spectral analysis (e.g. Huybers and Wunsch, 2009). 123 124 125 Fig. 2 shows a scatter-plot of the LR04 δ^{18} O benthic stack versus observed ice core CO₂ over the past 800 kyr. 126 Both data sets are binned to equivalent 3-kyr time steps (Methods). The Pearson's correlation coefficient (r) between the data sets is -0.82 (p < 0.05) indicating that ~68% of the variance in observed CO₂ is shared with the 127 128 LR04 δ^{18} O benthic stack. This strong relationship provides an initial rationale for using the LR04 δ^{18} O benthic 129 stack as an input parameter to predict CO₂ beyond 800 kyr. Mechanistically, multiple processes are expected to 130 contribute to the shared variance. A first order factor is the dependency of CO₂ solubility on ocean temperature 131 (e.g. Millero, 1995). From the simple solubility perspective, colder climate states with increased ice volume and 132 colder ocean temperatures will drive increased ocean uptake of CO₂ (Berends et al., 2021a). However, the 133 solubility effect only accounts for a portion of observed glacial CO₂ drawdown (Archer et al., 2000). Multiple additional contributors to the shared variance are proposed in the literature. These include (not exhaustively), 134 135 direct radiative forcing of ice volume changes by CO₂ (e.g. Shackleton et al., 1985); the impact of ice 136 volume/sea level changes on atmospheric CO₂ via ocean productivity and carbonate chemistry changes (e.g. 137 Broecker, 1982; Archer et al., 2000; Ushie and Matsumoto, 2012); CO2 drawdown during periods of high ice 138 volume by increased iron fertilisationfertilization (e.g. Röthlisberger et al., 2004; Martinez-Garcia et al., 2014) 139 and enhanced sea ice extent during periods of high ice volume capping the ventilation of CO₂ from the ocean 140 interior at high latitudes (Stephens and Keeling, 2000). 141 142 A quantitative separation and attribution of the processes linking global ice volume, ocean temperature and 143 atmospheric CO₂ on millennial to orbital timescales is not currently available (e.g. Archer et al., 2000; Sigman et al., 2010; Gottschalk et al., 2019) and will not be attempted here. Rather, we make the simple assumption that 144 the relationships between the LR04 benthic $\delta^{18}O$ stack and CO_2 can be extended beyond 800 kya and use 145 146 generalised least squares (GLS) regression modelling between benthic δ^{18} O and CO₂ to make a predictions of 147 CO₂ spanning 800–1500 kya. The deliberately simple implicit assumption, and null hypothesis, is that there is

4

no change to the feedback processes linking benthic $\delta^{18}O$ and CO_2 before and after the MPT.

148

This approach differs to previous more complex model studies that have attempted to reconstruct CO_2 using the LR04 benthic $\delta^{18}O$ stack as an input variable (van de Wal, 2011; Stap et al., 2016, Berends et al., 2021b). The latter studies use an inverse forward modelling approach, in which climate and ice sheet models of various complexities are used to capture physical relations between CO_2 , global temperature and ice volume. For example, in Berends et al., 2021b the offset between modelled and observed benthic $\delta^{18}O$ is used to calculate a value for atmospheric CO_2 that is iterated back to the inverse model. The CO_2 record which minimises the difference between the modelled and observed benthic stack is then taken as an estimate of how atmospheric CO_2 may have evolved to force coupled climate, deep ocean temperature and land ice volume changes that reproduce the observed benthic $\delta^{18}O$ signal. Accuracy of the reconstructions in the inverse modelling approach depends on the ability of the climate and ice sheet models used to capture the correct climate dynamics across the MPT. Our GLS method is a simpler statistical approach, designed with the specific null hypothesis in mind, that does not attempt to simulate the physics linking benthic $\delta^{18}O$ signal, land ice volume, global temperature and CO_2 . A range of approaches to reconstructing CO_2 have been called for and are of value in the context of forthcoming continuous ice core records across the MPT from oldest ice projects currently underway in Antarctica [IPICS 2020].



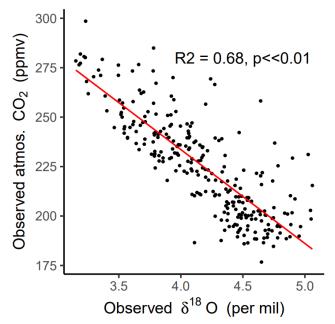


Figure 2: Scatter plot of the composite observed atmospheric CO₂ record (Bereiter *et al.*, 2015) against the LR04 benthic stack of marine δ^{18} O records (Lisiecki & Raymo, 2005). Red line is a linear line of best fit ($R^2 = 0.68$; p < 0.05).

To test the our null hypothesis, in advance of the recovery of a continuous ice core, we compare our predicted CO_2 record to two sets of low-resolution ice core data that exist outside the current 800 kyr observed CO_2 . These data come from direct CO_2 measurements from ancient "blue ice" from the Allan Hills in East Antarctica

(hereafter referred to as BI-CO₂) from ca. 1 Mya (Higgins *et al.*, 2015) and 1.5 Mya (Yan *et al.*, 2022). We use the term blue ice to describe deep, ancient glacial ice that has been brought nearer to the surface of an ice sheet by ice flow. Blue ice is sampled by cutting trenches or shallow drilling of up to several hundred meters (e.g. Higgins *et al.*, 2015). The vertical migration of blue ice is associated with high deformation making the ice samples stratigraphically complex and hard to date (Higgins *et al.*, 2015). As a result, blue ice records alone do not provide a continuous CO₂ record across the MPT. In the Discussion, wWe also compare our predicted record to existing proxy-CO₂ reconstructions from boron-isotope analysis of benthic foraminfera in marine sediment records (Chalk, *et al.*, 2017; Dyez *et al.*, 2018; Guillermic *et al.*, 2022), leaf wax δ¹³C carbon isotope ratios (Yamamoto *et al.*, 2022) and predictions from previous models of various complexities (van de Wal *et al.*, 2011; Willeit *et al.* 2019; Berends *et al.* (2021ba)). We conclude with discussion of the implications of our results and data-comparisons for the understanding MPT dynamics.

2 Methods

We use a generalised least squares (GLS) model to predict atmospheric CO_2 from the LR04 benthic $\delta^{18}O$ stack (Fig. 3A and B). We apply an AR(1) correlation factor to account for autocorrelation in the data. The AR(1) correlation factor yielded the lowest Akaike information criterion (AIC) value from a test of multiple correlation factors.

We use a generalised least squares (GLS) model with an auto-regressive (AR) factor 1 to predict atmospheric CO₂
 from the LR04 benthic δ¹⁸O stack (Fig. 3A and B). We use GLS because the assumptions of ordinary least squares
 (OLS) are violated by the presence of autocorrelation and heteroskedasticity in the regression errors. We selected
 the AR(1) correlation factor as it yielded the lowest Akaike information criterion (AIC) value from a test of
 multiple correlation factors. The AR(1) process assumes and accounts for dependence of error at a given point in
 time on the previous error term. In practise this makes the model assumptions more realistic and improves

201 parameter estimation where, as in the climate system, observations are dependent on past values.

To obtain common time steps and resolution between the predictor (LR04 benthic δ^{18} O stack) and response (CO₂) variables, we re-grid the LR04 benthic stack and Bereiter *et al.*, (2015) CO₂ data into time bins with a resolution of 3-kyr. The GLS regression model was then applied over the 0–800 kyr range of the predictor and response variables as follows:

$$CO_2 = 33.37 \times \delta^{18}O + 365.15$$
, autoregressive (AR) factor: 1

Based on the regression model, the $\delta^{18}O$ values of the LR04 Benthic Stack from 800-1500 kya were used to predict CO_2 concentration over this range (hereafter referred to as PRED- CO_2). To estimate the GLS model uncertainty and sensitivity we took a bootstrap approach, selecting a random 50% subset of our data and rerunning the model 1000 times to determine 95% confidence intervals for the predictions. To gauge the GLS model stability we took a bootstrap approach, selecting a random 50% subset of our data (with replacement) and re-running the model 1000 times to determine 95% confidence intervals for the predictions. While the GLS method itself addresses autocorrelation, the bootstrap method introduces variability such that each iteration of

the model has different combinations of the original data points (including repeated ones), this variability helps in assessing the robustness and sensitivity of the model e.g. to variable data and dating uncertainty.

218219220

221

222

223

224

225226

227

228

229

230

231

232

217

Uncertainties in the independent age scales of both the LR04 stack and the compiled CO_2 record are inherited by our GLS model and its predictions. The LR04 stack includes 57 globally-distributed benthic $\delta^{18}O$ sediment core records. The age models for these cores are independently constructed from the average sedimentation rates of each core, assuming global sedimentation rates have remained relatively stable, and with tuning to a simple ice model based on 21 June insolation at 65°N (Lisiecki & Raymo, 2005). The authors estimate uncertainty of 6 kyr from 1.5-1.0 Mya and 4 kyr from 1-0 Mya (Lisiecki & Raymo, 2005). The observed CO_2 composite ice core record for the past 800 kya (Bereiter at al., 2015) uses six independent dating methods for various core locations both spatially across Antarctica, and stratigraphically for different sections of the same core. The age uncertainty in the gas timescale has a median over the 0-800 kya 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 (median, 2σ , 5.78 ppm) (median ## ppm) to the bootstrap analysis with 1000 iterations of re computing the regression after removing a randomly chosen 50% of data for each iteration of the model (see Fig. 3B, C and Discussion).

233234235

3 Results

- Fig. 3B shows the time series of our LR04 benthic $\delta^{18}O$ stack-based GLS model predictions of atmospheric CO_2
- 237 (PRED-CO₂) over the past 800 kyr, in comparison to the observed ice core CO₂ record from Bereiter at al.,
- 238 (2015). The correlation coefficient (\mathbb{R}^2) between the predicted and observed records is 0.68 (p << 0.01). Our
- 239 PRED-CO₂ record out to 1.5 Mya with shaded 95% CIs from the bootstrap analysis is also shown, overlain with
- observed Allan Hills blue ice CO₂ (BI-CO₂) datasets of age 1000 ± 89 kya (Higgins et al., 2015) and 1.5 Mya ±
- 241 213 kyr (Yan et al., 2022).

242

- We evaluate the PRED-CO₂ record against the observed CO₂ data according to criteria of mean concentrations
- 244 across the common intervals, and mean concentrations in the glacial and interglacial subsets of the data. First,
- the mean CO₂ concentration over the common intervals (Fig 3C). From 0–800 kya the mean concentration in
- observed (Bereiter at al., 2015) and PRED-CO₂ data are in close agreement (225.2 \pm 3.03 ppm versus the
- predicted 225.1 \pm 2.5 ppm respectively; uncertainties are 95% confidence intervals, i.e. 1.96σ). In the 1000 ± 89
- 248 kya interval (i.e. averaged across the age uncertainty of the Higgins (2015) blue ice data) the BI-CO₂
- concentration is ~ 11 ppm higher than PRED-CO2 (246.7 \pm 8.4 ppm versus the predicted 235.5 \pm 3.9 ppm), this
- difference is not significant at the 95% confidence level. For the 1.5 Mya \pm 213 kyr interval, the mean BI-CO₂
- concentration is ~10 ppm lower than PRED-CO2 (231.9 \pm 5.6 ppm versus the predicted 241.7 \pm 2.5 ppm),
- 252 which is marginally significant at the 95% level. Comparisons of mean levels across intervals spanning multiple
- 253 glacial and interglacial cycles may be biassed biased if (as is likely) the blue ice data is not sampling glacial and
- interglacial values with the same uniformity as a continuous record.

To address this, we define the glacial and interglacial thresholds of PRED-CO₂ to be respectively the lower and upper 25^{th} percentiles of the LR04 δ^{18} O predictor variable (following Chalk et al., 2017). Filtering the observed (Bereiter at al., 2015) CO₂ record and our predicted CO₂ record according to these definitions we find a very close match for glacial (202.0 \pm 3.2 versus the predicted 199.7 \pm 1.7 ppm) and interglacial intervals (253.9 \pm 4.1 ppm versus the predicted 253.1 ± 2.3 ppm), over the past 800 kya (see Fig. 3D). For blue ice (BI₋₋₋CO₂) data, a corresponding LR04 isotope signal could not be confidently applied to the measured CO₂ concentration due to the uncertainties associated with blue ice datingaging; therefore, we defined the glacial and interglacial thresholds of blue ice data according to the top (interglacial) and bottom (glacial) 25th percentiles of actual CO₂. Applying this to the 1000 ± 89 kya interval finds that observed BI-CO₂ data is ~ 9 ppm higher than PRED-CO₂ during the glacial stages (226.2 \pm 4.0 ppm versus the predicted 217.6 \pm 2.3 ppm) and \sim 15 ppm higher than PRED-CO2 during the interglacial stages (271.3 \pm 4.5 versus the predicted 256.3 \pm 3.8 ppm). These differences are significant with respect to the constrained uncertainties. In contrast, during the 1.5 Mya \pm 213 kyr interval, the mean BI- CO2 concentration is not significantly different to PRED-CO2 in either glacial (217.6 \pm 2.3 versus the predicted 224.2 ± 6.6 ppm) or interglacial stages (256.3 ± 3.8 versus the predicted 261.1 ± 6.3 ppm). These comparisons, particularly the agreement at 1.5 Myr, indicate that PRED-CO₂ is not drifting systematically away from the existing observed BI-CO₂ data. In our view the disagreement at 1.0 Myr, where BI-CO₂ is elevated with respect to PRED-CO₂, does not give sufficient cause to reject the GLS model, it could of course be a failing in the model and/or could be due to potential biases in the blue ice data, for example elevated CO₂ concentrations due to in-situ CO₂ production in blue ice (see Discussion).

256

257258

259

260

261

262

263

264265

266267

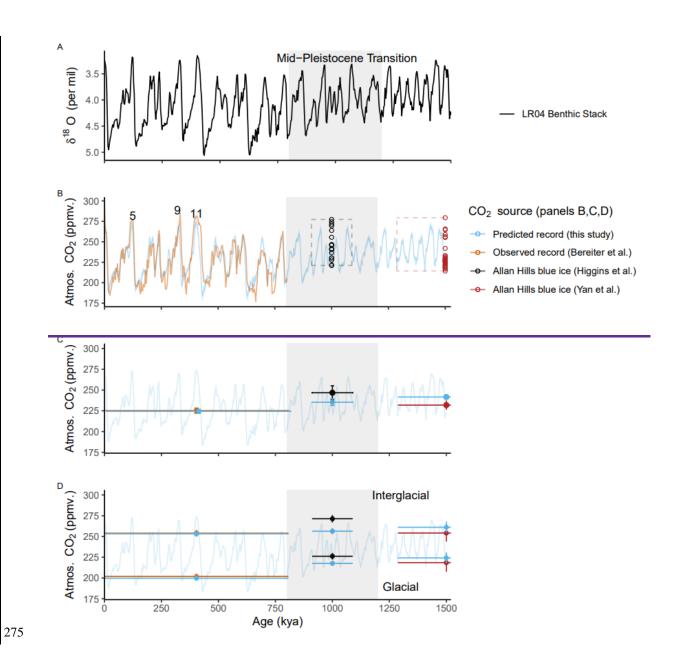
268269

270

271

272

273



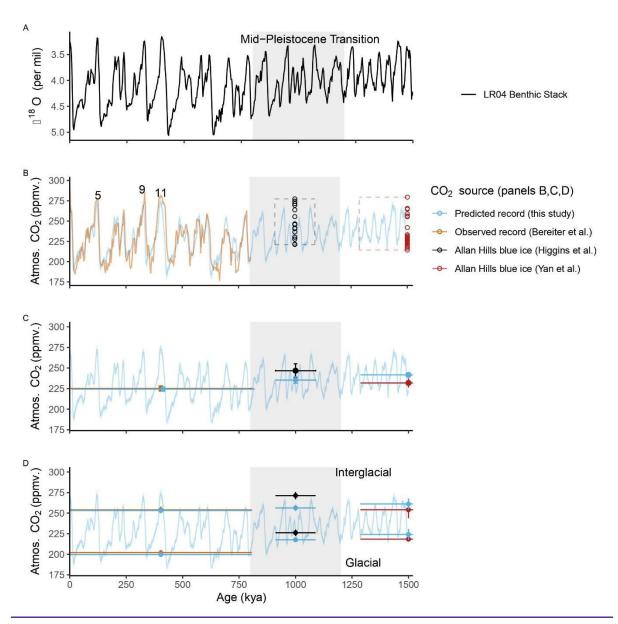


Figure 3: A) The LR04 Benthic Stack of 57 globally distributed δ¹⁸O records (Lisiecki & Raymo, 2005). B) Comparison of our PRED-CO₂ (ppm) record to the current continuous composite record (0–800 kya); and to direct CO₂ measurements from Allan Hills blue ice cores (BI-CO₂) ca. 1 Mya (± 89 kyr) (Higgins *et al.*, 2015) and ca. 1.5 Mya (± 213 kyr) (Yan *et al.*, 2022). Age uncertainty boundaries for the BI-CO₂ data are represented by dashed box boundaries. Marine isotope stages 5, 9, and 11 are numbered on the plot according to Lisiecki & Raymo (2005). Blue shading around PRED-CO₂ is the 95% CI from bootstrap analysis. C) Mean concentrations of the PRED-CO₂ and observed composite CO₂ records over the range of the observed composite record (offset for clarity), and the mean concentrations of the PRED-CO₂ and BI-CO₂ data at 1 Mya and again at 1.5 Mya averaged over the age uncertainty range of each BI-CO₂ data set. D) As for C) however filtered by the upper and lower 25th and 75th percentiles to estimate glacial and interglacial periods.

We now consider long-term trends in interglacial and (separately) glacial CO₂ levels across the past 1.5 Myr in PRED-CO₂ and in the existing ice core CO₂ data. For PRED-CO₂ there is no significant difference between CO₂

concentrations in the interglacial stages of the 1.5 Mya \pm 213 kya, 1000 ± 89 kya and 0-800 kya windows (Fig 4 D, blue bars). In the ice core observations, interglacial levels at 1.5 Mya in BI-CO₂ are also within the uncertainties of those in the 0-800 kya interval. Notably, the BI-CO₂ concentrations in the 1000 ± 89 kya interval appear elevated with respect to the 0-800 kyr and 1.5 Mya \pm 213 kya intervals, however this elevated (ca. 271 ppm) level is consistent with the observed interglacial CO₂ concentration during interglacials 5, 9 and 11 (Fig 3B). Overall, there is no indication in the observed ice core CO₂ data or in PRED-CO₂ for a long-term trend in *interglacial* CO₂ levels across the past 1.5 Myr.

297298299

300

301302

303

304

305

306

307

291

292293

294

295

296

In comparison, there are significant declines in glacial CO_2 levels across the MPT in PRED- CO_2 and the observed ice core data. For PRED- CO_2 , glacial CO_2 concentrations are not significantly different during the 1.5 Mya \pm 213 kya and 1000 \pm 89 kya windows. However, across the MPT, PRED- CO_2 glacial concentrations drop by ~18 ppm. This pattern is consistent with the observed data, where glacial CO_2 levels are also not significantly different between the 1.5 Mya \pm 213 kya and $1000 \pm$ 89 kya windows (217.6 \pm 2.3 and 226.2 \pm 4.0 ppm, respectively) and then fall by 24 ppm to the 0–800 kyr observed glacial mean of 202.0 \pm 3.2 ppm. Glacial-stage draw-down of CO_2 across the MPT in the absence of interglacial draw-down is consistent with previous observations based on the boron-isotope-based CO_2 reconstructions (e.g., Chalk *et al.*, 2017; Hönisch *et al.*, 2009 and see Discussion). In the following section we also compare PRED- CO_2 data to boron-isotope-based and other CO_2 proxy records covering the 0 to 1.5 Myr interval.

308309310

311

312

313

314

315

316

317318

319

320

321322

323

324

325

326

327

328

329

330

4 Discussion

Our objective with this manuscript was to generate the simplest reasonable model to predict CO₂ from the LR04 δ^{18} O benthic stack and to test the predictions against available observations. It is possible that the fit between observed and our predicted CO₂ data could be further improved using a non-linear approach. However, we refrain from a non-linear approach for several key reasons. First, a scatter plot of the LR04 δ^{18} O benthic stack versus observed ice core CO₂ over the past 800 kyr yields a Pearson's correlation coefficient (R) of -0.82 (Fig. 2), indicating that ~68% of the variance in observed CO₂ is shared with the benthic stack. This is similar to that reported in ; this is supported by ordinary linear least-squares modelling regression (Rr²=0.70) by Berends et al. (2021ba). Importantly, there is no evidence in this scatter plot for departure from the linear relationship at high or low CO₂ or benthic δ^{18} O levels. Second, following the approach of Chalk et al., 2017 and interpreting the upper 25th percentile of CO₂ data as representing mean interglacial stage CO₂ and the lower 25th percentile of CO₂ data as representing mean glacial stages CO₂ levels, we see that our predicted interglacial mean value for the past 800 kyr (253.1 \pm 2.3 ppm) closely overlaps with the observed interglacial mean value (253.9 \pm 4.1 ppm) and similarly, the predicted glacial stage mean (199.7 \pm 1.7 ppm) closely overlaps with the observed glacial stage mean (202.0 ± 3.2 ppm). Third, 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 CO2 values would be unlikely in the case of major non-linear dependencies between the LR04 predictor and CO₂ response variables. Fourth, 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 CO₂ variations still-remain poorly constrained (e.g. Archer et al.,

331 2000; Sigman et al., 2010; Gottschalk et al., 2019). Given this process-uncertainty, the GLS model fits our criteria of the simplest reasonable model. Further, the use of benthic δ^{18} O to predict atmospheric CO₂ has 332 333 precedence; in response to the EPICA challenge (Wolff et al., 2004), N. Shackleton-used <u>818Othis method to</u> 334 predicted atmospheric CO₂ out to 800 kyr, based on a number of benthic δ^{18} O records from the East Pacific 335 (Wolff, 2005). Furthermore, I inverse modelling of CO2 forced by the LR04 benthic stack hasves been 336 undertaken by van de Wal et a. (2011), and further expanded by Berends et al. (2021a) who utilised a simple least squares (LS) rather than a GLS regression, and van de Wal et al. (2011). 337 338 339 There are several caveats with blue ice data that may affect its use to evaluate our GLS model predictions. The 340 blue ice data may have been subject to diffusional smoothing of CO₂ (e.g. Yan et al., 2019), which would act in the direction of elevating the (lower 25th percentile) assumed glacial concentrations above the glacial 341 342 atmospheric values and reducing the (upper 25th percentile) assumed interglacial concentrations. There is also 343 the potential for artificially elevated CO₂ concentrations in blue ice due in-situ respiration of CO₂ due to microbial activity in detrital matter. Respiration effects are screened for by measurements of δ^{13} C of CO₂, 344 however it is difficult to demonstrate that all samples are unaffected (Yan et al., 2019). These uncertainties 345 346 support our argument that the GLS-model predictions are not rejected by the available observed BI-CO₂ data. 347 348 We consider the BI-CO₂ date to provide the most reliable measurements of CO₂ concentration, in the absence of 349 a continuous ice core record across the MPT. However, further comparison of our CO2 predictions can also be made against CO_2 proxy data from non-ice core archives (Fig 4A). We consider here $\delta^{11}B$ -based atmospheric 350 351 CO₂ reconstructions (Chalk et al., 2017, Dyez et al. 2018 and Guillermic et al. 2022) and a recent atmospheric CO_2 reconstruction from $\delta^{13}C$ of leaf wax (Yamamoto et al., 2022). The continuous $\delta^{11}B$ -based reconstructions 352 353 of Dyez et al., (2018) overlap PRED-CO₂ from ~1.38 – 1.5 Mya while the Chalk et al., (2017) reconstruction 354 overlaps PRED-CO₂ from 1.09 – 1.43 Mya. Discrete reconstructions from Guillermic et al. (2022) are distributed non-uniformly across the 800 to 1.5 Mya interval. For the two continuous $\delta^{11}B$ -based reconstructions 355 (Chalk et al., (2017) and Dyez et al., (2018)) the glacial CO₂ levels appear consistent with the PRED-CO₂ 356 record, within their reported 30-60 ppm uncertainties. However, $\delta^{11}B$ -based interglacial stages in these 357 358 reconstructions exceed those of the PRED-CO₂ record (Fig. 4A). The Guillermic et al. (2022) reconstructions 359 suggest a larger range of CO₂ concentrations than the overlapping intervals of PRED-CO₂ and of the two 360 continuous δ^{11} B-based reconstructions (Fig. 4A). The large range of the Guillermic *et al.* (2022) data and the high interglacial maxima in the Chalk et al (2017) and Dyez et al., (2018) data, all significantly exceed the 361 362 range and interglacial maxima from the BI-CO2 estimates. These discrepancies internally between different δ^{11} B-based CO₂ reconstructions and between the δ^{11} B-based reconstructions and the BI-CO₂ data, may be due to 363 uncertainties associated with the $\delta^{11}B$ proxy transfer function. The $\delta^{11}B$ -based CO₂ reconstructions are 364 dependent on assumptions about multiple components of the carbonate system, including local marine carbon 365

370

ca. 30 ppm (not shown).

366

367

368

369

chemistry and the CO₂ saturation state in the past and (Hönisch et al., 2009). Evidence that δ^{11} B-based

reconstructions may overestimate interglacial stage CO₂ is also seen in data from Chalk et al., (2017) spanning

ca. 0–250 kya, where the δ¹¹B-based interglacial CO₂ levels exceed the continuous ice core CO₂ record by up to

By comparison, the δ^{13} C of leaf wax data (Yamamoto *et al.*, 2022) has a similar glacial to interglacial range as PRED-CO₂, but a ca. 20ppm lower mean concentration than our predictions (Fig 4A). Hence, our PRED-CO₂ data fall lower than interglacial δ^{11} B-based interglacial levels but are higher than the δ^{13} C of leaf-wax based estimate. The strong spread between these different proxies and the large associated uncertainty of the alternative marine and leaf wax proxy-CO₂ reconstructions mean that Given the evidence that δ^{11} B-based reconstructions are known to overestimate atmospheric CO₂ concentration in the continuous ice core record, we do not find cause from the existing CO₂ proxy data to reject our predictions nor our associated null-hypothesis.

378379

380

381

382

383

384

385 386

387

388

389

390

391

392393

394

395

371372

373

374

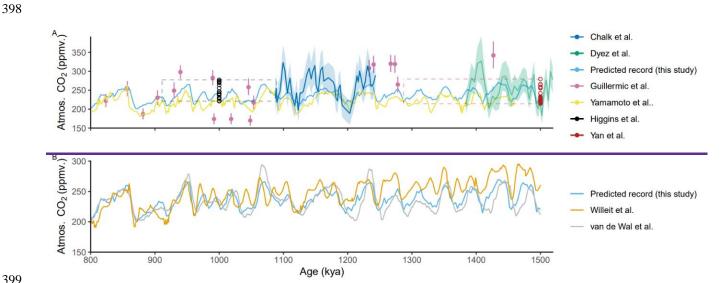
375

376

377

We also compare our predictions to existing more complex model simulations (Fig 4B.). First, against a transient simulation using an intermediate-complexity earth system model (CLIMBER-2) by Willeit et al. (2019). This study suggests a combination of gradual regolith removal and atmospheric CO₂ decline can explain the long-term climate variability over the past 3_Myr. Second, against a longer-term reconstruction by van de Wal et al. (2011), which uses benthic δ18O that utilises deep-sea benthic isotope records to reconstruct a continuous CO₂ record over the past 20 Myr. Third, a CO₂ reconstruction based on an inverse forwardmodelling approach forced by a simple least squares (LS) linear fit between the LR04 benthic stack, in which the forward model is and the current CO2 ice core record, and incrementally updated through interaction with Global Circulation Model snapshots and the ANICE 3-D ice-sheet-shelf model (Berends et al. 2021ba). Our simple GLS model demonstrates a similar long-term trend and timing of glacial-interglacial signals and an atmospheric CO₂ level that sits approximately mid-way between the van de Wal et al. (2011), and Willeit et al. (2019) models and is remarkably similar to the Berends et al. (2021b) reconstruction, despite their different approach. Notably the Berends et al. reconstruction shows . Berends et al. reconstruction shows-greater glacial to interglacial amplitude in the CO₂ signal compared to our GLS-model. The decreasing linear trend in CO2 in Willeit et al. (2019), which is not seen in the other reconstructions, was directly prescribed in that study to induce Northern Hemisphere glaciation at 2.6 Myr ago. The timing of the glacial cycles in our predictions match closely to those made by Berends et al. (2021a). threewo othermore complex models.

396397



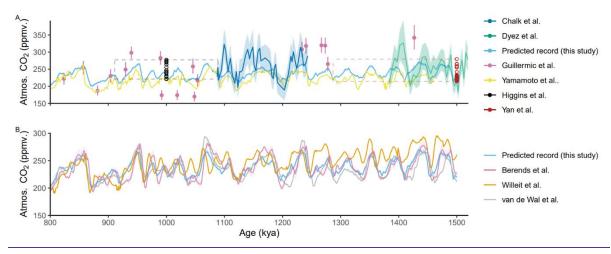


Figure 4: A) Predicted CO₂ (this work) compared to observed, proxy CO₂ estimates from a range of other sources: δ^{11} B-based pCO₂ reconstructions and measurements by Dyez *et al.* (2018), Guillermic *et al.* (2022); Chalk *et al.*, (2017); blue ice CO₂ measurements by Yan *et al.* (2019) and Higgins *et al.* (2015); δ^{13} C leaf wax proxy reconstructions by Yamamoto *et al.* (2022). The dashed boxes indicate the dating uncertainty and range of the respective BI-CO₂ records. B) Our predicted record compared to various model simulations: a regolith removal hypothesis simulation by Willeit *et al.* (2019); and <u>inverse-model based a high-resolution</u> CO₂ reconstructions by van de Wal *et al.* (2011), and ; and a least-squares linear regression based prediction (Berends et al., (2021ba)).

A complete and critical test of our and other CO_2 predictions awaits the upcoming analysis of the continuous oldest ice core records. We now discuss some potential applications of the PRED-CO2 record for hypothesis testing on the cause of the MPT.

PRED-CO₂ shows a long-term decline in glacial CO₂ across the MPT, but no long-term decrease in interglacial CO₂. This pattern is consistent with the boron-isotope-based CO₂ reconstructions shown earlier, where it is often described as an increase in the interglacial to glacial CO₂ difference (e.g., Chalk *et al.*, 2017; Hönisch *et al.*, 2009). Chalk *et al.*, (2017) concludes that the MPT was initiated by a change in ice sheet dynamics and that longer and higher-ice volume post-MPT ice ages are sustained by carbon cycle feedbacks, in particular dust fertiliszation of the Southern Ocean. That fact that our LR04-based prediction of CO₂ captures this same trend, of declining glacial CO₂-, with predicted glacial CO₂ fairly constant from 1.5 to ca. 1.0 Mya before declining from 1.0 to 0.6 kya, reflects that LR04 benthic stack also features an increase in the interglacial to glacial benthic δ^{18} O difference across this same intervale MPT, which is dominated by the glacial stage changes decline (Fig 3A.). Here, a comparison of PRED-CO2 to a realised continuous oldest ice core record will be of value. The agreement or disagreement would inform on the proportionality of the CO₂ coupling with ice volume; if there were a major new or non-linear process across the MPT that changed the nature of coupling between CO₂ and ice volume the PRED-CO2 and observed CO₂ records would be expected to diverge.

Another avenue to use the PRED-CO2 record for hypothesis testing on the cause of the MPT concerns the phase locking hypothesis. The phase locking hypothesis is proposed to explain the absence of precession-related (23

kyr) periods in the LR04 benthic stack prior to the MPT (Fig 1), 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 41 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.* (2022), lend some support to 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 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 in the post-MPT record. If Yan *et al.*, (2022) is correct and the phase locking hypothesis holds, then an implication is that prior to the MPT, Antarctic climate, Antarctic ice volume and by extension Southern Ocean climate conditions, would fall out of phase with the LR04 benthic stack. 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 major disagreement between our pre-MPT CO₂ predictions and a realised oldest ice continuous ice core CO₂ record.

5 Summary and Conclusions

In this study we have used a simple generalised least squares (GLS) model to predict atmospheric CO_2 from the LR04 benthic $\delta^{18}O$ stack for the period spanning the mid-Pleistocene transition, 800-1500 kyr. Our CO_2 prediction is therefore based on the assumption that the physical processes linking CO_2 , sea level, global ice volume and ocean temperature over the past 800 kyr do not fundamentally change across the 800-1500 kya time period. The null-hypothesis is deliberately simplistic on the basis that differences between our predictions and observed or proxy CO_2 records may be revealing of the physical processes involved in the mid-Pleistocene Transition.

 We made initial tests of the null hypothesis by comparing our predicted CO_2 record to existing discrete blue ice CO_2 records and other non-ice-core proxy- CO_2 records from the 800–1500 kyr interval. Our predicted CO_2 concentrations do not show any systematic departure from observed blue ice CO_2 concentrations. The predictions are marginally lower (during glacial *and* interglacial stages) than those observed in blue ice from 1000 ± 89 kya and marginally higher than observed in blue ice data from 1.5 Mya ± 213 kyr. Our predictions

- were generally lower than interglacial δ^{11} B-based-CO₂ reconstructions, but higher than recent δ^{13} C of leaf-wax
- based CO₂ reconstructions. Overall, we do not find clear evidence from the existing blue ice or proxy CO₂ data
- 473 to reject our predictions nor our associated null-hypothesis. The definitive test of our and other CO₂ predictions
- 474 therefore awaits the future analysis of the upcoming continuous oldest ice core records. The PRED-CO2 record
- presented here should provide a useful comparison to forthcoming oldest ice core records and opportunity to
- provide further constraints on the processes involved in the MPT.

- **Author contributions**
- 479 Project design by JRWM, JBP and TRV. Data analysis and writing led by JRWM with contributions from all
- 480 authors. Project design by JBP, TRV and JRWM and supervision by TRV and JBP. Data analysis and figures
- 481 by JRWM with input from all authors. Writing led by JRMV and JBP. All authors contributed to and agreed on
- the final version of the manuscript.

483 484

- **Competing interests**
- The authors declare that they have no competing interests.

486

- 487 **Disclaimer**
- 488 This study, to the best of the author(s) knowledge and belief, contains no material previously published or
- written by another person, except where due reference is made in the text of the study.

490 491

- Acknowledgements
- We acknowledge assistance from Simon Wotherspoon (Institute for Marine and Antarctic Studies) in
- 493 appropriate model selection methods. This research was supported by the Australian Government through
- 494 Australian Antarctic Science projects 4632, the Million Year Ice Core (MYIC) Project and by the Australian
- 495 Government Department of Industry Science Energy and Resources, grant ASCI000002.

496 497

- Data availability
- 498 PRED-CO2 data (0 to 1.5 Myr) will be publicly archived at the Australian Antarctic Data Centre
- 499 (https://data.aad.gov.au/ >>full link provided upon publication <<).

500

- 501 References
- Archer, D., Winguth, A., D. Lea, and Mahowald, N.: What caused the glacial/interglacial atmospheric
- 503 pCO₂ cycle?, Rev. Geophys., 38, 159–189, 2000, https://doi.org/10.1029/1999RG000066, 2000.

504

- Bazin, L., Landais, A., Lemieux-Dudon, B., Toye Mahamadou Kele, H., Veres, D., Parrenin, F., Martinerie, P.,
- Ritz, C., Capron, E., Lipenkov, V., Loutre, M.-F., Raynaud, D., Vinther, B., Svensson, A., Rasmussen, S.,
- 507 Severi, M., Blunier, T., Leuenberger, M., Fischer, H., Masson-Delmotte, V., Chappellaz, J., and Wolff, E.: An
- optimized multi-proxies, multi-site Antarctic ice and gas orbital chronology (AICC2012): 120-800 ka, Clim.
- 509 Past, 9, 1715-1731, https://doi.org/10.5194/cp-9-1715-2013, 2013.

510

- 511 Bereiter, B., Eggleston, S., Schmitt, J., Nehrbass-Ahles, C., Stocker, T. F., Fischer, H., Kipfstuhl, S., and
- 512 Chappellaz, J.: Revision of the EPICA Dome C CO2 record from 800 to 600 ky before present, Geophys. Res.
- 513 Lett., 42, 542-549, https://doi.org/10.1002/2014gl061957, 2015.

```
Berends, C. J., Köhler, P., Lourens, L. J., and van de Wal, R. S. W.: On the cause of the mid-Pleistocene transition., Rev. Geophys., 59, e2020RG000727. https://doi.org/10.1029/2020RG000727, 2021a.
```

Berends, C. J., de Boer, B., and van de Wal, R. S. W.: Reconstructing the evolution of ice sheets, sea level, and atmospheric CO2 during the past 3.6 million years. Clim. Past, 17, 361–377, http://doi.org/10.5194/cp-17-361-2021, 2021ba.

521 522

Berends, C. J., Köhler, P., Lourens, L. J., and van de Wal, R. S. W.: On the cause of the mid Pleistocene transition., Rev. Geophys., 59, e2020RG000727. https://doi.org/10.1029/2020RG000727, 2021b.

523 524

Berger, A., Li, X. S., and Loutre, M. F.: Modelling northern hemisphere ice volume over the last 3Ma, Quaternary. Sci. Rev., 18, 1-11, https://doi.org/10.1016/S0277-3791(98)00033-X, 1999.

527

528 Broecker, W.S.: Glacial to interglacial changes in ocean chemistry, Prog. Oceanogr., 11 (2), 151-197. 529 https://doi.org/10.1016/0079-6611(82)90007-6, 1982.

530

Chalk, T., Hain, M., Foster, G., Rohling, E., Sexton, P., Badger, M., Cherry, S., Hasenfratz, A., Haug, G.,
Jaccard, S., Martínez-García, A., Pälike, H., Pancost, R., and Wilson, P.: Causes of ice age intensification across
the Mid-Pleistocene Transition, P. Natl. Acad. Sci. USA., 114, 13114-13119,
https://doi.org/10.1073/pnas.1702143114, 2017.

535

Clark, P. U., Archer, D., Pollard, D., Blum, J. D., Rial, J. A., Brovkin, V., Mix, A. C., Pisias, N. G., and Roy, M.: The middle Pleistocene transition: characteristics, mechanisms, and implications for long-term changes in atmospheric pCO2, Quat. Sci. Rev., 25, 3150-3184, https://doi.org/10.1016/j.quascirev.2006.07.008, 2006.

539 540

Clark, P. U. and Pollard, D.: Origin of the Middle Pleistocene Transition by ice sheet erosion of regolith, Paleoceanography, 13, 1-9, https://doi.org/10.1029/97pa02660, 1998.

541542543

Dyez, K.A., Hönisch, B., and Schmidt, G.A.: Early Pleistocene obliquity-scale pCO₂ variability at ~1.5 million years ago. Paleoceanogr. Paleoclimatol., 33, no. 11, 1270-1291, https://doi.org/10.1029/2018PA003349, 2018.

544545

Elderfield, H., Ferretti, P., Greaves, S., Crowhurst, S., McCave, N., and Piotrowski, A.M.: Evolution of Ocean Temperature and Ice Volume Through the Mid-Pleistocene Climate Transition, Science, 337,704-709, https://doi.org/10.1126/science.1221294, 2012.

549

Gottschalk, J., Battaglia, G., Fischer, H., Frölicher, T.L., Jaccard, S.L., Jeltsch-Thömmes, A., Joos, F., Köhler,
 P., Meissner, K.J., Menviel, L., Nehrbass-Ahles, C., Schmitt, J., Schmittner, A., Skinner, L.C., and Stocker,
 T.G.: Mechanisms of millennial-scale atmospheric CO2 change in numerical model simulations, Quaternary.
 Sci. Rev., 220, 30-74, https://doi.org/10.1016/j.quascirev.2019.05.013, 2019.

554

Guillermic, M., Misra, S., Eagle, R., and Tripati, A.: Atmospheric CO2 estimates for the Miocene to Pleistocene
 based on foraminiferal δ11B at Ocean Drilling Program Sites 806 and 807 in the Western Equatorial Pacific,
 Clim. Past, 18(2), 183-207, https://doi.org/ 10.5194/cp-18-183-2022, 2022.

558

Hasenfratz, A. P., Jaccard, S. L., Martínez-García, A., Sigman, D. M., Hodell, D. A., Vance, D., Bernasconi, S. M., Kleiven, H. F., Haumann, F. A., and Haug, G. H.: The residence time of Southern Ocean surface waters and the 100,000-year ice age cycle, Science, 363, 1080, https://doi.org/10.1126/science.aat7067, 2019.

562

Higgins, J. A., Kurbatov, A. V., Spaulding, N. E., Brook, E., Introne, D. S., Chimiak, L. M., Yan, Y.,
 Mayewski, P. A., and Bender, M. L.: Atmospheric composition 1 million years ago from blue ice in the Allan
 Hills, Antarctica, P. Natl. Acad. Sci. USA., 112, 6887, https://doi.org/10.1073/pnas.1420232112, 2015.

566

Hönisch, B., Hemming, N. G., Archer, D., Siddall, M., and McManus, J. F.: Atmospheric Carbon Dioxide
 Concentration Across the Mid-Pleistocene Transition, Science, 324, 1551,
 https://doi.org/10.1126/science.1171477, 2009.

570

Huybers, P., & Wunsch, C. (2005). Obliquity pacing of the late Pleistocene glacial terminations. *Nature*, 434(7032), 491-494.

- 574 International Panel on Climate Change: Climate change 2001; IPCC third assessment report, IPCC, Geneva, 575 2001.
- 576
- International Partnerships in Ice Core Sciences: The oldest ice core: A 1.5 million year record of climate and greenhouse gases from Antarctica [White paper]. https://igbp-
- 579 scor.pages.unibe.ch/sites/default/files/download/docs/working_groups/ipics/white-papers/ipics_oldaa_final.pdf, accessed 06/12/2023, 2020.
- 581
- Jouzel, J., Masson-Delmotte, V., Cattani, O., Dreyfus, G., Falourd, S., Hoffmann, G., Minster, B., Nouet, J.,
- Barnola, J. M., Chappellaz, J., Fischer, H., Gallet, J. C., Johnsen, S., Leuenberger, M., Loulergue, L., Luethi, D.,
- Oerter, H., Parrenin, F., Raisbeck, G., Raynaud, D., Schilt, A., Schwander, J., Selmo, E., Souchez, R., Spahni,
- R., Stauffer, B., Steffensen, J. P., Stenni, B., Stocker, T. F., Tison, J. L., Werner, M., and Wolff, E. W.: Orbital
- and Millennial Antarctic Climate Variability over the Past 800,000 Years, Science, 317, 793,
- 587 https://doi.org/10.1126/science.1141038, 2007.
- 588
- Lisiecki, L. E. and Raymo, M. E.: A Pliocene-Pleistocene stack of 57 globally distributed benthic δ18O records, Paleoceanography, 20, PA1003, https://doi.org/10.1029/2004pa001071, 2005.
- 591
- Martínez-García, A., Sigman, D.M., Ren, H., Anderson, R.F., Straub, M., Hodell, D.A., Jaccard, S.L., Eglinton,
- T.I., and Haug, G.H.: Iron fertilization of the subantarctic ocean during the last ice age, Science, 343 (6177),
- 594 1347-1350, https://doi.org/10.1126/science.1246848, 2014.

- McClymont, E.L., Sosdian, S.M., and Rosell-Melé, A.: Pleistocene sea-surface temperature evolution: Early cooling, delayed glacial intensification, and implications for the mid-Pleistocene transition. Earth. Sci. Rev.,
- 598 123, 173-193, https://doi.org/10.1016/j.earscirev.2013.04.006, 2013.

599

Millero, F. J.: Thermodynamics of the carbon dioxide system in the oceans, Geochim. Cosmochim. Acta., 59, 601 661-677, https://doi.org/10.1016/0016-7037(94)00354-O, 1995.

602

- Morée, A. L., Sun, T., Bretones, A., Straume, E. O., Nisancioglu, K., and Gebbie, G.: Cancellation of the precessional cycle in δ¹⁸O records during the Early Pleistocene. Geophys. Res. Lett., 48,
- 605 e2020GL090035. https://doi.org/10.1029/2020GL090035, 2021.

606

- Petit, J. R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J. M., Basile, I., Bender, M., Chappellaz, J., Davis,
- M., Delaygue, G., Delmotte, M., Kotlyakov, V. M., Legrand, M., Lipenkov, V. Y., Lorius, C., PÉpin, L., Ritz,
- 609 C., Saltzman, E., and Stievenard, M.: Climate and atmospheric history of the past 420,000 years from the
- Vostok ice core, Antarctica, Nature, 399, 429-436, https://doi.org/10.1038/20859, 1999.

611

Raymo, M., Lisiecki, L., and Nisancioglu, K.: Plio-Pleistocene Ice Volume, Antarctic Climate, and the Global 18O Record, Science, 313, 492-495, https://doi.org/10.1126/science.1123296, 2006.

614

- Raymo, M., Ruddiman, W., and Froelich, P.: Influence of Late Cenozoic mountain building on ocean geochemical cycles, Geology, 16, 649-653, https://doi.org/10.1130/0091-
- 617 7613(1988)016<0649:IOLCMB>2.3.CO;2, 1988.

618

- Raymo, M. E.: The timing of major climate terminations, Paleoceanography, 12, 577-585,
- 620 https://doi.org/10.1029/97PA01169, 1997.

621 622

- Raymo, M. E. and Huybers, P.: Unlocking the mysteries of the ice ages, Nature, 451, 284-285,
- 623 https://doi.org/10.1038/nature06589, 2008.

624 625

- Röthlisberger, R., Bigler, M., Wolff, E. W., Joos, F., Monnin, E., and Hutterli, M. A.: Ice core evidence for the extent of past atmospheric CO₂ change due to iron fertilisation, Geophys. Res. Lett., 31, L16207,
- 627 https://doi.org/16210.11029/12004GL020338, 2004.

628

- 629 Ruddiman, W. F., Raymo, M. E., Martinson, D. G., Clement, B. M., and Backman, J.: Pleistocene evolution:
- Northern hemisphere ice sheets and North Atlantic Ocean, Paleoceanography, 4, 353-412,
- 631 https://doi.org/10.1029/PA004i004p00353, 1989.

- 633 Shackleton, N. J. and Pisias, N. G.: Atmospheric Carbon Dioxide, Orbital Forcing, and Climate. In: The Carbon
- 634 Cycle and Atmospheric CO2: Natural Variations Archean to Present, https://doi.org/10.1029/GM032p0303,
- 635 1985.

- Shugi, H., The older the ice, the better the science. Adv. Polar Sci., 23, 121-122,
- 638 https://doi.org/10.13679/j.advps.2022.0004, 2022.

639

Stephens, B.B., Keeling, R.F.: The influence of Antarctic sea ice on glacial–interglacial CO₂ variations. Nature, 404, 171–174, https://doi.org/10.1038/35004556, 2000.

642

Tzedakis, P. C., Crucifix, M., Mitsui, T., and Wolff, E. W.: A simple rule to determine which insolation cycles lead to interglacials, Nature, 542, 427-432, https://doi.org/10.1038/nature21364, 2017.

645

Ushie, H., and Matsumoto, K.: The role of shelf nutrients on glacial-interglacial CO₂: A negative feedback, Global Biogeochem. Cy., 26, GB2039, https://doi.org/10.1029/2011GB004147., 2012.

648

van de Wal, R. S. W., de Boer, B., Lourens, L. J., Köhler, P., and Bintanja, R.: Reconstruction of a continuous high-resolution CO2 record over the past 20 million years. Clim. Past, 7, 1459–1469. https://doi.org/10.5194/cp-7-1459-2011, 2011.

652

- Veres, D., Bazin, L., Landais, A., Toye Mahamadou Kele, H., Lemieux-Dudon, B., Parrenin, F., Martinerie, P.,
- Blayo, E., Blunier, T., Capron, E., Chappellaz, J., Rasmussen, S., Severi, M., Svensson, A., Vinther, B., and
- Wolff, E.: The Antarctic ice core chronology (AICC2012): an optimized multi-parameter and multi-site dating
- approach for the last 120 thousand years, Clim. Past, 9, 1733-1748, https://doi.org/10.5194/cp-9-1733-2013,
- 657 2013.

658

Willeit, M., Ganopolski, A., Calov, R., and Brovkin, V.: Mid-Pleistocene transition in glacial cycles explained by declining CO2 and regolith removal, Sci. Adv., 5, eaav7337, doi: 10.1126/sciadv.aav7337, 2019.

661

Wolff, E. W., Chappella, J., Fischer, H., Kull, C., Miller, H., Stocker, T. F., and Watson, A. J.: The EPICA challenge to the Earth system modeling community, EOS, 85, 363363, https://doi.org/10.1029/2004EO380003, 2004.

665

Wolff, E. W., Kull, C., Chappellaz, J., Fischer, H., Miller, H., Stocker, T. F., Watson, A. J., Flower, B., Joos, F., Köhler, P., Matsumoto, K., Monnin, E., Mudelsee, M., Paillard, D., and Shackleton, N.: Modeling past atmospheric CO2: results of a challenge, EOS, 86 (38), 341-345, http://doi.org/10.1029/2005EO380003, 2005.

669

Yamamoto, M., Clemens, S.C., Seki, O., Tsuchiya, Y., Huang, Y., O'ishi, R., and Abe-Ouchi, A.: Increased interglacial atmospheric CO2 levels followed the mid-Pleistocene Transition, Nat. Geosci., 15(4), 307–313, https://doi.org/10.1038/s41561-022-00918-1, 2022.

673

Yan, Y., Benderm M.I., Brook, E.J., Clifford, H.M., Kemeny, P.C., Kurbatov, A.V., Mackay, S., Mayewski, P.A., Ng, J., Severinghaus J.P., and Higgins, J.A.: Two-million-year-old snapshots of atmospheric gases from Antarctic ice, Nature, 574(7780), 663–666, https://doi.org/10.1038/s41586-019-1692-3, 2019.

677

Yan, Y., Kurbatov, A.V., Mayewski, P.A., Shackleton, S., and Higgins, J.A.: Early Pleistocene East Antarctic temperature in phase with local insolation. Nat. Geosci., 16, 50-55, https://doi.org/10.1038/s41561-022-01095-x, 2022.