**Causes of ice-age intensification across the Mid-Pleistocene Transition**

Thomas B. Chalk1,2,\*, Mathis P. Hain1\* Gavin L. Foster1, Eelco J. Rohling3,1, Philip F. Sexton4, Marcus P.S. Badger4,5, Soraya G. Cherry1, Adam P. Hasenfratz6, Gerald H. Haug7, Samuel L. Jaccard8, Alfredo Martínez-García7, Heiko Pälike9,1, Richard D. Pancost5, Paul A. Wilson1

**Affiliations:**

1 Ocean and Earth Science, University of Southampton, Waterfront Campus, National Oceanography Centre Southampton, Southampton, SO14 3ZH, UK

2 Department of Physical Oceanography, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, 02543, USA

3 Research School of Earth Sciences, The Australian National University, Canberra 2601, Australia

4 School of Environment, Earth and Ecosystem Sciences, The Open University, Milton Keynes, MK7 6AA, UK

5Organic Geochemistry Unit, School of Chemistry, the Cabot Institute, University of Bristol, Bristol, BS8 1TS, UK

6Geologisches Institut, ETH Zürich, Sonneggstr. 5, 8092 Zürich, Switzerland

7Max-Planck-Institut für Chemie, Hahn-Meitner-Weg 1, 55128 Mainz, Germany

8Institute of Geological Sciences and Oeschger Center for Climate Change Research, University of Bern, 3012 Bern, Switzerland

9MARUM – Center for Marine Environmental Sciences, University of Bremen, Leobener Strasse, 28359 Bremen, Germany

\*Corresponding Authors

**During the Mid-Pleistocene Transition (MPT; 1200–800 thousand years ago, kyrs) Earth’s orbitally paced ice-age cycles intensified, lengthened from ~40 to ~100 kyrs, and became distinctly asymmetrical. Testing hypotheses that implicate changing atmospheric CO2 levels as a driver of the MPT has proven difficult with available observations. Here we use orbitally resolved, boron-isotope CO2 data to demonstrate that the glacial-to-interglacial CO2 difference increased from ~43 to ~75 μatm across the MPT, mainly due to lower glacial CO2 levels. Through carbon-cycle modeling, we attribute this decline primarily to the initiation of substantive dust-borne iron fertilization of the Southern Ocean during peak glacial stages. We also observe a two-fold steepening of the relationship between sea level and CO2-related climate forcing that is suggestive of a change in the dynamics that govern ice-sheet stability, such as that expected from the removal of subglacial regolith or inter-hemispheric ice-sheet phase-locking. We argue that neither ice-sheet dynamics nor CO2 change in isolation can explain the MPT. Instead, we infer that the MPT was initiated by a change in ice-sheet dynamics, and that longer and deeper post-MPT ice ages were sustained by carbon-cycle feedbacks related to dust fertilization of the Southern Ocean as a consequence of larger ice sheets.**

Significance Statement: Conflicting sets of hypotheses highlight either the role of ice sheets or atmospheric carbon dioxide (CO2) in causing the increase in duration and severity of ice age cycles ~1 million years ago, during the Mid-Pleistocene Transition (MPT). We document, for the first time, early-MPT CO2 cycles that were smaller than during recent ice age cycles. Using model simulations we attribute this to post-MPT increase in glacial-stage dustiness and its effect on Southern Ocean productivity. Detailed analysis reveals the importance of CO2 climate forcing as a powerful positive feedback that magnified MPT climate change originally triggered by a change in ice sheet dynamics. These findings offer new insights into the close coupling of climate, oceans and ice sheets within the Earth System.

\body

**Introduction**

The Mid-Pleistocene Transition (MPT) marks a major shift in the response of Earth’s climate system to orbital forcing. During the early Pleistocene, glacial-interglacial (G-IG) climate cycles were paced by ~40 kyr obliquity cycles, whereas G-IG cycles after the MPT gradually intensified over multiple obliquity cycles (i.e. 80-120 kyr periodicity; 1,2) and acquired a distinctively asymmetric character with gradual glacial growth and abrupt glacial terminations that were paced by a combination of obliquity and precession (1). These changes gave rise to longer, colder, and dustier late Pleistocene ice ages with larger continental ice sheets and lower global sea level (3-5, Fig. 1). The MPT occurred in the absence of any significant change in the pacing or amplitude of orbital forcing, indicating that it arose from an internal change in the response of the climate system rather than a change in external forcing (1, 6, 7).

Proposed explanations for the MPT fall into two primary groups: those that invoke a change in ice-sheet dynamics, and those that call upon some subtle change in the climate system’s global energy budget. Two prominent hypotheses posit that either removal of the subglacial regolith beginning at about 1200 kyr (8, 9) or phase-locking of northern and southern hemisphere ice-sheets at about 1000 kyr(10) gave rise to deeper and ultimately longer G-IG climate cycles by allowing for a greater build-up of ice independent of a change in CO2 radiative climate forcing (scenario 1 in Fig. 2). Alternatively, it has been argued that an underlying change in the global carbon cycle could have triggered the MPT through a decline in ΔRCO2; i.e. the radiative climate forcing exerted by CO2 decline (11-13, scenario 2 in Fig. 2). The continuous 800-kyr-long ice-core record of atmospheric CO2 (i.e., compiled by ref. 14) is well correlated to, and shares spectral power with, orbital-scale changes in temperature, ice volume, sea level, and the oxygen isotopic composition of benthic foraminifera (Fig. 1; Fig. 3). State-of-the-art coupled climate-ice-sheet models can simulate climate cycles that are longer than single obliquity cycles, provided that mean CO2 concentrations lie within certain, model-dependent bounds (Ref. 15, 16; e.g. 200-260 μatm). These studies suggest that the absolute CO2 level attained during rising obliquity (i.e., during increasing high-latitude northern hemisphere summer insolation) may be a critical control that determines whether ice sheets are strictly locked to the ~40 kyr beat of obliquity or survive for longer periods. Recent work has provided some evidence for an overall CO2 decline since the MPT (11, 17) supporting this view. The study by Hönisch and colleagues (11), in particular, provides evidence that CO2 decline was most pronounced during glacial stages. Here we build on that work with the aim to resolve the coupling of CO2 and climate on orbital timescales in order to address major unanswered questions regarding the role of CO2 change in the MPT.

To better quantify the role of CO2 during the MPT, we present two orbitally resolved, boron-isotope-based CO2 records, generated using the calcite tests of surface-dwelling planktonic foraminifera from Ocean Drilling Program (ODP) Site 999 in the Caribbean (Fig. 3, Fig. S1, S2). Boron isotopes (δ11B) in foraminifera have proven to be a reliable indicator of past ocean pH (18, 19) and, with appropriate assumptions regarding a second carbonate-system parameter (Fig. S3, Methods), allow reconstruction of atmospheric CO2 levels. Site 999 likely remained near air-sea CO2 equilibrium through time (20), and this is further supported by agreement of our new data (blue and red in Figs. 1a and 3) with published low-resolution δ11B-derived CO2 data from ODP Site 668 in the equatorial Atlantic (11, purple squares in Figs. 1a and 3b), and with the ice-core CO2 compilation (14).

**Results**

Our two datasets span an early portion of the MPT from 1080 to 1250 kyr ago (eMPT; n= 51) and, for validation against the ice-core CO2 record, the Pleistocene interval from 0 to 260 kyr ago (LP260; n=59, including 32 recalculated data points from ref. 18), yielding a similar median sampling interval of ~3.5-4.5 kyr for both records. Our LP260 CO2 dataset has a confidence interval of ±20 μatm (2σ) and is offset by a mean of +7 μatm from the ice core CO2 data when accounting for both CO2 and age uncertainties (21, see Fig. 3b, and supplement section 2.3). Comparison between our two CO2 records reveals that eMPT glacials on average were associated with higher CO2 levels than LP260 glacials (eMPT 241±21 μatm vs. LP260 203±14 μatm; 2σ), whereas interglacial levels were indistinguishable (eMPT 284±17 vs. LP260 277±18 μatm; 2σ). This analysis uses highest and lowest 25th percentiles of δ18O values to define “glacial” and “interglacial” subsets of the data, although this pattern is independent of the thresholds we define (Fig. 4, Fig. S4). Our analysis reproduces the glacial-stage-specific decline in CO2 levels found in ref. 11, leading to similar reconstructed increases in the glacial-to-interglacial CO2 difference since the MPT (40±47 μatm and 32±35 μatm based on ref. 11 and our data, respectively; Fig. 4). The higher resolution of these datasets allows this approach to yield useful data about our time spans, despite the relatively large uncertainty on each individual data point. When analyzed in a similar way, recent direct measurements of CO2 from a stratigraphically disturbed section of ~1-million-year-old “blue ice” (17) offers a fully independent test for the two δ11B-based reconstructions and is consistent with these findings (Fig. 4, Fig. S4). Thus, all available evidence suggests that the MPT was associated with a transition in the global carbon cycle characterized mainly by enhanced glacial-stage drawdown of CO2.

We evaluate the reconstructed G-IG CO2 change across our study interval with a carbon cycle model inversion of Southern Ocean and Atlantic mechanisms thought to have contributed to the most recent late Pleistocene G-IG CO2 cycles (22). For this, we force the CYCLOPS carbon-cycle model (23) with ODP 1090 sedimentary iron mass-accumulation rates (24, FeMAR), ODP 1094 Ba/Fe ratios (25), and ODP 982/U1313 (Fig. S1) benthic ∆δ13C variations (26, 27), to represent, respectively: (a) Subantarctic dust-borne iron fertilization; (b) combined changes in polar Antarctic stratification, nutrient drawdown and export production; and (c) transitions in the geometry and depth structure of the Atlantic Meridional Overturning Circulation (AMOC) (Fig. S5). These mechanisms and their model sensitivities have been documented elsewhere (23). Here we invert the model and the forcing, to minimize the mismatch between simulated atmospheric CO2 levels and the ice-core CO2 record of the last 800 kyr (residual RMS error of 12.3 μatm; see supplement section 4.1), and then to predict atmospheric CO2 levels back to 1500 kyr (Fig. S5) for comparison with our new data.

We find that changes in the periodicity of simulated CO2 levels closely match those in the ice-core CO2 record, in the benthic foraminiferal oxygen isotope record, and in our δ11B-based CO2 reconstruction (Fig. S6). Within the relative age uncertainty between the model forcings and our δ11B record, we find that the model explains more than 60% of the variance observed in our eMPT CO2 reconstruction, in line with model and reconstruction uncertainties. The model inversion does not include any secular change in the silicate weathering cycle (see also ref. 11 and Supplement section 4.1), so that simulated CO2 change is exclusively related to carbon redistribution within the ocean-atmosphere system and associated CaCO3 compensation dynamics (22,23).

In good agreement with the δ11B-based CO2 reconstructions and the ice-core CO2 measurements, the model inversion yields (a) insignificant (-1±3 μatm; 2σ) eMPT to LP260 interglacial CO2 change, and (b) a -22±5 μatm (2σ) eMPT to LP260 decline in glacial-stage CO2 levels (Fig. 4, Fig. S4). In the model we can attribute most of the additional glacial CO2 drawdown to MPT intensification of glacial dust-borne iron fertilization of biological productivity and nutrient utilization in the Subantarctic Zone of the Southern Ocean (24, 28-30, see Fig. S5). AMOC shoaling also seems to have become more prevalent after ~1200 kyr, but contributes less to simulated CO2 change (23). The model reproduces relatively low reconstructed interglacial CO2 from 400 to 800 kyr because use of ODP 1094 Ba/Fe in the model inversion results in persistent polar Southern Ocean stratification, as suggested previously (25). Through our eMPT sample interval, the model reproduces the ~80-kyr CO2 periodicity that is evident in our eMPT δ11B data (Fig. S6), mainly because of an ~80-kyr periodicity in eMPT polar Antarctic stratification and nutrient cycling recorded in ODP 1094 Ba/Fe (25). While all three forcings (iron fertilization, Atlantic circulation, coupled polar Antarctic changes) contribute to the simulated changes in CO2 periodicities that are highly coherent with the MPT change in rhythm of the climate system, the iron fertilization influence dominates the MPT intensification of ice age CO2 drawdown (Fig. S5).

**Discussion**

MPT intensification of glacial-stage CO2 drawdown is consistent with stabilization of continental ice sheets during increasing orbital obliquity by reduced greenhouse gas forcing, thereby helping ice sheets to grow larger and for periods longer than one obliquity cycle (scenario 2 in Fig. 2). However, when we directly compare changes in sea level (SL) as a measure for ice volume against CO2 climate forcing (ΔRCO2) from our records (Fig. 2d), we find that, between eMPT and LP260, ice-sheet mass increased progressively more per CO2 lowering, thereby increasing the SL-ΔRCO2 slope in Figure 2. This suggests an increase in ice-sheet sensitivity to CO2 forcing across the MPT, with the caveat that eMPT may not fully capture pre-MPT conditions, though it agrees with the longer-term record of Hönisch and colleagues (11). This finding is robust regardless of which SL reconstruction is used (Fig. S7); in all cases the SL-to-ΔRCO2 relationships appear to be linear, with increasing slopes from eMPT to LP260. The steepening relationship is also evident when regressing δ11B-to-δ18O relationships, with both isotope ratios measured on the same sample material (Fig. S8). Using the SL record with the best coverage of both intervals, relative sea level from the Mediterranean Sea (4), we estimate 25±3 and 45±5 meters of sea-level lowering for each Wm–2 reduction in radiative forcing during eMPT and LP260, respectively. Such a pronounced increase in sensitivity implicates a change in ice-sheet dynamics as predicted by the regolith hypothesis (8, 9) or the establishment of marine-based ice sheet margins in East Antarctica (10, scenario 1 in Fig. 2).

The observed changes in the SL-to-ΔRCO2 relationships contain elements of both end-member scenarios shown in Figs. 2a and 2b, in which a greater slope is possibly related to changes internal to the ice sheets (scenario 1), and amplified glacial-to-interglacial CO2 climate forcing is linked (this study) to increased glacial dustiness that causes enhanced Southern Ocean iron fertilization (scenario 2). Therefore, we propose a hybrid scenario (Fig. 2c) that incorporates both heightened ice-sheet sensitivity to CO2 forcingand dust-driven ocean sequestration of CO2 torepresent the observed climate system change across the MPT.

First, we propose that – independent of orbital and CO2 forcing – a process internal to the climate system yielded greater glacial buildup of ice-sheets (e.g., regolith removal (8) or ice-sheet phase-locking (10)). Second, we infer that larger ice sheets led to increased glacial atmospheric dustiness (31,32), either directly through sea-level lowering, or indirectly because of atmospheric cooling, drying, and/or changes in surface winds. This in turn induced glacial iron fertilization of the Subantarctic Zone of the Southern Ocean, thereby effecting the 20-40 μatm increase in the amplitude of the G-IG CO2 cycles documented here (Fig. 4, see also ref. 11). In our hybrid scenario, the positive climate-dust-CO2 feedback is required to: (a) drive additional ice sheet growth; and (b) stabilize those ice sheets during the critical orbital phase of rising obliquity, ensuring the survival of ice sheets beyond single obliquity cycles. Therefore, regardless of the mechanism that served as the initial MPT trigger, our findings further illustrate the exquisite coupling that exists in the Earth System between climate change, ice-sheet mass, and the polar ocean mechanisms that regulate glacial-interglacial CO2 change.

**Materials and Methods**

*G. ruber* white *sensu stricto* (300–355 μm) were picked from sediments from ODP 999A (see Figure S1) and the age model was constructed by benthic oxygen isotopes from the same samples and XRF scanning data. Samples were measured for boron isotope composition using a Thermo Scientific Neptune MC-ICPMS at the University of Southampton according to methods described elsewhere (18). Analytical uncertainty is given by the external reproducibility of repeat analyses of Japanese Geological Survey Porites coral standard (JCP) at the University of Southampton and is typically <0.2‰ (at 95% confidence). Metal element–calcium ratios (Mg, B, Al) were analyzed using Thermo Element 2XR ICP-MS at the University of Southampton. Here, these data are used to assess adequacy of clay removal (Al/Ca <100 μmol/mol) and to generate down core temperature estimates. CO2 was calculated using a Monte Carlo approach (10,000 replicates) with estimates of salinity and ALK using a flat probability spanning a generous range (34-37 psu and 2100-2500 μmol/kg respectively). A normal distribution around proxy data was used for all other input variables (temperature, pH, δ11Bsw, δ11Bforam; see supplement section 2 for full details). The CO2 record was then probabilistically assessed using a Monte Carlo approach that considers uncertainties in both age and CO2 values, and that preserves the stratigraphy of the record, which minimizes age uncertainty in a relative sense between samples (shown as envelope in Fig.1 and 3). Each of 2,000 Monte Carlo iterations involved independent random resampling of each sample within its X and Y uncertainty distributions. The stratigraphic constraint prevents age reversals in this resampling procedure. Linear interpolation was performed between resampled points, and the distribution of values thus generated was analyzed per time-step for the modal value and its 95% probability interval, as well as the 95% probability envelope of data in the sampled distribution (using the 2.5th and 97.5th percentiles). Because uncertainties in both X and Y directions are considered, the record of probability maxima (modes) gives a smoothed representation of the record, with quantified uncertainties (see supplement section 3).

Inverse carbon cycle modeling was carried out using the CYCLOPS model (23), with the forward model forcing derived from pertinent paleoceanographic records (25-27) and the forcing scaling parameters inverted to minimize model misfit with respect to the ice core CO2 record of the last 800 kyrs. Significant linear correlation with and matching spectral content to our new boron isotope-based CO2 data confirm the skill of the model inversion (Figure S6). Detailed statistical analysis is carried out to identify and quantify changes in absolute glacial and interglacial CO2, as well as G-IG CO2 range, that are common to the model inversion results, our new high-resolution CO2 data and some previous datasets (11, 17) that are not well enough dated or lack the required temporal resolution for comparison in the time and/or frequency domains. This analysis is based on estimation of the population means of cumulative probability density of glacial and interglacial subsamples, which were selected based on either available benthic foraminiferal δ18O or CO2 rank (Figure 4). Factorial analysis of the validated model allows for the mechanistic attribution to Subantarctic iron fertilization of glacial stage-specific CO2 reduction associated with the MPT interval (see bottom panel Fig. S5), which is the pattern we identified as common between model and all three empirical datasets. More detailed description of inverse modeling, model/data cross-validation and statistical quantification of CO2 change can be found in the supplementary information sections 4 and 5, respectively.

**Acknowledgments:** This work used samples provided by the International Ocean Discovery Program, sponsored by the US National Science Foundation and participating countries under the management of the Joint Oceanographic Institutions. Research was supported by NERC studentship NE/I528626/1 to TBC, NERC fellowship NE/K00901X/1 to MPH, NE/H006273/1 to RDP, NE/I006346/1 to RDP and GLF, Australian Research Council Laureate Fellowship FL1201000050 to EJR, ERC CoG 617462 to HP, Swiss National Science Foundation Grant PP00P2-144811 and ETH Research Grant ETH-04 11-1 to SLJ, and NERC UK IODP Grant NE/F00141X/1 to PAW, NERC Grant NE/P011381/1 to GLF, MPH, PAW, EJR and TBC, and Royal Society Wolfson Awards to PAW and GLF. We thank J. A. Milton, M. Cooper, A. Michalik and members of the “boron-team” at the University of Southampton for analytical help, the IODP Gulf Coast core repository for sample provision, and R. James, E. McClymont, R. Greenop, W. Kordesch, J. Higgins and D. Sigman for discussion.

**Author Contributions**: TBC, MPH, GLF and PAW designed the study. TBC, SGC and APH produced the data, and MPH developed the model. MPH, TBC, GLF and EJR performed the statistical analyses. PFS produced the ODP 999 age model, and APH, AMG and SLJ the ODP 1094 age model. TBC and MPH led the writing of the manuscript. All authors contributed specialist knowledge to the study.

**Figure Captions**

**Figure 1 | Climate records across the MPT.** (a) CO2 records shown as follows: black line, ice-core compilation (14); blue, our δ11B-based LP260 data; red, our δ11B-based eMPT data and purple squares, low-resolution MPT δ11B record of ref. 11. (all with 2σ error bars/envelopes). The range of ice-core CO2 measurements (17) from stratigraphically disturbed “blue ice” and their approximate age are indicated. (b) Sea-level records, where orange indicates the Red Sea record (21), dark blue represents Mg/Ca-based deconvolution of deep-sea benthic foraminiferal oxygen isotope data (3), and pink shows a record from the Mediterranean Sea (4). (c) Dust Mass Accumulation Rate (MAR) in a Subantarctic Site ODP 1090 on the southern flank of the Agulhas Ridge (24). (d) LR04 benthic foraminiferal oxygen isotope stack (26). Warm intervals highlighted by grey bars.

**Figure 2 | Changing relationship between CO2 climate forcing and ice-sheet size.** Three scenarios (a,b,c) for the MPT intensification of glacial cycles, compared with observations (d). Reconstructed sea level is taken here to reflect continental ice-sheet size in relationship to CO2 climate forcing (∆RCO2) calculated (33) from our orbitally resolved CO2 data. In all panels red and blue represent conditions during our two sampling intervals before and after the MPT (i.e., eMPT and LP260), respectively. The end-member scenarios posit (a) a change in ice-sheet dynamics causing ice volume to become more sensitive to unchanged G-IG climate forcing, and (b) an unchanged sensitivity of ice-sheet size to forcing, with glacial intensification driven by additional CO2 drawdown. Neither one of these two scenarios adequately describes both observed changes of increased ice-sheet sensitivity (greater slope) and additional glacial CO2 drawdown (more negative climate forcing). Here we argue for a hybrid scenario with a change in ice-sheet dynamics (possibly due to regolith removal of ref. 8 or ice-sheet phase-locking of ref. 10) allowing ice sheets to grow larger and to trigger a positive ice-dust-CO2 feedback that promotes further glacial intensification. In panel (d), the regression confidence intervals account for uncertainty in both sea level and ΔRCO2 (see Supplement section 3), but to avoid clutter we only display the regression based on the Mediterranean SL reconstruction (ref. 4) and the uncertainty on the slope, rather than the individual data points. We refer the reader to Fig.S7 and Supplement section 3 for other SL records and full treatment of data uncertainties.

**Figure 3 | Reconstructed ice-age CO2 cycles before and after MPT.** (a) Boron-isotope data from ODP 999 (see Figure S1) shown in blue (LP260) and red (eMPT), along with the LR04 deep-sea benthic foraminiferal oxygen isotope stack (black, 26). (b) CO2 levels calculated from boron isotopes (same colours as above), compared to ice-core (black, ref. 14) and previous low-resolution boron-derived CO2 data (purple, ref. 11). Probabilistic assessments are shown as the coloured bands, with the probability maximum shown within a dark band that represents its 95% probability envelope (~±6ppm), and a lighter band that represents the full 95% envelope of the sampled distribution. As illustrated by the inset in the centre of the lower panel, comparison between our (red) eMPT and (blue) LP260 records reveals that glacials on average experienced higher CO2 levels during eMPT than LP260 (eMPT 241±21 μatm vs. LP260 203±14 μatm; 2σ), whereas interglacial levels were indistinguishable between the two time-slices (eMPT 284±17 vs. LP260 277±18 μatm; 2σ).

**Figure 4 | CO2 change since the MPT.** Quantified from different datasets: boron isotope data from ODP 999 (this study) and ODP 668 (11), CO2 directly measured on stratigraphically disturbed ~1-million-year-old “blue-ice” from the Allan Hills (17), and CYCLOPS model inversion (this study). For each dataset, we quantify (top) change in interglacial and (middle) glacial CO2 levels, as well as (bottom) the change in the magnitude of interglacial-glacial CO2 cycles. For this analysis, we define glacial and interglacial subsets of the datasets based on a 25% cut-off criterion, sub-sampling the data with the 25% lowest/highest δ18O (marine records) or CO2 (ice core, model). As further discussed in Supplement section 5, the results are robust for a wide range of cut-off values (Fig. S4). Thick black bars denote 1σ uncertainty of the estimated CO2 change while thin black bars denote the one-sided test of the sign of CO2 change at 95% significance level. We note that the ODP 668 uncertainties do not encompass the underlying alkalinity and seawater boron isotope composition assumptions, which are included in the uncertainty propagation for our new ODP 999 data. The Allan Hills ice may not capture the full range of CO2 levels (17).

References:

1 Huybers P. Combined obliquity and precession pacing of late Pleistocene deglaciations. *Nature,* 480 229-232, (2011).

2 Clark, P. U. *et al.* The middle Pleistocene transition: characteristics, mechanisms, and implications for long-term changes in atmospheric pCO2. *Quaternary Science Reviews* **25**, 3150-3184 (2006).

3 Elderfield, H. *et al.* Evolution of ocean temperature and ice volume through the Mid-Pleistocene climate transition. *Science* **337**, 704-709 (2012).

4 Rohling, E. *et al.* Sea-level and deep-sea-temperature variability over the past 5.3 million years. *Nature* **508**, 477-482 (2014).

5 McClymont, E. L., Sosdian, S. M., Rosell-Melé, A. & Rosenthal, Y. Pleistocene sea-surface temperature evolution: Early cooling, delayed glacial intensification, and implications for the mid-Pleistocene climate transition. *Earth-Science Reviews* **123**, 173-193 (2013).

6 Imbrie J. *et al.* On the structure and origin of major glaciation cycles: 2. The 100,000-year cycle. Paleoceanography 8(6), 699-735 (1993).

7 Pisias NG & Moore T The evolution of Pleistocene climate: a time series approach. *Earth and Planetary Science Letters* 52(2):450-458, (1981).

8 Clark, P. U. & Pollard, D. Origin of the Middle Pleistocene Transition by ice sheet erosion of regolith. *Paleoceanography* **13**, 1-9, (1998).

9 Snyder, C. W. Evolution of global temperature over the past two million years. Nature, (2016)

10 Raymo ME & Huybers P. Unlocking the mysteries of the ice ages. *Nature,* 451, 284-285, (2008).

11 Hönisch, B., Hemming, N. G., Archer, D., Siddall, M. & McManus, J. F. Atmospheric Carbon Dioxide Concentration Across the Mid-Pleistocene Transition. *Science* **324**, 1551-1554, (2009).

12 Raymo ME, Ruddiman WF, & Froelich PN Influence of late Cenozoic mountain building on ocean geochemical cycles. *Geology* 16(7):649-653, (1988).

13 Berger A, Li X, & Loutre M Modelling northern hemisphere ice volume over the last 3Ma. *Quaternary Science Reviews* 18(1):1-11, (1999).

14 Bereiter, B. *et al.* Revision of the EPICA Dome C CO2 record from 800 to 600 kyr before present. *Geophysical Research Letters* **42**, 542-549, (2015).

15 Abe-Ouchi, A. *et al.* Insolation-driven 100,000-year glacial cycles and hysteresis of ice-sheet volume. *Nature* **500**, 190-193 (2013).

16 Ganopolski, A. & Calov, R. The role of orbital forcing, carbon dioxide and regolith in 100 kyr glacial cycles. *Climate of the Past* **7** (2011).

17 Higgins, J. A. *et al.* Atmospheric composition 1 million years ago from blue ice in the Allan Hills, Antarctica. *Proceedings of the National Academy of Sciences* **112**, 6887-6891, (2015).

18 Foster, G. L. Seawater pH, pCO2 and CO32- variations in the Caribbean Sea over the last 130 kyr: A boron isotope and B/Ca study of planktic forminifera. *Earth and Planetary Science Letters* **271**, 254-266, (2008).

19 Hemming, N. G. & Hönisch, B. A critical review and recent advances in the boron isotope paleo-pH proxy. *Geochimica Et Cosmochimica Acta*, A129-A129 (2005).

20 Martinez-Boti, M. A. *et al.* Plio-Pleistocene climate sensitivity evaluated using high-resolution CO2 records. *Nature* **518**, 49-54, (2015).

21 Grant, K. M. *et al.* Sea-level variability over five glacial cycles. *Nat Commun* **5**, (2014).

22 Sigman, D. M., Hain, M. P. & Haug, G. H. The polar ocean and glacial cycles in atmospheric CO2 concentration. *Nature* **466**, 47-55 (2010).

23 Hain, M. P., Sigman, D. M. & Haug, G. H. Carbon dioxide effects of Antarctic stratification, North Atlantic Intermediate Water formation, and subantarctic nutrient drawdown during the last ice age: Diagnosis and synthesis in a geochemical box model. *Global Biogeochemical Cycles* **24**, GB4023, (2010).

24 Martínez-Garcia, A. *et al.* Southern Ocean dust-climate coupling over the past four million years. *Nature* **476**, 312-315 (2011).

25 Jaccard, S. *et al.* Two modes of change in Southern Ocean productivity over the past million years. *Science* **339**, 1419-1423 (2013).

26 Lisiecki, L. E. & Raymo, M. E. A Pliocene-Pleistocene stack of 57 globally distributed benthic 18O records. *Paleoceanography*, (2005).

27 Lang, D. C. *et al.* The transition on North America from the warm humid Pliocene to the glaciated Quaternary traced by eolian dust deposition at a benchmark North Atlantic Ocean drill site. *Quaternary Science Reviews* **93**, 125-141 (2014).

28 Ridgwell, A. Implications of the glacial CO2 “iron hypothesis” for Quaternary climate change. *Geochemistry Geophysics Geosystems* 4(9), 1076, (2003)

29 Martínez-Garcia, A. *et al.* Iron Fertilization of the Subantarctic Ocean During the Last Ice Age. *Science* **343**, 1347-1350 (2014).

30 Martin, J. H., Gordon, R. M. & Fitzwater, S. E. Iron in Antarctic waters. *Nature*, 156-158 (1990).

31 McGee, D., Broecker, W. S. & Winckler, G. Gustiness: The driver of glacial dustiness? *Quaternary Science Reviews* **29**, 2340-2350 (2010).

32 Kohfeld, K. E. & Harrison, S. P. DIRTMAP: the geological record of dust. *Earth-Science Reviews* **54**, 81-114, (2001).

33 Myhre, G., Highwood, E. J., Shine, K. P. & Stordal, F. New estimates of radiative forcing due to well mixed greenhouse gases. *Geophysical Research Letters* **25**, 2715-2718, (1998).

**Supplementary references**

34 Foster, G. L. & Rae, J. W. B. Reconstructing Ocean pH with Boron Isotopes in Foraminifera. *Annual Review of Earth and Planetary Sciences* **44**, 207-237, (2016).

35 Takahashi T*, et al.* Climatological mean and decadal change in surface ocean pCO2, and net sea–air CO2 flux over the global oceans. *Deep Sea Research Part II: Topical Studies in Oceanography* 56(8–10):554-577. (2009)

36 Henehan, M. J. *et al.* Calibration of the boron isotope proxy in the planktonic foraminifera *Globigerinoides ruber* for use in palaeo-CO2 reconstruction. *Earth and Planetary Science Letters* **364**, 111-122 (2013).

37 Edgar, K. M., Anagnostou, E., Pearson, P. N. & Foster, G. L. Assessing the impact of diagenesis on δ11B, δ13C, δ18O, Sr/Ca and B/Ca values in fossil planktic foraminiferal calcite. *Geochimica et Cosmochimica Acta* **166**, 189-209 (2015).

38 Paillard, D., Labeyrie, L. & Yiou, P. Analyseries 1.0: a Macintosh software for the analysis of geographical time-series. *Eos* **77**, 379 (1996).

39 Schmidt, M. W., Vautravers, M. J. & Spero, H. J. Western Caribbean sea surface temperatures during the late Quaternary. *Geochemistry, Geophysics, Geosystems* **7**, Q02P10, (2006).

40 Barker, S., Greaves, M. & Elderfield, H. A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. *Geochemistry, Geophysics, Geosystems* **4** (2003).

41 Yu, J. M. & Elderfield, H. Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state. *Earth and Planetary Science Letters*, 73-86, (2007).

42 Rae, J. W., Foster, G. L., Schmidt, D. N. & Elliott, T. Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system. *Earth and Planetary Science Letters* **302**, 403-413 (2011).

43 Foster, G. L. *et al.* Interlaboratory comparison of boron isotope analyses of boric acid, seawater and marine CaCO3 by MC-ICPMS and NTIMS. *Chemical Geology* **358**, 1-14, (2013).

44 Evans, D. & Müller, W. Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular change in seawater Mg/Ca. *Paleoceanography* **27**, PA4205, (2012).

45 Fantle, M. S. & DePaolo, D. J. Sr isotopes and pore fluid chemistry in carbonate sediment of the Ontong Java Plateau: Calcite recrystallization rates and evidence for a rapid rise in seawater Mg over the last 10 million years. *Geochimica et Cosmochimica Acta* **70**, 3883-3904, (2006).

46 Delaney, M. L., WH Bé, A. & Boyle, E. A. Li, Sr, Mg, and Na in foraminiferal calcite shells from laboratory culture, sediment traps, and sediment cores. *Geochimica et Cosmochimica Acta* **49**, 1327-1341 (1985).

47 Klochko, K., Kaufman, A. J., Yao, W. S., Byrne, R. H. & Tossell, J. A. Experimental measurement of boron isotope fractionation in seawater. *Earth and Planetary Science Letters*, 276-285, (2006).

48 Catanzaro, E. J. *Boric acid: isotopic and assay standard reference materials*. Vol. 17 (National Bureau of Standards, Institute for Materials Research, 1970).

49 Hemming, N. G., Reeder, R. J. & Hanson, G. N. Mineral-fluid partitioning and isotopic fractionation of boron in synthetic calcium carbonate. *Geochimica et Cosmochimica Acta* **59**, 371-379, (1995).

50 Hemming, N. G. & Hanson, G. N. Boron isotopic composition and concentration in modern marine carbonates. *Geochimica Et Cosmochimica Acta*, 537-543 (1992).

51 Dickson, A. G. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep Sea Research Part A. Oceanographic Research Papers* **37**, 755-766, (1990).

52 Foster, G. L., von Strandmann, P. & Rae, J. W. B. Boron and magnesium isotopic composition of seawater. *Geochemistry Geophysics Geosystems* **11**, (2010).

53 Foster, G. L., Lear, C. H. & Rae, J. W. B. The evolution of pCO2, ice volume and climate during the middle Miocene. *Earth and Planetary Science Letters* **341–344**, 243-254, (2012).

54 Raitzsch, M. & Hönisch, B. Cenozoic boron isotope variations in benthic foraminifers. *Geology*, (2013).

55 Lemarchand, D., Gaillardet, J., Lewin, E. & Allegre, C. Boron isotope systematics in large rivers: implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic. *Chemical Geology* **190**, 123-140 (2002).

56 Toggweiler, J. Variation of atmospheric CO2 by ventilation of the ocean's deepest water. *Paleoceanography* **14**, 571-588 (1999).

57 Farrell, J. W. & Prell, W. L. Pacific CaCO3 Preservation and δ18O Since 4 Ma: Paleoceanic and Paleoclimatic Implications. *Paleoceanography* **6**, 485-498, (1991).

58 Catubig, N. R., Archer, D. E., Francois, R., Howard, W. R. & Yu, E.-F. Calcium carbonate global LGM Burial rate data. (1998).

59 R: A language and environment for statistical computing (R Foundation for Statistical Computing, Vienna, Austria (2010).

60 seacarb: seawater carbonate chemistry with R. R package version 3.0. (2011).

61 York D, Evensen NM, Martı́nez ML, Delgado JDB, & Derek Y, Unified equations for the slope, intercept, and standard errors of the best straight line Least-squares fitting of a straight line. *American Journal of Physics* 72(3):367-375 (2004).

62 De Boer B, Stocchi P, & Van De Wal R A fully coupled 3-D ice-sheet-sea-level model: algorithm and applications. *Geoscientific Model Development* 7(5):2141-2156., (2014)

63 Archer, D. Modeling the calcite lysocline. *Journal of Geophysical Research: Oceans* **96**, 17037-17050 (1991).

64 Sigman, D. M., McCorkle, D. C. & Martin, W. R. The calcite lysocline as a constraint on glacial/interglacial low‐latitude production changes. *Global Biogeochemical Cycles* **12**, 409-427 (1998).

65 Robinson, R. S. *et al.* Diatom‐bound 15N/14N: New support for enhanced nutrient consumption in the ice age subantarctic. *Paleoceanography* **20** (2005).

66 Franois, R. *et al.* Contribution of Southern Ocean surface-water stratification to low atmospheric CO2 concentrations during the last glacial period. *Nature* **389**, 929-935 (1997).

67 Robinson, R. S., Brunelle, B. G. & Sigman, D. M. Revisiting nutrient utilization in the glacial Antarctic: Evidence from a new method for diatom‐bound N isotopic analysis. *Paleoceanography* **19** (2004).

68 Studer, A. S. *et al.* Antarctic Zone nutrient conditions during the last two glacial cycles. *Paleoceanography* **30**, 845-862 (2015).

69 Duplessy, J. *et al.* Deepwater source variations during the last climatic cycle and their impact on the global deepwater circulation. *Paleoceanography* **3**, 343-360 (1988).

70 Sarnthein, M. *et al.* Changes in East Atlantic Deepwater Circulation over the last 30,000 years: Eight time slice reconstructions. *Paleoceanography* **9**, 209-267, (1994).

71 Sigman, D. M., Lehman, S. J. & Oppo, D. W. Evaluating mechanisms of nutrient depletion and 13C enrichment in the intermediate‐depth Atlantic during the last ice age. *Paleoceanography* **18** (2003).

72 Lynch-Stieglitz, J. *et al.* Atlantic meridional overturning circulation during the Last Glacial Maximum. *Science*, 66-69, (2007).

73 Hain, M.P., Sigman, D.M. & Haug, G.H. in *Treatise on Geochemistry, 2nd ed.*, Vol. 8, 485-517, Elsevier (2014).

74 Pena LD & Goldstein SL. Thermohaline circulation crisis and impacts during the mid-Pleistocene transition. *Science*. (2014)

75 Shipboard Scientific Party. Site 1094. In *Proceedings of the Ocean Drilling Program, Initial Reports, Volume 177, Ch. 9, 1–73 [Gersonde, R. and Hodell, D. A. and Blum, P. et al. (eds.)]. College Station TX, USA*. (1999).

76 Powell, M. J. An efficient method for finding the minimum of a function of several variables without calculating derivatives. *The computer journal* **7**, 155-162 (1964).

77 Brent, R. P. Some efficient algorithms for solving systems of nonlinear equations. *SIAM Journal on Numerical Analysis* **10**, 327-344 (1973).

78 Brent, R. P. *Algorithms for minimization without derivatives*. (Courier Corporation, 2013).

79 Fletcher, R. & Reeves, C. M. Function minimization by conjugate gradients. *The computer journal* **7**, 149-154 (1964).