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

Maxence Guillermic¹,², Sambuddha Misra³,⁴, Robert Eagle¹,², Aradhna Tripati¹,²

¹Department of Atmospheric and Oceanic Sciences, Department of Earth, Planetary, and Space Sciences, Center for Diverse Leadership in Science, Institute of the Environment and Sustainability, University of California – Los Angeles, Los Angeles, CA 90095 USA
²Laboratoire Géosciences Océan UMR6538, UBO, Institut Universitaire Européen de la Mer, Rue Dumont d'Urville, 29280, Plouzané, France
³Indian Institute of Science, Centre for Earth Sciences, Bengaluru, Karnataka 560012, India
⁴The Godwin Laboratory for Palaeoclimate Research, Department of Earth Sciences, University of Cambridge, UK

Correspondence to: Maxence Guillermic (maxence.guillermic@gmail.com) and Aradhna Tripati (atripati@g.ucla.edu)
ABSTRACT

Constraints on the evolution of atmospheric CO₂ levels throughout Earth’s history are foundational to our understanding of past variations in climate. Despite considerable effort, records vary in their temporal and spatial coverage and estimates of past CO₂ levels do not always converge, and therefore new records and proxies are valuable. Here we reconstruct atmospheric CO₂ values across major climate transitions over the past 16 million years using the boron isotopic composition (δ¹¹B) of planktic foraminifera from 89 samples obtained from two sites in the West Pacific Warm Pool, Ocean Drilling Program (ODP) Sites 806 and 807 measured using high-precision multi-collector inductively-coupled plasma mass spectrometry. We compare our results to published data from Pacific Site 872, also in the Western Equatorial Pacific, that goes back to 22 million years ago. These sites are in a region that today is near equilibrium with the atmosphere and are thought to have been in equilibrium with the atmosphere for the interval studied. We show that data from this region is consistent with ice core data and other boron-based studies. The data show evidence for elevated pCO₂ during the Middle Miocene and Early to Middle Pliocene, and reductions in pCO₂ of ~200 ppm during the Middle Miocene Climate Transition, ~250 ppm during Pliocene Glacial Intensification, and ~50 ppm during the Mid-Pleistocene Climate Transition. There is possible evidence for a larger reduction in glacial pCO₂ during the Mid-Pleistocene Transition compared to interglacial pCO₂, and a minimum in pCO₂ during glacial MIS 30. Our results are consistent with a coupling between pCO₂, temperature and ice sheet expansion from the Miocene to Recent.

Highlights

In this study, we reconstruct atmospheric pCO₂ using δ¹¹B data from ODP Sites 806 and 807 and compare them with ice core data, demonstrating the fidelity of our approach. We therefore apply the same framework to older samples to create a long-term pH and pCO₂ reconstruction for the past 16 million years, and recalculate pCO₂ for ODP Site 872 from 17 to 22 million years ago. We find major increases in surface water pH and decreases in atmospheric pCO₂ were associated with decreased temperature in the Western Equatorial Pacific, including associated with major episodes of ice sheet expansion in the high latitudes, providing more robust quantitative constraints on the past coupling between pCO₂, temperature, and cryosphere stability.
Keywords

Boron isotopes, CO₂, ODP Site 806, ODP Site 807, Miocene, climate
1. Introduction

Due to concerns about the long-term consequences of anthropogenic emissions and associated climate change (IPCC, 2014, 2018), efforts have been made to quantify past atmospheric CO$_2$ and examine past relationships between CO$_2$ and temperature. Such data are not only critical for constraining Earth-system sensitivity (Lea, 2004; Lunt et al., 2010; Pagani et al., 2010; Hansen et al., 2012, 2013, Foster and Rohling, 2013; Schmittner et al., 2011; Tierney et al., 2020), but are also of broad interest because such data can help us understand the evolution of climate and geological systems through Earth’s history (Tripati et al., 2011; Foster et al., 2017; Tripati and Darby, 2018). However, discrepancies between proxy reconstructions still exist, including for major climate transitions of the Cenozoic. In particular, there remains a pressing need for robust and higher-resolution atmospheric CO$_2$ records from sites that are in equilibrium with the atmosphere.

High-resolution and direct determinations of atmospheric CO$_2$ are available for the last 800 kyr through analysis of air bubbles extracted from ice-cores, but these records are limited to the availability of cores (Petit et al., 1999; Siegenthaler et al., 2005; Lüthi et al., 2008; Bereiter et al., 2015). A window into atmospheric CO$_2$ levels comes from 1 million-year-old blue ice (Higgins et al., 2015) and more recently a snapshot from the early Pleistocene period (Yan et al., 2019). Most reconstructions of CO$_2$ for prior to 800 ka are based on indirect terrestrial and marine proxies. Stomata indices for fossil leaves (Van der Burgh, 1993; Royer, 2001), carbon isotope ratios ($\delta^{13}$C) of paleosols (Retallak et al., 2009), $\delta^{13}$C of alkenones (Pagani et al., 2005; Zhang et al., 2013), B/Ca ratios of surface-dwelling foraminifera (Yu and Hönisch, 2007; Foster, 2008; Tripati et al., 2009, 2011), and boron isotope ratios ($\delta^{11}$B) of surface-dwelling foraminifera (Pearson and Palmer, 2000; Hönisch et al., 2009; Bartoli et al., 2011; Foster, 2008, 2012; Foster and Sexton, 2014; Chalk et al., 2017; Sosdian et al., 2018; Dyez et al., 2018) have been used to estimate atmospheric CO$_2$.

Each of the above proxy methods has sources of systematic errors that we do not attempt to exhaustively document as they have been discussed in-depth elsewhere (e.g., Pagani et al., 2005; Tripati et al., 2011; Guillermic et al., 2020). However, we note that significant developments in the boron-based proxies include improvements to the accuracy and precision of measurements using multi-collector inductively coupled mass spectrometry (MC-ICP-MS) compared to early work with thermal ionization.
mass spectrometry (TIMS), where there were large instrumental mass fractionations and challenges with laboratory intercomparison (Foster et al., 2013; Farmer et al., 2016; Aggarwal and You, 2017). There was also the realization that temperature-dependent K_D to interpreting B/Ca sensitivities observed from the field of sediment trap, core-top, and downcore studies (Yu and Hönisch, 2007; Foster et al., 2008; Tripathi et al., 2009, 2011; Babila et al., 2010; Osborne et al., 2020) differ from foraminiferal culture experiments (Allen et al., 2011, 2012) and inorganic calcite (Mavromatis et al., 2015); this type of discrepancy has also been observed with other elemental proxies (e.g., Mg/Ca). Such differences may be due to differences in growth rates (Sadekov et al., 2014), ontogenetic changes, a correlation in the field between temperature and other hydrographic variables that obscure robust statistical determination of parameter relationships, culture conditions resulting in organisms being stressed, and/or other factors.

The marine CO_2 proxy that appears to be subject to the fewest systematic uncertainties, based on our current understanding, is the boron isotopic composition (δ^{11}B) of planktic foraminifera as measured using MC-ICPMS and TE-NTIMS (Hain et al., 2018). This proxy provides constraints on seawater pH, if temperature, salinity, seawater δ^{11}B, and the appropriate mono-specific calibration between δ^{11}B_{carbonate} and δ^{11}B_{borate} are constrained (Pearson and Palmer, 2000; Foster et al., 2008; Sosdian et al., 2018; Raitzsch et al., 2018; Guillermic et al., 2020). Seawater pH can be used to calculate seawater pCO_2 if there are constraints on a second parameter of the carbonate system (e.g. alkalinity, DIC). Atmospheric pCO_2 can then be constrained if the site being examined is in air-sea CO_2 equilibrium.

Given the evolution of the field, there are relatively few studies generating high-precision boron-based records over major climate transitions in the Cenozoic using recent analytical methods, that incorporate our current understanding of the proxy (e.g., Greenop et al., 2014; Martinez-Boti et al., 2015b; Chalk et al., 2017; Dyez et al., 2018; de la Vega et al., 2020). Furthermore, of the existing studies using boron-based proxies, an additional uncertainty frequently exists, namely the short time interval of study (e.g., emphasizing on a climate transition) (Martinez-Boti et al., 2015b; Chalk et al., 2017) and whether the study sites remain in air-sea CO_2 equilibrium with the atmosphere (Martinez et al., 2015a). And although estimation of atmospheric pCO_2 from seawater pH using this proxy is relatively straightforward, reconstructions are still impacted by uncertainties including the lack of robust constraints on a second

5
parameter of the carbonate system, and our limited understanding of secular variations in the $\delta^{11}B$ of seawater (Tripati et al., 2011; Greenop et al., 2017; Sosdian et al., 2018; Rae et al., 2021).

Therefore, to provide additional constraints on the evolution of atmospheric $pCO_2$ from the Miocene through Pleistocene, we developed new records from the western tropical Pacific. We use foraminiferal $\delta^{11}B$ and trace elements in the planktic foraminiferal species *Trilobus sacculifer* and *Globigerinoides ruber* to reconstruct past seawater pH and atmospheric CO$_2$ at Ocean Drilling Program (ODP) Sites 806 and 807 in the Western Equatorial Pacific (WEP) over the last 16 million years (Myr). The sites are located on the western border of the tropical Pacific Ocean, the largest open-oceanic region on the globe, and the warmest open ocean region at present.

These two sites have been examined in other boron-based studies (Wara et al., 2003; Tripati et al., 2009, 2011; Shankle et al., 2020), as has the region more broadly (Pearson and Palmer, 2000), because it is understood to be in equilibrium with the atmosphere and have relative stable hydrography. The region experiences equatorial divergence but is not strongly affected by upwelling and has a current estimated annual air-sea CO$_2$ flux of +28 ppmv (Takahashi et al., 2014). The pre-industrial air-sea CO$_2$ flux is calculated to be +16 ppm, (GLODAP database corrected from anthropogenic inputs), with a value of 298 ppm, compared to the Vostok ice core value of 282 ppm at 1.08 ka. This $pCO_2$ difference is similar to our $pCO_2$ uncertainty (an average of ~17 ppm for the youngest samples). If trade winds were much stronger, and equatorial divergence greater, than this could drive some disequilibrium in the past. However, a few lines of evidence suggest the region was in quasi-equilibrium in the past: 1) zonal temperatures are at a maximum in pre-industrial times and during the Pleistocene, and we are able to reconstruct atmospheric $pCO_2$ values from the ice cores, 2) temperature proxies indicate the region is relatively stable with respect to temperature compared to other parts of the ocean, and also indicate a weak and stable zonal temperature gradient during the Miocene and Pliocene which would support air-sea stable conditions and air-sea equilibrium (e.g., Nathan and Leckie, 2009; Zhang et al. 2014; Liu et al., 2019).

This study builds on low-resolution prior reconstructions for these sites (Wara et al., 2003; Tripati et al., 2009, 2011; Shankle et al., 2020), Site 872 in the tropical Pacific (Sosdian et al., 2018), and other published boron isotope work, to provide additional data to constrain past seawater pH and pCO$_2$ for the
WEP using MC-ICP-MS, thereby providing an invaluable new perspective on reconstructing past atmospheric CO2 via marine sediment archives. We explore various constraints on the second carbonate system parameter using a number of different scenarios, following on the systematic work done by Tripati et al. (2009) and (2011) for B/Ca. We interpret these data using recent constraints on seawater δ11B (Lemarchand et al., 2000; Raitzsch and Hönisch, 2013; Greenop et al., 2017). For temperature estimation, we utilize a multi-variable model for Mg/Ca (Gray and Evans, 2019), that builds on prior work with clumped isotopes in planktic foraminifera for Site 806 and other WEP sites demonstrating that for the Last Glacial Maximum to recent, salinity-corrected Mg/Ca values are needed to yield convergent estimates of mixed-layer temperatures (Tripati et al., 2014).

2. Materials and Methods

Below we describe site locations, analytical methods used, and figures of merit. The supplemental methods section describes screening for potential contamination, equations used for calculations, and error propagation.

2.1 Site locations

Samples are from three ODP holes recovered during Leg 130 in the WEP (Fig. 1, Table 1): Hole 806A (0°19.140'N, 159°21.660'E, 2520.7 m water depth), Hole 806B (0°19.110'N, 159°21.660'E, 2519.9 m water depth), and Hole 807A (3°36.420'N, 156°37.500'E, 2803.8 m water depth) (Berger et al., 1993). Sites 806 and 807 are not likely to have experienced major tectonic changes over the last 20 million years.

2.2 Preservation

Microfossils in sediments at these sites, as with any sedimentary sequences, have the potential to be influenced by diagenesis. Despite evidence of authigenic carbonate formation, recent modeling work concluded the influence of dissolution and reprecipitation at Sites 806 and 807 was relatively minor (Mitnik et al., 2018). Prior work has also found minimal impacts on the B/Ca ratio of Pliocene foraminifera from Site 806 (White and Ravelo, 2020), and on the Mg/Ca ratio of Miocene D. altispera shells at Site 806 (Sosdian et al., 2020). The weight/shell ratio is commonly used to monitor dissolution,
and the only published record at Site 806 for the Pliocene does not show a trend consistent with dissolution of *T. sacculifer* (Wara et al., 2005). We do note that while the “coccolith size-free dissolution” index reported in Si and Rosenthal (2019) indicates higher dissolution rates in the Miocene, their records were thought to be biased from changes in foraminifera assemblages as discussed in White and Ravelo (2020).

To further assess the potential impact of dissolution in our geochemical data, the weight/shell ratio was examined in our samples. The weight/shell data used to monitor dissolution does not exhibit any trend within the interval studied consistent with dissolution. Absolute weights/shell are increasing in the Miocene, which is not consistent with dissolution influencing the record (Fig. 2E). Additionally, reconstructed pH and pCO$_2$ values also exhibit reasonable correspondence with the Vostok ice core data. Downcore $\delta^{11}$B values from Sites 806 and 807 are similar, despite evidence for higher authigenic carbonate at Site 807 relative to Site 806 (Mitnik et al., 2018). Further, the consistency of our boron isotope and Mg/Ca results with at the two sites with each other, and to the published data from Site 872 (Sosdian et al., 2018), each with different sedimentation rates, are not consistent with diagenesis being a primary driver of the record. Comparison of raw data, and derived parameters, is shown in Figs. 2 and 7.

### 2.3 Age models

The age model for Site 806 from 0-1.35 Ma is based on Medina-Elizalde and Lea (2005); calculated ages correspond well with ages from the Lisiecki and Raymo LR04 stack (Fig. 2A). The fourth polynomial regression-based biostratigraphy from Lear et al. (2015) was used for the rest of the record, following other work (Sosdian et al., 2020). Ages for Site 807 are based on published biostratigraphy (Berger et al., 1993) for 807 with additional constraints placed by Zhang et al., (2007) for the interval from 0-0.55 Ma.

### 2.4 Species and trace element cleaning

Samples were picked and cleaned to remove clays at UCLA (Los Angeles, CA) and the University of Western Brittany (Plouzané, France). 50-100 foraminifera shells were picked from the 300-400µm fraction size for *T. sacculifer* (w/o sacc) and from the 250-300 µm for *G. ruber* (white sensu stricto). Picked foraminifera were gently crushed, clays removed, and checked for coarse-grained silicates.
Samples were then cleaned using a full reductive and oxidative cleaning protocol following Barker et al. (2003). A final leach step with 0.001N HCl was done prior dissolution in 1N HCl. Boron purification used a published microdistillation protocol (see Misra et al., 2014b, Guillermic et al., 2020 for more detailed methods).

2.5 Chemical purification and geochemical analysis

Chemical separation was performed in a boron-free clean lab at the University of Cambridge (Cambridge, UK). Calcium concentrations were measured on an ICP-AES®Ultima 2 HORIBA at the Pôle Spectrometrie Océan (PSO), UMR6538 (Plouzané, France). Elemental ratios (e.g. X/Ca ratios) were analyzed on a Thermo Scientific®Element XR HR-ICP-MS at the PSO, Ifremer (Plouzané, France). Boron isotopic measurements were carried out on a Thermo Scientific®Neptune+ MC-ICP-MS equipped with $10^{13}$ Ohm resistor amplifiers (Lloyd et al., 2018) at the University of Cambridge (Cambridge, UK).

2.6 Standards

Variations in B isotope ratios are expressed in conventional delta ($\delta$) notation with $\delta^{11}$B values reported against the reference standard NIST SRM 951 (NIST, Gaithersburg, MD, USA):

$$\delta^{11}B (‰) = 1000 \times \left( \frac{^{11}B/^{10}BSample}{^{11}B/^{10}BNIST SRM 951} - 1 \right) \quad \text{eq. 1}$$

Multiple analyses of external standards were performed to ensure data quality. For boron isotopic measurements, JCp-1 (Geological Survey of Japan, Tsukuba, Japan, Gutjahr et al., 2020) was used as a carbonate standard, and NEP, a *Porites sp* coral from University of Western Australia and Australian National University was also used (McCulloch et al., 2014). A boron isotope liquid standard, ERM® AE121 (certified $\delta^{11}$B = 19.9 ± 0.6 ‰, SD), was used to monitor reproducibility and drift during each session (Vogl and Rosner, 2012; Foster et al., 2013; Misra et al., 2014b). For trace elements, external reproducibility was determined using the consistency standard Cam-Wuellerstorfi (University of Cambridge) (Misra et al., 2014b).
2.7 Figures of Merit

2.7.1 δ\(^{11}\)B analyses

Samples measured for boron isotopes typically ranged in concentration from 10 ppb B (~5ng B) to 20 ppb B samples (~10ng B). Sensitivity was 10mV/ppb B (eg. 100mV for 10ppb B) in wet plasma at 50µl/min sample aspiration rate. The intensity of \(^{11}\)B for a sample at 10 ppb B was typically 104 ± 15 mV (2 SD, typical session) and closely matched the 98 ± 6 mV (2 SD, typical session) of the standard. Procedural boron blanks ranged from 15 pg B to 65 pg B (contributed to less than 1% of the sample signal). The acid blank during analyses was measured at ≤ 1mV on the \(^{11}\)B (which also is < 1% of the sample intensity), and no memory effect was seen within and across sessions.

External reproducibility was determined by analyzing the international standard JCp-1 (Gutjahr et al., 2020) and a \textit{Porites sp.} coral (NEP). The boron isotopic composition of JCp-1 was measured at 24.06 ± 0.20‰ (2 SD, n=6) within error of published values of 24.37 ± 0.32‰, 24.11± 0.43‰ and 24.42 ± 0.28‰ from Holcomb et al. (2015), Farmer et al. (2016) and Sutton et al. (2018), respectively. Average values are δ\(^{11}\)B\textsubscript{NEP} = 25.72 ± 0.79‰ (2 SD, n=31) determined over 13 different analytical sessions, with each number representing a separately processed sample from this study. These results are within error of published values of 26.20 ± 0.88‰ (2 SD, n = 27) and 25.80 ± 0.89‰ (2 SD, n = 6), from Holcomb et al. (2015) and Sutton et al. (2018), respectively. Data are reported in Supplementary Table B.

2.7.2 X/Ca analyses

Trace element (TE) analyses were conducted at a Ca concentration of either 10 or 30 ppm. Typical blanks for a 30 ppm Ca session were: \(^7\)Li < 2%, \(^{11}\)B < 7%, \(^{25}\)Mg < 0.2% and \(^{43}\)Ca < 0.02%. Additionally, blanks for a 10 ppm Ca session were: \(^7\)Li < 2.5%, \(^{11}\)B < 10%, \(^{25}\)Mg < 0.4% and \(^{43}\)Ca < 0.05%. Analytical uncertainty of a single measurement was calculated from the reproducibility of the CamWuellestorfi standard: 0.6 µmol/mol for Li/Ca, 8 µmol/mol for B/Ca and 0.02 mmol/mol for Mg/Ca (2 SD, n=48). Data are reported in Supplementary Table B.

2.8 Calculations
Detailed calculations can be found in the supplemental materials. Briefly, Mg/Ca was used to reconstruct sea surface temperature (SST) using the framework from Gray and Evans. (2019) correcting for influences of pH and salinity. $\delta^{11}B_{\text{carbonate}}$ was corrected using an empirical $\delta^{11}B_{\text{carbonate}}$-weight/shell ratio relationship. $\delta^{11}B_{\text{borate}}$ was determined using species dependent sensitivities of $\delta^{11}B_{\text{carbonate}}$ to $\delta^{11}B_{\text{borate}}$ (Guillermic et al., 2020). pH was calculated using the $\delta^{11}B_{\text{borate}}$ with different scenarios of secular seawater $\delta^{11}B$ changes (Lemarchand et al., 2002; Raitzsch and Hönisch, 2013; Greenop et al., 2017). $pCO_2$ was reconstructed using pH based $\delta^{11}B_{\text{carbonate}}$ and different scenarios of Alkalinity (Tyrell and Zeebe, 2004; Ridgwell and Zeebe, 2005; Caves et al. 2016 and Rae et al. 2021). Further details including equations are in the Supplement.

3. Results and discussion

3.1 Geochemical results

Geochemical data used in this study are presented in Figure 2. Mg/Ca data (Fig. 2C) are consistent with previously published Mg/Ca values for Site 806 on *T. sacculifer* (Wara et al., 2005; Tripati et al., 2009; Nathan and Leckie, 2009). Although the record we generated does not overlap with Site 872, they are time-adjacent, and there is a good correspondence with our Mg/Ca data and the published Mg/Ca record from *T. trilobus* at Site 872 (Sosdian et al., 2018). Mg/Ca from a different species, *D. altispira* (Sosdian et al., 2020), is also plotted with an offset, for comparison.

Comparison with Site 872 data that is part of the compilation from Sosdian et al. (2018) shows that their $\delta^{11}B$ data are in line with our dataset (Figure 2B), and all sites examined in the WEP (Sites 806, 807, and 872) are above the lysocline (Kroenke et al. 1991). The $\delta^{11}B$ data for *T. sacculifer* exhibit a significant decrease (4.2‰) from the Miocene to present. Figure 2B also compares the $\delta^{11}B$ data used in this study with published data from other sites, and shows that raw $\delta^{11}B$ data for the WEP can be lower than values for other regions.

3.2 Reproducing $pCO_2$ from ice cores

Validation of air-sea equilibrium in the WEP during the relatively large amplitude late Pleistocene glacial/interglacial cycles was a primary goal for our work. In order to validate our approach, we
reconstructed pCO2 for the last 800 kyr (Fig. 3). The two critical diagnostics we use for method validation are: 1) that the reconstruction of pCO2 is representative of recent atmospheric CO2, and 2) that the boron-based reconstruction empirically reproduces the record from ice cores. For the last 800 kyr, reconstructed pCO2 values for Holes 806A and B and Site 807 are mostly within error of the records from the Vostok and EPICA Dome C ice cores (Fig. 3, Petit et al., 1999, Siegenthaler et al., 2005, Lüthi et al., 2008; compilation from Bereiter et al., 2015), with the exception of two data points at 47 and 79 ka that have lower pCO2 in comparison to ice core values. Crossplots comparing our data are presented in Figs. 3C, 3D, 3E; the slope and intercept are not statistically different from a 1:1 line (p=0.69 and p=0.48). Between MIS 7 and 6, our reconstructions exhibit a decrease in temperature (ΔT) of 1.2°C, an increase in pH (ΔpH) of 0.08 and a decrease in pCO2 (ΔpCO2) of 58 ppm. Between stage 3 and 1, we observed an increase of temperature of 2.0°C, a decrease of pH of 0.13 and an increase in pCO2 of 76 ppm. We also compare results with recent reconstructions in Figs. S1 and S2 (Sosdian et al., 2018; Rae et al., 2021). These results highlight that we are able to reproduce absolute measurements of atmospheric pCO2 of the ice core record, and reproduce the amplitude of changes between transitions, with uncertainties typical for this type of work (Hönisch et al., 2019). We note that reconstructed pCO2 uncertainties could potentially be reduced using independent temperature proxies for the WEP such as clumped isotope thermometry (Tripati et al., 2010; 2014), a technique that is not sensitive to the same sources of error as Mg/Ca thermometry, and therefore is an area planned for future work.

### 3.3 Sea surface temperature in the WEP

Mg/Ca data for the WEP are consistent between studies at Site 806 (Wara et al., 2005; Tripati et al., 2009, 2011; Nathan and Leckie, 2009) and Site 872 (Sosdian et al., 2018). The Mg/Ca in *T. sacculifer* has to date not shown a pH dependency (Gray and Evans, 2019) but Mg/Ca of *G. ruber* does and was therefore corrected from this effect (see supplemental material). Data for both species were corrected from salinity and seawater Mg/Ca changes. Mg/Ca-temperatures for Site 872 was reconstructed using published data and the same framework we use here, and are presented in Figure 4. Recalculated values for Site 872 are from *D. altispera*, with an offset applied relative to *T. sacculifer*, and show similar variations to our record for the MCO-MMCT periods (Sosdian et al., 2020). Temperatures from Tex86
and $^{13}$C are plotted for comparison but those records are limited to the last 12 and 5 Myrs respectively (Zhang et al., 2014).

The Mg/Ca data support high temperatures of $35.2 \pm 1.3$ °C (2SD, n=11) for the early Miocene until the MMCT, with relatively small (ca. 1°C) change from into the MCO, and larger changes out of the MCO. Similarly warm SST for the MCO were reconstructed in the North Atlantic at Site 608 from Tex$^{86}$ (Super et al., 2018). Despite a gap in our compilation from 11.5 to 9.5 Ma, there is a SST decrease of $\sim 6$°C from the MCO to $\sim 7$ Ma where temperatures similar to present day values are observed. A decline in temperature during the MMCT is coincident with the timing of a constriction of the Indonesian Seaway, the pre-closure of the trans-equatorial circulation and subsequent formation of a proto-warm pool (Nathan and Leckie, 2009; Sosdian et al., 2020). From 12 to 7 Ma, the Mg/Ca-SST record diverges from Tex$^{86}$ and $^{13}$C$^{37}$-based reconstructions, with higher temperatures. At the same time, a record for the North Atlantic showed a decrease of $\sim 10$°C from the MCO to $\sim 9$ Ma (Super et al., 2018). From 7 Ma to present, the record from multiple proxies – Mg/Ca, Tex$^{86}$, and $^{13}$C$^{37}$, in the WEP agree.

3.4 Scenarios of seawater $^{11}$B and alkalinity used for $pCO_2$ reconstructions

Figures 5 and 6 show the different histories of seawater $^{11}$B and alkalinity used for calculations, respectively. Details of calculations are in the Supplemental methods. Following the approach of Tripati et al. (2009, 2014) and recent literature (Sosdian et al., 2018; Rae et al., 2021), we explored multiple scenarios for the evolution of seawater boron geochemistry (Fig. 5) and alkalinity for calculations of $pCO_2$ (Figs. 6, S1 and S2). During the interval overlapping with the ice core record, we observe that the choice of model used does not make a significant difference in reconstructed values. During earlier time intervals, we see there is a greater divergence, reflecting larger uncertainties in seawater $^{11}$B and alkalinity further back in Earth history.

Prior to 10 Ma and during the early Pliocene ($\sim 4.5$ to 3.5 Ma), calculations of $pCO_2$ diverge from published values largely because of the different assumptions each study has used for past seawater $^{11}$B (Fig. 5). However, we find that when the uncertainty in reconstructed pH is fully propagated, the differences in reconstructed pH values calculated using each of the $^{11}$B$_{seawater}$ histories is not significantly different (Fig. 5 and 6; see also Hönisch et al., 2019). In contrast to the results from Greenop et al. (2017),
the record from Raitzsch and Hönisch, (2013) exhibits substantial variations on shorter timescales. Such variability is a challenge to reconcile with the Li isotope record of Misra and Froelich, (2012), given that Li has a shorter residence time than boron while having similar sources and sinks. For the remainder of this study, we use the $\delta^{11}$B$_{\text{seawater}}$ history from Greenop et al. (2017) because it is in good agreement with seawater $\delta^7$Li (Misra and Froelich, 2012). The recent calculations of seawater pH (Sosdian et al., 2018; Rae et al., 2021) agree with values from our study when uncertainties are taking into account (Fig. 5).

The four alkalinity models used in this study diverge prior to 9 Ma, with a maximum difference at ~13 Ma that is also reflected in reconstructed pCO$_2$ values (Fig. 6). However, all four models yield pCO$_2$ estimates that are within error of each other when the full uncertainty is considered. Uncertainty in the evolution of seawater alkalinity and seawater $\delta^{11}$B leads to differences in the absolute values of pCO$_2$ reconstructed (Fig. S2), and a divergence in pCO$_2$ values reconstructed that is largest in the Miocene. The two scenarios that produce the highest divergence in values are those calculated using constant alkalinity relative to those calculated using values from McCaves et al. (2016), with a maximum difference at 15.06 Ma of up to 250 ppm CO$_2$, and with the latter model producing lower values (Fig. 6). Thus, for the MCO, alkalinity is a critical parameter in calculations of absolute pCO$_2$ values. For the Miocene and earlier intervals, improved constraints on past secular variations of seawater $\delta^{11}$B and alkalinity will yield more accurate reconstructions of pCO$_2$.

For the remainder of this paper, we use the model of Caves et al. (2016) to estimate alkalinity and $\delta^{11}$B$_{\text{seawater}}$ determined by Greenop et al. (2017). We note that two recent syntheses of boron isotope data have been published and compare our results to these findings (Figs. 8 and S2). Sosdian et al. (2018) reports values that are in line with our results in the Miocene but this study does not replicate results from ice cores. Rae et al. (2021) presents reconstructed values that are higher in the Miocene, due to the utilization of different scenarios of seawater $\delta^{11}$B and alkalinity compared to this work.

### 3.5 Time intervals

#### 3.5.1 Miocene

The study of Miocene climate is thought to provide a useful analog for changes associated with global warming and melting of polar ice, in concert with ocean circulation (Holbourn et al., 2013). The
Miocene epoch (23-5.3 Ma) is characterized by a warm interval, the Miocene Climate Optimum (~17-14.7 Ma - MCO), and an abrupt cooling during the Middle Miocene Climate Transition (~14-13 Ma – MMCT) that led to the expansion of ice on Antarctica and Greenland. Climate modeling supports a role for decreasing CO₂ in this transition (DeConto and Pollard, 2003). However, reconstructions for the Miocene are still relatively limited (Sosdian et al., 2018; Rae et al., 2021). Current boron isotope and alkenone-based pCO₂ reconstructions support higher pCO₂ during the MCO and a decrease over the MMCT (Sosdian et al. 2018; Stoll et al., 2019; Tanner et al., 2020), consistent with what was previously inferred from B/Ca (Tripathi et al., 2009, 2011).

We applied the same framework we used for calculations at Sites 806 and 807 to published boron isotope data from Site 872 (Sosdian et al., 2018) in order to extend the WEP record to the early Miocene (Figs. 7, 8). The Miocene data between Sites 806 and 872 do not overlap as both are low in resolution, but do show excellent correspondence in their trends in δ¹¹B and reconstructed pH. For example, the closest datapoints in time at the two sites are at 15.6 Ma at Site 806 with a δ¹¹B=14.47± 0.21 ‰, and at 16.7 Ma at Site 872, with a δ¹¹B=15.12± 0.25 ‰. The pH values we reconstruct are within error of published estimates from Site 872 (Sosdian et al. 2018, Figs. 7D and 8D). Collectively, these data suggest the early Miocene WEP was characterized by a mixed-layer pH of 8.1 ± 0.1 (2 SD, n=4) between 19.4 and 21.8 Ma, which decreased to reach a minimum during the MCO of 7.7 (±0.11 ‰).

Given the sensitivity in absolute pCO₂ to assumptions about the second carbonate system parameter, a few scenarios were explored for the combined 806/807/872 reconstructed pH values. For all alkalinity scenarios we used, reconstructed pCO₂ shows an increase from the Early Miocene to the MCO, with the highest values in the MCO. Recalculated pCO₂ for Site 872 between 19.4 and 21.8 Ma is 232 ± 92 ppm (2 SD, n=4), lower but within error of the ones presented in Sosdian et al. (2018) and also within error of a constant alkalinity scenario (Fig 8D). The main difference between reconstructions is when comparing the same data recalculated in Rae et al. (2021) that show higher pCO₂ between 19.4 and 21.8 Ma, with an average value of 591 ± 238 ppm (2 SD, n=4) for Site 872, because of the different assumptions used in their study and ours. This difference is important because that would imply a relatively high and stable pCO₂ from the early Miocene to MCO, which would imply a decoupling between pCO₂ and temperature with no pCO₂ change during an interval of decreasing benthic δ¹⁸O.
However, our reconstructed pCO$_2$ increase towards the MCO is in line with the observed benthic $\delta^{18}O$ decrease and $\delta^{13}C$ increase and suggest a coupling between temperature and pCO$_2$ over this period. We note that overall, Mg/Ca-SSTs are warm (>32°C), and there are relatively small changes in Mg/Ca-SST from the early Miocene into the MCO in the WEP.

The highest pCO$_2$ values we reconstruct are during the MCO (Fig. 6E). For the MCO, our estimates are 511 ± 201 ppm (2 SD, n=3, Table 2). The middle Miocene values we reconstruct are in line with previous studies (Greenop et al., 2014; Sosdian et al., 2018). Published $\delta^{11}B$-based reconstructions also support higher pCO$_2$ for the MCO of ~350-400 ppm (Foster et al., 2012) or 300-500 ppm (Greenop et al., 2014) that was recalculated by Sosdian et al. (2018) to be ~470-630 ppm depending on the model of $\delta^{11}B_{\text{seawater}}$ chosen. During the MCO relative maxima in pCO$_2$, our data support very warm sea surface temperatures in the WEP (35.6°C ± 0.6°C 2SD, n=3; Fig. 8C), that merits further examination in future studies. In fact, the highest temperatures recorded in our samples occur when there is a minimum in the global composite record of $\delta^{18}O$ of benthic foraminifera (Zachos et al., 2001, 2008; Tripati and Darby, 2018).

During the MMCT, we find evidence for changes in pCO$_2$ and temperature in the WEP (Fig. 8). From 13.5 to 12.7 Ma, we reconstruct an increase of pH ~0.21 and a major decrease of pCO$_2$ of ~215 ppm during an interval highlighted by Flower and Kennett, (1996), who observed changes in $\delta^{18}O$ indicative of rapid East Antarctic Ice Sheet growth, and enhanced organic carbon burial with a maximum $\delta^{13}C$ reached at ~13.6 Ma (Shevenell et al., 2004; Holbourn et al., 2007). As discussed in section 3.4 the alkalinity model used for the calculations have an important impact during the Miocene which is likely responsible for the different absolute pCO$_2$ values over the MCO. In comparison, a scenario of constant alkalinity would lead to a pCO$_2$ during the MCO of 714 ± 313 ppm (2 SD, n=3) and a decrease of ~540 ppm during the MMCT. Both those reconstructions could simulate the large-scale advance and retreat of Antarctic ice with such low pCO$_2$ values (Gasson et al., 2016). At the same time, we find evidence for a decline in SST of 3.4°C to a minimum of 33.3°C. The synchronous shifts in the $\delta^{13}C$ and $\delta^{18}O$ of benthic foraminifera are consistent with increased carbon burial during colder periods, thus feeding back into decreasing atmospheric CO$_2$, and supporting the hypothesis that the drawdown of atmospheric CO$_2$ can in part, be explained by enhanced export of organic carbon.
The resolution of our data during the late Miocene is low, with a data gap from 12.5 to 9.2 Ma, and another gap between 6.5 and 5 Ma. We note the pCO₂ peak at ~9 Ma observed by Sosdian et al. (2018) is not seen in our record although this is likely due to the low resolution of our dataset. Between 9.5 and 7.1 Ma we find evidence for a decrease in atmospheric CO₂ of 100 ppm associated with a decrease in temperature of 1.3 °C. pCO₂ estimates derived from alkenones for Site 1088 (Tanner et al., 2020) do not show the same trend as boron-based reconstructions from the WEP or other regions (Figure 6), but this perhaps is unsurprising given the oceanographic setting of Site 1088.

3.5.2 Pliocene

Oxygen isotope data from a global benthic foraminiferal stack show that the Pliocene epoch (5.3-2.6 Ma) was initially characterized by warm conditions followed by the intensification of glaciation that occurred in several steps, including during MIS M2 (3.312-3.264 Ma), followed by the Middle Pliocene Warm Period (Lisiecki and Raymo, 2005). The Middle Pliocene Warm Period (mPWP – 3.29-2.97 Ma) is considered a relevant geological analogue for future climate change given ~3°C warmer global temperatures and sea levels that were ~20 m higher than today (Dutton et al., 2015; Haywood et al., 2016), and is a target for model intercomparison projects, for which accurate paleo-atmospheric pCO₂ estimates are critical (Haywood et al., 2016).

Figure 9 shows that during the Early Pliocene warm interval, from 4.7 to 4.5 Ma, we calculate high pCO₂ values of 419 ± 119 ppm (2 SD, n=3, Table 2). The pCO₂ data we report provide a higher data density for the Early Pliocene, with a trend that is in line with the reconstruction from Rae et al. (2021). Our data support values of 530 ± 110 ppm over the mPWP (2 SD, n = 4), higher than previously published data (Figs. 9, S2 and Table 2), although we acknowledge our low data density may not fully sample variability over this period. The similarity between our reconstructed values and those published for Site 871 in the Indian Ocean (Sosdian et al., 2018) suggests that changes in Indonesian through-flow do not induce substantial changes in air-sea exchange in the WEP.

The warmth and local pCO₂ maxima of the mPWP (mid-Pliocene Warm Period) was followed by a strong decrease of temperature in upwelling and high latitude regions during from 3.3-2.7 Ma, coincident with glacial intensification in the Northern Hemisphere. This climate transition was
hypothesized to be driven by the closure of the Panama seaway the opening of the high latitudes and subsequent modifications of oceanic circulation (Haug and Tiedemann, 1998). However, modeling from Lunt et al. (2008) supports an additional major role for CO2 in the glaciation. pCO2 thresholds have been proposed to explain the intensification of Northern Hemisphere Glaciation, with values proposed ranging from 280 ppm (DeConto et al., 2008) to 200 to 400 ppm (Koening et al., 2011).

The pCO2 concentrations that we calculate indicates a reduction to 350 ppm by 2.7 Ma, ~280 ppm by 2.6 Ma, and ~210 ppm by 2.4 Ma, in several steps. These results support roughly a halving of CO2 values when compared to values of ~530 ppm at 3.3 Ma. These values are consistent with the pCO2 thresholds proposed by both DeConto et al. (2008) and Koening et al. (2011) for the intensification of Northern Hemisphere glaciation and the low atmospheric CO2 (280 ppmv) scenario from Lunt et al. (2008). Mg/Ca SST decline from 30°C to 26°C, supporting an Earth System sensitivity of ~4°C/doubling of CO2 over this range, although given uncertainties, higher values of ~6°C/doubling of CO2 that have recently been proposed (Tierney et al., 2020) can not be excluded.

We speculate that associated with Pliocene glacial intensification, at 4.42, 3.45 and 2.67 Ma, it is possible that the declines in CO2 and ice growth in turn drove substantial changes in pole-to-equator temperature gradients and winds, that in turn may have impacted iron cycling (Watson et al., 2000; Robinson et al., 2005; Martinez-Garcia et al., 2011), stratification (Toggweiler, 1999; Sigman et al., 2010), and other feedbacks that impact the amplitude of glacial/interglacial cycles and have been implicated as factors that could have contributed to Pliocene glacial intensification. Specifically, as the mean climate state of the planet became cooler, and glacial-interglacial cycles became larger in amplitude, enhanced windiness and dust transport and upwelling during glacial (Martinez-Boti et al., 2015b) may have enhanced iron fertilization and subsequent carbon export (Martinez-Garcia et al., 2011). While data resolution are limited, we speculate this could explain why glacial/interglacial amplitudes in WEP pCO2 values decrease from the MPWP towards the Pleistocene, whereas variations in δ18O are increasing – a speculation that could be tested with increased data resolution.
3.5.3 Pleistocene

During the Pleistocene (2.58-0.01 Ma), the climate system experienced a transition in glacial/interglacial (G/I) variability from low amplitude, higher frequency and obliquity-dominated oscillations (i.e., ~ 41 kyr) of the late Pliocene to the high amplitude, lower frequency and eccentricity-dominated cycles (i.e., ~100 kyr) of the last 800 kyr. This transition is termed the Middle Pleistocene Transition (1.2-0.8 Ma – MPT). Questions have been raised about the role of atmospheric CO2 during this transition, including using boron-based proxies (Hönisch et al., 2009; Tripati et al., 2011; Chalk et al., 2017). Previous boron isotope studies for ODP Sites 668 and 999 in the tropical Atlantic Ocean have suggested that a decline in atmospheric CO2 did occur during glacial periods in the MPT, but not during interglacials (Hönisch et al., 2009; Chalk et al., 2017; Dyez et al., 2018).

Our pCO2 concentrations for Sites 806/807 reported here are in good agreement with those determined from ice cores from the early Pleistocene (Yan et al., 2019, Figs. 9 and 10), and with the boron-derived pCO2 from a recent compilation (Rae et al., 2021). Results for the MPT are broadly in the range of values reported by Hönisch et al. (2009) and Chalk et al. (2017). Although our data are relatively limited, we note they have greater resolution for the middle and later part of the transition than prior publications that have drawn conclusions about the MPT (Hönisch et al., 2009; Chalk et al., 2017; Dyez et al., 2018) (Fig. 10D) and therefore we explore their implications.

Taken alone, or when combined with the published data from Chalk et al. (2017) (that is also based on MC-ICPMS), our results support a possible reduction of both glacial and interglacial pCO2 values. We also find evidence that during the MPT, glacial pCO2 declined rapidly from 189 (±30) ppm at MIS 36 (Chalk et al., 2017) to reach a minimum of 170 (±52) ppm during MIS 30. We note that pCO2 concentrations are within error when uncertainty is fully propagated, and then remained relatively stable until the end of the MPT whereas interglacial pCO2 values decrease gradually to reach post-MPT values.

In our record for the last 16 Myr, the lowest pCO2 is recorded at MIS 30 during the MPT, with values of 164 (±44) ppm, which supports an atmospheric CO2 threshold that leads to ice sheet stability. During this transition, the pCO2 threshold needed to build sufficiently large ice sheets that were able to survive the critical orbital phase of rising obliquity to ultimately switch to a 100 kyr world, was likely reached at MIS 30. The multiple feedbacks resulting from stable ice sheets (iron...
fertilization/productivity/changes in albedo/changes in deep water formation) might have sustained larger mean global ice volumes over the subsequent 800 kyr. An asymmetrical decrease between pCO$_2$ values during interglacials relative to glacial, with glacial exhibiting the largest change across the MPT, would have led to increased sequestration of carbon during glacial in the 100 kyr world, as discussed by Chalk et al. (2017), with increased glacial dust input and iron fertilization.

3.6 Changes in volcanic activity and silicate weathering, and long-term pCO$_2$

On million-year timescales, atmospheric CO$_2$ is mainly controlled by volcanic activity and silicate weathering. Over the last 16 Myr, two relative maxima in atmospheric pCO$_2$ are observed in our record, one during the MCO (at 15.67 Ma) and a second around the late Miocene/early Pliocene (beginning at 4.7 and 4.5 Ma) (Fig. 11), though the timing for the latter is not precise. The strong pCO$_2$ increase from the early Miocene to MCO is timely with increasing volcanic activity (Foster et al. 2012), associated with the eruption of the Columbia River Flood Basalts (Hooper et al., 2002; Kasbohm and Schoene, 2018), with recent geochronologic evidence published supporting higher eruption activity between 16.7 and 15.9 Ma (Kasbohm and Schoene, 2018) reinforcing the idea of an episodic pCO$_2$ increase during the MCO due to volcanic activity.

The second CO$_2$ peak could correspond to observed global increased volcanism in the early/middle Pliocene (Kennett and Thunell, 1977; Kroenke et al., 1993), and/or a change of silicate weathering regime. Strontium and lithium isotopes ($^{87/86}$Sr and $\delta^7$Li) have been used as proxy for silicate weathering activity. Although the strontium isotope record exhibits a monotonous increase, lithium isotope data (Misra and Froelich, 2012) are more variable with a transition from a period of increase seawater $\delta^7$Li (e.g. non-steady state weathering) to stable seawater $\delta^7$Li (e.g., steady state weathering) beginning at roughly 6.8 Ma (Fig. 11).

It is also interesting to note that the changes in $\delta^7$Li (Fig. 11B) in the early Miocene to the MCO are in line with changes in pCO$_2$. Before 18.5 Ma, the pCO$_2$ is relatively stable, $\delta^7$Li is increasing representative of a non-steady state weathering. From 18.6 to 16.7 the $\delta^7$Li decrease of about 2‰, this decrease can inform on decreasing weathering rate and this decrease is associated with an increase in pCO$_2$. Between 16.7 and 15.9 Ma, when the eruption of the Columbia River Flood Basalts is maximum
the δ⁷Li increases, in line with higher weathering due to higher atmospheric CO₂ and the presence of fresh
silicate rocks. The δ⁷Li decreases again until the end of the MCO ~14.7 Ma, in line with a decrease in the
eruption rate and sustaining high atmospheric CO₂, then, a constant increase is observed until the early
Pliocene where the change toward a steady in weathering regime occurs, this increase in δ⁷Li is also
consistent with the decrease in pCO₂ observed until the early Pliocene.

3.9 Outlook and Conclusions

We developed a reconstruction of atmospheric pCO₂ based on δ¹¹B of planktic foraminifera from
ODP Sites 806 and 807 located in the Western Equatorial Pacific for the past 16 million years and
extended the record to 22 Ma by processing data from Site 872. Our study represents the first long-term
reconstruction for the Neogene derived from boron isotopes from the Pacific Ocean. We build on past
efforts to reconstruct atmospheric pCO₂ using different proxies from this region, including from carbon
isotopes in marine organic matter (Rayno et al., 1996) and alkenones (Pagani et al., 2010), as well as
foraminiferal B/Ca ratios (Tripati et al., 2009, 2011), all of which have been shown to have a number of
complexities and potential sources of systematic error (e.g., Tripati et al., 2011). It also builds on efforts
using boron isotopes in other regions using MC-ICP-MS (Seki et al., 2010; Foster et al., 2012, 2014;
Greenop et al., 2014; Martinez-Boti et al., 2015b; Stap et al., 2016; Chalk et al., 2017; Dyez et al., 2018;
de la Vega et al., 2020), and our recent work constraining fractionation factors and measuring small
samples of foraminifera. Although the record is not continuous, with variable resolution, it captures both
long-term and short-term variability associated with several key transitions and demonstrates the utility
of these sites for future higher resolution study.

As expected, these data generally reproduce the pCO₂ record from ice cores, consistent with the
sites being in equilibrium with the atmosphere. The MCO has higher pCO₂ than reconstructions from
other sites, with values estimated as 511 ± 201 ppm (2 SD, n=3), likely linked to the eruption of the
Columbia River Flood Basalts, with values declining into the early Pliocene, including during Pliocene
glacial intensification. The changes in pCO₂ we observed are in line with changes in δ⁷Li, proxy of silicate
weathering, future modellisation on those records will provide helpful insights.
We find support for a larger reduction in glacial $p$CO$_2$ during the MPT compared to interglacial pCO$_2$, and a minimum in pCO$_2$ during glacial MIS 30. These findings confirm a role for CO$_2$ in the transition from a 41 kyr to a 100 kyr world.

Higher-resolution boron isotope records from the WEP would allow for further resolution of these changes. Additional constraints on temperature, such as from clumped isotopes (Tripati et al., 2010) in the WEP (Tripati et al., 2014), could allow for uncertainties in $p$CO$_2$ estimates from boron isotopes to be reduced and for new constraints on Earth system climate sensitivity. Future constraints on the vertical structure of the tropical Pacific during these transitions may also potentially be illuminating.

**Code/ data availability**

All data are available in the supplemental materials.

**Author Contribution**

AT wrote the proposals that funded the work and provided the samples. All authors contributed to the experimental design. MG performed the measurements with assistance from SM. MG conducted the data analysis. MG drafted the paper, which was edited by all authors. Interpretation was led by MG, AT, and SM with input from RE.

**Competing interests**

The authors declare that they have no conflict of interest.

**Acknowledgments**

The authors wish to thank the Tripati Lab, including Lea Bonnin and Alexandra Villa, for assistance with picking samples; the IODP core repository for provision of samples; Mervyn Greaves for technical support and use of laboratory space at the University of Cambridge; Yoan Germain, Emmanuel Ponzevera, Céline Liorzou and Oanez Lebeau for technical support and use of laboratory space at IUEM and Ifremer (Plouzané, France). We thank Thomas Chalk, another anonymous reviewer, and Hubertus Fischer for their helpful comments on the manuscript, and Mathis Hain for discussion of this work.
Financial support

This research is supported by DOE BES grant no. DE-FG02-13ER16402 to AKT, by the International Research Chair Program that is funded by the French government (LabexMer ANR-10-LABX-19-01) to AKT and RAE, and IAGC student research grant 2017.

6. References


GraphPad Prism version 7.00 for Windows, GraphPad Software, La Jolla California USA, www.graphpad.com


Hain, M. P., Foster, G. L., & Chalk, T.: Robust constraints on past CO2 climate forcing from
the boron isotope proxy. Paleoceanography and Paleoclimatology, 33(10), 1099-1115,
2018.

Academy of Sciences, 109(37), 2012.

Hansen J., Sato M., Russell G. and Kharecha P.: Climate sensitivity, sea level and
2013.

Haug, G. H., & Tiedemann, R.: Effect of the formation of the Isthmus of Panama on Atlantic


Hemming N. G. and Hanson G. N.: Boron isotopic composition and concentration in modern

new boron isotope-pH calibration for Orbulina universa, with implications for
understanding and accounting for ‘vital effects.’ Earth Planet. Sci. Lett. 454, 282–292,
2016.

Henehan M. J., Rae J. W. B., Foster G. L., Erez J., Prentice K. C., Kucera M., Bostock H. C.,
Calibration of the boron isotope proxy in the planktonic foraminifera Globigerinoides

Y., Mayewski P. A. and Bender M. L.: Atmospheric composition 1 million years ago
from blue ice in the Allan Hills, Antarctica. Proc. Natl. Acad. Sci. 112, 6887–6891,
2015.

Holbourn A., Kuhnt W., Frank M. and Haley B. A.: Changes in Pacific Ocean circulation
following the Miocene onset of permanent Antarctic ice cover. Earth Planet. Sci. Lett.


Hönisch, B. and Hemming, N. G., Ground-truthing the boron isotope-paleo-pH proxy in
planktonic foraminifera shells: Partial dissolution and shell size effects,

deMenocal, P., Rosenthal, Y., D. Russel, a.: Elderfield, H.: The influence of salinity on
Mg/Ca in planktic foraminifers–Evidence from cultures, core-top sediments and

dioxide concentration across the mid-pleistocene transition. Science 324, 1551–1554,
2009.

Horita J., Zimmermann H. and Holland H. D.: Chemical evolution of seawater during the


Figure captions

Figure 1: Modern hydrography of sites. A. Map of air-sea pCO₂ (ΔpCO₂, ppm, data from Takahashi et al. (2014) and plotted using Ocean Data View from Schlitzer, (2016) showing the location of ODP Sites 806 and 807 (black circles) and Site 872 (black square, Premoli et al., 1993). Depth profiles are for preindustrial parameters. B. pH calculated from GLODAP database and corrected from anthropogenic inputs. C. Boron isotopic composition of borate ion (δ¹¹Bborate) with associated propagated uncertainties.

Figure 2: Foraminiferal data for the Miocene to Recent. A. Benthic foraminiferal δ¹⁸O data (blue line – stack from Lisiecki and Raymo, 2005; black line – compilation from Zachos et al., 2008). B. δ¹¹B of T. sacculifer (blue circles) and G. ruber (blue triangles) at Sites 806 (light blue), 807 (dark blue), Grey filled square are data from Site 872 located in the WEP (Sosdian et al., 2018). Open symbols are for G. ruber. C. Mg/Ca ratios of T. sacculifer and G. ruber at Sites 806, 807 and fourth-order polynomial regression from Sosdian et al. (2020) representing secular variations of Mg/Ca. E. Calculated weight per shell for T. sacculifer and G. ruber. For Panels B-D: Circles = T. sacculifer, Triangles = G. ruber.

Figure 3: A. Reconstruction of surface pCO₂ for the past 0.8 Myr from T. sacculifer at ODP Sites 806 and 807. Planktonic foraminiferal δ¹⁸O at site 806 with isotope stages labeled (black line – Medina-Elizalde and Lea, 2005) and benthic foraminiferal δ¹⁸O stack (grey line - Lisiecki and Raymo, 2005). B. pCO₂ values calculated from boron isotopes (colored symbols - this study) with data from the literature (open gray triangles – data recalculated in Rae et al., 2021) and ice core pCO₂ (black line – Bereiter et al., 2015). Data from the two sites we examined reproduces the absolute values and amplitude of atmospheric pCO₂ as determined from ice cores, thereby validating our methodology. C. Cross plot for the last 0.8 Myr of δ¹¹B₅. sacculifer from this study and δ¹⁸O₇. ruber from site 806 (Medina-Elizalde and Lea, 2005) (Linear regression: p=0.7). D. Cross plot for the last 0.8 Myr of pCO₂ T. sacculifer from this study and δ¹⁸O G. ruber from site 806 (Medina-Elizalde and Lea, 2005) (Linear regression: p=0.9) and E. Cross plot for the last 0.8 Myr of pCO₂ T. sacculifer from this study and pCO₂ Vostok (from ice core, Bereiter et al., 2015) (Linear regression: p=0.3, R²=0.09).

Figure 4: Compilation of temperature from site 806 in the WEP. Mg/Ca based temperature were derived using the same framework (see supplemental information). Blue filled symbols are from Sites 806 and 807, filled gray squares are data from Site 872 (Sosdian et al., 2018). Open symbols are SST derived from Mg/Ca at Site 806 (Wara et al., 2005; Tripati et al., 2009; Nathan and Leckie, 2009). Tex86 and UK′37 are also plotted for comparison (Zhang et al., 2014). Blue line is a smooth line (Lowess) going through the data.

Figure 5: Different models for the evolution of the boron geochemistry explored as part of this work. Due to the 1‰ uncertainty propagated for δ¹¹B₅. seawater, all scenarios yield reconstructed seawater pH values that are within error of each other. Propagated uncertainties were calculated using eq. S14 (see Supplement). A. Different models for δ¹¹B₅. seawater used for the reconstruction of pCO₂ in this study (blue – Lemarchand et al., 2000; green – Greenop et al., 2017; red – Raitzsch and Hönisch, 2013). B. Reconstructed pH based on our measured δ¹¹B₅. carbonate values using different models for δ¹¹B₅. seawater (blue – Lemarchand et al., 2000; green – Greenop et al., 2017; red – Raitzsch and Hönisch, 2013), compilation pH from Sosdian et al. (2018) (open squares) and Rae et al. (2021) (open triangles) are also shown for comparison.

Figure 6: Different models for the evolution of a second carbonate (e.g. alkalinity) system parameter explored as part of this work. The propagated uncertainties were calculated using eq. S16 (see Supplement). A. Different models for alkalinity used for the reconstruction of pCO₂ in this study
Reconstructed pCO2 using constant alkalinity scenario from Tyrell and Zeebe, (2004) and $\delta^{11}\text{B}_{\text{seawater}}$ from Greenop et al. (2017). Data presented are from this study. Open triangles are compilation from Rae et al. (2021), black symbols are from site 872.

Stars indicate pCO2 values reconstructed from alkenones by Tanner et al. (2020) (simulation 6) at Site 1088 in the Southern Ocean.

**Figure 7:** Proxy data for the past 22 million years in the Western Equatorial Pacific compared to benthic oxygen isotope data. A. Benthic $\delta^{18}\text{O}$ (blue line – stack from Lisiecki and Raymo, 2005; black line – compilation from Zachos et al., 2008). B. Benthic $\delta^{13}\text{C}$ (black line – compilation from Zachos et al., 2008). C to E, colored is indicating the site (filled light blue=806, filled dark blue=807), symbols represent the species (circle=$T$. sacculifer and triangle=$G$. ruber), filled grey squares are recalculated data based on Sosdian et al. (2018) at site 872. C. SST reconstructed at ODP Sites 806 and 807 using Mg/Ca ratios (see supplemental informations for reconstruction details), open symbols are reconstructed temperature based on literature Mg/Ca at site 806 (see text or Fig. 4). D. Seawater pH reconstructed from $\delta^{13}\text{B}$ of $T$. sacculifer and $G$. ruber using $\delta^{11}\text{B}_{\text{seawater}}$ from Greenop et al. (2017) (refer to text and supplement for calculations, this study), open squares are compilation data from Sosdian et al. (2018) and open triangles are compilation from Rae et al. (2021). E. Reconstructed pCO2 (ppm) using boron-based pH and alkalinity from Caves et al. (2016), data presented are from this study. Propagated uncertainties are given by eq. S17 for the dark blue envelope, while the light blue envelope are the uncertainties calculated based on eq. S16 (taking into account uncertainty on $\delta^{11}\text{B}_{\text{seawater}}$). Cross symbols are original pCO2 calculated in Sosdian et al. (2018) at site 872; asterix symbols are calculated pCO2 at site 872 from Rae et al. (2021).

**Figure 8:** Proxy data from 22 to 6 million years, including the Middle Miocene Climate Transition (MMCT) and Miocene Climate Optimum (MCO), in the Western Equatorial Pacific compared to benthic oxygen isotope data. A. Benthic $\delta^{18}\text{O}$ (black line – compilation from Zachos et al., 2008). B. Benthic $\delta^{13}\text{C}$ (black line – compilation from Zachos et al., 2008). C and D, colored is indicating the site (filled light blue=806, filled dark blue=807), symbols represent the species (circle=$T$. sacculifer and triangle=$G$. ruber), filled grey squares are recalculated data based on Sosdian et al. (2018) at site 872. C. SST reconstructed at ODP Sites 806 and 807 using Mg/Ca ratios (see supplemental informations for reconstruction details), open symbols are reconstructed temperature based on literature Mg/Ca at site 806 (see text or Fig. 4). D. Reconstructed pCO2 (ppm) from this study (blue symbols) using boron-based pH and alkalinity from Caves et al. (2016) and $\delta^{11}\text{B}_{\text{seawater}}$ from Greenop et al. (2017). Orange datapoints and envelope are calculated pCO2 and associated uncertainty from our study using our framework and a constant alkalinity scenario. Open squares are compilation data from Sosdian et al. (2018). Cross symbols are original pCO2 calculated in Sosdian et al. (2018) at site 872; asterix symbols are calculated pCO2 at site 872 from Rae et al. (2021).

**Figure 9:** Proxy data from 7 to 1 million years, including the Warm Pliocene Transition (WPT), in the Western Equatorial Pacific compared to benthic oxygen isotope data. A. Benthic $\delta^{18}\text{O}$ (black line – compilation from Zachos et al., 2008). B. Benthic $\delta^{13}\text{C}$ (black line – compilation from Zachos et al., 2008). C and D, colored is indicating the site (filled light blue=806, filled dark blue=807), symbols represent the species (circle=$T$. sacculifer and triangle=$G$. ruber), filled grey squares are recalculated data based on Sosdian et al. (2018) at site 872. C. SST reconstructed at ODP Sites 806 and 807 using Mg/Ca ratios (see supplemental informations for reconstruction details), open symbols are reconstructed temperature based on literature Mg/Ca at site 806 (see text or Fig. 4). D. Reconstructed pCO2 (ppm) from this study (blue symbols) using boron-based pH and alkalinity from Caves et al.
Propagated uncertainties are given by eq. S17 for the dark blue envelope, while the light blue envelope reflects the uncertainties calculated based on eq. S16 (taking into account uncertainty on $\delta^{11}\text{B}_{\text{seawater}}$). Open squares are pCO$_2$ compilation from Sosdian et al. (2018), open triangles are from compilation from Rae et al. (2021). In black are published estimates from ice core data (circles - Yan et al., 2019).

Figure 10: Proxy data from 1.5 to 0.5 million years, including the Middle Pleistocene Transition (MPT), in the Western Equatorial Pacific compared to benthic oxygen isotope data. A. Benthic $\delta^{18}$O (blue line – stack from Lisiecki and Raymo, 2005). B. Benthic $\delta^{13}$C (black line – compilation from Zachos et al., 2008). C and D colored is indicating the site (filled light blue=806, filled dark blue=807), symbols represent the species (circle=$T$. sacculifer and triangle=$G$. ruber), filled grey squares are recalculated data based on Sosdian et al. (2018) at site 872. C. SST reconstructed at ODP Sites 806 and 807 using Mg/Ca ratios (see supplemental informations for reconstruction details), open symbols are reconstructed temperature based on literature Mg/Ca at site 806 (see text or Fig. 4). D. Reconstructed pCO$_2$ (ppm) from this study (blue symbols) using boron-based pH and alkalinity from Caves et al. (2016). Propagated uncertainties are given by eq. S17. In black are published estimates from ice core data (line – Bereiter et al., 2015; black circles - Yan et al., 2019). Open triangles are from compilation from Rae et al. (2021).

Figure 11: Proxy data from 1.5 to 0.5 million years, including the Middle Pleistocene Transition (MPT), in the Western Equatorial Pacific compared to benthic oxygen isotope composites. A. Benthic $\delta^{18}$O (blue line – compilation from Lisiecki and Raymo, 2005, black line – compilation from Zachos et al. 2008). B. Records from Lithium isotopes ($\delta^{7}$Li, orange, Misra and Froelich, 2012) and Strontium isotopes ($^{87/86}$Sr, grey, Hodell et al., 1991, Farrel et al., 1995, Martin et al., 1999, Martin et al., 2004), both proxies for silicate weathering. Orange arrows represent the different weathering regimes as indicated by the $\delta^{7}$Li, black crosses are indication when changes in weathering regime occurs. C. Reconstructed pCO$_2$ (ppm) using boron-based pH and alkalinity from Caves et al. (2016), colored is indicating the site (filled light blue=806, filled dark blue=807), symbols represent the species (circle=$T$. sacculifer and triangle=$G$. ruber), filled grey squares are recalculated data based on Sosdian et al. (2018) at site 872. Propagated uncertainties are given by eq. S17 for the dark blue envelope, while the light blue envelope are the uncertainties calculated based on eq. S16 (taking into account uncertainty on $\delta^{11}\text{B}_{\text{seawater}}$). Also shown are timing of major events. The rose band and dark rose band indicate eruption of the Columbia River flood basalts (Hooper et al., 2002) and time of maximum eruption (Kasbohm and Schoene, 2018), respectively.
Table 1: Core information.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Leg</th>
<th>Hole</th>
<th>N (°)</th>
<th>E (°)</th>
<th>Depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODP</td>
<td>130</td>
<td>807</td>
<td>3.61</td>
<td>156.62</td>
<td>2804</td>
</tr>
<tr>
<td>ODP</td>
<td>130</td>
<td>806</td>
<td>0.32</td>
<td>159.37</td>
<td>2520</td>
</tr>
</tbody>
</table>
### Table 2: Comparison of reconstructed pCO$_2$ values for key intervals in the last 16 Myr.

<table>
<thead>
<tr>
<th>Interval</th>
<th>pCO$_2$ (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mid-Pleistocene transition (1.2-0.8 Ma)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIS (IG)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCO$_2$ (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIS (IG)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCO$_2$ (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mid-Pleistocene transition (1.2-0.8 Ma)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIS (IG)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCO$_2$ (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Early Pliocene Warm Period (4.7-4.5 Ma)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCO$_2$ (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Middle Pliocene Warm Period (3.9-2.97 Ma)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCO$_2$ (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Miocene Climate Optimum (17-14 Ma)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCO$_2$ (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Mid-Pleistocene transition (1.2-0.8 Ma)**

<table>
<thead>
<tr>
<th>Time (Ma)</th>
<th>pCO$_2$ (ppm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2-0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8-0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6-0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4-0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2-0.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1
Figure 3

(A) Graph showing changes in δ¹⁸O values of G. ruber and T. sacculifer over time, with data points indicating fluctuations.

(B) Graph depicting pCO₂ (ppm) over time, with markers denoting different datasets.

(C) Scatter plot of δ¹¹B of T. sacculifer versus δ¹⁸O of G. ruber.

(D) Scatter plot showing correlation between Ln(pCO₂/δ¹¹B/278) and δ¹⁸O of G. ruber.

(E) Scatter plot of pCO₂ (ppm) versus pCO₂ (µatm) with 1:1 line indicating direct correlation.

Other studies: Rae et al. 2021.
Other studies - Sopdan et al. 2018
Other studies - Rae et al. 2021
Figure 8

(A) Graph showing δ¹⁸O (%). The Miocene is indicated with a gray shaded area.

(B) Graph showing δ¹³C (%).

(C) Graph showing SST (°C). The Miocene is indicated with a gray shaded area.

(D) Graph showing pCO₂ (ppm). The Miocene is indicated with a gray shaded area.

Sites
- Site 806 G11233
- Site 806 G11193
- Site 872 recalculated
- Site 872 Sosdian et al. 2018
- Site 872 Rae et al. 2021
- Other studies Sosdian et al. 2018
Figure 10
Figure 11