Atmospheric CO$_2$ estimates for the last 17 million years based on foraminiferal $\delta^{11}$B at Ocean Drilling Program Sites 806 and 807 in the Western Equatorial Pacific

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ABSTRACT

Constraints on the evolution of atmospheric CO\textsubscript{2} levels throughout Earth’s history are foundational to our understanding of past variations in climate. Despite considerable effort, estimates of past CO\textsubscript{2} levels do not always converge. Here we reconstruct atmospheric CO\textsubscript{2} values across major climate transitions over the past 17 million years using the boron isotopic composition (\(\delta^{11}\text{B}\)) of planktic foraminifera from 89 samples obtained from two sites in the West Pacific Warm Pool, Ocean Drilling Program (ODP) Sites 806 and 807. These sites are in a region that today is in equilibrium with the atmosphere, despite equatorial divergence, and is likely to have been in equilibrium with the atmosphere for the interval studied. We use high-precision multi-collector inductively-coupled plasma mass spectrometry and show that data from these sites can reproduce the ice core record. Estimates of early Miocene pCO\textsubscript{2} are generally higher than published reconstructions from other sites, while values for the Pliocene and Pleistocene are more similar to other datasets. We find evidence for reductions in pCO\textsubscript{2} of \(\sim 280\) µatm during the Middle Miocene Climate Transition, \(\sim 270\) µatm during Pliocene Glacial Intensification, and \(\sim 50\) µatm during the Mid-Pleistocene Climate Transition. There is possible evidence for a larger reduction in glacial pCO\textsubscript{2} during the Mid-Pleistocene Transition compared to interglacial pCO\textsubscript{2}, and a minimum in pCO\textsubscript{2} during glacial MIS 30. Our results are consistent with a strong coupling between pCO\textsubscript{2}, temperature and ice sheet expansion throughout the past 17 million years.

Highlights

In this study, we are able to accurately reproduce pCO\textsubscript{2} data from ice cores, demonstrating the fidelity of our approach. We therefore apply the same framework to older samples to create a long-term pH and pCO\textsubscript{2} reconstruction for the past 17 million years. We find major increases in surface water pH and decreases in atmospheric pCO\textsubscript{2} 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 pCO\textsubscript{2}, temperature, and cryosphere stability.

Keywords

Boron isotopes, CO\textsubscript{2}, 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 CO₂ and examine past relationships between CO₂ 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 CO₂ records from sites that are in equilibrium with the atmosphere.

Relatively high-resolution and direct determinations of atmospheric CO₂ 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; Luthi et al., 2008). A window into atmospheric CO₂ levels comes from 1 million-year-old blue ice (Higgins et al., 2015) and more recently from the Pliocene period (Yan et al., 2019). Most reconstructions of CO₂ 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 (δ¹³C) of paleosols (Retallak et al., 2009), δ¹³C 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 (δ¹¹B) of surface-dwelling foraminifera (Pearson and Palmer., 2000; Hönisch et al., 2009; Bartoli et al., 2011; Foster et al., 2012; Foster and Sexton, 2014; Chalk et al., 2017; Sosdian et al., 2018) have been used to estimate atmospheric CO₂.

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; Tripati 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 is the boron isotopic composition ($\delta^{11}B$) of planktic foraminifera as measured
using MC-ICPMS and TE-NTIMS. This proxy provides constraints on seawater pH, if
temperature, salinity, seawater $\delta^{11}B$, and the appropriate mono-specific calibration between
$\delta^{11}B_{\text{carbonate}}$ and $\delta^{11}B_{\text{borate}}$ 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, the number of studies generating high-precision and
high-resolution boron-based records over major climate transitions in the Cenozoic using the
recent analytical methods, and incorporating our current understanding of proxy systematics
are relatively few (Foster et al., 2012; Martinez-Boti et al., 2015b; Chalk et al., 2017, 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 parameter of the carbonate system, and our limited
understanding of secular variations in the $\delta^{11}B$ of seawater (Tripati et al., 2011; Sosdian et al.,
2018; Greenop et al., 2017).

Therefore, to provide additional constraints on the evolution of atmospheric $pCO_2$
from the Miocene through recent, 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 17 million years (myr). The two sites we examined 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. Currently this region is in air-sea CO$_2$ equilibrium despite equatorial divergence (Takahashi et al., 2014).

This work represents the first reconstructions of past seawater pH and pCO$_2$ for the WEP using MC-ICPMS, thereby providing an invaluable new perspective on reconstructing past atmospheric CO$_2$ 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 $\delta^{11}$B (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 ODP Leg 130 in the WEP (Fig. 1, Table 1): ODP 806A (0°19.140'N, 159°21.660'E, 2520.7 m water depth), ODP 806B (0°19.110'N, 159°21.660'E, 2519.9 m water depth), and ODP 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.

The WEP sites used in this study are currently close to equilibrium with the atmosphere (Takahashi et al., 2014) (despite equatorial divergence), and given their location, are likely to have remained so throughout the study interval. We do note, however, that the
thermocline is deep today, and that changes in thermocline depth have been inferred for the WEP (Nathan and Leckie., 2009; Ford et al., 2015). Any potential changes in depth and properties coupled with changes in upwelling, have the potential to influence equilibrium at this site. While this is the case, changes could be smaller in the WEP compared to other regions, due to the relatively small amplitude changes in temperature and salinity (e.g., compared to higher latitude sites, or eastern boundary current regions).

2.2 Age models

Sites 806 and 807 have high quality age models (Shackleton et al., 1991). The age model for Site 806 from 0-1.35 Ma is based on Lea et al. (2000), while from 1.352-5.875 Ma it is based on Lisiecki and Raymo, (2005), and Wara et al. (2005) is the source of information for sediments older than 5.875 Ma. 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 0-0.550 Ma.

2.3 Species and trace element cleaning

Samples were picked and cleaned to remove clays at UCLA (Los Angeles, CA) and the University of Western Brittany (Plouzane, 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).

2.4 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 $10^{13}$ amplifiers (Lloyd et al., 2018) at the University of Cambridge (Cambridge, UK).

2.5 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):

$$\delta^{11}B (‰) = 1000 \times \left( \frac{^{11}B_{\text{Sample}}}{^{10}B_{\text{NIST SRM 951}}} - 1 \right)$$  \hspace{1cm} \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., 2014) 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 $\delta^{11}B = 19.9 \pm 0.6$ ‰, 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).

2.6 Figures of Merit

2.6.1 $\delta^{11}B$ analyses

Samples measured for boron isotopes typically ranged in concentration from 10 ppb B (~5 ng B) to 20 ppb B samples (~10 ng B). Sensitivity was 10 mV/ppb B (eg. 100 mV for 10 ppb B) in wet plasma at 50 µl/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) 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 ≤ 1 mV 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., 2014) and a 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 $\delta^{11}\text{B}_{\text{NEP}} = 25.72 \pm 0.79\%$ (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 $26.20 \pm 0.88\%$ (2 SD, $n=27$) and $25.80 \pm 0.89\%$ (2 SD, $n=6$), from Holcomb et al. (2015) and Sutton et al. (2018), respectively. Data are reported in Table 2.

2.6.2 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: $^7\text{Li} < 2\%$, $^{11}\text{B} < 7\%$, $^{25}\text{Mg} < 0.2\%$ and $^{43}\text{Ca} < 0.02\%$. Additionally, blanks for a 10 ppm Ca session were: $^7\text{Li} < 2.5\%$, $^{11}\text{B} < 10\%$, $^{25}\text{Mg} < 0.4\%$ and $^{43}\text{Ca} < 0.05\%$. 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 Table 2.

2.7 Calculations

Details of calculations are in the Supplemental methods. We explored multiple scenarios for the evolution of seawater $\delta^{11}\text{B}$ and alkalinity for calculations of $\rho\text{CO}_2$. 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 (Fig. S2). During earlier time intervals, we see there is a greater divergence, reflecting larger uncertainties in seawater $\delta^{11}\text{B}$ and alkalinity further back in Earth history.

During the early Pliocene (~4.5 to 3.5 Ma) and prior to 10 Ma, calculations of $\rho\text{CO}_2$ diverge largely because of disagreement between studies estimating past seawater $\delta^{11}\text{B}$ (Fig. S2). However, we also found that reconstructed pH values that utilize each of the $\delta^{11}\text{B}_{\text{seawater}}$ histories are not significantly different, when the uncertainty in reconstructed pH is fully propagated (Fig. S2 and S3; 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 short 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 $\delta^{11}\text{B}_{\text{seawater}}$ history from Greenop et al. (2017) because it is in good agreement with seawater $\delta^7\text{Li}$ (Misra and Froelich, 2012).
The three alkalinity models used diverge prior to 9 Ma, with a maximum difference at ~13 Ma that is also reflected in reconstructed pCO$_2$ (Fig. S3). However, all three models yield pCO$_2$ estimates that are within error of each other when the full uncertainty is considered (Fig. S3). For the remainder of the text, we utilize the model of Caves et al. (2016) for alkalinity and the $^{81}$B$_{\text{seawater}}$ determined by Greenop et al. (2017), as these represent the best constrained histories for each available at this time.

3. Results and discussion

3.1 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 pCO$_2$ for the last 800 kyr (Fig. 2). The two critical diagnostics we use for method validation are: 1) that the reconstruction of pCO$_2$ is representative of recent atmospheric CO$_2$, and 2) that the boron-based reconstruction empirically reproduces the record from ice cores. As shown in Fig. 2, absolute values for the last glacial/interglacial cycle are within error of the ice core record (Petit et al., 1999 and others) at both sites. For the last 800 kyr, reconstructed pCO$_2$ values for Holes 806A and B and Site 807 are within error of the Vostok ice core (Petit et al., 1999 and others). Between MIS 7 and 6, our reconstructions exhibit a decrease in temperature ($\Delta T$) of 2.4°C, an increase in pH ($\Delta pH$) of 0.08 and a decrease in pCO$_2$ ($\Delta$ pCO$_2$) of 58 µatm. Between stage 3 and 1, we observed an increase of temperature of 2.5°C, a decrease of pH of 0.13 and an increase in pCO$_2$ of 76 µatm. These results highlight that we are able to reproduce absolute measurements of atmospheric pCO$_2$ within error 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 pCO$_2$ 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.

3.2 Long–term record for the past 17 myr

Our reconstruction is consistent with published Mg/Ca estimates of early Pliocene to recent temperatures at Site 806 (Medina-Elizalde et al., 2005, Wara et al., 2005; Tripati et al., 2009, 2011). Our reconstruction is also consistent with the work of Nathan and Leckie,
(2009) for time slices at ~7.3 and ~6.2 Ma, though we note that the SST in our study is slightly higher (~2°C) than what was reported for the middle/late Miocene by Nathan and Leckie, 2009 and Zhang et al., 2014, which could reflect the different methods used for reconstructing temperature. Our temperature record over the last 17 myr for the WEP (Fig. 3C) shows a gradual decrease between 17 and 6.5 Ma from 36.7°C ± 0.6°C (2 SD, n=4) for the Miocene Climate Optimum (MCO) to values of 28.8 ± 3.4°C (2 SD, n=67) over the last 6.5 myr. From 6.5 Ma to present, we reconstruct a slight decrease in SSTs, with more variability after the Mid-Pleistocene Transition (MPT). Raw δ¹¹B data (Fig. S1B) exhibit a significant decrease (4.2‰) with increasing age for T. sacculifer from 16.5 Ma to present. Reconstructed pH for the MCO are 7.80 ± 0.10 (SD, n=4), with an increase of ~0.27 to a Holocene value of 8.18 ± 0.11 (n=2) (Fig. 3D).

3.3 Miocene

The study of Miocene (23-5.3 Ma) 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 is characterized by a warm interval, the Miocene Climate Optimum (~17-14 Ma - MCO), and an abrupt cooling during the Middle Miocene Climate Transition (~15-13 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, proxies for CO₂ yield conflicting reconstructions for the MCO and MMCT. Alkenone-based reconstructions do not show any variations over the MCO and MMCT with pCO₂ below 300 ppm (Zhang et al., 2013). However, it is a challenge to simulate the large-scale advance and retreat of Antarctic ice with such low pCO₂ values (Gasson et al., 2016). In contrast, published δ¹¹B-based reconstructions supports higher pCO₂ for the MCO of ~350-400 ppm (Foster et al., 2012), 300-500 ppm (Greenop et al., 2014) or ~470-630 ppm (Sosdian et al., 2018), although it is unclear if these values accurately reflect the atmosphere given the sites may or may not have been in equilibrium with the atmosphere.

Some of the highest pCO₂ values we reconstruct are during the MCO (Fig. 3E). For the MCO, our estimates are 479 ± 173 µatm (2 SD, n=4, Table 3). The middle Miocene values we reconstruct are in line with previous studies (Greenop et al., 2014; Sosdian et al., 2018). Sosdian et al. (2018) report values of 470 to 630 ppm depending on the model of δ¹¹B_{seawater} chosen. We attribute the differences in δ¹¹B-based pCO₂ to the choice of
reconstruction methods and/or the different oceanographic settings at each site. All of the
boron isotope-based reconstructions do not support reconstructions from alkenones for the
Miocene (Pagani et al., 1999; 2005; Zhang et al., 2013). As thoughtfully discussed by Badger
et al. (2019), the response of CO₂ derived from alkenones is muted compared to boron-based
reconstructions of CO₂, and this is possibly due to changes in coccolithophore calcification
based on recent studies (Bolton and Stoll, 2013; Bolton et al., 2016). During the MCO
relative maxima in pCO₂, our data support very warm sea surface temperatures in the WEP
(36.7°C ± 0.6°C 2SD, n=4; Fig. 5C), 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 δ¹⁸O of benthic foraminifera (Zachos et al., 2001, 2008; Tripati
and Darby, 2018).

During the MMCT, we find evidence for changes in pCO₂ and temperature in the
WEP (Fig. 4). From 13.5 to 12.9 Ma, we reconstruct an increase of pH ~0.24 and a major
decrease of pCO₂ of ~243 µatm during an interval highlighted by Flower and Kennett,
(1996), who observed changes in δ¹⁸O indicative of rapid East Antarctic Ice Sheet growth,
and enhanced organic carbon burial with a maximum δ¹³C reached at ~13.6 Ma (Shevenell et
al., 2004; Holbourn et al., 2007). 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 δ¹³C and δ¹⁸O of benthic
foraminifera are consistent with increased carbon burial during colder periods, thus feeding
back into decreasing atmospheric CO₂, and supporting the hypothesis that the drawdown of
atmospheric CO₂ can in part, be explained by enhanced export of organic carbon.

3.4 Late Miocene

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 8.8 and 6.5 Ma we find evidence for a decrease in
atmospheric CO₂ of 205 µatm associated with a decrease in temperature of 3.1 °C.

3.5 CO₂ during Pliocene Warmth

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).

Figure 5 shows that during the Early Pliocene warm interval, from 4.7 to 4.5 Ma, we calculate high pCO2 values of 541 ± 124 ppm (2 SD, n=3, Table 3).

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). Our data support values of 515 ± 119 µatm (2 SD, n = 4) are consistent with previously published δ11B-derived pCO2 from ODP Site 999 (Martinez-Boti et al., 2015b) but are higher than Bartoli et al. (2011), which was 320 ± 130 (2 SD, n=8) for Site 999, potentially due to instrument offset between N-TIMS and MC-ICP-MS (Martinez-Boti et al., 2015b). Our values are higher in comparison to boron isotope estimates from de La Vega et al. (2020) for Site 999 and calculations based on Martinez-Boti et al., (2015b.) This can suggest differences in air-sea equilibrium between sites. The pCO2 trends in this study are similar to previous ones, the reconstructed pCO2 show larger amplitude in our study. pCO2 concentrations determined from ice cores from the early Pleistocene have recently been published (Yan et al., 2019, Figs. 4 and 5), and those values are in good agreement with our boron-derived pCO2 at site 806/807 reported here, and with previous boron-based studies (Hönisch et al., 2009; Stap et al., 2016; Chalk et al., 2017).

3.6 Pliocene Glacial Intensification

The warmth and local pCO2 maxima of the MPWP 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. 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 µatm (DeConto et al., 2008) to 200 to 400 µatm (Koening et al., 2011).

From 3.3 to 3.0 Ma, our boron isotope-derived estimates of pCO2 are typically 150 µatm higher than Bartoli et al. (2011), and de la Vega., (2020). This study, Martinez-Boti et
al. (2015b) and de la Vega et al., (2020) used an MC-ICP-MS so it is possible the differences reflect changes in air-sea equilibrium recorded at Site 999 compared to Sites 806/807.

The reconstruction for the WEP exhibits multiple steps during the decline in pCO₂, with a minimum observed at 4.42 Ma (360 (±117/85) µatm), at 3.45 Ma (323 (±100/75) µatm) and at 2.67 Ma (269 (±77/59) µatm) (Fig. 6). Those atmospheric CO₂ concentrations 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 CO₂ (280 ppmv) scenario from Lunt et al. (2008). 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), stratification (Togweiller, 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 periods may have enhanced iron fertilization and subsequent carbon export. This could explain why glacial/interglacial amplitudes in WEP pCO₂ values decrease from the MPWP towards the Pleistocene, whereas variations in δ¹⁸O are increasing.

3.7 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 (0.8-1.2 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 have suggested that a decline in atmospheric CO₂ did not occur during the MPT (Hönisch et al., 2009, Chalk et al., 2017).

Although our pCO₂ results for the MPT (Fig. 9D) are broadly in the range of values reported by Hönisch et al. (2009) and Chalk et al. (2017), we have higher data coverage for
the middle and later part of the transition (Fig. 6). 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 reduction of both glacial and interglacial pCO₂ values. We also find evidence that during the MPT, glacial pCO₂ declined rapidly from 189 (±30) µatm at MIS 36 (Chalk et al., 2017) to reach a minimum of 164 (±35) µatm during MIS 30 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 17 myr, the lowest pCO₂ is recorded at MIS 30 during the MPT, with values of 164 (±44) µatm, 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 pCO₂ values during interglacials relative to glacialis, with glacialis exhibiting the largest change across the MPT, would have led to increased sequestration of carbon during glacialis in the 100 kyr world, as discussed by Chalk et al. (2017), with increased glacial dust input and iron fertilization.

3.8 Changes in volcanic activity and silicate weathering, and long-term pCO₂

On million-year timescales, atmospheric CO₂ is mainly controlled by volcanic activity and silicate weathering. Over the last 17 myr, two relative maxima in atmospheric pCO₂ are observed in our record, one during the MCO and a second around the late Miocene/early Pliocene (Fig. 7), though the timing for the latter is not precise due to a data gap for this period. The high CO₂ levels of the MCO are hypothesized (Foster et al., 2012) to coincide with increasing volcanic activity, 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). The second CO₂ 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 (⁸⁷/⁸⁶Sr and δ⁷Li) have been used as proxy for silicate weathering activity. Although the strontium isotope
record exhibits a monotonous increase (Fig. 7), lithium isotope data (Misra and Froelich, 2012) are more variable with a transition from a period of increase seawater δ⁷Li (e.g. non-steady state weathering) to stable seawater δ⁷Li (e.g., steady state weathering) beginning at roughly 6.8 Ma (Fig. 7).

3.9 History of the WEP

The patterns observed in our study are also in line with major changes in the equatorial Pacific dynamic reported from other studies over these timescales (Figure 8). The development of the warm pool and transient changes between La Madre (La-Nina-like) to El Padre (El-Nino-like conditions) have been inferred from geological records (Nathan and Leckie, 2009), including foraminiferal assemblage data and asymmetric carbonate preservation between the west and the east equatorial Pacific (Chaisson and Ravelo, 2000; Nathan and Leckie, 2009), and sea surface and sub-surface temperature proxies (Wara et al, 2005; Rickaby and Halloran, 2005; Seki et al., 2012; Ford et al., 2012, 2015; Drury et al., 2018).

The increase in CO₂ in the late Miocene and early Pliocene in our record corresponds to the timing of the biogenic bloom in the Eastern equatorial Pacific that has been linked to a global biogenic bloom (Hermoyan and Owen, 2001). These blooms have been hypothesized to arise from an increase in nutrients (Hermoyan and Owen, 2001) that arose due to higher rates of weathering as well as change in oceanic circulation due to Indonesian and Central American Seaways constrictions (Gupta and Thomas, 1999; Grant and Dickens, 2002 amongst many others). The change in silicate weathering regime inferred from the record of δ⁷Li (Misra and Froelich, 2012) would also be consistent with this hypothesis.

3.9 Outlook

This study is the first to report a long-term pCO₂ record for the WEP derived from boron isotopes. Using samples from ODP Sites 806 and 807, we build on past efforts to reconstruct atmospheric pCO₂ from carbon isotopes in marine organic matter (Rayno et al., 1996), alkenones (Pagani et al., 2010), and B/Ca (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; de la Vega et al., 2020). Future constraints
on the vertical structure of the WEP during these transitions will potentially be illuminating. Comparison to records from different parts of the ocean will also help us better understand how air-sea disequilibria has changed through time.

4. Conclusions

[1] We developed a reconstruction of atmospheric pCO\textsubscript{2} based on $\delta^{11}$B of planktic foraminifera from Sites 806 and 807 located in the Western Equatorial Pacific for the Miocene to Recent. The record is at present the most data-rich and continuous boron-isotope reconstruction in the literature for a single region over the last 20 myr s, with variable resolution that captures both long-term and short-term variability associated with several key transitions.

[2] As expected, these data reproduce the pCO\textsubscript{2} record from ice cores, consistent with the sites being in equilibrium with the atmosphere.

[3] The MCO has higher pCO\textsubscript{2} than reconstructions from other sites, with values estimated as $479 \pm 173$ µatm (2 SD, n=4), potentially linked to the eruption of the Columbia River Flood Basalts, with values declining into the early Pliocene.

[4] Major drops in pCO\textsubscript{2} occurred at 12.9, 4.42, 3.45 and 2.71 Ma, including during Pliocene glacial intensification.

[5] We find support for a larger reduction in glacial pCO\textsubscript{2} during the MPT compared to interglacial pCO\textsubscript{2}, and a minimum in pCO\textsubscript{2} during glacial MIS 30. These findings support a role for CO\textsubscript{2} in the transition from a 41 kyr to a 100 kyr world.

[6] Higher-resolution boron isotope records from the WEP will allow for further testing of these findings. Additional constraints on temperature, such as from clumped isotopes in the WEP (Tripati et al., 2014), could allow for uncertainties in pCO\textsubscript{2} estimates from boron isotopes to be reduced.

Acknowledgments

The authors wish to thank the Tripati Lab, including Lea Bonnin, and Alexandra Villa, for assistance with picking samples; the IODP 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).
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.

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


IPCC: Global Warming of 1.5 °C- edited by Intergovernmental Panel on Climate Change, 2018.


Figure caption

**Figure 1:** A. Map of air-sea pCO$_2$ (ΔpCO$_2$, µatm, data from Takahashi et al., 2014 and map realized on Ocean Data view, Shlitzer, 2016) showing the location of ODP Sites 806 and 807 (black circles). Depth profiles for preindustrial parameters, B. pH calculated from GLODAP database and corrected from anthropogenic inputs, C. boron isotopic composition of borate ion (δ$^{11}$B$_{borate}$) with associated propagated uncertainties.

**Figure 2:** Reconstruction of surface pCO$_2$ for the past 0.8 My from *T. sacculifer* at ODP Sites 806 and 807. This plot compares pCO$_2$ from boron isotopes (this study, colored symbols) with data from the literature (black and grey symbols) and ice core pCO$_2$ (LePetit at al., 2009; black line). Data from the two sites we examined reproduces the absolute values and amplitude of atmospheric pCO$_2$ as determined from ice cores, thereby validating our methodology.

**Figure 3:** Proxy data for the past 17 million years in the Western Equatorial Pacific compared to benthic oxygen isotope composites. A. Benthic δ$^{18}$O (blue line - Lisiecki and Raymo, 2005; black line – compilation from Zachos et al., 2008). B. Benthic δ$^{13}$C (black line – compilation from Zachos et al., 2008). C to E, colored is indicating the site (open grey=806, filled grey=807), symbols represent the species (circle=*T. sacculifer* and triangle=*G. ruber*). C. SST reconstructed at ODP Sites 806 and 807 using Mg/Ca ratios and equation S6 and S7 (this study). D. Seawater pH reconstructed from δ$^{11}$B of *T. sacculifer* and *G. ruber* using δ$^{11}$B$_{seawater}$ from Greenop et al. (2017) (refer to text and supplement for calculations, this study). E. Reconstructed pCO$_2$ (µatm) using boron-based pH and alkalinity from Caves et al. (2016), data presented are from this study. Propagated uncertainties are given by eq. 18 for the dark (green or blue) envelope, while the light (green or blue) envelope are the uncertainties calculated based on eq. 17 (taking into account uncertainty on δ$^{11}$B$_{seawater}$). Only data from this study are shown.

**Figure 4:** Proxy data from 17 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 composites. A. Benthic δ$^{18}$O (black line – compilation from Zachos et al., 2008). B. Benthic δ$^{13}$C (black line – compilation from Zachos et al., 2008). C and D, colored is indicating the site (open grey=806, filled grey=807), symbols represent the species (circle=*T. sacculifer* and triangle=*G. ruber*). C. SST reconstructed at ODP Sites 806 and 807 using Mg/Ca ratios and equation S6 and S7 (this study). D. Reconstructed pCO$_2$ (µatm) using boron-based pH and alkalinity from Caves et al. (2016), data presented are from this study. Propagated uncertainties are given by eq. 18 for the dark (green or blue) envelope, while the light (green or blue) envelope are the uncertainties calculated based on eq. 17 (taking into account uncertainty on δ$^{11}$B$_{seawater}$).

**Figure 5:** Proxy data from 7 to 1 million years, including the Warm Pliocene Transition (WPT), in the Western Equatorial Pacific compared to benthic oxygen isotope composites. A. Benthic δ$^{18}$O (black line – compilation from Zachos et al., 2008). B. Benthic δ$^{13}$C (black line – compilation from Zachos et al., 2008). C and D, colored is indicating the site (open grey=806, filled grey=807), symbols represent the species (circle=*T. sacculifer* and triangle=*G. ruber*). C. SST reconstructed at ODP Sites 806 and 807 using Mg/Ca ratios and equation S6 and S7 (this study). D. Reconstructed pCO$_2$ (µatm) using boron-based pH and alkalinity from Caves et al. (2016), data presented are from this study. Propagated uncertainties are given by eq. 18 for the dark (green or blue) envelope, while the light (green or blue) envelope are the uncertainties calculated based on eq. 17 (taking into account uncertainty on δ$^{11}$B$_{seawater}$).

**Figure 6:** 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 δ$^{18}$O (blue line – compilation from Lisiecki and Raymo, 2005). B. Benthic δ$^{13}$C (black line – compilation from Zachos et al., 2008). C and D, colored is indicating the site (open grey=806, filled grey=807), symbols represent the species (circle=*T. sacculifer* and triangle=*G. ruber*). C. SST reconstructed at ODP Sites 806 and 807 using Mg/Ca ratios and equation S6 and S7 (this study). D.
Reconstructed pCO₂ (µatm) using boron-based pH and alkalinity from Caves et al. (2016), data presented are from this study. Propagated uncertainties are given by eq. 18 for the dark (green or blue) envelope, while the light (green or blue) envelope are the uncertainties calculated based on eq. 17 (taking into account uncertainty on δ¹¹B seawater).

**Figure 7:** 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 δ¹⁸O (blue line – compilation from Lisiecki and Raymo, 2005, black line – compilation from Zachos et al. 2008). B. B. Records from Lithium isotopes (δ⁷Li, orange, Misra and Froelich, 2012) and Strontium isotopes (^⁸⁷/⁸⁶Sr, 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 δLi, black crosses are indication when changes in weathering regime occurs. C. Reconstructed pCO₂ (µatm) using boron-based pH and alkalinity from Caves et al. (2016), data presented are from this study. Propagated uncertainties are given by eq. 18 for the dark (green or blue) envelope, while the light (green or blue) envelope are the uncertainties calculated based on eq. 17 (taking into account uncertainty on δ¹¹B seawater). Colored is indicating the site (open grey=806, filled grey=807), symbols represent the species (circle = T. sacculifer and triangle= G. ruber). Rose band and dark rose band represent time of eruption of the Columbia river flood basalts (Hooper et al., 2002) and time of maximum eruption (Kasbohm and Schoene, 2018), respectively. Blue bands represent hypothesized La Madre intervals and red bands represent hypothesized El Padre intervals (Farrell et al., 1995; Chaisson and Ravelo, 2000; Nathan and Leckie, 2009; Ford et al., 2012; Drury et al., 2018). The biogenic bloom in the EEP (Farrell et al., 1995) and in the WEP (Berger et al., 1991), is hypothesized to have been driven by enhanced weathering that increased nutrient delivery to the global ocean (Hermoyian and Owen, 2001).
Table 1: Boxe 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>
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<td>807</td>
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<td>156.62</td>
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<td>159.37</td>
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<td>Age (Ma)</td>
<td>pODC</td>
<td>pH</td>
<td>Reconstruction Parameters</td>
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<td>30.0</td>
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Table 2: Analytical data and reconstructed parameters for ODP Sites 806 and 807.
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<th>Depth 3</th>
<th>Depth 4</th>
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<td>Average weight of individual shell</td>
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<tr>
<td>SST</td>
<td>Sea surface Temperature determined from Mg/Ca ratios, see text for calculations</td>
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<td>Error 2</td>
<td>Propagated error for pH and pCO2 calculated from eq. S16 and eq. S18, respectively</td>
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<tr>
<td>Up</td>
<td>Propagated error above symbol</td>
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<tr>
<td>Down</td>
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<td></td>
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</table>
Table 3: Comparison of reconstructed pCO₂ values for key intervals in the last 17 My.

### Mid-Pleistocene transition (1.2-0.8 My)

<table>
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<tr>
<th>MIS (G)</th>
<th>pCO₂ (µatm)</th>
<th>Reference</th>
<th>MIS (IG)</th>
<th>pCO₂ (µatm)</th>
<th>Reference</th>
<th>pCO₂ amplitude IG-G (µatm)</th>
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<td>222</td>
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</tr>
<tr>
<td>24</td>
<td>nd</td>
<td>This study</td>
<td>25</td>
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<td>nd</td>
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<tr>
<td>26</td>
<td>168</td>
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<td>27</td>
<td>nd</td>
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<tr>
<td>30</td>
<td>164</td>
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<td>295</td>
<td>Hönisch et al., 2009 (N-TIMS)</td>
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<tr>
<td>32</td>
<td>218</td>
<td>Chalk et al., 2017</td>
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<td>323</td>
<td>Chalk et al., 2017</td>
<td>105</td>
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<td></td>
<td>39</td>
<td>306</td>
<td>This study</td>
<td>nd</td>
</tr>
</tbody>
</table>

### Early Pliocene Warm Period (4.7-4.5 My)

- pCO₂ (µatm): 541 ± 124
- Reference: This study (2 SD, n=3)

### Middle Pliocene Warm Period (3.29-2.97 My)

- pCO₂ (µatm): 515 ± 119
- Reference: This study (2 SD, n=4)

- pCO₂ (µatm): 320 ± 130
- Reference: Martinez-Boti, 2015b (2 SD, n=8)

### Miocene Climate Optimum (17-14 My)

- pCO₂ (µatm): 479 ± 173
- Reference: This study (2 SD, n=4)

- pCO₂ (µatm): 350-400
- Reference: Foster et al., 2012

- pCO₂ (µatm): 300-500
- Reference: Greenop et al., 2014

- pCO₂ (µatm): 470-630
- Reference: Sosdian et al., 2018
Figure 1
Figure 2

T. sacculifer (806), this study
T. sacculifer (807), this study
Hönisch et al., 2009
Seki et al., 2010
Stap et al., 2016
Chalk et al., 2017
Foster et al., 2014
Vostok ice core
Figure 3
Figure 4
Figure 5

A. 

B. 

C. 

D. 

- Chalk et al., 2017 (999A)
- Stap et al., 2016 (1264)
- Martinez-Boti et al., 2015b and de la Vega et al., 2020 (999A)
- Yan et al., 2019 (ice core)
- Hönisch et al., 2009 (668B)
- Bartoli et al., 2011 (999A)
Figure 6

(A) δ¹⁸O (‰) vs. Age (Ma)

(B) δ¹³C (‰) vs. Age (Ma)

(C) SST (°C) vs. Age (Ma)

(D) pCO₂ (µatm) vs. Age (Ma)

Sites:
- Site 806
- Site 807

Research Studies:
- Hönicke et al., 2009 (668B)
- Foster et al., 2014 (999A)
- Seki et al., 2010 (999A)
- Chalk et al., 2017 (999A)
- Yan et al., 2019 (ice core)
- Site 807
- Site 806
Figure 7

Steady state weathering Non steady state weathering

Miocene climate optimum MCO

Middle Miocene climate transition MCT

Mid-Pleistocene transition MPT

Warm Pliocene transition WPT

Columbia river flood basalts

Site 806
Site 807

Chalk et al., 2017 (999A)
Stap et al., 2016 (1264)
de La Vega 2020
Martinez Boti., 2015b (999)
Foster et al., 2014 (999A)

Greenop et al., 2014 (761B)
Badger et al., 2013
Foster et al., 2012 (962A)
Foster et al., 2012 (761B)
Bartoli et al., 2011 (999A)
Seki et al., 2010 (999A)
Hönisch et al., 2009 (668B)
SUPPLEMENTAL INFORMATIONS

Atmospheric CO$_2$ reconstruction for the last 17 Ma based on foraminiferal $\delta^{11}$B measurements for Ocean Drilling Program Sites 806 and 807 in the Western Equatorial Pacific warm pool

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Supplemental Methods

1.1 Potential contamination

We found no evidence for contamination of TE (including Mg/Ca) arising from the presence of silicate minerals or Mn-Fe-Oxide coatings. Contamination of samples by silicate minerals was monitored using Fe/Mg ratios. Samples with Fe/Mg > 0.1 mol/mol are typically rejected due to potential contamination by silicate minerals (Barker et al., 2003). Our samples have an average Fe/Mg of 0.034 ± 0.07 mol/mol (2 SD, n=106), indicating that silicate minerals have been efficiently removed during our cleaning. Contamination by clays was monitored using Ti/Ca no correlations were found between Ti/Ca and Mg/Ca \( (R^2=0.0066) \) or with B/Ca \( (R^2=0.0237) \). Contamination by Mn-Fe oxides is detected using Mn/Ca ratios and Fe/Ca ratios. Our samples have Mn/Ca ratios of 0.12 ± 0.11 mmol/mol (2 SD, n=108) consistent with previous published data of cleaned samples (Wara et al., 2005). No correlations was observed between Mg/Ca and Fe/Ca \( (R^2=0.0841) \) or between Mg/Ca and Mn/Ca \( (R^2=0.0161) \). No significant correlation was observed between B/Ca and Mn/Ca \( (R^2=0.0011) \) or B/Ca and Fe/Ca \( (R^2=0.0132) \) ratios.

2.7 Calculations of temperature, salinity, pH, and \( \rho \text{CO}_2 \)

Analyses of \( ^{\delta^{11}}B \), \( ^{\delta^{18}}O \) and elemental ratios (eg., Mg/Ca, B/Ca) were used to reconstruct the chemical and physical properties of seawater over the last 17 My of the Western Equatorial Pacific (Fig. S1).

2.7.1 Salinity reconstruction

Salinity was reconstructed using the relative sea level (RSL) reconstruction from Stap et al. (2017) and equation 2:

\[
S = S_{\text{modern}}/3800*(3800+\text{RSL}) \quad \text{eq. 2}
\]

\( S_{\text{modern}} \) is the modern salinity corresponding to the depth habitat of the foraminifera at the site of interest. The depths used were 125 m for \( T. \text{sacculifer} \) and 80m for \( G. \text{ruber} \) (Rickaby et al., 2005; Guillermic et al., 2020). At Site 806, values for \( S_{\text{modern}} \) of 35.38 was used for \( T. \text{sacculifer} \) and 35.01 was used for \( G. \text{ruber} \). At Site 807, a value of 35.05 was used for \( T. \text{sacculifer} \).

2.7.2 Temperature
Paleotemperatures were calculated using Mg/Ca ratios of planktic foraminifera. A number of factors have been shown to impact Mg/Ca ratios and calculated paleotemperature. Factors identified in prior studies include salinity and pH effects on Mg/Ca, seawater Mg/Ca ratios, cleaning methodology, dissolution, and basin-specific equations, as discussed in more detail below. Below we describe some of the prior work that was factored into the regional mono-specific equations we used for calculating temperature from Mg/Ca.

### 2.7.2.1 Prior work showing evidence for salinity and pH effects on Mg/Ca-T

Studies have found that Mg/Ca ratios in foraminifera are impacted by salinity (Nürnberg et al., 1996; Hönisch et al., 2013) and pH or [CO$_3^{2-}$] (Russell et al., 2004; Kisakürek et al., 2008; Evans et al., 2016; Gray et al., 2018; Gray and Evans, 2019). Based on culture experiments, Gray and Evans (2019) reported impacts of both salinity and pH on *G. ruber* but only a salinity effect on *T. sacculifer*, and derived the following equations:

\[
\text{SST (} T. \text{sacculifer}) = (\ln(\frac{Mg}{Ca}_{\text{test}}) - 0.054 * (S - 35) + 0.24)/0.062 \quad \text{eq. 3}
\]

\[
\text{SST (} G. \text{ruber}) = (\ln(\frac{Mg}{Ca}_{\text{test}} - 0.036 * (S - 35) + 0.87 * (pH - 8) + 0.03)/0.064 \quad \text{eq. 4}
\]

### 2.7.2.2 Prior work showing evidence for variations in Mg/Ca ratios of seawater

Over timescales of $10^6$-$10^7$ years, Mg/Ca$_{sw}$ can vary. Evidence from evaporites, carbonate veins, fossil corals and models suggests that seawater Mg/Ca$_{sw}$ ratios have varied through time with variations of ~3 mol/mol (Horita et al., 2002; DeFantle and Paolo, 2006; Coggon et al., 2011; Brennan et al., 2013; Gothman et al., 2015). These studies do not agree on the timing of changes in Mg/Ca$_{sw}$. Gothman et al. (2015) made measurements of corals and also compiled different seawater archives including carbonate veins, gastropods, brachiopods, fish teeth, and found that values of Mg/Ca$_{sw}$ of 2.5 mol/mol occurred ~25 My. To correct for secular variations in Mg/Ca$_{sw}$ we used the approach of O’Brien et al. (2014), theoretical work from Evans and Muller, (2012), and the Mg/Ca$_{sw}$ record of Gothman et al. (2015). The equations we utilized are adapted from Dekens et al. (2002):

\[
\text{SST (} T. \text{sacculifer}) = (\ln(\frac{Mg}{Ca}_{\text{test}} * \frac{Mg}{Ca}_{sw}) - 0.37 * \frac{Mg}{Ca}_{sw})/0.09 + 0.36 * C + D \quad \text{eq. 5}
\]
Specifically H refers to the power components of the power law relationship between the Mg partition coefficient and Mg/Ca_{sw}, with a value of 0.41 for *T. sacculifer* (Delaney et al., 1985) which we also assume is the same for *G. ruber*. C is the depth of the site. D refer to a basin-specific offset, which is 2 °C for *T. sacculifer* and 2.9 °C for *G. ruber* for the Pacific Ocean, (Table S1).

### 2.7.2.3 Prior work on reductive cleaning effects on Mg/Ca

The use of a reductive step in cleaning has been shown to lower Mg/Ca_{test} ratios in planktic (Barker et al., 2003; Bian et al., 2010; Johnstone et al., 2016) and benthic foraminifera (Yu et al., 2007a), and contribute to offsets between studies using different methodologies. A decrease in Mg/Ca_{test} of 6-9% was reported for *T. sacculifer* by Bian et al. (2010), and of 5% by Johnstone et al. (2016). A decrease of 4% was reported for *G. ruber* by Johnstone et al. (2016).

### 2.7.2.4 Mg/Ca-SST equations used for this study

Based on the above equations from Gray and Evans (2019) (eq. 3 and 4), we incorporated a term to account for changes in the Mg/Ca ratio of seawater, and based on results from Dekens et al., (2002) we incorporated two terms to account for dissolution (C) and basin-specific offsets (D), and used an iterative approach for our calculations to account for pH effect on *G. ruber* (Gray and Evans, 2019). The equations we used are:

\[
SST (T. sacculifer) = \left( \frac{\text{Mg/Ca}_{\text{test}} \times \text{Mg/Ca}_{\text{sw}0}}{\text{Mg/Ca}_{\text{sw}0}} \right) - \ln(0.37 \times \frac{\text{Mg/Ca}_{\text{sw}0}}{\text{Mg/Ca}_{\text{sw}0}}) / 0.09 + 0.61 \times C + D
\]

\[
\text{eq. 6}
\]

\[
SST (G. ruber) = \left( \frac{\text{Mg/Ca}_{\text{test}} \times \text{Mg/Ca}_{\text{sw}0}}{\text{Mg/Ca}_{\text{sw}0}} \right) - \ln(0.37 \times \frac{\text{Mg/Ca}_{\text{sw}0}}{\text{Mg/Ca}_{\text{sw}0}}) / 0.09 + 0.61 \times C + D
\]

\[
\text{eq. 7}
\]

\[
SST (G. ruber) = \left( \frac{\text{Mg/Ca}_{\text{test}} \times \text{Mg/Ca}_{\text{sw}0}}{\text{Mg/Ca}_{\text{sw}0}} \right) - \ln(0.37 \times \frac{\text{Mg/Ca}_{\text{sw}0}}{\text{Mg/Ca}_{\text{sw}0}}) / 0.09 + 0.61 \times C + D
\]

\[
\text{eq. 8}
\]
With H being the power components of the power relationship between the Mg partition coefficient and Mg/Ca, 0.41 for T. sacculifer (Delaney et al., 1985). We use the same value for G. ruber. C is the depth of the core (km). In order to take the impact of reductive cleaning into account we applied a decrease of 5% for G. ruber and T. sacculifer (Bian et al., 2010 and Johnstone et al., 2016).

Given evidence for a pH effect on Mg/Ca-SST calibration for G. ruber, we used an iterative approach for our calculations, following Gray and Evans, (2019). Up to 4 iterations were needed to achieve a difference in SST with the previous iteration of <0.05°C and a difference in pH of <0.001. For this iterative approach, we first calculate pH from foraminiferal δ¹¹B, then calculate SST from pH, then calculate pH with SST, and then repeat.

### 2.8 δ¹¹Bborate from δ¹¹Bcarbonate

The use of δ¹¹B in foraminiferal carbonate to calculate seawater δ¹¹Bborate, and derived pH and pCO₂ values, has been shown to accurately replicate pCO₂ records independently determined from ice cores and using oceanographic data, if several factors are taken into account (Chalk et al., 2017; Guillermic et al., 2020). These factors include mono-specific calibrations, size fraction or shell weight, basin, and water depth. In order to accurately reconstruct seawater pH (and pCO₂) from δ¹¹B of foraminifera, mono-specific calibrations are needed to convert δ¹¹Bcarbonate to δ¹¹Bborate. Recent culture and field-based calibrations have refined the sensitivities of δ¹¹Bcarbonate to δ¹¹Bborate for different foraminiferal species (Henehan et al., 2016; Raitzsch et al., 2018; Guillermic et al., 2020). For T. sacculifer and G. ruber, the sensitivities of δ¹¹Bcarbonate to δ¹¹Bborate are 0.82 and 0.58, respectively (Raitzsch et al., 2018; Guillermic et al., 2020). As with Mg/Ca, the intercepts are prone to large uncertainties and are commonly adjusted based on core-top data, in order to yield the expected pre-industrial pH or pCO₂ value at the site being examined (Chalk et al., 2017; Sosdian et al., 2018). The rationale for this correction is the impact of the depth habitat on microenvironment pH and subsequent δ¹¹Bcarbonate (Hönisch and Hemming, 2004; Guillermic et al., 2020) and/or preferential dissolution of gametogenic calcite (Ni et al., 2007). It is also possible that these offsets may reflect observed size effects on G. ruber as well as T. sacculifer (Henehan et al., 2013; Hönisch et al., 2019). For T. sacculifer, a relationship between shell size and δ¹¹Bcarbonate has been observed in the WEP (Hönisch and Hemming, 2004; Ni et al., 2007). Hönisch and Hemming, (2004) also reported that values for the 515-865 µm size fraction yielded values of 21.76 ‰,
and determined a size-fraction specific relationship. Here, we modify this approach to develop
a shell-weight specific relationship:

\[
\text{Size offset (‰)} = 21.76 - (0.06522 \times \text{Weight/shell (µg)} + 17.38) \quad \text{eq. 9}
\]

We adapted the equation for \textit{T. sacculifer} from Guillermic et al. (2020):

\[
\delta^{11}B_{\text{borate}} = \left[ (\delta^{11}B_{T. \text{sacculifer}} + \text{Size offset}) - 4.09 (\pm 0.86) \right] / 0.83 (\pm 0.48) \quad \text{eq. 10}
\]

Due to the lack of coretop measurements for \textit{G. ruber} from this study, we selected three control
points at Marine isotope stages (MIS) 30, 37 and 39 (Lisiecky and Raymo, 2005) times when
both \textit{T. sacculifer} and \textit{G. ruber} were measured to determine appropriate offsets for both
\(\text{Mg/Ca} \) and \(\delta^{11}B \) that yield (Table S1 and S2) the best agreement between the species. This was
used to adapt the equation from Guillermic et al. (2020) for \textit{G. ruber}:

\[
\delta^{11}B_{\text{borate}} = \left[ (\delta^{11}B_{G. \text{ruber}} + 2.0) - 9.11 (\pm 0.73) \right] / 0.58 (\pm 0.91) \quad \text{eq. 11}
\]

2.9 Constants

Temperature, salinity and pressure were used to calculate the different dissociation
constants and parameters. We used \(K_1, K_2 \) from Lueker et al. (2000), \(K_B \) from Dickson, (1990),
\(K_{SO_4} \) from Dickson, (1990), \(KF \) from Peres and Fraga, (1987) and total boron from Lee et al.
(2010).

2.10 pH calculations

The quantitative estimation of pH using downcore \(\delta^{11}B_{\text{carbonate}} \) requires: 1) calculations
of the borate isotopic composition of seawater (\(\delta^{11}B_{\text{borate}} \)), 2) constraints on the secular variation
of the boron isotopic composition of seawater (\(\delta^{11}B_{\text{seawater}} \)), 3) the fractionation factor (\(\alpha \))
between \(\text{B(OH)}_3 \) and \(\text{B(OH)}_4^- \) and 4) the calculations of acid/base equilibrium constants based
temperature, salinity and pressure. To translate our \(\delta^{11}B \) measurements to pH, we used the
following relationship (Hemming and Hanson, 1992):

\[
pH = pK_B^* - \log \left( \frac{\delta^{11}B_{\text{sea}} - \delta^{11}B_{\text{borate}}}{\delta^{11}B_{\text{sea}} - \alpha \delta^{11}B_{\text{borate}} - \epsilon} \right) \quad \text{eq. 12}
\]

\(pK_B^* \) is the dissociation constant between the two boron species (8.5975 at 25 °C and a salinity
of 35 psu, Dickson, 1990). A fractionation between \(\text{B(OH)}_3 \) and \(\text{B(OH)}_4^- \) (\(\epsilon \)) of 27.2 ± 0.6 ‰
was empirically determined by Klochko et al. (2006) in seawater and confirmed independently
using a different method by Nir et al. (2015).

A few studies have attempted to reconstruct secular variations of \( \delta^{11}\text{B}_{\text{seawater}} \)
(Lemarchand et al., 2000; Foster et al., 2012; Raitzsch and Hönisch, 2013; Greenop et al.,
2017). For our work, we first compared different scenarios (Fig. S1A). These scenarios are
modeled values of \( \delta^{11}\text{B}_{\text{seawater}} \) based on constraints on the boron budget from Lemarchand et al.
(2000) (labeled as scenario L02), a second modeled history that assumed changes in seawater
pH from Raitzsch and Hönisch (2013) (labeled as scenario R&H13), and a third scenario that
also considered constraints on pH gradients from \( \delta^{13}\text{C} \) measurements published by Greenop et
al. (2017) (labeled as scenario G17).

2.11 pCO\textsubscript{2} calculations

The carbonate system has two degrees of freedom, meaning that if two parameters of the
carbonate system are known all the others can be calculated. For this study, we utilized pH
calculated using \( \delta^{11}\text{B}_{\text{borate}} \), and total alkalinity (TA) as a second parameter that are shown in
Fig. S2A. We used three different alkalinity scenarios for our calculations (Tyrell and Zeebe,
all calculations, we used CO\textsubscript{2}sys from Pierrot et al. (2006).

2.12 Error propagation for temperature (T), pH and pCO\textsubscript{2}

The main source of uncertainty in reconstructed pCO\textsubscript{2} comes from the errors in pH. Table
S3 summarizes the sensitivity of pH and pCO\textsubscript{2} to different variables. The individual
uncertainties were propagated in quadrature to combined uncertainties for temperature (\( \delta T \)),
pH (\( \delta \text{pH} \)) and pCO\textsubscript{2} (\( \delta \text{pCO}_2 \)) (eq. 13, 14, 15, 16 and 17). Minimum and maximum propagated
uncertainties were derived separately for pH and pCO\textsubscript{2}. \( \delta \text{pCO}_2 \) (A) is the full uncertainty
propagation, \( \delta \text{pCO}_2 \) (B) is the uncertainty propagation without taking into account the \( \delta^{11}\text{B}_{\text{sw}} \).
Both are shown in the figures and discussed below.

\[
\delta T_{G.\text{rub}} = \sqrt{(\delta T_{\text{Mg/Ca}})^2 + (\delta T_{\text{Salinity}})^2 + (\delta T_{\text{pH}})^2} \quad \text{eq. 13}
\]

\[
\delta T_{T.\text{saculifer}} = \sqrt{(\delta T_{\text{Mg/Ca}})^2 + (\delta T_{\text{Salinity}})^2} \quad \text{eq. 14}
\]
\[ \delta p\text{H (A)} = \sqrt{(\delta \text{pH}_{\text{Temperature}})^2 + (\delta \text{pH}_{\text{Salinity}})^2 + (\delta \text{pH}_{\delta^{11}\text{B}_{\text{sw}}})^2 + (\delta \text{pH}_{\delta^{11}\text{B}_{\text{carbonate}}})^2} \]

*eq. 15*

\[ \delta \text{pH (B)} = \sqrt{(\delta \text{pH}_{\text{Temperature}})^2 + (\delta \text{pH}_{\text{Salinity}})^2 + (\delta \text{pH}_{\delta^{11}\text{B}_{\text{carbonate}}})^2} \]

*eq. 16*

\[ \delta \text{pCO}_2 (A) = \sqrt{(\delta \text{pCO}_2_{\text{Temperature}})^2 + (\delta \text{pCO}_2_{\text{Salinity}})^2 + (\delta \text{pCO}_2_{\delta^{11}\text{B}_{\text{sw}}})^2 + (\delta \text{pCO}_2_{\delta^{11}\text{B}_{\text{carbonate}}})^2 + (\delta \text{pCO}_2_{\text{Alkalinity}})^2} \]

*eq. 17*

\[ \delta \text{pCO}_2 (B) = \sqrt{(\delta \text{pCO}_2_{\text{Temperature}})^2 + (\delta \text{pCO}_2_{\text{Salinity}})^2 + (\delta \text{pCO}_2_{\delta^{11}\text{B}_{\text{carbonate}}})^2 + (\delta \text{pCO}_2_{\text{Alkalinity}})^2} \]

*eq. 18*

With for example, “\(\delta \text{pCO}_2_{\text{Temperature}}\)” being the uncertainty in \(\text{pCO}_2\) due to temperature.
Tables and Figures

Table S1: Control points for a 2‰ offset used for G. ruber.

Table S2: Comparaison of the control points reconstructions between T. sacculifer and G. ruber for MIS 30, 37 and 39, using different offsets (see text).

Table S3: Sensitivity tests for reconstructed pH and pCO2 (G17, Caves-16), all results are given as the minimum and maximum variation (%) observed in our data.

Figure S1: Results for the past 17 million years. A. Benthic δ¹⁸O (blue line - Lisiecki and Raymo, 2005; black line – compilation from Zachos et al., 2008). B. δ¹¹B of T. sacculifer and G. ruber at sites 806, 807. C. B/Ca ratios. D. Mg/Ca ratios. E. Calculated weight per shell to assess dissolution for T. sacculifer and G. ruber.

Figure S2: Pannel A) shows the various scenarios of δ¹¹B seawater tested for pCO₂ reconstruction, in green Greenop et al. (2017) (G17), red Raitzsch and Hönisch, (2013) (R&H13) and in blue Lemarchand et al. (2000) (L02). Pannel B) is the reconstructed pH based our δ¹¹B carbonate records associated with the different scenarios. The propagated uncertainties were calculated using eq. S14. Due to the 1‰ uncertainty propagated for δ¹¹B seawater, all scenarios of reconstructed seawater pH are within error of each other

Figure S3: Pannel A) shows the various scenarios of Alkalinity (e.g. second carbonate parameter) tested for pCO₂ reconstruction, in orange R-05 (Ridgwell and Zeebe, 2005), in violet T&Z-04 (Tyrell and Zeebe, 2004) and in green Caves-16 (Caves et al., 2016). Pannel B) is the reconstructed pCO₂ records (based on δ¹¹B seawater from scenario G17) associated with the different alkalinity scenarios, orange (Ridgwell and Zeebe, 2005), violet (T&Z-04) and green (Caves-16). The propagated uncertainties were calculated using eq. S15.
<table>
<thead>
<tr>
<th>Species</th>
<th>Sample</th>
<th>mcd</th>
<th>mbsf</th>
<th>Shell Wt</th>
<th>Age</th>
<th>SST</th>
<th>error</th>
<th>Salinity</th>
<th>TA</th>
<th>pH</th>
<th>Error</th>
<th>pCO2</th>
<th>Error max</th>
<th>Error min</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>G. ruber</em></td>
<td>806</td>
<td>B</td>
<td>3</td>
<td>5</td>
<td>6</td>
<td>22.06</td>
<td>22.06</td>
<td>16.1</td>
<td>1.046</td>
<td>26.4</td>
<td>1.8</td>
<td>35.3</td>
<td>2241</td>
<td>8.16</td>
</tr>
<tr>
<td><em>T. sacculifer</em></td>
<td>806</td>
<td>B</td>
<td>3</td>
<td>5</td>
<td>6</td>
<td>22.06</td>
<td>22.06</td>
<td>18.2</td>
<td>1.048</td>
<td>25.9</td>
<td>0.9</td>
<td>35.6</td>
<td>2230</td>
<td>8.28</td>
</tr>
<tr>
<td><em>G. ruber</em></td>
<td>806</td>
<td>B</td>
<td>4</td>
<td>1</td>
<td>71</td>
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<td>26.21</td>
<td>17.0</td>
<td>1.240</td>
<td>26.6</td>
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<td>35.1</td>
<td>2230</td>
<td>8.09</td>
</tr>
<tr>
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<td>B</td>
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<td>56</td>
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<td>26.06</td>
<td>22.2</td>
<td>1.233</td>
<td>29.8</td>
<td>0.9</td>
<td>35.6</td>
<td>2228</td>
<td>8.08</td>
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Table S2: Comparison of the control points reconstructions between *T. sacculifer* and *G. ruber* for MIS 30, 37 and 39, using different offsets (see text).

<table>
<thead>
<tr>
<th>Offset (‰)</th>
<th>ΔpCO₂ (µatm)</th>
<th>ΔpH (tot scale)</th>
<th>ΔT (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>105</td>
<td>-0.14</td>
<td>-0.02</td>
</tr>
<tr>
<td>1.85</td>
<td>37</td>
<td>-0.02</td>
<td>-3.75</td>
</tr>
<tr>
<td>2.0</td>
<td>26</td>
<td>-0.01</td>
<td>-0.36</td>
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<tr>
<td>2.1</td>
<td>100</td>
<td>-0.003</td>
<td>0.06</td>
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<td>1.85</td>
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<td>0.01</td>
<td>-3.65</td>
</tr>
<tr>
<td>2.0</td>
<td>20</td>
<td>0.02</td>
<td>-0.27</td>
</tr>
<tr>
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<td>86</td>
<td>0.02</td>
<td>0.31</td>
</tr>
<tr>
<td>1.85</td>
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<td>0.03</td>
<td>-3.39</td>
</tr>
<tr>
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<td>0.47</td>
<td>-0.005</td>
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<tr>
<td>2.1</td>
<td>100</td>
<td>0.17</td>
<td>0.47</td>
</tr>
</tbody>
</table>
Table S3: Sensitivity tests for reconstructed pH and pCO$_2$ (G17, Caves-16), all results are given as the minimum and maximum variation (%) observed in our data.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH ($G. ruber$)</th>
<th>pH ($T. sacculifer$)</th>
<th>pCO$_2$ ($G. ruber$)</th>
<th>pCO$_2$ ($T. sacculifer$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity</td>
<td>0.07-0.08 %</td>
<td>0.12-0.13 %</td>
<td>0.8-1.5 %</td>
<td>0.8-1.4 %</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.02-0.3%</td>
<td>0.02-0.7%</td>
<td>5-11%</td>
<td>5-7%</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>0.07-0.1%</td>
<td>0.1-0.6%</td>
<td>0.8-1.2%</td>
<td>0.8-1.5%</td>
</tr>
<tr>
<td>δ$_{11}^{18}$ Carbonate</td>
<td>1-2%</td>
<td>1-1.5%</td>
<td>0.02-1.5%</td>
<td>0.02-1.5%</td>
</tr>
<tr>
<td>δ$_{11}^{18}$ Seawater</td>
<td>0.8-1.4%</td>
<td>0.12-0.13%</td>
<td>0.12-0.16%</td>
<td>0.12-0.13%</td>
</tr>
</tbody>
</table>

Table S3: Sensitivity tests for reconstructed pH and pCO$_2$ (G17, Caves-16), all results are given as the minimum and maximum variation (%) observed in our data.
Figure S1: Results for the past 17 million years. A. Benthic δ¹⁸O (blue line - Lisiecki and Raymo, 2005; black line – compilation from Zachos et al., 2008). B. δ¹¹B of T. sacculifer and G. ruber at sites 806, 807. C. B/Ca ratios. D. Mg/Ca ratios. E. Calculated weight per shell to assess dissolution for T. sacculifer and G. ruber from this study.
Figure S2: Pannel A) shows the various scenarios of δ^{11}B_{seawater} tested for pCO_2 reconstruction, in green Greenop et al. (2017) (G17), red Raitzsch and Hönisch, (2013) (R&H13) and in blue Lemarchand et al. (2000) (L02). Pannel B) is the reconstructed pH based our δ^{11}B_{carbonate} records associated with the different scenarios. The propagated uncertainties were calculated using eq. S14. Due to the 1‰ uncertainty propagated for δ^{11}B_{seawater}, all scenarios of reconstructed seawater pH are within error of each other.
Figure S3: Pannel A) shows the various scenarios of Alkalinity (e.g. second carbonate parameter) tested for pCO$_2$ reconstruction, in orange R-05 (Ridgwell and Zeebe, 2005), in violet T&Z-04 (Tyrell and Zeebe, 2004) and in green Caves-16 (Caves et al., 2016). Pannel B) is the reconstructed pCO$_2$ records (based on $\delta^{11}$B$_{seawater}$ from scenario G17) associated with the different alkalinity scenarios, orange (Ridgwell and Zeebe, 2005), violet (T&Z-04) and green (Caves-16). The propagated uncertainties were calculated using eq. S15.