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Climate of the Past
Discussions

Atmospheric CO_2 estimates for the Miocene to Pleistocene based on foraminiferal $\delta^{11}B$ at Ocean Drilling Program Sites 806 and 807 in the Western Equatorial Pacific

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Climate of the Past Discussions

ABSTRACT

Constraints on the evolution of atmospheric CO_2 levels throughout Earth's history are foundational to our understanding of past variations in climate. Despite considerable effort, estimates of past CO_2 levels do not always converge and therefore new records and proxies are valuable. Here we reconstruct atmospheric CO_2 values across major climate transitions over the past 17 million years using the boron isotopic composition ($\delta^{11}B$) 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 and are thought 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_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_2 of ~280 µatm during the Middle Miocene Climate Transition, ~270 µatm during Pliocene Glacial Intensification, and ~50 µatm during the Mid-Pleistocene Climate Transition. There is possible evidence for a larger reduction in glacial pCO_2 during the Mid-Pleistocene Transition compared to interglacial pCO_2, and a minimum in pCO_2 during glacial MIS 30. Our results are consistent with a coupling between pCO_2, temperature and ice sheet expansion throughout the past 17 million years.

Highlights

In this study, we are able to accurately reproduce pCO_2 data from ice cores using $\delta^{11}B$ data from ODP Sites 806 and 807, demonstrating the fidelity of our approach. We therefore apply the same framework to older samples to create a long-term pH and pCO_2 reconstruction for the past 17 million years. We find major increases in surface water pH and decreases in atmospheric pCO_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_2, temperature, and cryosphere stability.

Keywords

Boron isotopes, CO_2, ODP Site 806, ODP Site 807, Miocene, climate

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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.

Relatively 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). A window into atmospheric CO_2 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 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 et al., 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

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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, based on our current understanding, 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 $\delta^{11}B_{carbonate}$ and $\delta^{11}B_{borate}$ 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, 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 Pleistocene, we developed new records from the western tropical

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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. The west Pacific warm pool is a region that is in air-sea CO_2 equilibrium (Takahashi et al., 2014), and is thought to have been so throughout the Cenozoic so has been targeted for past atmospheric CO_2 reconstructions (Pearson and Palmer, 2000; Tripati et al., 2009, 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.

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The WEP sites used in this study are in equilibrium with the atmosphere today (Takahashi et al., 2014), and given their location, are thought to have been throughout the Cenozoic (Pearson and Palmer, 2000; Tripati et al., 2009, 2014). 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 should be smaller in the WEP compared to other regions, due to the relatively small amplitude of changes in temperature and salinity (e.g., compared to eastern boundary current regions or higher latitude sites).

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).

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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).

2.5 Standards

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

$$\delta^{11}B\ (‰) = 1000 \times \left(\frac{^{11}B/^{10}B_{Sample}}{^{11}B/^{10}B_{NIST\ SRM\ 951}} - 1\right) \qquad \textbf{eq. 1}$$

Multiple analyses of external standards were performed to ensure data quality. For boron isotopic measurements, JC_P-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 ± 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 (~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 JC_P-1 (Gutjahr et al., 2014) and a *Porites sp.* coral (NEP). The boron isotopic composition of JC_P-1

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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 $\delta^{11}B_{NEP}$ = 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.

2.6.2 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}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.

2.7 Calculations

Figure 2 shows the planktic $\delta^{11}B$ and B/Ca data compared to other records (benthic $\delta^{18}O$, planktic Mg/Ca, and shell weight), while Figures 3 and 4 show the different histories of seawater $\delta^{11}B$ and alkalinity used for calculations, respectively. Details of calculations are in the Supplemental methods. Following the approach of Tripati et al. (2009, 2014), we explored multiple scenarios for the evolution of seawater boron geochemistry (Fig. 3) and alkalinity for calculations of pCO_2 (Fig. 4). 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. 5). During earlier time intervals, we see there is a greater divergence, reflecting larger uncertainties in seawater $\delta^{11}B$ and alkalinity further back in Earth history.

During the early Pliocene (~4.5 to 3.5 Ma) and prior to 10 Ma, calculations of pCO_2 diverge largely because of disagreement between studies estimating past seawater $\delta^{11}B$ (Fig. 5). However, we also found that reconstructed pH values that utilize each of the $\delta^{11}B_{seawater}$ histories are not significantly different, when the uncertainty in reconstructed pH is fully propagated (Fig. 5 and 6; see also Hönisch et al., 2019). In contrast to the results from

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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 $\delta^{11}B_{seawater}$ history from Greenop et al. (2017) because it is in good agreement with seawater $\delta^{7}Li$ (Misra and Froelich, 2012).

The three alkalinity models used diverge prior to 9 Ma, with a maximum difference at ~13 Ma that is also reflect in reconstructed pCO_2 (Fig. 6). However, all three models yield pCO_2 estimates that are within error of each other when the full uncertainty is considered (Fig. 6). For the remainder of the text, we utilize the model of Caves et al. (2016) for alkalinity and the $\delta^{11}B_{seawater}$ determined by Greenop et al. (2017), as these represent the best constrained estimates for these parameters 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. 5). 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. For the last 800 kyr, reconstructed pCO_2 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. 5, Petit et al., 1999, Siegenthaler et al., 2005, Lüthi et al., 2008). Absolute values for the last glacial/interglacial cycle are also within error of the ice cores values, with the exception of two data points at 47 and 79 ka that have lower pCO_2 in comparison to ice core values. Between MIS 7 and 6, our reconstructions exhibit a decrease in temperature (ΔT) of 2.4°C, an increase in pH (ΔpH) of 0.08 and a decrease in pCO_2 (ΔpCO2) 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

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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

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. 6C) 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 $\delta^{11}B$ data (Fig. 2B) 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. 6D).

3.3 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 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 CO_2 in this transition (DeConto and Pollard, 2003). However, proxies for CO_2 yield conflicting reconstructions for the MCO and MMCT. Alkenone-based reconstructions do not show any variations over the MCO and MMCT with pCO_2 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 pCO_2 values (Gasson et al., 2016). In contrast, published $\delta^{11}B$-based reconstructions supports higher pCO_2 for the MCO of ~350-400 ppm (Foster et al., 2012),

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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 pCO_2 values we reconstruct are during the MCO (Fig. 6E). For the MCO, our estimates are 479 ± 173 µatm (2 SD, n=4, Table 2). 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 $\delta^{11}B_{seawater}$ chosen. We attribute the differences in $\delta^{11}B$-based pCO_2 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 CO_2 derived from alkenones is muted compared to boron-based reconstructions of CO_2, 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 pCO_2, our data support very warm sea surface temperatures in the WEP (36.7°C ± 0.6°C 2SD, n=4; Fig. 7C and 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. 7). Fom 13.5 to 12.9 Ma, we reconstruct an increase of pH ~0.24 and a major decrease of pCO_2 of ~243 µatm 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). 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.

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 pCO_2 peak at ~9 Ma observed

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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 CO_2 of 205 µatm associated with a decrease in temperature of 3.1 °C.

3.5 CO_2 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 pCO_2 values of 541 ± 124 ppm (2 SD, n=3, Table 2).

The Middle Pliocene Warm Period (MPWP – 3.29-2.97 Ma) is considered a relevant geological analogue for future climate change given ~3ºC 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 pCO_2 estimates are critical (Haywood et al., 2016). Our data support values of 515 ± 119 µatm (2 SD, n = 4) are marginally consistent with previously published $\delta^{11}B$-derived pCO_2 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 pCO_2 trends in this study are similar to previous ones, the reconstructed pCO_2 show larger amplitude in our study. pCO_2 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 pCO_2 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 pCO_2 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

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latitudes and subsequent modifications of oceanic circulation (Haug and Tiedemann, 1998). However, modeling from Lunt et al. (2008) supports an additional major role for CO_2 in the glaciation. pCO_2 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 pCO_2 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 pCO_2, with a minimum observed at 4.42 Ma (360 ($\pm^{117}_{85}$) µatm), at 3.45 Ma (323 ($\pm^{100}_{75}$) µatm) and at 2.67 Ma (269 ($\pm^{77}_{59}$) µatm) (Fig. 9). Those atmospheric CO_2 concentrations are consistent with the pCO_2 thresholds proposed by both DeConto et al. (2008) and Koening et al. (2011) for the intensification of Northern Hemisphere glaciation and the low CO_2 (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 CO_2 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 glacials may have enhanced iron fertilization and subsequent carbon export. This could explain why glacial/interglacial amplitudes in WEP pCO_2 values decrease from the MPWP towards the Pleistocene, whereas variations in $\delta^{18}O$ 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

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been raised about the role of atmospheric CO_2 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 CO_2 did not occur during the MPT (Hönisch et al., 2009; Chalk et al., 2017; Dyez et al., 2018).

Although our pCO_2 results for the MPT 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. 9D). 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 pCO_2 values. We also find evidence that during the MPT, glacial pCO_2 declined rapidly from 189 (±30) µatm at MIS 36 (Chalk et al., 2017) to reach a minimum of 164 ($\pm^{44}_{35}$) µatm during MIS 30, the pCO_2 concentrations are however within error when uncertainty is fully propagated,and then remained relatively stable until the end of the MPT whereas interglacial pCO_2 values decrease gradually to reach post-MPT values.

In our record for the last 17 Myr, the lowest pCO_2 is recorded at MIS 30 during the MPT, with values of 164 ($\pm^{44}_{35}$) µatm, which supports an atmospheric CO_2 threshold that leads to ice sheet stability. During this transition, the pCO_2 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 glacials, with glacials exhibiting the largest change across the MPT, would have led to increased sequestration of carbon during glacials 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 pCO_2

On million-year timescales, atmospheric CO_2 is mainly controlled by volcanic activity and silicate weathering. Over the last 17 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. 10), though the timing for the latter is not precise. The high CO_2 levels of the MCO are hypothesized (Foster et al., 2012) to coincide with increasing volcanic activity, associated with the eruption of the Columbia River

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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 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 δ^7Li) 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 δ^7Li (e.g. non-steady state weathering) to stable seawater δ^7Li (e.g., steady state weathering) beginning at roughly 6.8 Ma (Fig. 10).

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 CO_2 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 δ^7Li (Misra and Froelich, 2012) would also be consistent with this hypothesis.

3.9 Outlook and Conclusions

We developed a reconstruction of atmospheric pCO_2 based on $\delta^{11}B$ of planktic foraminifera from ODP Sites 806 and 807 located in the Western Equatorial Pacific for the

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past 17 million years. 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 pCO_2 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 pCO_2 record from ice cores, consistent with the sites being in equilibrium with the atmosphere. The MCO has higher pCO_2 than reconstructions from other sites, with values estimated as 479 ± 173 µatm (2 SD, n=4), potentially linked to the eruption of the Columbia River Flood Basalts, with values declining into the early Pliocene. Major drops in pCO_2 occurred at 12.9, 4.42, 3.45 and 2.71 Ma, including during Pliocene glacial intensification. We find support for a larger reduction in glacial pCO_2 during the MPT compared to interglacial pCO_2, and a minimum in pCO_2 during glacial MIS 30. These findings support 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 pCO_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.

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Figure captions

Figure 1: Modern hydrography of sites. **A.** Map of air-sea pCO_2 (ΔpCO_2, µatm, 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). Depth profiles are for preindustrial parameters, **B.** pH calculated from GLODAP database and corrected from anthropogenic inputs, **C.** Boron isotopic composition of borate ion ($\delta^{11}B_{borate}$) with associated propagated uncertainties.

Figure 2: Foraminiferal data for the Miocene to Recent. A. Benthic foraminiferal $\delta^{18}O$ data (blue line – stack from Lisiecki and Raymo, 2005; black line – compilation from Zachos et al., 2008). B. $\delta^{11}B$ of *T. sacculifer* and *G. rube*r at Sites 806, 807. C. B/Ca ratios. D. Mg/Ca ratios. E. Calculated weight per shell for *T. sacculifer* and *G. ruber*. For Panels B-E: Circles = *T. sacculifer,* Triangles = *G. ruber.*

Figure 3: Different models for the evolution of the boron geochemistry explored as part of this work. Due to the 1‰ uncertainty propagated for $\delta^{11}B_{seawater}$, 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 $\delta^{11}B_{seawater}$ used for the reconstruction of pCO_2 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 $\delta^{11}B_{carbonate}$ values using different models for $\delta^{11}B_{seawater}$.

Figure 4: Different models for the evolution of a second carbonate 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 pCO_2 in this study (orange - Ridgwell and Zeebe, 2005; violet - Tyrell and Zeebe, 2004; green - Caves et al., 2016. B. Reconstructed pCO_2 based on our measured $\delta^{11}B_{carbonate}$ values using different models for alkalinity and $\delta^{11}B_{seawater}$ from Greenop et al., 2017.

Figure 5: Reconstruction of surface pCO_2 for the past 0.8 My from *T. sacculifer* at ODP Sites 806 and 807. Also shown is benthic foraminiferal $\delta^{18}O$ with isotope stages labeled (black line – stack from Lisiecki and Raymo, 2005). pCO_2 values calculated from boron isotopes (colored symbols - this study) with data from the literature (gray symbols: circles - Honisch et al., 2009; half filled circles - Seki et al. 2010; triangles – Foster et al., 2014; diamonds - Stap et al., 2016; squares – Chalk et al., 2017) and ice core pCO_2 (black line - LePetit at al., 2009). 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 6: Proxy data for the past 17 million years in the Western Equatorial Pacific compared to benthic oxygen isotope data. **A.** Benthic $\delta^{18}O$ (blue line – stack from Lisiecki and Raymo, 2005; black line – compilation from Zachos et al., 2008). **B.** Benthic $\delta^{13}C$ (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 $\delta^{11}B$ of *T. sacculifer* and *G. ruber* using $\delta^{11}B_{seawater}$ 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. S17 for the dark (green or blue) envelope, while the light (green or blue) envelope are the uncertainties calculated based on eq. S16 (taking into account uncertainty on $\delta^{11}B_{seawater}$).

Figure 7: 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 data. **A.** Benthic $\delta^{18}O$ (black line – compilation from Zachos et al., 2008). **B.** Benthic $\delta^{13}C$ (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

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S6 and S7 (this study). **D.** Reconstructed pCO_2 (µatm) from this study (blue symbols) using boron-based pH and alkalinity from Caves et al. (2016). 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 $\delta^{11}B_{seawater}$). In grey are $\delta^{11}B$-derived estimates from the literature (open triangles – Foster et al., 2012 for Site 761B; half-filled diamonds – Foster et al., 2012 for Site 962A; open circles – Badger et al., 2013 for locality in Malta; half-filled triangles – Greenop et al., 2014 for Site 761B; filled diamonds - Stap et al., 2016 for Site 1264).

Figure 8: 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 $\delta^{18}O$ (black line – compilation from Zachos et al., 2008). **B.** Benthic $\delta^{13}C$ (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. S17 for the dark (green or blue) envelope, while the light (green or blue) envelope are the uncertainties calculated based on eq. S16 (taking into account uncertainty on $\delta^{11}B_{seawater}$). In black are published estimates from ice core data (circles - Yan et al., 2019). In grey are $\delta^{11}B$-derived estimates from the literature (light grey circles – Honisch et al., 2009 for Site 668B; half-filled circles – Seki et al., 2010 for Site 999A; medium grey circles – Bartoli et al., 2011 for Site 999A; unfilled triangles – Martinez-Boti et al., 2015b for Site 999A; squares – Chalk et al., 2017 for Site 999A; half-filled diamonds – Dyez et al., 2018 for Site 668B; grey triangles - de la Vega et al., 2020 for Site 999A).

Figure 9: 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 (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 equations 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. S17 for the dark (green or blue) envelope, while the light (green or blue) envelope are the uncertainties calculated based on eq. S16 (taking into account uncertainty on $\delta^{11}B_{seawater}$). In black are published estimates from ice core data (line - LePetit at al., 2009; circles - Yan et al., 2019). In grey are $\delta^{11}B$-derived estimates from the literature (grey circles – Honisch et al., 2009 for Site 668B; half-filled circles – Seki et al., 2010 for Site 999A; squares – Chalk et al., 2017 for Site 999A; half-filled diamonds – Dyez et al., 2018 for Site 668B).

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 composites. **A.** Benthic $\delta^{18}O$ (blue line – compilation from Lisiecki and Raymo, 2005, black line – compilation from Zachos et al. 2008). **B.** 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 (µatm) using boron-based pH and alkalinity from Caves et al. (2016), data presented are from this study (circle - *T. sacculifer* and triangle - *G. ruber*). Propagated uncertainties are given by eq. S17 for the dark (green or blue) envelope, while the light (green or blue) envelope are the uncertainties calculated based on eq. S16 (taking into account uncertainty on $\delta^{11}B_{seawater}$). In grey are $\delta^{11}B$-derived estimates from the literature (light grey circles – Honisch et al., 2009 for Site 668B; half-filled circles – Seki et al., 2010 for Site 999A; medium grey circles – Bartoli et al., 2011 for Site 999A; unfilled triangles – Foster et al., 2012 for Site 761B; top half-filled diamonds – Foster et al. 2012 for Site 962A; open squares – Badger et al., 2013 for locality in Malta;

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left-filled triangle – Greenop et al., 2014 for Site 761B; upside down triangle – Foster et al., 2014 for Site 999A; grey triangles – Martinez-Boti et al., 2015b for Site 999A; grey diamonds – Stap et al., 2016 for Site 1264; grey squares – Chalk et al., 2017 for Site 999A; bottom half-filled diamonds – Dyez et al., 2018 for Site 668B; grey triangles - de la Vega et al., 2020 for Site 999A). 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. Light grey bands represent hypothesized La Nina-like intervals and dashed dark grey bands represent hypothesized El Nino-like intervals (Farell 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 (Farell 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).

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Table 1: Boxe core information.

Cruise	Leg	Hole	N (°)	E (°)	Depth (m)
ODP	130	807	3.61	156.62	3638
ODP	130	806	0.32	159.37	2521

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Table 2: Comparison of reconstructed pCO_2 values for key intervals in the last 17 Myr.

Mid-Pleistocene transition (1.2-0.8 Ma)

MIS (G)	pCO_2 (µatm)	Reference	MIS (IG)	pCO_2 (µatm)	Reference	pCO_2 amplitude IG-G (µatm)
20	171	This study	**21**	245	This study	74
22	180	This study	**23**	222	This study	42
24	*nd*		**25**	288	This study	*nd*
26	168	This study	**27**	*nd*		*nd*
28	165	This study	**29**	*nd*		*nd*
30	164	This study	**31**	295	Hönisch et al., 2009 (N-TIMS)	131
32	218	Chalk et al., 2017	**33**	323	Chalk et al., 2017	105
34	197	Chalk et al., 2017	**35**	315	Chalk et al., 2017	118
36	189	Chalk et al., 2017	**37**	295	This study, Chalk et al., 2017	106
			39	306	This study	*nd*

Early Pliocene Warm Period (4.7-4.5 Ma)

pCO_2 (µatm)	Reference
541 ± 124	This study (2 SD, n=3)

Middle Pliocene Warm Period (3.29-2.97 Ma)

pCO_2 (µatm)	Reference
515 ± 119	This study (2 SD, n=4)
320 ± 130	Martinez-Boti, 2015b (2 SD, n=8)

Miocene Climate Optimum (17-14 Ma)

pCO_2 (µatm)	Reference
479 ± 173	This study (2 SD, n=4)
350-400	Foster et al., 2012
300-500	Greenop et al., 2014
470-630	Sosdian et al., 2018

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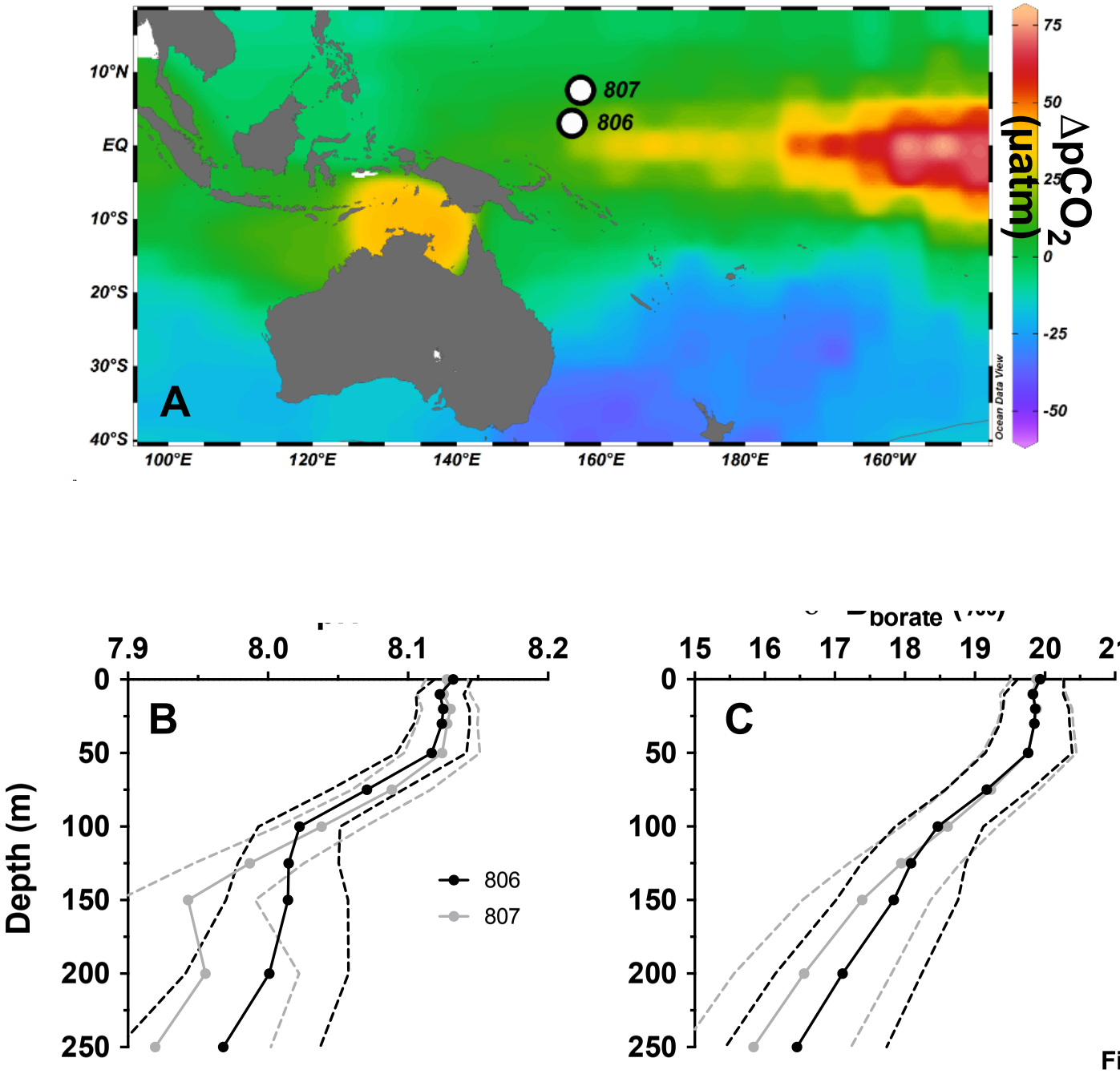

Figure 1

https://doi.org/10.5194/cp-2020-158
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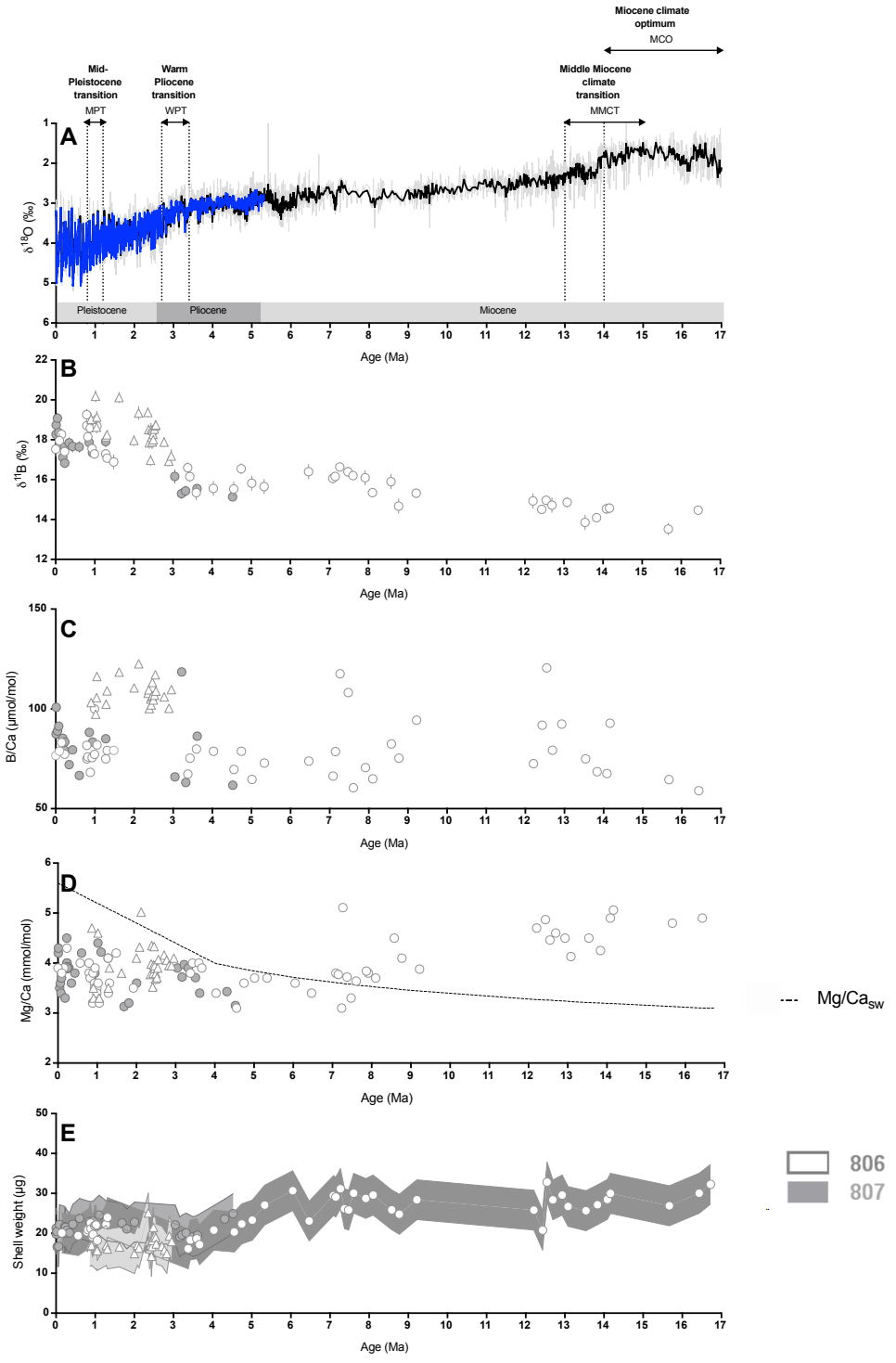

Figure 2

https://doi.org/10.5194/cp-2020-158
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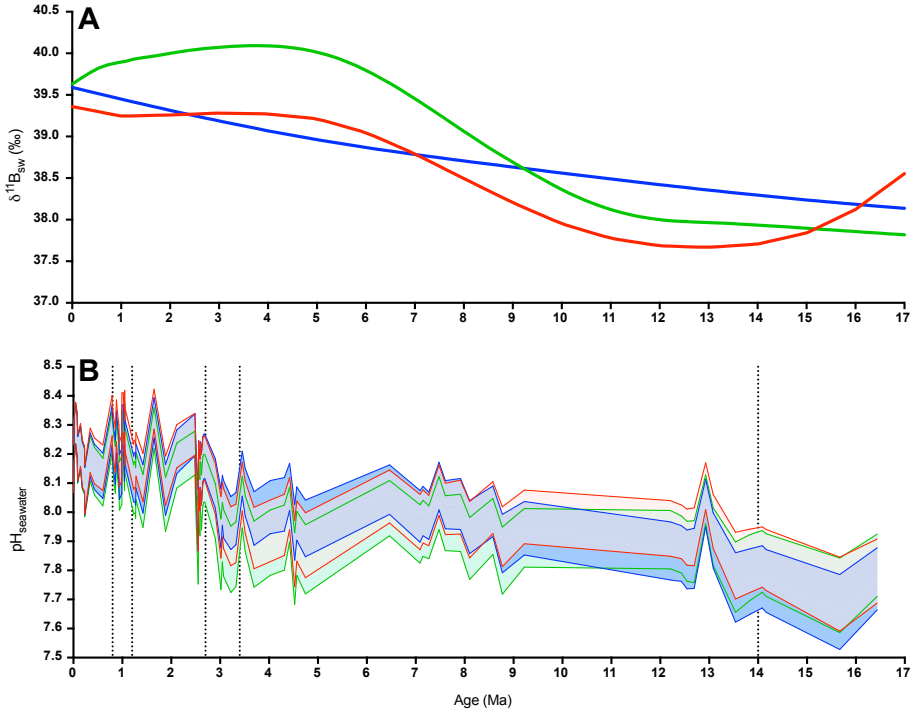

Figure 3

https://doi.org/10.5194/cp-2020-158
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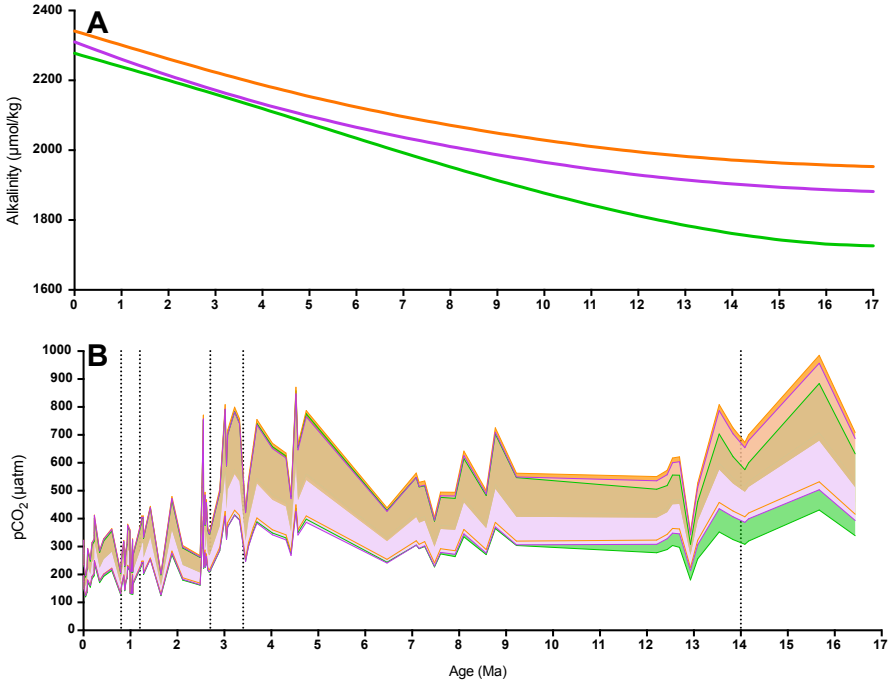

Figure 4

https://doi.org/10.5194/cp-2020-158
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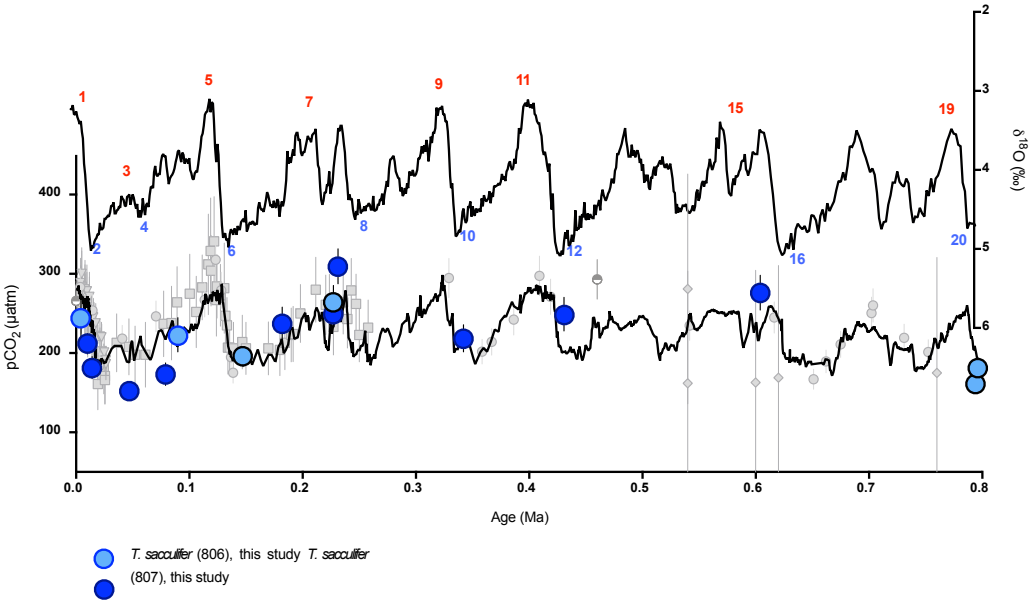

Figure 5

https://doi.org/10.5194/cp-2020-158
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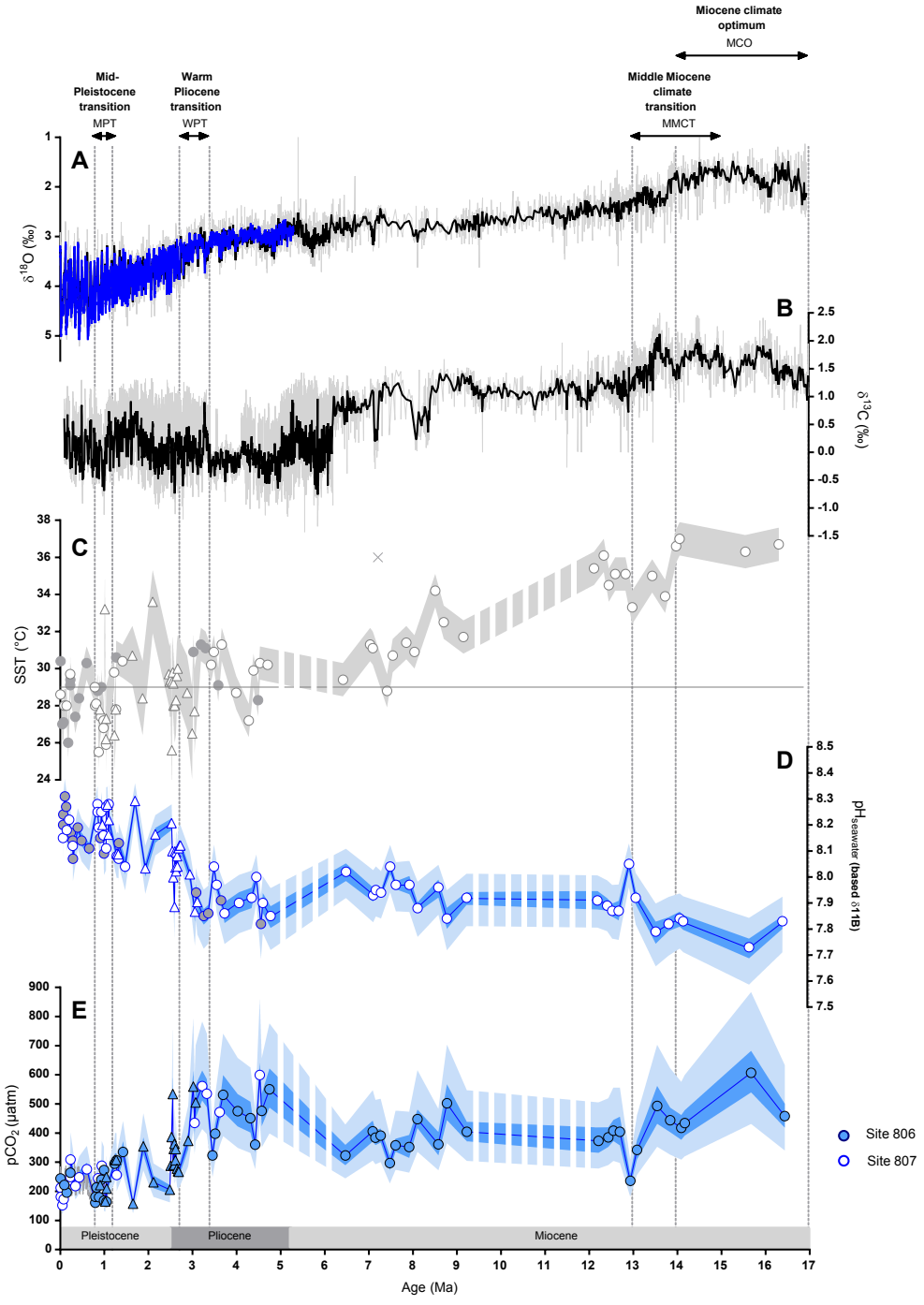

Figure 6

https://doi.org/10.5194/cp-2020-158
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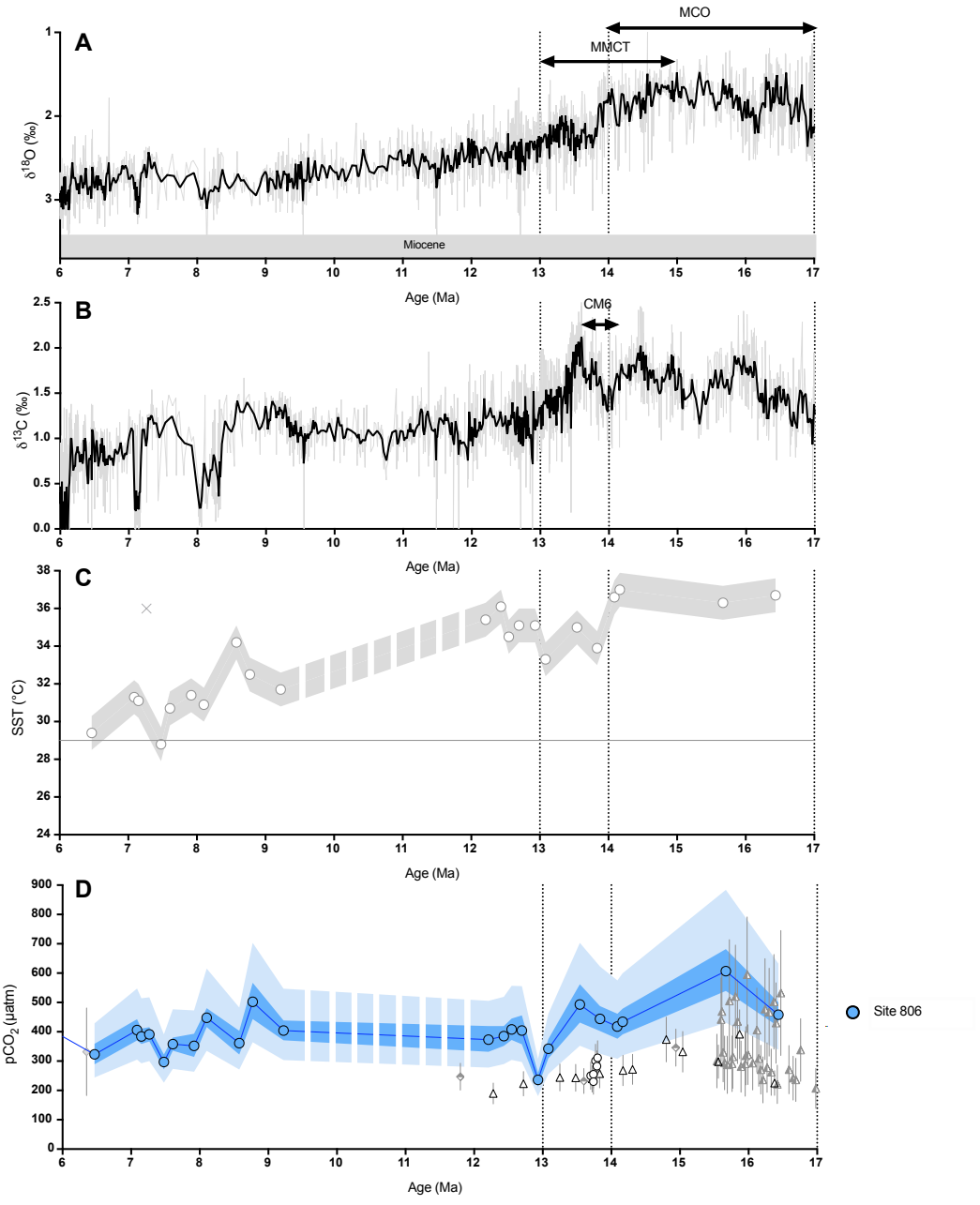

Figure 7

https://doi.org/10.5194/cp-2020-158
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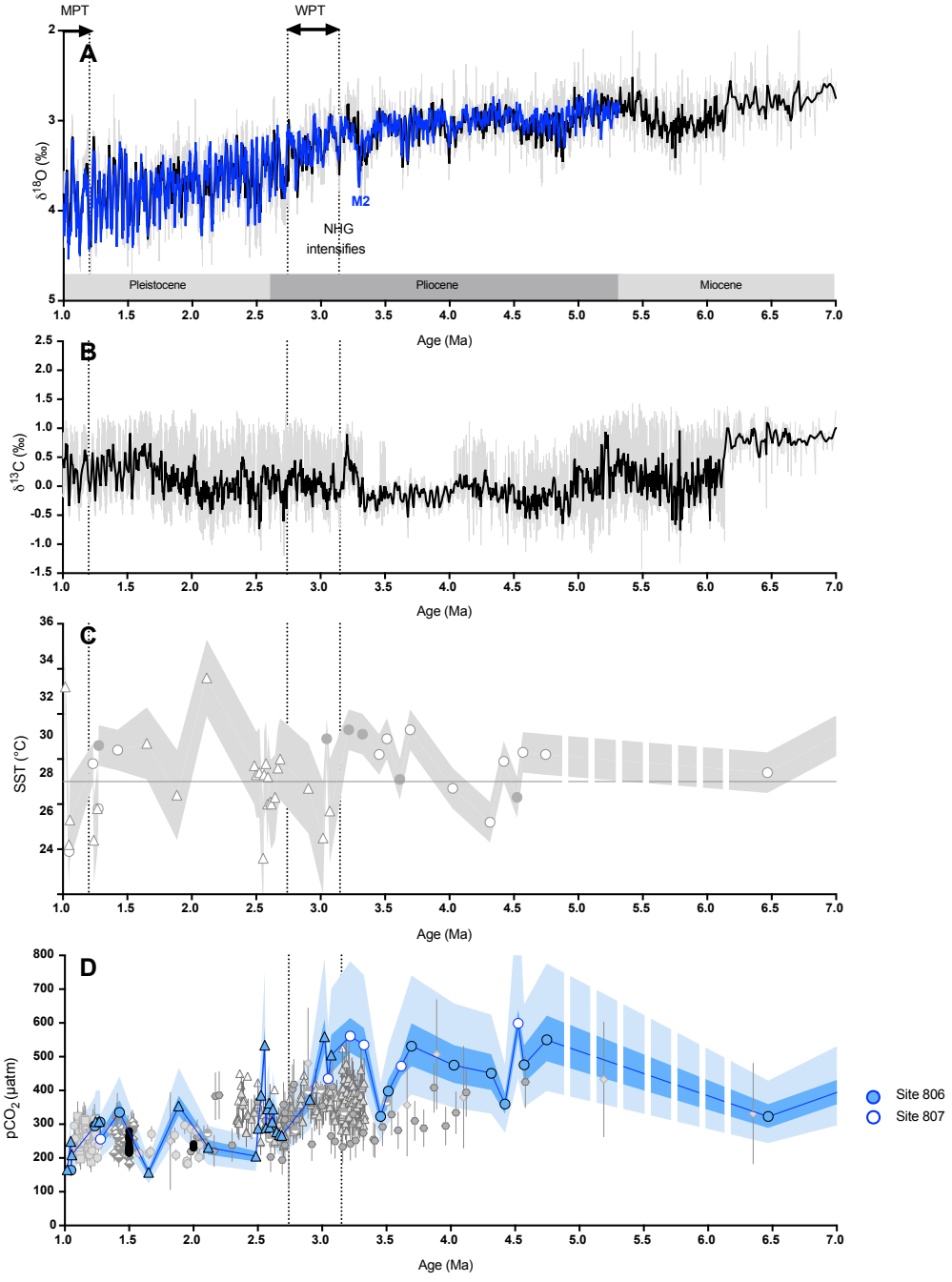

Figure 8

https://doi.org/10.5194/cp-2020-158
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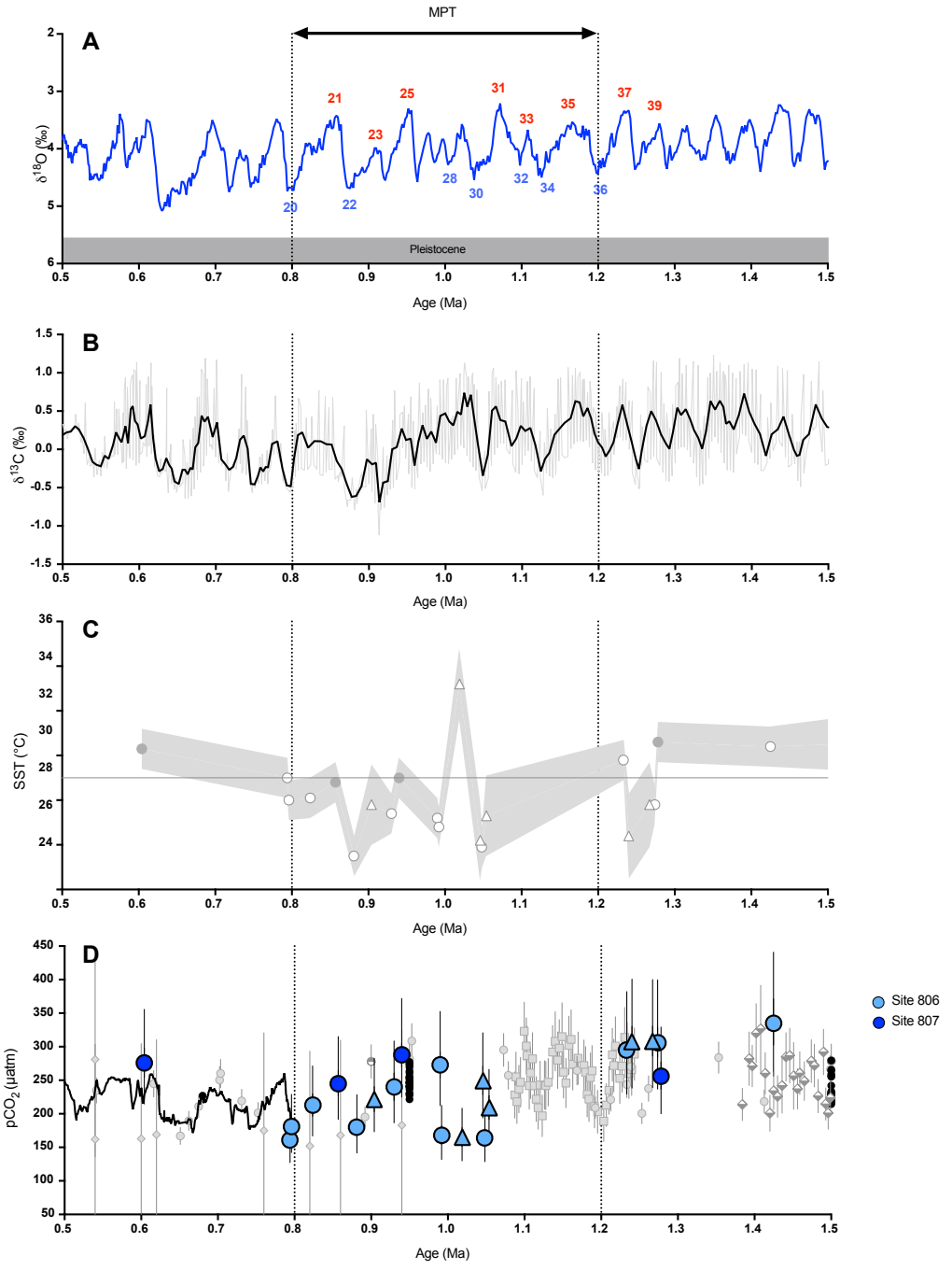

Figure 9

https://doi.org/10.5194/cp-2020-158
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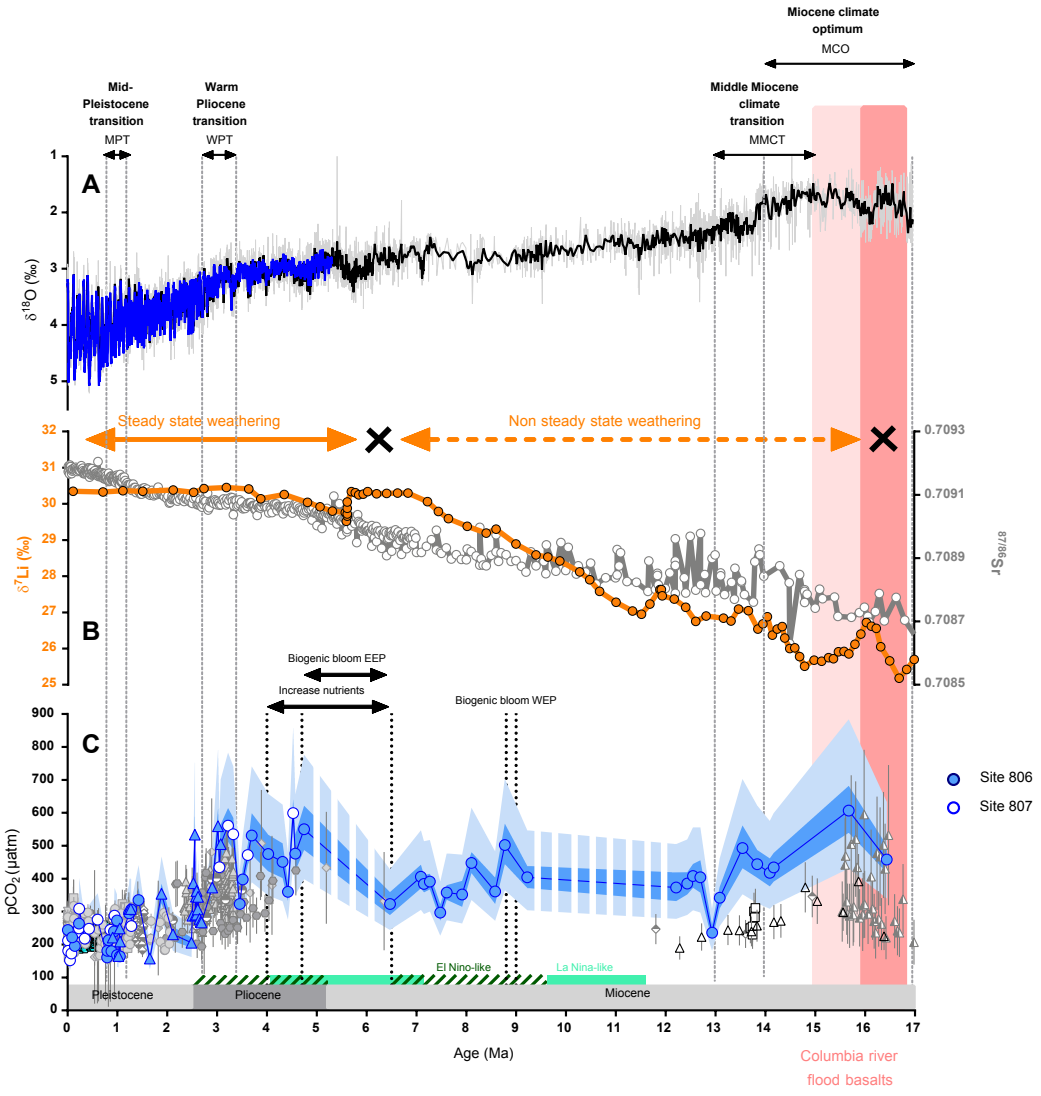

Figure 10