Eccentricity-paced atmospheric carbon-dioxide variations across the middle Miocene climate transition

Markus Raitzsch¹,², Jelle Bijma², Torsten Bickert¹, Michael Schulz¹, Ann Holbourn³, Michal Kučera¹

¹MARUM – Zentrum für Marine Umweltwissenschaften, Universität Bremen, Leobener Straße, 28359 Bremen, Germany
²Alfred-Wegener-Institut, Helmholtz-Zentrum für Polar-und Meeresforschung, Am Handelshafen 12, 27570, Bremerhaven, Germany
³Christian-Albrechts-Universität, Institut für Geowissenschaften, 24118 Kiel, Germany

Correspondence to: Markus Raitzsch (mraitzsch@marum.de)

Abstract. The middle Miocene climate transition ~14 Ma marks a fundamental step towards the current “icehouse” climate, with a ~1 ‰ δ¹⁸O increase and a ~1 ‰ transient δ¹³C rise in the deep ocean, indicating rapid expansion of the East Antarctic Ice Sheet associated with a change in the operation of the global carbon cycle. The variation of atmospheric CO₂ across the carbon-cycle perturbation has been intensely debated as proxy records of pCO₂ for this time interval are sparse and partly contradictory. Using boron isotopes (δ¹¹B) in planktonic foraminifers from drill site ODP 1092 in the South Atlantic, we show that long-term pCO₂ variations between ~14.3 and 13.2 Ma were paced by 400 k.y. eccentricity cycles, with decreasing pCO₂ at high eccentricity and vice versa. Our data support results from a carbon-cycle model study, according to which increased monsoon intensity at high eccentricity enhanced weathering and river fluxes in the tropics, resulting in increasing carbonate and organic carbon burial and hence decreasing atmospheric CO₂. In this scenario, a combination of the eccentricity-driven climatic cycle and enhanced meridional deep-ocean circulation during Antarctic ice-sheet expansion may have both contributed to the pCO₂ rise following Antarctic glaciation, acting as a negative feedback on the progressing glaciation and helping to stabilize the climate system on its way to the late Cenozoic “icehouse” world.

1 Introduction

With rapid cooling of Antarctica and associated expansion of the East Antarctic Ice Sheet (EAIS), the middle Miocene climate transition (MMCT) ~14 Ma marks a fundamental step towards the current “icehouse” climate (Woodruff and Savin, 1991; Flower and Kennett, 1994). The transition is characterized by a δ¹⁸O increase of ~1 ‰ in the deep ocean between 13.9 and 13.8 Ma and a positive (~1 ‰) δ¹³C excursion between 13.9 and 13.5 Ma indicating a fundamental change in global carbon-cycle dynamics (Shevenell et al., 2004; Holbourn et al., 2005, 2007). The carbon-isotope maximum (CM) event CM6 is the last and most prominent of at least six maxima within a long-lasting δ¹³C excursion, the “Monterey Excursion”, spanning ~16.9 to ~13.5 Ma and apparently paced by long-term changes in the 400 k.y. eccentricity cycle of the Earth’s orbit (Vincent and Berger, 1985; Holbourn et al., 2007). These δ¹³C maxima hint at a major reorganization of the marine carbon
cycle, and the temporal coincidence of CM6 with expansion of the Antarctic ice sheet indicates that the glaciation may have been caused by cooling due to reduced CO\textsubscript{2} radiative forcing (Greenop et al., 2014).

The CM events within the Monterey Excursion have been traditionally considered as episodes of increased organic-carbon (C\textsubscript{org}) burial resulting in \textsuperscript{12}C-depleted seawater, atmospheric CO\textsubscript{2} drawdown and associated cooling and buildup of continental ice (Vincent and Berger, 1985; Flower and Kennett, 1993, 1994; Badger et al., 2013). In a recent study, it was proposed that a more sluggish meridional Pacific Ocean overturning circulation, due to reduced deep-water formation in the Southern Ocean, enhanced the weathering of \textsuperscript{13}C-enriched shelf carbonates, and that the expansion of the terrestrial carbon reservoir may have been responsible for the \textdelta\textsuperscript{13}C excursion CM6, associated with a decrease in pCO\textsubscript{2} (Ma et al., 2018).

Another explanation for the CM events refers to the “missing sink” mechanism (Lear et al., 2004), where large areas of Antarctic silicate rocks are covered by ice caps, which reduce chemical weathering and, thus, limit their potential as a sink for atmospheric CO\textsubscript{2} (Pagani et al., 1999; Lear et al., 2004; Shevenell et al., 2008). While all scenarios result in increasing marine \textdelta\textsuperscript{13}C, the former two act as positive feedbacks (falling CO\textsubscript{2}) promoting ice-sheet expansion, and the latter as a negative feedback (rising CO\textsubscript{2}) preventing global climate from evolving to an even colder state.

The nature of the carbon cycle perturbation could be better constrained if we knew the evolution of atmospheric CO\textsubscript{2} across the MMCT. Understanding the role of the carbon cycle in this cooling step is a key to assess Earth-system sensitivity to CO\textsubscript{2} forcing and the long-term stability of the Antarctic ice sheet under rising CO\textsubscript{2} concentrations. However, most proxy records for the history of pCO\textsubscript{2} across the MMCT are incomplete or at low resolution, thus prohibiting resolution of the CM events (Pagani et al., 1999; Kürschner et al., 2008; Foster et al., 2012; Ji et al., 2018; Sosdian et al., 2018; Super et al., 2018) and making it difficult to identify the mechanism responsible for the major step into the “icehouse” world. The only high-resolution pCO\textsubscript{2} reconstruction across CM6 is based on alkenone \textdelta\textsuperscript{13}C data from a Miocene outcrop on Malta (Badger et al., 2013), but it does not reveal a significant change.

Therefore, to better understand atmospheric CO\textsubscript{2} evolution over the period of EAIS growth, we generated a high-resolution reconstruction based on \textdelta\textsuperscript{11}B measurements of fossil planktonic foraminifers from the South Atlantic (Figs. 1, 2). The boron isotopic composition of biogenic carbonates is a reliable recorder of ambient pH, which in turn is closely linked to atmospheric pCO\textsubscript{2} in oligotrophic surface waters. Our record fully captures the carbon isotope excursions CM5b and CM6, which include the major expansion of the EAIS.

1 Material and Methods

1.1 Sampling strategy

This research used samples from Ocean Drilling Program (ODP) Site 1092, located at 46.41 S and 7.08 E (Fig. 1) in a water depth of 1973 m. The interval studied (~178-184 mcd, see Table S1) consists of nannofossil ooze with excellent carbonate preservation, as shown by SEM-imaged undissolved coccoliths, which are susceptible to corrosion (Fig. 2). The shown example is from ~13.8 Ma, where pH was low, but shell preservation is similarly good throughout the entire record.
Approximately 200 specimens of the cold-water dwelling planktonic foraminifer *G. bulloides* were picked for δ\(^{11}\)B analysis from 35 processed 10 cm\(^3\) sediment samples. In addition, about 5 to 8 specimens of the benthic foraminifer *Cibicidoides wuellerstorfi* were picked from 14 intervals to reconstruct deep-sea pH (Table S1). Today, surface-water p\(\text{CO}_2\) at Site 1092 is close to equilibrium with the atmosphere (\(\Delta p\text{CO}_2\text{sea-air} < -30 \mu\text{atm}\) (Takahashi et al., 1993, 2009)). Plankton tow data revealed that *G. bulloides* generally lives within the upper 100 m of the water column (Mortyn and Charles, 2003). Based on DIC (dissolved inorganic carbon) and TA (total alkalinity) from seasonal TCO2+TALK (Goyet et al., 2000), and temperature and salinity from WOA13 data sets, modern gradients in pH and p\(\text{CO}_2\) are small at this site within the upper 200 m of the water column. During the austral spring season, when the shell flux of *G. bulloides* is highest (Jonkers and Kučera, 2015; Raitzsch et al., 2018), the differences in pH and p\(\text{CO}_2\) within this depth range are -0.03 and 17 \(\mu\text{atm}\), respectively. Hence, we expect *G. bulloides* to be a reliable recorder of subsurface pH and p\(\text{CO}_2\).

1.2 Age model

The age model used in this study is adopted from Kuhnert et al. (2009), but was revised to bring it in line with the astronomically tuned stable isotope record of the reference IODP Site U1338 (Holbourn et al., 2014) (Fig. 3, Table S2). In addition, chron C5ADn (top) identified at 182.51 mcd and originally dated to 14.178 Ma (Censarek and Gersonde, 2002) was tied to 14.081 Ma from the age model of Site U1338 (Holbourn et al., 2014). For direct comparison of our p\(\text{CO}_2\) record with the boron-based reconstructions available from the literature, the age models of ODP 761 (Holbourn et al., 2004, Foster et al., 2012, Sosdian et al., 2018) and the Blue Clay Formation of Ras-il-Pellegrin on Malta (Abels et al., 2005; Badger et al., 2013) were also re-tuned to match the reference curve U1338 (Table S2). Based on these revised age models, the δ\(^{18}\)O and δ\(^{13}\)C profiles of Sites 1092, ODP 791 and the Blue Clay Formation generally show a good agreement with those of Site U1338 (Fig. 3).

1.3 Boron isotope analysis

Foraminifer shells were cleaned following the protocol of Barker et al. (2003). Trace metal and boron isotope (δ\(^{11}\)B) were measured following Raitzsch et al. (2018). Briefly, the cleaned samples were dissolved in 60 \(\mu\text{L}\) of 1 N HNO\(_3\) and micro-distilled on a hotplate to separate boron from the carbonate matrix. The microdistillation method has been proven to yield a B recovery of \(\sim100\%\), a low procedural blank, and accurate results, even at low B concentrations (Gaillardet et al., 2001; Wang et al., 2010; Misra et al., 2014; Raitzsch et al., 2018). The distillate containing only boron was diluted with 2 \% HNO\(_3\) and analyzed for isotopes in triplicate using a Nu Plasma II multi-collector ICPMS at AWI (Bremerhaven, Germany) that is equipped with a customized detector array of 16 Faraday cups and 6 secondary electron multipliers (SEM), also termed ion counters (IC). \(^{11}\)B and \(^{10}\)B were collected in IC5 and IC0, respectively, at a boron concentration of \(\sim3\) ppb. As three of the SEMs were later replaced by Daly detectors, \(^{11}\)B and \(^{10}\)B of *C. wuellerstorfi* samples were collected in D5 and D0, respectively, at a boron concentration of \(\sim2\) ppb. \(^{11}\)B/\(^{10}\)B was standardized against concentration-matched NBS 951 using the standard-sample-standard bracketing technique, and frequent analysis of control standard AE121 with an isotopic
composition similar to that of foraminifers was monitored to ensure accuracy of measurement. Measurement uncertainties are reported as 2 standard deviations (2σ) derived from triplicate measurements or as ±0.30 ‰ (for SEM-analyzed samples) and ±0.25 ‰ (for Daly-analyzed samples) determined from the long-term reproducibility (2σ) of the control standard, whichever is larger (see Table S1).

1.4 Reconstruction of pH and pCO₂ from δ¹¹B

Planktonic δ¹¹B was converted to sea-surface pH (Fig. S1) using the δ¹¹B_foram/δ¹¹B_borate relationship for *G. bulloides* (Raitzsch et al., 2018), where δ¹¹B_borate is determined by the dissociation constant *pK₆* and δ¹¹B seawater. *pK₆* is dependent on salinity, temperature and pressure. Mg/Ca was taken from Kuhnert et al. (2009) for temperature estimates, and pressure was chosen from 50 m water depth, the assumed average calcification depth of *G. bulloides*. To account for seawater Mg/Ca, which was approximately 3.2 mol/mol ~14 Ma ago (Stanley and Hardie, 1999; Horita et al., 2002), Mg/Ca temperatures were corrected by applying a correction factor of 0.825 to the pre-exponential constant of the Mg/Ca-temperature equation of Mashiotta et al. (1999). This correction factor was previously determined for *G. sacculifer* by Evans and Müller (2012), but we assume that the effect of seawater Mg/Ca on shell Mg/Ca is similar for *G. bulloides*, since both have similar Mg/Ca ratios. However, the difference between Mg/Ca_sw-corrected and non-corrected Mg/Ca absolute temperatures is in the order of 1.7 °C, but the relative changes are nearly identical.

Relative salinity changes were estimated by converting δ¹⁸O, derived from planktonic foraminiferal δ¹⁸O and Mg/Ca temperatures (Shackleton, 1974), to salinity using a δ¹⁸O: salinity gradient of 1.1 ‰ (the change in δ¹⁸O per salinity unit). This minimum gradient is required to keep the upper ocean density difference across the Subantarctic Front to enable the formation of Antarctic Intermediate Water (Kuhnert et al., 2009), which existed as Southern Component Intermediate Water (SCIW) since at least ~16 Ma (Shevenell and Kennett, 2004) and spread into all oceans adjacent to the Southern Ocean (Wright et al., 1992). However, since the computed absolute salinity values are unrealistically low, an offset of 17.2 (psu) was added to the entire salinity record to achieve post-glaciation values similar to today. The reconstructed relative salinity change across the MMCT at Site 1092 is slightly more than 1 (psu), which is equivalent to the salinity gradient across the Subantarctic front today. Deep-sea pH from *C. wuellerstorfi* δ¹¹B_foram shown in Fig. S1 was calculated using a δ¹¹B_foram: δ¹¹B_borate relationship of 1:1 (Rae et al., 2011), deep-sea temperatures derived from Mg/Ca (data courtesy of H. Kuhnert) using the species-specific calibration of Raitzsch et al. (2008), a salinity of 34 (psu), and a paleo-water depth of 1794 m.

The most critical parameter for correct conversion to pH is δ¹¹B_seawater, which is fortunately well constrained for the middle Miocene. We used a δ¹¹B_seawater value of 37.80 ‰, which is the mean value from different independent studies and in close agreement with each other to within 0.1 ‰ (1σ) (Pearson and Palmer, 2000; Foster et al., 2012; Raitzsch and Hönisch, 2013; Greenop et al., 2017), and also comparable to the 38.5 ‰ modeled by Lemarchand et al. (2000).

To calculate pCO₂ from sea-surface pH, a second carbonate system parameter needs to be constrained. For this study, we used a sea-surface TA of 2000 µmol/kg, which is in line with various carbon cycle model results (Tyrrell and Zeebe, 2004;
To assess whether a pH effect on Mg/Ca-derived temperatures and, in turn, pH-corrected temperature influences estimated $pCO_2$ as shown by Gray and Evans (2019), we used a slightly modified version of their ‘MgCaRB’ package written in ‘R’. Briefly, this program corrects Mg/Ca for the effects of salinity and pH and the resulting change in the temperature effect on $pK_B$ and hence on pH, until the change in both parameters between two iterations fall below certain threshold values. The original R code from Gray and Evans (2019) uses sediment age and associated error to determine past salinity and its uncertainty, based on the secular seawater salinity model from Spratt and Lisiecki (2016). Hence, the model is limited to the last ~800 ka. To adopt the code for our Miocene study, we slightly modified ‘MgCaRB.d11B.R’ from Gray and Evans (2019) by allowing for directly use estimated salinities and associated uncertainties. In addition, the seawater B isotopic composition was changed from 39.61 ‰ to the Miocene value of 37.80 ‰ (see code in the supplement). While the Miocene relative salinity variations can be constrained from changes in benthic foraminiferal $\delta^{18}O$, the absolute salinity levels are difficult to determine. Hence this approach only allows for comparing relative differences between the conventionally and the iteratively corrected $pCO_2$ estimates. For this reason, the temperature and $pCO_2$ values of the two approaches were brought in coincidence at the start of the record (Fig. S2).

Uncertainties of $pCO_2$ estimates were fully propagated from individual uncertainties in pH (converted from 2σ measurement uncertainty of $\delta^{11}B$), TA ($\pm100$ µmol/kg), temperature ($\pm1$ °C), and salinity ($\pm1$ psu) using the ‘seacarb’ package (Lavigne et al., 2011) programmed in ‘R’. The applied temperature uncertainty is similar to the mean difference of ~2 °C between the non-corrected and pH-corrected Mg/Ca temperatures (Fig. S2), while the TA uncertainty is similar to the mean standard deviation of ±130 µmol/kg between different TA models and clearly encompassing the standard deviation of ±50 µmol/kg for each model across the MMCT (Sosdian et al., 2018). The applied salinity uncertainty encompasses the potential salinity change across the MMCT. We did not apply uncertainties for Mg/Ca$_{sw}$ and $\delta^{11}B_{sw}$, since both are systematic errors and would just shift the $pCO_2$ record in either direction.

3. Results

3.1 Carbon dioxide record

Our boron-based record indicates a steady $pCO_2$ increase from ~390 to 520 ± 60 µatm between 14.25 and 14.08 Ma and a subsequent decrease to ~360 µatm until 13.87 Ma, culminating after the onset of the major ice-sheet expansion (Fig. 4E). It should be noted that this ~160 µatm drop in $pCO_2$ occurred at a time of northward shifting Southern Ocean fronts, which is only related to a step-like drop in sea-surface temperature (SST) and salinity around 14 Ma at this site (Fig. 4C) (Kuhnert et al., 2009). At 13.82 Ma, when SST had already reached a lower stable level and after the inception of the ~1 ‰ rise in benthic $\delta^{18}O$ (Fig. 4A), $pCO_2$ increased rapidly by ~120 µatm and displayed high-amplitude variations of more than 50 µatm until 13.57 Ma. This transient rise in $pCO_2$ ended with a decrease to ~360 µatm and much reduced variability after 13.53 Ma.
Sea-surface pH values within the entire record range from 7.87 to 8.07 ± 0.05 (Figs. 4D and S1), while deep-sea pH varies between 7.68 and 7.82 ± 0.07 over the same interval. Interestingly, the pH offset between the surface and deep ocean is nearly identical to the modern gradient and does not change substantially within our Miocene record (Fig. S1).

It is possible that the overall absolute $p$CO$_2$ values and the glacial rise after 13.82 Ma are overestimated by up to ~80 µatm and ~30 µatm, respectively, since pH might affect planktonic foraminiferal Mg/Ca and hence the sea-surface temperature estimations (Fig. S2) (Gray and Evans, 2019). Since differences in relative $p$CO$_2$ changes are not substantial and absolute values are within uncertainties between both reconstructions, confirming the overall robustness of our $p$CO$_2$ record, we report the uncorrected data here.

The $p$CO$_2$ variations within the studied time interval show a remarkable agreement with variations in δ$^{13}$C that correspond to CM5b and CM6 (Fig. 5). Accordingly, the maxima at ~14.1 and 13.7 Ma as well as the minima at ~13.9 and 13.5 Ma indicate that atmospheric CO$_2$ levels were paced by the 400 k.y. eccentricity cycle, as also demonstrated by evolutive harmonic and power spectral analyses (Fig. 6).

### 3.2 Sensitivity tests

Given that we propose an eccentricity-modulated change in TA input to the ocean, which might have affected our $p$CO$_2$ reconstruction, we carried out several sensitivity tests. The first tests demonstrate that either constant salinity, a ~1 unit change in salinity, or TA co-varying with salinity using a modern TA-S relationship, has no discernible effect on $p$CO$_2$ estimates (Fig. 7A). As ODP Site 1092 was apparently influenced by a northward migration of the Southern Ocean fronts, we tested the potential impact on calculated $p$CO$_2$ by varying TA with temperature. Even at an unrealistically high total change of 400 µmol/kg, calculated relative $p$CO$_2$ changes are very similar after the EAIS expansion at ~13.9 Ma (Fig. 7B).

Given the modern sea-surface TA gradient across the polar frontal system of ~100 µmol/kg (higher in the south), we conclude that the increasing influence of southern-sourced surface waters on $p$CO$_2$ estimates at our study site is comparatively small. When in our simulations TA was varied with pH or eccentricity (both on short and long periodicity) by ±100 µmol/kg, $p$CO$_2$ reconstructions are almost identical among each other (Figs. 7C-7H). On the other hand, at TA variations of ±400 µmol/kg, the $p$CO$_2$ estimates may differ substantially between the different scenarios, but the general shape of the record remains more or less the same. Given that total variations in TA of 800 µmol/kg are very unlikely, we suggest that periodic changes in monsoon-driven TA do not affect our $p$CO$_2$ estimates significantly.

### 4. Discussion

#### 4.1 Comparison with other $p$CO$_2$ records

Our $p$CO$_2$ data broadly agree with reconstructed long-term trends based on planktonic foraminiferal δ$^{14}$B (Foster et al., 2012) and paleosol δ$^{13}$C (Ji et al., 2018), despite a few differing values before CM5b and during CM6 (Fig. 3). The boron isotope...
data from the Mediterranean Sea by Badger et al. (2013) also show decreasing $pCO_2$ values after 13.8 Ma, but no rebound after 13.75 Ma and no rise after 13.85 Ma, although these discrepancies may be due to the different sampling resolutions. In contrast, the $pCO_2$ reconstructions from high-resolution alkenone $\delta^{13}C$ data from Badger et al. (2013) are similar to the estimates of Super et al. (2018), which are considerably lower than the boron-based reconstructions and do not exhibit significant changes CM6. This might be related to the insensitivity of the alkenone proxy at low to moderate $pCO_2$ levels (Badger et al., 2019). It is worth noting that our $pCO_2$ record reveals a striking match with the box model output presented in Ma et al. (2011), suggesting a linear response of weathering-controlled nutrient input to changes in orbital parameters with attendant variations in ocean carbon reservoir during the middle Miocene.

### 4.2 The role of eccentricity in the carbon cycle

The $pCO_2$ increase preceding and following the EAIS expansion closely tracks the global $\delta^{13}C$ history of CM5b and CM6 (Fig. 4), emphasizing a fundamental link between changes in the ocean carbon cycle and atmospheric carbon dioxide. The CM peaks correspond to minima in the 400 k.y. eccentricity cycle, suggesting that $\delta^{13}C$ variations were related to changes in monsoon and weathering intensity (Holbourn et al., 2007; Ma et al., 2011). Monsoon intensity is paced by solar radiation variations caused by precessional cycles but their amplitude variations are modified by eccentricity. More precisely, higher eccentricity results in larger precession amplitudes and hence in larger wet/dry variations in the tropics (e.g., Wang, 2009), stronger physical and chemical weathering, and ultimately in an increased input of particulate organic material, dissolved inorganic carbon, alkalinity and nutrients to the oceans (e.g., Clift and Plumb, 2008; Ma et al., 2011; Wan et al., 2009). The potential influence of alkalinity variations on our $pCO_2$ record is shown in Fig. 7 and evaluated in section 3.2.

The increased nutrient supply enhanced the primary production and organic carbon burial, which in turn lowered $pCO_2$. At the same time, the burial of shallow and total calcium carbonate (CaCO$_3$) increased, while CaCO$_3$ burial in the deep ocean decreased (Holbourn et al., 2007). However, as the net burial of CaCO$_3$ (enriched in $^{13}C$) in relation to $C_{org}$ (depleted in $^{13}C$) increased at high eccentricity, $\delta^{13}C_{DIC}$ values decreased, which is in line with the global isotope signature (Holbourn et al., 2007; Ma et al., 2011).

The increase in carbonate burial in shallow seas should have removed alkalinity from seawater, and thus lowered pH and released CO$_2$ to the atmosphere (e.g., Zeebe and Wolf-Gladrow, 2001) during 100 k.y. eccentricity maxima, but the resolution of our record is too low to detect this. On longer timescales (400 k.y. cycles), however, increased alkalinity input from rivers, dissolution of deep-sea carbonates, and the enhanced burial of $C_{org}$ in tropical regions during eccentricity maxima might have contributed to the long-term decrease in $pCO_2$. This agrees well with the box model output from Ma et al. (2011), suggesting that during the long-eccentricity maxima $pCO_2$ decreased when the monsoon was most intense and the organic carbon burial and river fluxes were high. Conversely, weathering and nutrient supply to the ocean in low latitudes decreased when eccentricity was low, resulting in a net decrease in the CaCO$_3$-to-$C_{org}$ burial ratio and hence in CO$_2$ release and higher $\delta^{13}C$. 


4.3 Enhanced glacial deep-water ventilation

The MMCT bears similarities to the Eocene-Oligocene transition (EOT) ~34 Ma ago, when Antarctic ice-expansion was also accompanied by a large positive δ¹³C excursion, in terms of both magnitude and duration (Coxall et al., 2005). The δ¹³C excursion following Antarctic glaciation was accompanied by a transient $p$CO$_2$ rise of more than 300 µatm (Pearson et al., 2009; Heureux and Rickaby, 2015), which bears similarity to the $p$CO$_2$ rise during the mid-Miocene EAIS expansion, although the amplitude was much larger. A modeling study suggested that a sea-level-fall-induced shelf-basin carbonate burial fractionation and a temporal enhancement of deep-water formation (by 150 %) in the Southern Ocean were sufficient to produce both the positive δ¹³C excursion and a transient $p$CO$_2$ rise by ~80 µatm in the EOT (McKay et al., 2016). Similarly, ocean circulation may have intensified during the Miocene EAIS expansion, as the latitudinal temperature gradient increased and atmospheric circulation strengthened. This is supported by benthic foraminifers, Mn/Ca and XRF data from Southeast Pacific sites, which indicate improved deep-water ventilation and carbonate preservation after 13.9 Ma, particularly during colder climate phases (Holbourn et al., 2013). Improved deep-water ventilation may also have led to enhanced advection of silica-rich waters toward low latitudes, culminating in an increased upwelling and diatom productivity between 14.04 and 13.96 Ma and between 13.84 and 13.76 Ma in the equatorial East Pacific, as indicated by massive opal accumulation found at IODP Site U1338 (Holbourn et al., 2014). We speculate that increased upwelling may have resulted in CO$_2$ outgassing, if the supply exceeded consumption by primary productivity.

5. Conclusions

We conclude that $p$CO$_2$ variations across the MMCT were paced by 400 k.y. eccentricity cycles, where $p$CO$_2$ decreased at high eccentricity and rose when eccentricity was low (Fig. 4). At high eccentricity, the global monsoon and hence weathering intensity increased (e.g., Wang, 2009), causing an increased input of dissolved inorganic carbon, alkalinity and nutrients to the oceans. The resulting increase in the CaCO$_3$-to-C$_{org}$ burial ratio lowered $p$CO$_2$ and decreased δ¹³C$_{DIC}$. The $p$CO$_2$ decrease between 14.08 and 13.87 Ma might have facilitated the initiation of EAIS expansion starting at ~13.9 Ma. Conversely, the CO$_2$ rise after the onset of EAIS expansion, possibly caused by decreased weathering fluxes at low eccentricity and hence net decrease in the CaCO$_3$-to-C$_{org}$ burial ratio, could have acted as a negative feedback on the progressing Antarctic glaciation. In this way, the radiative forcing due to the temporary $p$CO$_2$ rise may have helped to stabilize the climate system on its way to the late Cenozoic “icehouse” world. Our results also highlight the need for more high-resolution $p$CO$_2$ records across the middle Miocene climate transition.

Data availability

The boron isotope data collected for this study are available from Table S1, the tie points used for the revised age model are listed in Table S2, and the modified R code of ‘MgCaRB’ (Gray and Evans, 2019) is available from S1 in the supplement.
Author contribution

MR and JB conceived the study (conceptualization). MR carried out measurements, analyzed the data, and performed data statistics (data curation, formal analysis, investigation). JB provided access to analytical instruments at AWI (resources). MR raised funding for the project (funding acquisition). MR produced the figures for the manuscript (visualization), and wrote the first draft of the manuscript (writing – original draft). All authors interpreted, edited, and reviewed the manuscript (writing – review & editing).

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgement

We thank the Ocean Drilling Program for providing samples from ODP Leg 177, and M. Maeke for washing the sediments and picking foraminifer shells. A. Benthien, B. Müller, K.-U. Richter, and U. Richter are thanked for their assistance in the lab. This study is part of a research project (RA 2068/3-1) granted to MR by the German Research Foundation (Deutsche Forschungsgemeinschaft DFG).

References

Abels, H. A., Hilgen, F. J., Krijgsman, W., Kruk, R. W., Raffi, I., Turco, E. and Zachariasse, W. J.: Long-period orbital control on middle Miocene global cooling: Integrated stratigraphy and astronomical tuning of the Blue Clay Formation on Malta, Paleoceanography, 20, PA4012, doi:10.1029/2004PA001129, 2005.
Badger, M. P. S., Lear, C. H., Pancost, R. D., Foster, G. L., Bailey, T. R., Leng, M. J. and Abels, H. A.: CO₂ drawdown following the middle Miocene expansion of the Antarctic Ice Sheet, Paleoceanography, 28(1), 42–53, doi:10.1002/palo.20015, 2013.
Badger, M. P. S., Chalk, T. B., Foster, G. L., Bown, P. R., Gibbs, S. J., Sexton, P. F., Schmidt, D. N., Pälike, H., Mackensen, A. and Pancost, R. D.: Insensitivity of alkenone carbon isotopes to atmospheric CO₂ at low to moderate CO₂ levels, Clim. Past, 15(2), 539–554, doi:https://doi.org/10.5194/cp-15-539-2019, 2019.
Barker, S., Greaves, M. and Elderfield, H.: A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, Geochem. Geophys. Geosyst., 4(9), 8407, doi:10.1029/2003GC000559, 2003.
Caves, J. K., Jost, A. B., Lau, K. V. and Maher, K.: Cenozoic carbon cycle imbalances and a variable weathering feedback, Earth Planet. Sci. Lett., 450, 152–163, doi:10.1016/j.epsl.2016.06.035, 2016.
Censarek, B. and Gersonde, R.: Miocene diatom biostratigraphy at ODP Sites 689, 690, 1088, 1092 (Atlantic sector of the Southern Ocean), Mar. Micropaleontol., 45(3–4), 309–356, doi:10.1016/S0377-8398(02)00034-8, 2002.
Clift, P. D. and Plumb, R. A.: The Asian Monsoon: Causes, History and Effects, Cambridge University Press., 2008.
Coxall, H. K., Wilson, P. A., Palike, H., Lear, C. H. and Backman, J.: Rapid stepwise onset of Antarctic glaciation and deeper calcite compensation in the Pacific Ocean, Nature, 433(7021), 53–57, doi:10.1038/nature03135, 2005.

Evans, D. and Müller, W.: Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular change in seawater Mg/Ca, Paleoceanography, 27(4), doi:10.1029/2012PA002315, 2012.

Flower, B. P. and Kennett, J. P.: Middle Miocene ocean-climate transition: High-resolution oxygen and carbon isotopic records from Deep Sea Drilling Project Site 588A, southwest Pacific, Paleoceanography, 8(6), 811–843, doi:10.1029/93PA02196, 1993.

Flower, B. P. and Kennett, J. P.: The middle Miocene climatic transition: East Antarctic ice sheet development, deep ocean circulation and global carbon cycling, Paleogeogr. Paleoclimatom. Paleoecol., 108, 537–555, doi:https://doi.org/10.1016/0031-0182(94)90251-8, 1994.

Foster, G. L., Lear, C. H. and Rae, J. W. B.: The evolution of pCO₂, ice volume and climate during the middle Miocene, Earth Planet. Sci. Lett., 341–344, 243–254, doi:10.1016/j.epsl.2012.06.007, 2012.

Goyet, C., Healy, R., Ryan, J. and Kozyr, A.: Global Distribution of Total Inorganic Carbon and Total Alkalinity below the Deepest Winter Mixed Layer Depths, ORNL/CDIAC-127, NDP-076. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee. [online] Available from: https://digital.library.unt.edu/ark:/67531/metadc724552/m1/7/ (Accessed 18 May 2017), 2000.

Gray, W. R. and Evans, D.: Nonthermal Influences on Mg/Ca in Planktonic Foraminifera: A Review of Culture Studies and Application to the Last Glacial Maximum, Paleocean. Paleoclimat., 34(3), 306–315, doi:10.1029/2018PA003517, 2019.

Greenop, R., Foster, G. L., Wilson, P. A. and Lear, C. H.: Middle Miocene climate instability associated with high-amplitude CO₂ variability, Paleoceanography, 29(9), 2014PA002653, doi:10.1002/2014PA002653, 2014.

Greenop, R., Hain, M. P., Sosdian, S. M., Oliver, K. I. C., Goodwin, P., Chalk, T. B., Lear, C. H., Wilson, P. A. and Foster, G. L.: A record of Neogene seawater δ¹¹B reconstructed from paired δ¹¹B analyses on benthic and planktic foraminifera, Clim. Past, 13(2), 149–170, doi:10.5194/cp-13-149-2017, 2017.

Heureux, A. M. C. and Rickaby, R. E. M.: Refining our estimate of atmospheric CO₂ across the Eocene–Oligocene climatic transition, Earth Planet. Sci. Lett., 409, 329–338, doi:10.1016/j.epsl.2014.10.036, 2015.

Holbourn, A., Kuhnt, W., Simo, J. A. (Toni) and Li, Q.: Middle Miocene isotope stratigraphy and paleoceanographic evolution of the northwest and southwest Australian margins (Wombat Plateau and Great Australian Bight), Paleogeogr. Paleoclimatom. Paleoecol., 208(1), 1–22, doi:10.1016/j.palaeo.2004.02.003, 2004.

Holbourn, A., Kuhnt, W., Schulz, M. and Erlenkeuser, H.: Impacts of orbital forcing and atmospheric carbon dioxide on Miocene ice-sheet expansion, Nature, 438, 483–487, doi:https://doi.org/10.1038/nature04123, 2005.

Holbourn, A., Kuhnt, W., Schulz, M., Flores, J.-A. and Andersen, N.: Orbitally-paced climate evolution during the middle Miocene “Monterey” carbon-isotope excursion, Earth Planet. Sci. Lett., 261, 534–550, doi:https://doi.org/10.1016/j.epsl.2007.07.026, 2007.

Holbourn, A., Kuhnt, W., Frank, M. and Haley, B. A.: Changes in Pacific Ocean circulation following the Miocene onset of permanent Antarctic ice cover, Earth and Planetary Science Letters, 365, 38–50, doi:10.1016/j.epsl.2013.01.020, 2013.

Holbourn, A., Kuhnt, W., Lyle, M., Schneider, L., Romero, O. and Andersen, N.: Middle Miocene climate cooling linked to intensification of eastern equatorial Pacific upwelling, Geology, 42(1), 19–22, doi:10.1130/G34890.1, 2014.
Horita, J., Zimmermann, H. and Holland, H. D.: Chemical evolution of seawater during the Phanerozoic: Implications from the record of marine evaporites, Geochim. Cosmochim. Acta, 66(21), 3733–3756, doi:10.1016/S0016-7037(01)00884-5, 2002.

Ji, S., Nie, J., Lechler, A., Huntington, K. W., Heitmann, E. O. and Breecker, D. O.: A symmetrical CO$_2$ peak and asymmetrical climate change during the middle Miocene, Earth Planet. Sci. Lett., 499, 134–144, doi:10.1016/j.epsl.2018.07.011, 2018.

Jonkers, L. and Kučera, M.: Global analysis of seasonality in the shell flux of extant planktonic Foraminifera, Biogeosciences, 12(7), 2207–2226, doi:10.5194/bg-12-2207-2015, 2015.

Kuhnert, H., Bickert, T. and Paulsen, H.: Southern Ocean frontal system changes precede Antarctic ice sheet growth during the middle Miocene, Earth Planet. Sci. Lett., 284(3–4), 630–638, doi:10.1016/j.epsl.2009.05.030, 2009.

Kürschner, W. M., Kvaček, Z. and Dilcher, D. L.: The impact of Miocene atmospheric carbon dioxide fluctuations on climate and the evolution of terrestrial ecosystems, PNAS, 105(2), 449–453, doi:https://doi.org/10.1073/pnas.0708588105, 2008.

Laskar, J., Robutel, P., Joutel, F., Gastineau, M., Correia, A. C. M. and Levrard, B.: A long-term numerical solution for the insolation quantities of the Earth, Astron. Astrophys., 428(1), 25, doi:10.1051/0004-6361:20041335, 2004.

Lavigne, H., Epitalon, J.-M. and Gattuso, J.-P.: seacarb: seawater carbonate chemistry with R. [online] Available from: http://CRAN.R-project.org/package=seacarb, 2011.

Lemarchand, D., Gaillardet, J., Lewin, É. and Allègre, C. J.: The influence of rivers on marine boron isotopes and implications for reconstructing past ocean pH, Nature, 408, 951–954, doi:10.1038/35050058, 2000.

Lear, C. H., Rosenthal, Y., Coxall, H. K. and Wilson, P. A.: Late Eocene to early Miocene ice sheet dynamics and the global carbon cycle, Paleoceanography, 19, PA4015, doi:10.1029/2004PA001039, 2004.

Ma, W., Tian, J., Li, Q. and Wang, P.: Simulation of long eccentricity (400-kyr) cycle in ocean carbon reservoir during Miocene Climate Optimum: Weathering and nutrient response to orbital change, Geophys. Res. Lett., 38(10), doi:10.1029/2011GL047680, 2011.

Ma, X., Tian, J., Ma, W., Li, K. and Yu, J.: Changes of deep Pacific overturning circulation and carbonate chemistry during middle Miocene East Antarctic ice sheet expansion, Earth Planet. Sci. Lett., 484, 253–263, doi:10.1016/j.epsl.2017.12.002, 2018.

Mashiotta, T. A., Lea, D. W. and Spero, H. J.: Glacial-interglacial changes in Subantarctic sea surface temperature and δ$^{18}$O-water using foraminiferal Mg, Earth Planet. Sci. Lett., 170, 417–432, doi:10.1016/S0012-821X(99)00116-8, 1999.

McKay, D. I. A., Tyrrell, T. and Wilson, P. A.: Global carbon cycle perturbation across the Eocene-Oligocene climate transition, Paleoceanography, 31(2), 311–329, doi:10.1002/2015PA002818, 2016.

Misra, S., Owen, R., Kerr, J., Greaves, M. and Elderfield, H.: Determination of δ$^{13}$B by HR-ICP-MS from mass limited samples: Application to natural carbonates and water samples, Geochim. Cosmochim. Acta, 140, 531–552, doi:10.1016/j.gca.2014.05.047, 2014.

Mortyn, P. G. and Charles, C. D.: Planktonic foraminiferal depth habitat and δ$^{18}$O calibrations: Plankton tow results from the Atlantic sector of the Southern Ocean, Paleoceanography, 18(2), 1037, doi:10.1029/2001PA000637, 2003.
Myers, S. R.: Astrochron: An R Package for Astrochronology. [online] Available from: https://cran.r-project.org/package=astrochron, 2014.

Pagani, M., Freeman, K. H. and Arthur, M. A.: Late Miocene Atmospheric CO\textsubscript{2} Concentrations and the Expansion of C4 Grasses, Science, 285, 876–879, doi:10.1126/science.285.5429.876, 1999.

Pearson, P. N. and Palmer, M. R.: Atmospheric carbon dioxide concentrations over the past 60 million years, Nature, 406, 695–699, doi:10.1038/35021000, 2000.

Pearson, P. N., Foster, G. L. and Wade, B. S.: Atmospheric carbon dioxide through the Eocene–Oligocene climate transition, Nature, 461(7267), 1110–1113, doi:10.1038/nature08447, 2009.

Rae, J. W. B., Foster, G. L., Schmidt, D. N. and Elliott, T.: Boron isotopes and B/Ca in benthic foraminifera: Proxies for the deep ocean carbonate system, Earth Planet. Sci. Lett., 302(3–4), 403–413, doi:10.1016/j.epsl.2010.12.034, 2011.

Raitzsch, M. and Hönsch, B.: Cenozoic boron isotope variations in benthic foraminifers, Geology, 41(5), 591–594, doi:https://doi.org/10.1130/G34031.1, 2013.

Raitzsch, M., Kuhnert, H., Groeneveld, J. and Bickert, T.: Benthic foraminifer Mg/Ca anomalies in South Atlantic core top sediments and their implications for paleothermometry, Geochem. Geophys. Geosyst., 9(5), Q05010, doi:https://doi.org/10.1029/2007GC001788, 2008.

Raitzsch, M., Bijma, J., Benthien, A., Richter, K.-U., Steinhoefel, G. and Kučera, M.: Boron isotope-based seasonal paleo-pH reconstruction for the Southeast Atlantic – A multispecies approach using habitat preference of planktonic foraminifera, Earth Planet. Sci. Lett., 487, 138–150, doi:https://doi.org/10.1016/j.epsl.2018.02.002, 2018.

Ridgwell, A.: A Mid Mesozoic Revolution in the regulation of ocean chemistry, Mar. Geol., 217(3–4), 339–357, doi:16/j.margeo.2004.10.036, 2005.

Shackleton, N. J.: Attainment of isotopic equilibrium between ocean water and the benthonic foraminifera genus \textit{Uvigerina}: isotopic changes in the ocean during the last glacial, Cent. Nat. Rech. Sci. Colloq. Int., 219, 203–209, 1974.

Shevenell, A. E. and Kennett, J. P.: Paleoceanographic Change During the Middle Miocene Climate Revolution: An Antarctic Stable Isotope Perspective, in The Cenozoic Southern Ocean: Tectonics, Sedimentation, and Climate Change Between Australia and Antarctica, pp. 235–251, American Geophysical Union (AGU), 2004.

Shevenell, A. E., Kennett, J. P. and Lea, D. W.: Middle Miocene Southern Ocean Cooling and Antarctic Cryosphere Expansion, Science, 305, 1766–1770, doi:10.1126/science.1100061, 2004.

Shevenell, A. E., Kennett, J. P. and Lea, D. W.: Middle Miocene ice sheet dynamics, deep-sea temperatures, and carbon cycling: A Southern Ocean perspective, Geochem. Geophys. Geosyst., 9(2), Q02006, doi:10.1029/2007GC001736, 2008.

Sosdian, S. M., Greenop, R., Hain, M. P., Foster, G. L., Pearson, P. N. and Lear, C. H.: Constraining the evolution of Neogene ocean carbonate chemistry using the boron isotope pH proxy, Earth Planet. Sci. Lett., 498, 362–376, doi:10.1016/j.epsl.2018.06.017, 2018.

Spratt, R. M. and Lisiecki, L. E.: A Late Pleistocene sea level stack, Clim. Past, 12(4), 1079–1092, doi:https://doi.org/10.5194/cp-12-1079-2016, 2016.

Stanley, S. M. and Hardie, L. A.: Hypercalcification: Paleontology links plate tectonics and geochemistry to sedimentology, GSA Today, 9, 2–7, 1999.
Super, J. R., Thomas, E., Pagani, M., Huber, M., O’Brien, C. and Hull, P. M.: North Atlantic temperature and pCO₂ coupling in the early-middle Miocene, Geology, 46(6), 519–522, doi:10.1130/G40228.1, 2018.

Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W. and Sutherland, S. C.: Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: A comparative study, Glob. Biogeochem. Cyc., 7(4), 843–878, doi:10.1029/93GB02263, 1993.

Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., Hales, B., Friederich, G., Chavez, F., Sabine, C., Watson, A., Bakker, D. C. E., Schuster, U., Metzl, N., Yoshikawa-Inoue, H., Ishii, M., Midorikawa, T., Nojiri, Y., Körtzinger, A., Steinhoff, T., Hoppe, M., Olafsson, J., Arnason, T. S., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., Wong, C. S., Delille, B., Bates, N. R. and de Baar, H. J. W.: Climatological mean and decadal change in surface ocean pCO₂, and net sea–air CO₂ flux over the global oceans, Deep-Sea Res. II, 56(8–10), 554–577, doi:10.1016/j.dsr2.2008.12.009, 2009.

Tyrrell, T. and Zeebe, R. E.: History of carbonate ion concentration over the last 100 million years, Geochim. Cosmochim. Acta, 68(17), 3521–3530, doi:10.1016/j.gca.2004.02.018, 2004.

Vincent, E. and Berger, W. H.: Carbon dioxide and polar cooling in the Miocene: the Monterey hypothesis, in The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present, pp. 455–468, American Geophysical Union, Washington, DC. [online] Available from: https://doi.org/10.1029/GM032p0455, 1985.

Wan, S., Kürschner, W. M., Clift, P. D., Li, A. and Li, T.: Extreme weathering/erosion during the Miocene Climatic Optimum: Evidence from sediment record in the South China Sea, Geophys. Res. Lett., 36(19), doi:10.1029/2009GL040279, 2009.

Wang, B.-S., You, C.-F., Huang, K.-F., Wu, S.-F., Aggarwal, S. K., Chung, C.-H. and Lin, P.-Y.: Direct separation of boron from Na- and Ca-rich matrices by sublimation for stable isotope measurement by MC-ICP-MS, Talanta, 82(4), 1378–1384, doi:10.1016/j.talanta.2010.07.010, 2010.

Wang, P.: Global monsoon in a geological perspective, Chin. Sci. Bull., 54(7), 1113–1136, doi:10.1007/s11434-009-0169-4, 2009.

Wright, J. D., Miller, K. G. and Fairbanks, R. G.: Early and Middle Miocene stable isotopes: Implications for Deepwater circulation and climate, Paleoceanography, 7(3), 357–389, doi:10.1029/92PA00760, 1992.

Woodruff, F. and Savin, S.: Mid-Miocene isotope stratigraphy in the deep sea: high resolution correlations, paleoclimatic cycles, and sediment preservation, Paleoceanography, 6, 755–806, doi:https://doi.org/10.1029/91PA02561, 1991.

Zeebe, R. E. and Tyrrell, T.: History of carbonate ion concentration over the last 100 million years II: Revised calculations and new data, Geochim. Cosmochim. Acta, 257, 373–392, doi:10.1016/j.gca.2019.02.041, 2019.

Zeebe, R. E. and Wolf-Gladrow, D. A.: CO₂ in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier Oceanography Series, Amsterdam., 2001.
Figure 1: Azimuthal view of the location of ODP Site 1092 (water depth 1973 m) on the Meteor Rise in the South Atlantic Ocean, north of the modern polar front. Also shown are locations of DSDP Site 608, ODP Site 761, IODP Site U1338 and Ras-il-Pellegrin on Malta, for which $pCO_2$ records are displayed in Fig. 5.
Figure 2. SEM images of collected *G. bulloides* for δ¹¹B analysis (representative example from 177-1092B-18-4, 69-71 cm). (A) Whole shell; (a) close-up image reveal intact coccoliths covering the shell surface indicating lack of post-depositional dissolution. (B) Shell fragments after chemical cleaning; (b) close-up image shows absence of non-shell material.
Figure 3. Age models of ODP Site 1092, ODP Site 761 and Blue Clay Formation (Ras-il-Pellegrin, Malta), which were re-tuned with respect to the reference curve of IODP Site U1338 (Holbourn et al., 2014), based on their δ\(^{18}\)O (upper panel) and δ\(^{13}\)C (lower panel) records. Thick line of the Ras-il-Pellegrin record is from Abels et al. (2005), and thin line from Badger et al. (2015). Arrows mark tie points from this study, which are listed in Table S2. Dashed lines delimit CM events 5b and 6.
Figure 4. Proxy records of the middle Miocene climate transition. (A) Benthic oxygen isotope curve from ODP Site 1092 (in red) used in this study and from eastern Pacific IODP Site U1338 (in blue) used as a reference (Holbourn et al., 2014). (B) The same as in A) but for carbon isotopes. The carbon maximum events CM5b and CM6 are indicated. (C) Site 1092 sea-surface temperatures reconstructed from *G. bulloides* Mg/Ca ratios (Kuhnert et al., 2009), with ±1 °C uncertainty band. (D) Raw boron isotope data of *G. bulloides*. Shaded area indicates 2σ uncertainties of measurement. (E) Estimated $pCO_2$ of surface waters (derived from) using pH derived from (D), a total alkalinity (TA) of 2000 ± 100 µmol/kg, and a $\delta^{11}B_{sw}$ value of 37.80 ‰. Secondary axis represents pH.
and shaded area delimits fully propagated $pCO_2$ uncertainties (). (F) Eccentricity of the Earth’s orbit from Laskar et al. (2004) and lowpass-filtered 400 k.y. signal (grey line).
Figure 5. Eccentricity of the Earth’s orbit from Laskar et al. (2004) (upper panel) and comparison of \( p\text{CO}_2 \) estimates from this study with literature data (lower panel). Note that the boron-based \( p\text{CO}_2 \) data from Foster et al. (2012) and Badger et al. (2013) were re-calculated using a TA of 2000 µmol/kg and a \( \delta^{11}\text{B}_\text{sw} \) value of 37.80 ‰ for consistency with our data. In addition, the age models from these studies were also revised for direct comparison with our record (Fig. 3). All other records are based on their original data and age models.
Figure 6. Evolutive harmonic analysis (EHA) and power spectral analysis of $pCO_2$ record from ODP Site 1092, using the Thomson multitaper method (MTM). The red line in the left panel is the lowpass-filtered 400 k.y. signal using cosine-tapered window. Analyses were performed using the R package ‘Astrochron’ (Myers, 2014).
Figure 7. Sensitivity tests of pH-derived $pCO_2$ estimations. (A) Effect of varying salinity (derived from $\delta^{18}O$ changes) and TA (at modern correlation with S) on estimated $pCO_2$. (B) Effect of TA on $pCO_2$ estimates, when TA is correlated (green) or anti-correlated (orange) with sea-surface temperature at a total range of 400 µmol/kg. (C-H) Effect of TA on $pCO_2$ estimates, when TA is (anti-)correlated with pH or eccentricity at maximum ranges of ±100 (orange) and ±400 µmol/kg (green). The grey line in all panels represents the box model output from Ma et al. (2011). Shaded areas represent propagated 2σ uncertainties. Note that the red line is the record shown in Figs. 4E and 5.