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Oligocene-early Miocene paradox of pCO_2 inferred from alkenone carbon isotopic fractionation and sea surface temperature trends

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Abstract. Atmospheric carbon dioxide decline is hypothesized to drive the progressive cooling over the Cenozoic. However, at multimillion-year timescales during the Oligocene to Miocene time interval the existing reconstructions, most based on the phytoplankton carbon isotopic fractionation (ε_p) proxy, differ from what is expected to drive the climate observations.

Here, we produce two new long-term records of ε_p over the Oligocene to early Miocene time interval from widely separated locations at IODP Site 1406 and ODP 1168 and increase the resolution of determinations at the equatorial Atlantic ODP 925. These new results confirm a global footprint of ε_p shift occurring during this interval. Abrupt 3 ‰ declines are found from 27 to 24.5 Ma and 24 to 22.5 Ma, and minimum ε_p is attained at 19 Ma. Between 28.7 and 29.7 Ma at IODP 1406, a higher resolution sampling reveals orbital scale 100 kyr cyclicity in ε_p. Making use of alkenone-based sea surface temperature (SST) estimates and benthic $\delta^{18}O$ estimated extracted from the same samples, we perform a direct comparison with ε_p to evaluate the relationship with climate dynamics. We observe that across the long Oligocene to early Miocene interval the two sites' relationships contrast with what is expected if CO_2 was the main driver of ε_p and average earth surface temperature evolution was registered at the local surface SST and global benthic $\delta^{18}O$. Moreover, at orbital timescale, ε_p and benthic $\delta^{18}O$ appear to follow an inverse relationship, although located within the multimillion-year period with the strongest direct correlation between these variables (>25.5 Ma). To evaluate the physiological, non- CO_2 influences on ε_p, we use modern cultures to evaluate the impact of changing cell size and growth rate on the trends in ε_p. Although at specific time intervals, those drivers seem to explain part of the ε_p divergence with SST or benthic $\delta^{18}O$, most periods remain largely divergent, particularly the late Oligocene warming. We infer that a common CO_2 forcing is likely the dominant control on the coherent temporal trends in ε_p at widely separated sites, which experienced contrasting temperature evolution and likely experienced different variations in nutrient availability. While CO_2 changes likely caused significant changes in radiative forcing, SST variation at the examined sites may have been conditioned by regional heat transport, and the relationship between benthic $\delta^{18}O$ and ε_p could reflect variable phasing between ice growth and global temperature.

Short summary. We reconstructed from sediments of different ocean sites phytoplankton carbon isotopic fractionation (ε_p), mainly linked to CO_2 variations, during the Oligocene to early Miocene. Records confirm long-term trends but show contrasting relationships with the sea surface temperatures evolution. We evaluate the role of non-CO_2 physiological factors such as temperature and nutrients at each site ε_p, highlighting the complexity of interpreting climate dynamics and CO2 reconstructions.

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1 Introduction

Geological records provide key context to current assessments of the consequences of rising atmospheric CO_2 on ice sheet stability and oceanic temperatures (Foster et al., 2017; Golledge, 2020; Zachos et al., 2008). The Oligocene to Miocene time interval has been proposed to represent a nonlinear transition between the 'greenhouse' and 'icehouse' stages of Earth history (Miller et al., 1991; Zachos et al., 2001) useful to evaluate the Earth system climate sensitivity to the hypothesized progressive CO_2 drawdown of the Cenozoic (Deconto et al., 2008; Zhang et al., 2013). However, the long term decline in CO_2 estimated by existing proxy records contrasts with the rather stable climatic state with multimillion year warming and cooling trends defined by the temperature trends in the deep ocean (Cramer et al., 2011; Lear et al., 2000), and surface ocean (Guitián et al., 2019; Liu et al., 2009; O'Brien et al., 2020) and with estimated Antarctic Ice sheet volume and sea level (Lear et al., 2004; Liebrand et al., 2017; Miller et al., 2020).

Most of the Oligocene and early Miocene pCO_2 estimates are derived from the sensitivity of marine algae to CO_2 (Henderiks and Pagani, 2008; Pagani et al., 1999, 2000; Pagani et al., 2005; Super et al., 2018; Zhang et al., 2013) based on the carbon isotopic fractionation in organic matter during photosynthesis (ε_p) of marine phytoplankton (Rau et al., 1996), typically measured in biomarkers from haptophyte algae. This fractionation can be reconstructed in the past from sediments by the analysis of $\delta^{13}C$ of the organic lipids and reconstruction of the $\delta^{13}C$ of the DIC in the seawater from which biomass was produced. Fractionation (ε_p) is predicted to be higher when CO_2 availability is high relative to cellular carbon demand. A decrease in atmospheric CO_2 and consequently in CO_2 of the surface ocean should therefore lead to a decrease in ε_p globally. However, in addition to CO_2, the ε_p in phytoplankton is affected by physiological factors such as the rate of carbon fixation, which may vary over time in a given location due to variations in temperature or the supply of light. One approach to evaluate the relative contribution of physiological factors vs CO_2 is to produce ε_p records from sites of widely contrasting oceanographic setting, where the CO_2 signal may be expected to be common to both locations but the environmental factors such as nutrient availability might not be expected to change in unison. The existing ε_p-based CO_2 estimations for the Oligocene are derived from ~1 m.y. resolution measurements from two sites on the south American margin of the equatorial and South Atlantic; in the early Miocene an additional North Atlantic record provides data (CenCO2PIP Consortium, 2023). In this study, we produce a new long-term record of ε_p over the Oligocene to Miocene time interval at two new, widely separated locations: IODP Site 1406 in the subtropical North Atlantic off the Newfoundland coast, and ODP 1168 in the Southern Ocean off of Tasmania. We also increase the resolution of determinations at the equatorial Atlantic ODP 925.

Our new <1 m.y. resolution ε_p records from these two mid- latitude locations allow us to directly compare ε_p with estimates of SST derived from alkenones extracted from the same samples, since unlike very warm tropical locations, the $U^{k'}_{37}$ index still retains sensitivity to temperature in the mid-latitudes during the Oligocene and early Miocene. Additionally, we compare ε_p with benthic $\delta^{18}O$ available from the same sediments, an indicator of high-latitude temperature and Antarctic ice sheet extent and/or volume. These long-term relationships are contrasted with higher resolution analysis during the middle Oligocene at IODP 1406. The dataset allows a robust evaluation of the relationship between ε_p and climate dynamics for this time interval. We further discuss the significance of the observed ε_p record with the implications for the phytoplankton sensitivity over multimillion year timescales over the Cenozoic.

1.2 An overview of alkenone ε_p pCO_2 proxy

The carbon isotopic fractionation in phytoplankton during photosynthesis is affected not only by the $CO_{2[aq]}$ but also by physiological factors related to the cellular uptake of carbon. These were initially modelled from the assumption of diffusive carbon acquisition in phytoplankton cells (Rau et al., 1996), where higher ε_p could be induced by higher $CO_{2(aq)}$, lower instantaneous growth rates, or a higher cellular surface area to volume ratio. Both cellular permeability and the carbon isotopic fractionation by the Rubisco enzyme have been assumed to be constant, with Rubisco fractionation typically estimated between 25 and 29 ‰ for alkenone producers (Pagani et al., 2014). Traditional attempts to reconstruct pCO_2 from ε_p have simplified

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this original diffusive model by relating ε_p and CO_2 with a single factor *b* defined to include all physiological parameters affecting the fractionation, and ε_f representing the fractionation of the Rubisco enzyme (Jasper and Hayes, 1994).

The *b*-value has been estimated from modern photic zone and culture samples, for which $CO_{2(aq)}$ is independently known. For sedimentary alkenones, previous pCO_2 calculations have either, (1) assumed the modern *b*-value for that oceanographic setting remained constant in the past (e.g. Zhang et al., 2013), (2) applied modern relationships between *b* and phosphate and a simulated paleo-surface ocean phosphate concentration at the site (Pagani et al., 2011), or (3) estimated the difference between the modern *b* value at the site and the paleo-setting *b* value from productivity proxies or proxies for coccolithophore size (Bolton et al., 2016; Henderiks and Pagani, 2007). Despite the appeal of this approach, a recent re-evaluation of cultures and field observations suggest the *b* term is not well predicted by growth rate, light or cell size alone in a diffusive model. Additional effects occur from carbon concentration mechanisms (CCM) on carbon uptake at lower CO_2 concentrations, which cause a deviation in the CO_2 dependence from the theoretical hyperbolic relationship (Hernández-Almeida et al., 2020; Stoll et al., 2019). A further challenge to the physical diffusive model is that the Rubisco fractionation in coccolithophores has been measured in-vitro as 11 ‰ rather than 25‰ (Boller et al., 2011), suggesting that fractionations larger than 11‰ may reflect the operation of additional enzymatic fractionations (Wilkes et al., 2018). The lower Rubisco fractionation has implications for the sensitivity of ε_p to CO_2 (e.g. as explored in (González-Lanchas et al., 2021)).

A meta-analysis of experimental culture data (Stoll et al., 2019) suggests that ε_p features a logarithmic dependence on CO_2, rather than the hyperbolic dependence implied by (Rau et al., 1997). This approach does not resolve the mechanisms for the observed slope of ε_p dependence on CO_2, but over the range of $CO_{2(aq)}$ from 5 to 30 µM, it provides an empirical relationship for interpreting the magnitude of $CO_{2(aq)}$ change implied by a given ε_p change. The culture dataset illustrates more broadly how ε_p is the sum of its dependencies on ln(CO_2), ln(light), and growth rate and cell radius:

$$(1)\quad \varepsilon_p = 2.66\ln(CO_2) + 2.33\ln(light) - 6.98\,\mu_i - 1.28\,\text{radius} + 6.26$$

where $CO_{2(aq)}$ is in µM, light is in µE, growth rate is day^{-1} and radius is in microns (see Stoll et al. (2019) for confidence intervals on the regression).

From this empirical culture calibration, two challenges remain for the estimation of past CO_2 from ε_p measurements derived from sedimentary alkenones. First, its use would require an estimation of the cell radius, light during the season and depth of alkenone production, and the growth rate. While cell size can be estimated from coccolith length, determining the absolute light and growth rate is rarely possible. Since the equation is a linear sum of these influences, these non-CO_2 variables may be integrated into the intercept (e.g. as in González-Lanchas et al. (2021)), where the intercept (*I*) would decrease with higher growth rates and larger cell sizes and increase with higher light.

$$(2)\quad \varepsilon_p = 2.66\ln(CO_2) + I$$

Yet, as with Eq. (1), there remains the challenge of determining which value should be used for the intercept for past conditions, and whether a constant or variable *I* is more appropriate for a given site since there are limited proxies for algal growth rate. Recent culture studies document a 0.5 ‰ decrease in ε_p per 1°C warming (Torres Romero et al., 2024), a magnitude which is indistinguishable from the prediction of growth rate effect on ε_p and the modeled temperature dependence of coccolithophore growth rates (Krumhardt et al., 2017). This suggests that growth rate, and *I*, may vary over time at a given location if temperature is variable. Therefore, records of SST from alkenone unsaturation or other proxies provide the opportunity to deconvolve the effects of temperature-driven growth rate variations on ε_p even when the absolute growth rate is not known.

In this study, given the potential for oceanographic conditions at the studied sites to differ significantly from those in the modern ocean at these locations, and the concomitant high uncertainties in estimating an appropriate *b* value for the traditional

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approach or *I* for Eq. (2), we do not calculate the past absolute CO_2 concentration from our ε_p measurements. Instead, we account for the potential influence of temperature-driven growth rate changes on our ε_p records using alkenone temperature estimates derived from the same samples. Similarly, we evaluate the potential impact of cell size variations on the ε_p changes. Then, we employ the sensitivity of ε_p to CO_2 in Eq. (2) to estimate possible relative changes in CO_2 in the case where the other nutrient-stimulated growth rate or light influences on ε_p were constant during the studied interval at each site evaluating evidences for this assumption.

2 Sites and sediments

We have selected two widely separated paleo locations for this study, from the mid latitude North Atlantic ocean and the high to mid latitudes of the Southern Ocean, from IODP 1406 (40°21.0′N, 51°39.0′W; 3,814 mbsl), ODP 1168 (43° 36.5'S, 144° 24.7'E, and 2463 mbsl) (Fig. 1). A total of 43 and 34 sediment sampling spreading from 30 Ma to 17 Ma at each site were selected. Additionally, higher resolution sampling at IODP 1406 was performed within the 29-30 Ma time window. We also measured an additional six sample set from equatorial Site ODP 925 (4◦12.25'N, 43◦29.33'W, 3042 mbsl) in order to increase the million-year scale resolution of the previous longest Oligocene record in alkenone carbon fractionation (Zhang et al., 2013). The age model for Sites 1406 and 1168 has been updated using new $^{87}Sr/^{86}Sr$ isotope stratigraphy (Stoll et al., 2024) and the age-modelling software Bacon (Blaauw and Christen, 2011). The new age model for IODP Site 1406 is comparable to previously published chronologies (e.g. as in Guitián et al. (2019) and Van Peer et al. (2017)) but clarifies the duration of the upper Miocene hiatus between 33.3 m and 34.7 m core depths (CCSF-A) as extending from 18.5 to 21 Ma. The ODP Site 1168 age model was revised with the Sr isotope stratigraphy in the interval from 562 to 278 mbsf. The Site 1168 chronology is significantly shifted for most of the Oligocene to early Miocene compared with previous biostratigraphically-based age models and shipboard magnetostratigraphy (Pfuhl and McCave, 2003). Strontium isotope stratigraphy identifies a condensed interval from 22.5 to 21.6 Ma, but suggests sustained sedimentation thereafter through 16 Ma. The age model is most uncertain between 27 and 25 Ma where the Sr isotopic curve has a low rate of change. For the two ODP 1168 samples deeper than the Sr isotope measurements, and those from Site ODP 925 we use previous age constraints as published previously by Guitián et al. (2020). The paleolatitude reconstruction for the Oligocene to early Miocene barely changes the position of Atlantic sites, in contrast, ODP 1168 moved from 55°S to 48°S between 30 and 15 Ma (Torsvik et al., 2012; van Hinsbergen et al., 2015). Paleodepth estimates for coastal site ODP 1168 suggest a gradual deepening from the Eocene onwards (Exon et al., 2001).

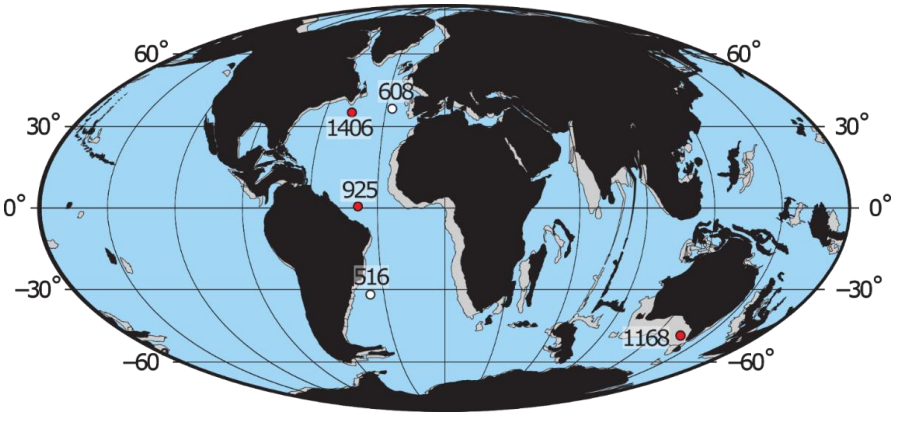

Figure 1. Location of the study sites. Reconstructed map of continental distribution over the 30 Ma (grey) – 17 Ma (black) time interval. Modified after the plate tectonic reconstruction service ODSN.

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3 Methods

3.1 Alkenone purification, quantification and $\delta^{13}C$ analysis

Biomarkers from sediments of IODP 1406 and ODP 1168 were extracted from 30g of freeze-dried sediment using an Accelerated Solvent Extractor 350 with CH_2Cl_2/MeOH (9:1 v/v) solvent for four static cycles at 100°C and further silica gel column chromatography protocols for purification of the ketone fraction containing the alkenones (see Guitián et al. (2019) for details).

Alkenone ratios were obtained with a Thermo Scientific Trace 1310 Gas Chromatograph (GC)-FID. Originally, for IODP 1406 and 1168 samples the GC-FID was equipped with a non-polar (60 m × 0.25 mm × 0.25 µm) capillary column (ZB-1ms, Zebron™) at ETH Zurich and at Lamont-Doherty Earth Observatory from Columbia University (Guitián et al., 2019; Guitián and Stoll, 2021). However, ODP Site 1168 samples older than 22.4 Ma featured more complex chromatograms and a high diversity of compounds. To reduce the effects of coelution, samples were additionally analyzed on a 105m column RTX-200ms at ETH Zurich, which improved separation of long chain ketones (Rama-Corredor et al., 2018). The following temperature program was used: 1 min at 50°C, temperature gradient of 40°C/min to 200°C and 5°C/min to 300°C, hold for 45min, and increased to 320°C at 10°C/min and hold for 8min. Carrier gas was Helium at a flow rate of 1.5ml/min. In-house standards and replicates injected at every sequence ensured instrument precision. A subset of IODP Site 1406 and samples younger than 22.4 Ma from Site 1168 were re-measured with the RTX-200 to ensure replicability (Table S1). Method used for each organic analysis is described in the supplementary material dataset.

Sea surface temperature was calculated from $U^{k\prime}_{37}$ ratio using the Bayspline calibration (Tierney and Tingley, 2018) for all samples in IODP 1406 and for the young set of samples in ODP 1168. Because for those, we find $U^{k\prime}_{37}$ ratios within the analytical uncertainty using both columns, we report the original ZB-1 results for all Site 1406 samples and Site 1168 samples younger than 22.4 Ma / 408.22 m depth. The RTX-200 column provided substantially improved resolution of C38 peaks, allowing quantification of $C_{38:2}$ and $C_{38:3}$ ME peaks, but for samples between the ages of 23.1 and 29.1 Ma in ODP 1168 it did not perform well enough for the C37 peaks. Therefore, for this set we provide temperatures estimated from the $U^{k\prime}_{38ME}$ ratio applying the Novak et al. (2022) core top calibration. For the ODP 925 equatorial site samples, the $C_{37:3}$ methyl ketone is under the detection limit, therefore we further purified and analyzed the extracted organics as in Guitián et al. (2019) to get the temperatures from the TEX86 ratio using the BAYSPAR calibration by (Tierney and Tingley, 2015).

Compound-specific $\delta^{13}C$ measurements were performed on a Thermo Scientific Trace 1310 Gas Chromatograph coupled to a Thermo Scientific GC Isolink II, a Conflo IV, and a Delta V Plus Mass Spectrometer at ETH Zurich. Oxygen was flushed through the combustion reactor for one hour at the beginning of each sequence and seed oxidized for one minute before each injection. Alkenones from ODP Site 1168 and IODP 1406 were analyzed on a GC equipped with a non-polar capillary column (60 m × 0.25 mm × 0.25 µm) (ZB-1ms, Zebron™) and 5-m guard column. Helium was used as carrier gas flow with 2-ml/min. GC oven was set at 90°C ramped to 250 at 25°C/min, to 313°C at 1°C/min and finally to 320°C at 10°C /min. The GC oven was then maintained isothermally for 20 min. A subset of IODP 1406 samples were measured additionally at the Lamont-Doherty Earth Observatory on equivalent instrumentation but with some modifications for improved sensitivity (Baczynski et al., 2018) and following similar GC procedures, with similar results.

From ODP Site 1168, a subset of samples older than 24.5 Ma featuring more complex chromatograms were rerun on a GC-irMS equipped with a RTX-200 ms column. GC oven was set at 50°C ramped to 275°C at 40°C/min, to 295°C at 0.5°C, hold for 22 min, and finally ramped to 320°C at 10°C/min and hold for 5 min. Flow rate was 1.5ml/min. Comparison of a subset of samples from Site 1406 and ODP 1168 younger than 22.4 ma showed that $\delta^{13}C$ C37:2 were similar on both ZB-1 and RTX-200 columns. We consequently report here $\delta^{13}C$ C37:2 from the ZB-1 runs, with the exception of the samples from Site 1168 older than 22.4 Ma. All values are reported here in parts per mil (‰) relative to VPDB (Vienna Pee Dee Belemnite). Sample

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replicates, in-house alkenone standard (provided by G. O'Neil, Western Washington University, and C. M. Reddy, Woods Hole Oceanographic Institution), and known isotopic mixtures A5 and B4 (supplied by A. Schimmelmann, Univ. of Indiana) were simultaneously measured to determine the analytical accuracy of the measurement and an uncertainty of 0.5 ‰.

3.2 Estimation of aqueous carbon dioxide $\delta^{13}C$

Isotopic composition of $CO_{2[aq]}$ is estimated from the temperature dependent fractionation between DIC and aqueous CO_2 during alkenone production of Rau et al. (1996) based on Mook et al. (1974) and Freeman and Hayes (1992):

$$(3)\quad \delta^{13}C_{[CO2]aq} = \delta^{13}C_{DIC} + 23.644 - \left(\frac{9701.5}{T}\right)$$

The $\delta^{13}C$ DIC may be estimated from the $\delta^{13}C$ of calcium carbonate of benthic foraminifera with the assumption of a constant and known offset between the $\delta^{13}C$ DIC of the deep and surface ocean, or from bulk sediment calcium carbonate that is mostly derived from coccolithophores and planktonic foraminifera. Site 1406 and 925 features sufficient well preserved benthic foraminifera, mainly epifaunal *Cibicidoides* spp. larger than 200 µm, $\delta^{13}C$ of surface ocean DIC can be calculated here applying a constant offset of 2 ‰ of measurements from the same samples following previous Miocene and Oligocene studies (Guitián et al., 2019; Pagani et al., 2011; Zhang et al., 2013). However, at ODP Site 1168 benthic foraminifera were scarce for picking for isotopes in many intervals and the progressive evolution of water depth at the site may change the $\delta^{13}C$ offset between the benthic environment and the surface ocean over time. Consequently, to follow the same approach for all studied records we calculate the $\delta^{13}C$ DIC from the $\delta^{13}C$ of the bulk carbonate, which is dominated by *Reticulofenestra* coccoliths (Guitián et al., 2020). Because there is no divergence of vital effects between small and large coccoliths in the late Oligocene to early Miocene (Bolton and Stoll, 2013), we propose that the offset between coccolith $\delta^{13}C$ and DIC is likely to remain constant. We subtract 0.5 ‰ from the $\delta^{13}C_{bulk}$ to calculate $\delta^{13}C_{DIC}$, based on average alkenone-producing coccoliths cultured at DIC <4 mM compiled in Stoll et al. (2019). Support for estimating photosynthetic fractionation from coccolith $\delta^{13}C$ is provided by recent culture studies of *G. oceanica* (Torres Romero et al., 2024).

Stable isotopes of carbonates were measured as described in in Guitián et al. (2019) with the guidelines from Breitenbach and Bernasconi (2011) for small carbonate samples on a GAS BENCH II Delta V Plus irMS from Thermo Scientific with international (NBS-19 & 18) and in-house carbonate as standards achieving a precision of 0.07 ‰.

3.3 Calculation of $\varepsilon_{p\ 37.2}$

Carbon isotopic fractionation (ε_p), describes the fractionation occurring during photosynthesis when carbon is fixed into algal cellular biomass ($\delta^{13}C_{org}$) from the ambient aqueous CO_2 ($\delta^{13}C_{CO2aq}$) (Freeman and Hayes, 1992):

$$(4)\quad \varepsilon_p = \left(\frac{(\delta^{13}C_{[CO2]aq} + 1000)}{(\delta^{13}C_{org} + 1000)} - 1\right) * 1000$$

Organic $\delta^{13}C$ is obtained from the $\delta^{13}C$ analysis of haptophyte specific alkenone di-unsaturated $C_{37.2}$. Culture experiments showed that the lipid organic matter is depleted in ^{13}C relative to the whole cell isotopic composition by 4.2 ‰, a correction that needs to be applied (Popp et al., 1998; Wilkes et al., 2018):

$$(5)\quad \delta^{13}C_{org} = [(\delta^{13}C_{37:2} + 1000) * ((4.2/1000) + 1) - 1000]$$

Uncertainties were propagated by a full Monte Carlo (n = 10000) simulation following (Tanner et al., 2020).

To compare our new records with previous data spanning the same time interval, we discuss published ε_p datasets recently compiled by the paleo CO_2 community (CenCO2PIP Consortium, 2023), from DSDP 516 in the South Atlantic (Pagani et al., 2000; Pagani et al., 2011; Pagani et al., 2005), DSDP 608 in the North Atlantic (Super et al., 2018), and the equatorial site from ODP 925 (Zhang et al., 2013). For these, we ensure that ε_p for the published records is calculated from biomarker-based

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paleothermometers. The most recent publications from DSDP 608 and 925 used GDGT-derived estimations from TEX-86. To better compare our results with DSDP 516, where originally temperatures were derived from $\delta^{18}O$ of planktic foraminifera for the Miocene section and GDGTS for part of the Oligocene, we have updated the ε_p calculations using a running averaging of the recent higher resolution GDGT temperature reconstructions from Auderset et al. (2022) at the same site.

For our data of paired ε_p and alkenone SST, we calculate the shift in ε_p which is expected from temperature-stimulated growth rates. We adjusted each samples ε_p absolute value by using the relationship of -0.48 ‰ per 1°C SST difference relative to the record average (Torres Romero et al., 2024). We complete a similar exercise for cell radius, calculating the deviation in ε_p relative to the median cell size, for each point using the culture dependence of ε_p on cell radius (Stoll et al., 2019). Biogenic silica (bioSi) was determined on 20 samples from ODP 1168 following methods described previously in Guitián et al. (2020).

4 Results and Discussion

4.1 Trends in ε_p in the Oligocene to early Miocene

4.1.1 New ε_p records from sites 1406 and 1168

In both long-term records from Site 1406 and Site 1168, $\delta^{13}C$ of $C_{37.2}$ alkenones range from very low values near -30 ‰ in the early Oligocene (28-30 Ma) increasing to -24 ‰ by 18-20 Ma (Fig. 2). The new calculated ε_p decrease from the Oligocene to the early Miocene, defined most precisely at the highest resolution North Atlantic Site 1406, features abrupt 3 ‰ declines from 26.5 to 25.4 Ma and 24 to 22.8 Ma. Newly obtained ODP 925 ε_p determinations within the interval 25 Ma to 19 Ma are in agreement with previous determinations at this site (Zhang et al., 2013) resolving steps at 26 ma and 21 Ma. The trends in ε_p calculated from benthic $\delta^{13}C$ are similar to those calculated from the coccolith-dominated bulk $\delta^{13}C$. In the high resolution section from 28.8 to 29.6 Ma in Site 1406 there is no long-term trend, but orbital scale ε_p variations exceed 1.5 ‰ in amplitude (Fig. 3, Fig. S1). Several~100 ky orbital scale variations of 0.75 ‰ benthic $\delta^{18}O$ and bulk $\delta^{18}O$ are sampled, as expected for this time window of high 100 ky power in benthic $\delta^{18}O$ in other sites (Liebrand et al., 2017).

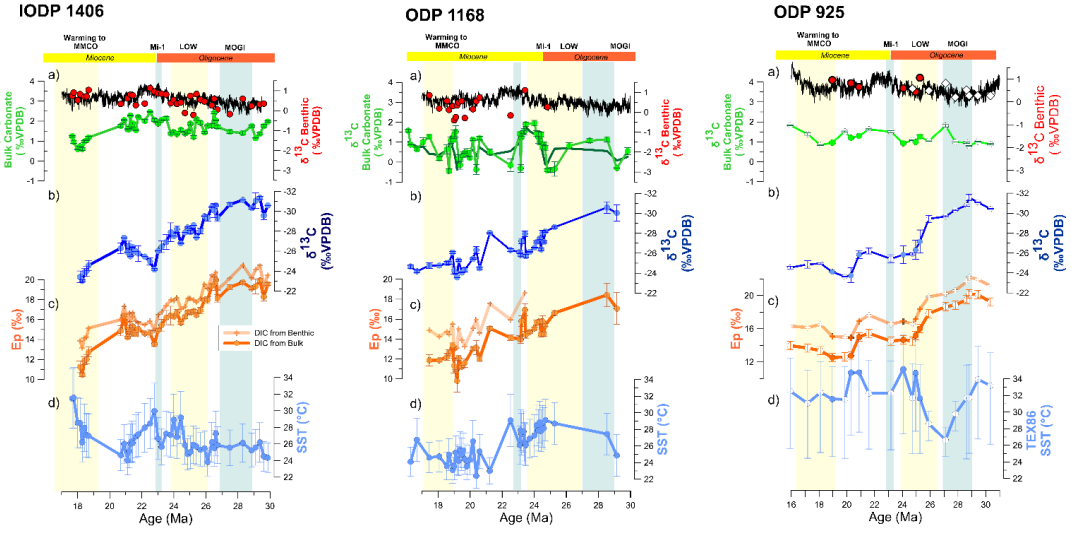

Figure 2: Analytical results of this study. a) Carbonate stable isotopes for benthic foraminifera (red symbols), data from this work for each site; black line shows results from Westerhold et al., (2020) and bulk sediment carbonate (green color). b) Alkenone $C_{37.2}$ $\delta^{13}C$. c) Calculated alkenone carbon fractionation, solid line DIC $\delta^{13}C$ is derived from bulk carbonate, transparent line from picked benthic foraminifera at the same samples. d) Temperature estimates. IODP 1406, including SST and benthic $\delta^{18}O$ dataset from Guitian et al., (2019); ODP 1168, dark green $\delta^{13}C$ bulk carbonate shows the 4-point moving average used to calculate εp at the site; ODP 925, filled circles are new measurements for this study, white symbols are published data (Zhang et al., 2013), being ε_p

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recalculated following method described in text. Note SST is derived from GDGT at this site. SST errors bars: 1406- 1σ, 1168-$U^{k'}_{37}$- 1σ, 1168-$U^{k'}_{38ME}$-2σ, 925-TEX$_{86}$-2σ.

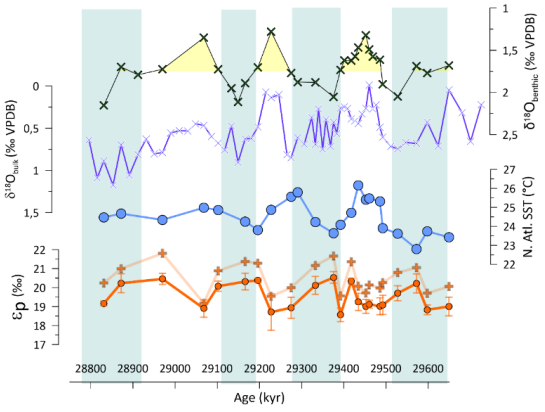

Figure 3. High resolution sampling from IODP 1406, showing $\delta^{18}O$ of bulk carbonate and benthic foraminifera, alkenone SST estimates, and ε_p calculated from bulk carbonate (circles) and benthic foraminifera assuming a constant offset (crosses).

4.1.2 Comparison of 1168 and 1406 ε_p records with published Atlantic records

The overall decline in ε_p through the time interval of our records, is broadly comparable to the trend in published ε_p datasets recently compiled by the paleo CO_2 community (CenCO2PIP Consortium, 2023), which exhibits a long term decrease in the late Oligocene through the transition to the Miocene and an overall low and stable early Miocene (Fig. 4). However, several factors complicate a detailed comparison of our new and the previously published records.

Rapid ε_p shift comparison might be hindered by site chronology uncertainties. Although all records are presented here on the GTS 2012 (Gradstein et al., 2012), ODP 1168 and IODP 1406 age models rely on Sr isotope stratigraphy (Stoll et al., 2024), whereas ODP 925, DSDP 516 and ODP 608 are based exclusively on biostratigraphic and magnetostratigraphic reversals datums (Curry et al., 1995). As seen in sites 1168 and 1406, Sr isotopic stratigraphy can adjust age determinations by 0.5 to 1 Myr. or even up to 2 Myr. at few cases.

Additionally, differences in the absolute value of ε_p among records may also reflect contrasting approaches to the reconstruction of DIC $\delta^{13}C$ in the different studies. At DSDP 608, the DIC $\delta^{13}C$ was reconstructed from surface-dwelling foraminifera *G. quadrilobatus* (Pagani et al., 1999), while at DSDP 516 the Miocene section was estimated from planktic foraminifera and most of the Oligocene samples DIC $\delta^{13}C$ was determined from fine fraction (Pagani et al., 2000; Pagani et al., 2005). Published ODP 925 ε_p has been recalculated here with DIC $\delta^{13}C$ derived from bulk carbonates of nearby samples, to resolve the previous divergent estimates from planktic and benthic foraminifera (Zhang et al., 2013).

The longest record from **DSDP Site 516** exhibits a general ε_p decline from the Oligocene to early Miocene. However, due to lower resolution at this site, we cannot evaluate if there is an abrupt 3 ‰ decline from 26 to 24.5 Ma as seen in sites 1406 and 925. A steep ε_p decline between at 21 and 20 Ma in Site 516 may be within age uncertainty of the decrease observed at ODP 1168 and ODP 925; additional Sr isotope stratigraphy at Site 516 in this time interval could help test the synchronicity. The late Oligocene at DSDP 516 features a 5‰ peak in ε_p between 24.5 and 24.9 Ma, which is not reflected at 1406, or 1168 sites. The early Miocene record at DSDP **Site 608** shows a more variable ε_p with a much steeper decline through the early Miocene and higher amplitude variation compared to other sites. The characteristic minimum in ε_p from 18 to 17 Ma is potentially within the age model uncertainty of the minimum in ε_p at 19 Ma in 1168 and the minimum identified at Site 1406 at 18.5 Ma. Updated stratigraphy could contrast more robustly the timing of these events. If there is high amplitude short term variability

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in ε_p in the early Miocene as in the Oligocene time interval (Fig. 2), there is also the potential for low resolution sampling to undersample high frequency temporal variability and generate aliasing artefacts.

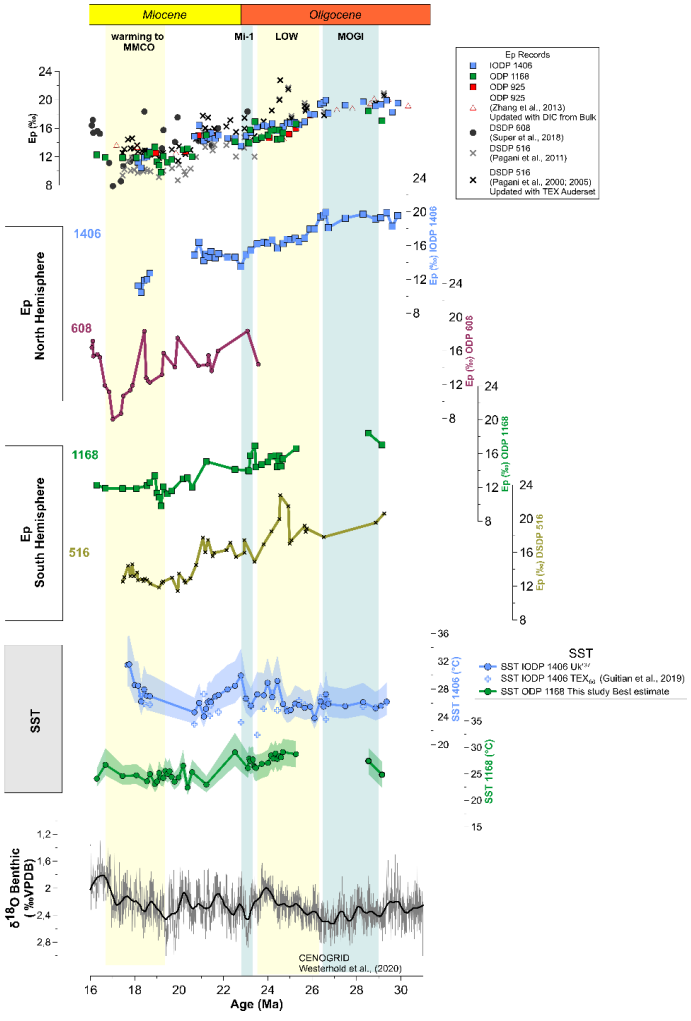

Figure 4: Oligocene to Miocene global long term ε_p trends. Comparison of the new obtained ε_p records with previously published alkenone measurements. All ε_p estimates have been recalculated following the methodology described in text with data source described on Table S2.

4.2 CO_2 vs size and nutrient effects on ε_p

In addition to CO_2, ε_p may be influenced by changes in cell surface area to volume ratio and cellular growth rate regulated by light and nutrients. There is no long-term trend in mean coccolith size in these records (Guitián et al., 2020) and estimating the impact of it on the ε_p records shows a negligible effect on long-term trends (Fig. 5). At discrete time intervals of IODP Site 1406, the size effect reduces most values older than 27 Ma and produce a steeper decrease on ε_p towards the Oligocene Miocene transition.

For the statistical model of Eq. (1), it is complex to identify proxy records for any possible effect of nutrient-stimulation of growth rate or changes in the mean light conditions at the depth of growth. In modern spatial gradients in the ocean, these factors are often coupled, so that settings characterized by deep mixing and high nutrient supply rates to stimulate growth, are also characterized by lower mean light levels due to the deeper mixing, both factors lowering ε_p.

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As one possible nutrient indicator, a higher concentration of biogenic silica (bioSi) in sediments may reflect a higher rate of bioSi delivery to the seafloor due to higher export production produced by siliceous organisms (mainly diatoms) in the ocean (Ragueneau et al., 2000). In the modern ocean, regions with abundant dissolved Si in the photic zone are regions also characterized by higher concentrations of macronutrients such as P and N. At IODP 1406, bioSi concentrations generally increase from the Oligocene to earliest Miocene, potentially indicating a gradual increase in the concentration of dissolved Si in surface waters at the site (Fig. 5). If the increase in dissolved silica observed at the North Atlantic is correlated to an increase in dissolved P or N, it could contribute to increase in growth rate, and therefore likely increase in biomass and chlorophyll, which would reduce light in the water column both being part of the observed long term decrease of ε_p. However, the actual correlation between bioSi and ε_p is not that strong (Fig. S2), suggesting that while increased nutrient concentrations could contribute to the long-term evolution of ε_p, the specific steps of ε_p decline are less likely to be driven by increased nutrients and growth rate.

The drivers for increasing bioSi burial rates at Site 1406 are not clear, although they could reflect a global increase in nutrient delivery. Important changes in the rate of continental weathering within the Oligocene- early Miocene are often interpreted from the evolution of radiogenic isotopes of Sr, Li and Os (Misra and Froelich, 2012) including the steep rise in $^{87}Sr/^{86}Sr$, although the precise origin of the late Eocene and Miocene increase in $^{87}Sr/^{86}Sr$ remains under discussion (Rugenstein et al., 2019). On a global scale, the nutrient delivery may be conditioned by the riverine supply of P from continental erosion and weathering of P containing minerals. On the time scales examined in our records, much longer than the residence time of P, the net effect on nutrient concentrations depends on the balance of the supply and the nutrient removal in sediments.

While a significant increase in erosion and weathering and nutrient inventory is one mechanism to contribute to the long term decline in ε_p via enhanced algal growth rates, an increase in erosion and weathering can itself contribute to a CO_2 drawdown by CO_2 consumption through silicate weathering and enhanced burial of organic carbon in delta regions (Raymo and Ruddiman, 1992). If the biogenic Si increase at 1406 were representative of a global trend, an increase in nutrient supply may have contributed to ε_p decline through both CO_2 decline and increased nutrient stimulation of phytoplankton growth. A global decline in ε_p solely from increased weathering and nutrient concentrations without a CO_2 decline would require that in the Oligocene, the nutrient release from silicate weathering was less coupled to carbon burial than in the late Neogene. If the periodically glaciated margin of Antarctica is a major locus for increased erosion and weathering in the Oligocene (Reilly et al., 2002), release of nutrients and radiogenic isotopes may have occurred in the continental margins, but with much less organic carbon burial than the modern Himalaya system due to limited terrestrial biomass on Antarctica and temperature and sea-ice limited oceanic biomass production in the marine regions.

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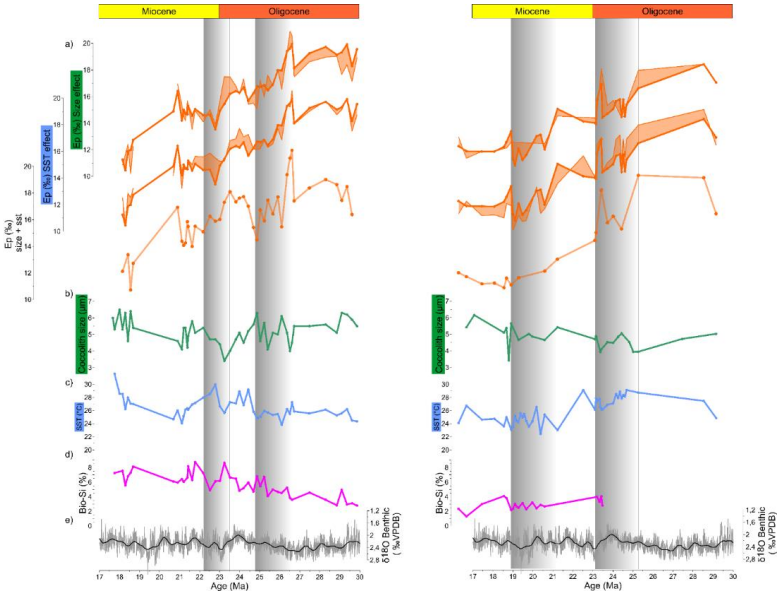

335 **Figure 5: Timeseries of ε_p at IODP 1406 and ODP 1168 including a) the measured ep record (solid line) and the estimated ε_p resulted once size and temperature effect is applied following Torres et al., (2024), and Stoll et al., (2019) (transparent shadows). b) Coccolith size record from Guitian et al., (2020); c) SST estimates d) Biogenic silica measurements (Guitian et al., (2020) and this study); e) reference CENOGRID benthic $\delta^{18}O$ curve (Westerhold et al., 2020)**

On the other hand, the long term trend of increased bioSi is not observed in the Southern ocean Site 1168 (Fig. 5). The available 340 Miocene bioSi at ODP 1168 is stable with no change across the steep ε_p drop from the latest Oligocene to early Miocene. The increasing distance of Site 1168 from the coastline with basin subsidence may have decreased the availability of Si from the early Oligocene through the early Miocene, imparting a local effect superimposed on any potential global trend. However, likely not only Si but also other nutrients would decrease with increasing distance from the coast. If the long term trend in ε_p at both 1406 and 1168 sites were conditioned by increased nutrient availability, faster growth rates, and lower light levels it 345 would require bioSi accumulation rates at Site 1168 to be decoupled from the overall changes in nutrient availability, which we consider less likely. Consequently, we propose that the similarity in trend and magnitude of the long term ε_p decline in both sites (and in tropical Site 925), is more consistent with a global forcing of ε_p, which may be most plausibly driven by a significant decrease in atmospheric CO_2 and CO_2aq.

4.3 Relationship between ε_p and SST and benthic $\delta^{18}O$

350 The new ε_p data from Site 1406 and Site 1168 provide the first records of ε_p from the early Oligocene to early Miocene with alkenone unsaturation indices as independent estimations of SST for the precise time intervals of ε_p determination. Since they are biomarkers derived from the same organism, alkenone-derived SST estimates correspond to the same season and growth depth as the alkenone ε_p determinations. There are two processes which may influence the relationship between temperature and ε_p. First, higher temperatures lead to higher phytoplankton carbon fixation rates, decreasing ε_p. Secondly, higher CO_2 355 would increase ε_p and through radiative forcing lead to warmer global average temperature and SSTs. The expected relationship between ε_p and SST from either process could be obscured by a superposition of temperature effects on growth rate and a climatic correlation of ε_p with mean air temperature.

4.3.1 Million year scale relationships

Across the overall time interval, Site 1406 ε_p is weakly inversely correlated with SST, whereas Site 1168 ε_p is weakly positively 360 correlated with SST (Fig. 6; Fig. S3, Table S3). Our estimation of the growth rate effect due to warmer temperatures shows

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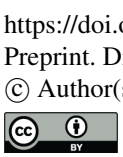

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that it has a very limited impact on the long term ε_p trend, amplifying slightly the long-term excursion in ODP 1168 and imparting a minor increase in ε_p in the late Oligocene 25.5 to 24 Ma in IODP 1406 but otherwise not affecting the sign of the overall trend (Fig. 5, 6, Fig. S3). At our studied sites across the 30 to 17 Ma time interval, the long term average warming of 2-3°C is insufficient to account for the 7 ‰ decline in ε_p due to a temperature-driven growth rate effect.

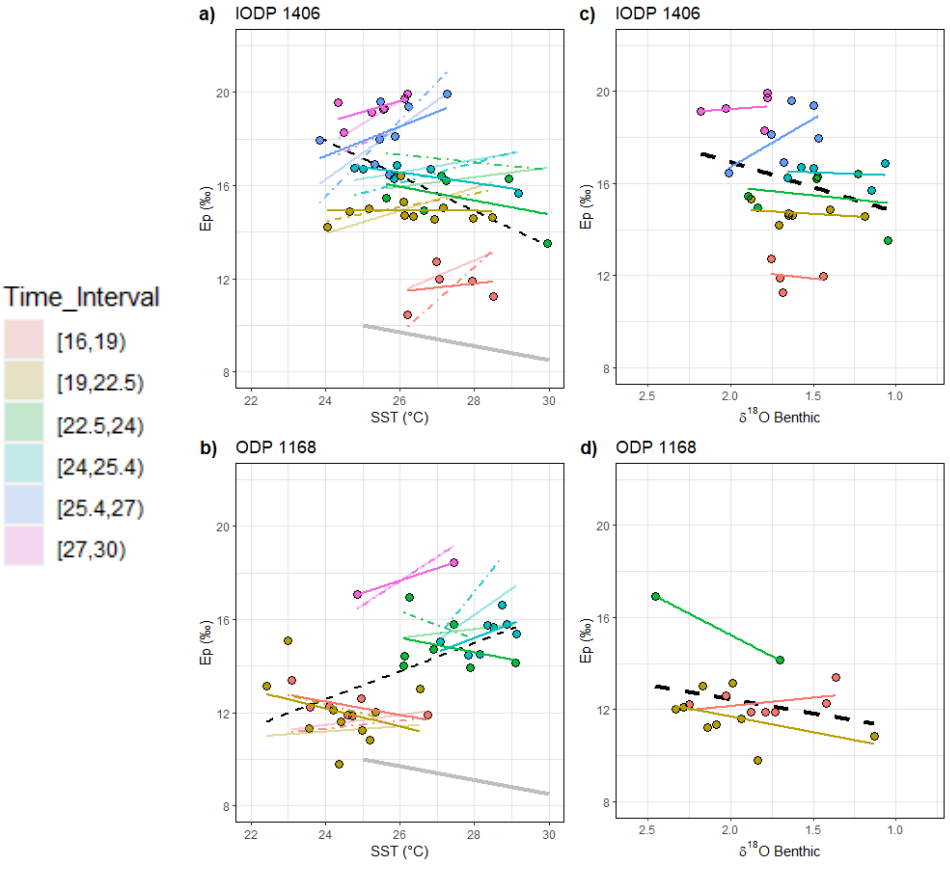

Figure 6. Relationship between calculated ε_p and SST and benthic $\delta^{18}O$ for the same samples from IODP 1406 and ODP 1168. Dashed dark line in the plot background shows the regression of the overall dataset. Grey line in a) b) shows empirical temperature-growth rate effect in temperature described in the text (Torres et al., 2024) as the ε_p change with growth rate if CO_2 were constant. Colored lines shows the regression at specific time intervals for the measured ε_p (solid), ε_p with the temperature effect removed (transparent), and ε_p with both the temperature and size effect removed (dashed). See Fig. S3 for overall dataset relationships.

Yet aside from the overall inverse correlation at IODP 1406, during certain time intervals the correlation is positive. Before 25.4 Ma, there is a general positive correlation between ε_p and alkenone SST (Fig. 6, Table S3); for the intervals 27 to 30 and 25.4 to 27 Ma in Site 1406 with a slope of **0.7** (n=6, n=10). This is also true for the 25.4 to 24 Ma interval in 1168 with 0.6 slope (n=6). This slope is significantly greater when the influence of size and temperature-growth rate effects on ε_p are removed. In other time intervals, there is a negligible slope or negative slope with measured ε_p, for example -0.3 (24 to 22.5 Ma in both sites, n=7, n=4) or during the drop after 19 Ma at IODP1406 appear to occur at times of warming temperature (slope= 0.2, n=5) that slightly improves when the ε_p is adjusted to size and temperature.

Over the studied time interval, this relationship similarly shows insignificant correlation for the previously published ε_p, records with updated age models and ε_p calculations (Fig. S4), although temperatures estimates are derived from GDGT which might not reflect the same depth and/or season of coccolithophore growth. Negative covariance is observed at DSDP 608 from

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19 to 16 ma, at DSDP 516 before 21 Ma and for the few samples from 27 to 24 ma at ODP 925. Some of these intervals feature significant temperature changes of 4 to 5°C, and therefore the temperature-growth rate effect on ε_p may be significant, and the negative slopes observed in some intervals are consistent with this being the dominant effect (gray line in Fig. 6a and 6b). At 1406, during the older intervals of positive correlation of SST and ε_p, potentially the growth rate stimulation due to higher SST was balanced by a decrease of nutrient availability during warmer temperatures as suggested by the bioSi evolution (Fig. S2), whereas during younger time intervals, temperature exerted a dominant effect on growth rate.

Benthic $\delta^{18}O$ was measured in multiple time intervals in Site 1406. Benthic $\delta^{18}O$ has been proposed to reflect global surface temperature (Evans et al., 2024; Hansen et al., 2013) and as such may be less sensitive than SST to regional reorganizations of heat transport. Alternatively, benthic $\delta^{18}O$ has been proposed to be highly sensitive to the areal extent of the Antarctic ice sheet due to its cooling effect on surface ocean temperatures in regions of deepwater formation (Bradshaw et al., 2021; Lisiecki and Raymo, 2005; Shackleton, 1987). If the global surface temperature change translated to changes in surface ocean temperatures at Site 1406 and Site 1168, we would expect the temperature-growth rate effect to generate a direct correlation between benthic $\delta^{18}O$ and ε_p. If the radiative forcing effect on global temperature change were dominant, we would expect an inverse correlation between ε_p and benthic $\delta^{18}O$. As for SST, only the time intervals older than 25.4 Ma exhibit the inverse correlation expected from radiative forcing, whereas other intervals suggest neutral slope which may reflect the superposition of growth rate and CO_2-radiative effects on ε_p.

4.3.2 Relationships between ε_p, temperature and benthic $\delta^{18}O$ at orbital timescales

In the high resolution sampling between 29.0 and 29.6 Ma, despite a significant 1 ‰ range in $\delta^{18}O$ benthic and $\delta^{18}O$ bulk, we likewise observe no inverse relationship between ε_p and $\delta^{18}O$ benthic, or between ε_p and $\delta^{18}O$ bulk (Fig. 7). We also observe no significant correlation between ε_p and alkenone SST. Because the magnitude of SST variation is small over this time interval, the impact of temperature-stimulated carbon fixation rates is not a significant impact on the relationship between ε_p and any of these variables – a temperature-corrected ε_p record for the 29 to 29.6 Ma interval would still not exhibit an inverse relationship between ε_p and $\delta^{18}O$ benthic as observed in the late Pleistocene glacial cycles (Hernández-Almeida et al., 2023). If ε_p variations are dominantly responding to CO_2, our results suggest that low CO_2 is not contributing to greater ice volume and/or colder ocean temperatures on 100 ky cycles and that the relationship between Antarctic ice growth and CO_2 may be more complex at this time.

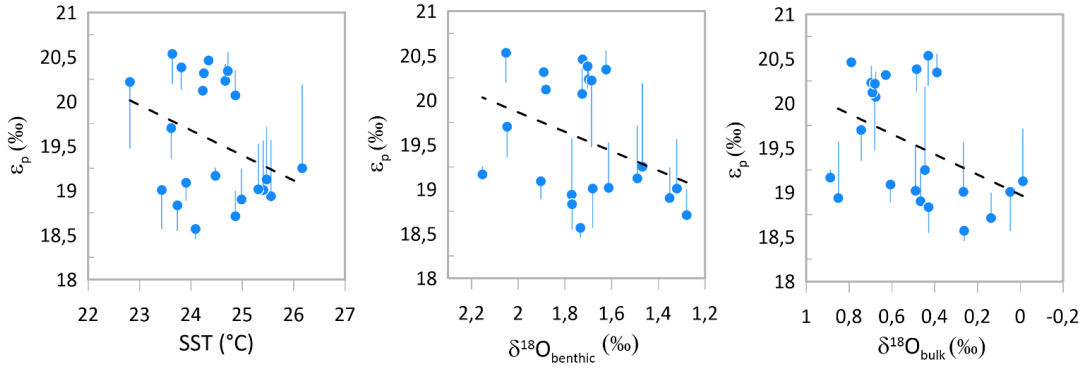

Figure 7. Relationship between calculated ε_p and temperature (r2=-0.34), $\delta^{18}O$ from benthic foraminifera (r2=0.42), and $\delta^{18}O$ from bulk carbonates (r2=0.37) for the high resolution interval samples from IODP 1406. Vertical error bars shows the temperature effect on ε_p following findings from cultures (Torres et al., 2024). Dashed line shows the linear regression for all plotted samples.

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4.4 A Climate and CO_2 paradox from the Oligocene to early Miocene

The long term trends between 30 and 16 Ma based on new ε_p data at two sites and recalculation of previous ε_p studies with uniform methods cannot be attributed to a temperature effect on growth rate and ε_p, nor to changes in the cell size of the alkenone producing community. Both effects are small in magnitude according to the sensitivities observed in cultures and do not alter the long-term trend (Fig. 5). Therefore, the long-term ε_p decline must have a significant global driver, with the most obvious being a decline in pCO_2.

Although the calculation of absolute CO_2 concentrations from ε_p in the Oligocene and early Miocene remains challenging, the logarithmic dependence of ε_p on $CO_{2[aq]}$ observed in cultures allows us to estimate the relative changes in CO_2 if the sensitivity of ε_p to CO_2 in the Oligocene were similar to modern cultured species. If we incorporate a temperature correction on growth rate (Krumhardt et al., 2017) equivalent to the magnitude from cultures (Torres Romero et al., 2024) and apply the 50th percentile estimate of the modern culture ε_p dependence on ln $[CO_{2[aq]}]$ of 2.66, it implies major changes in CO_2 concentrations, with potentially 4 halvings of CO_2 concentration from 29 to 16 Ma (Fig. 8). Modern General Circulation Models (GCM) estimate climate sensitivity at 3 to 5°C per doubling or halving of CO_2, which if representative for the Oligocene to early Miocene, would imply 12 to 20°C of cooling of earth's mean surface temperature. Although ocean is 70% of the globe and temperature changes are 1.3- to 1.8-fold less than land temperature (Sutton et al., 2007), such a large temperature change of at least 10.4°C would be expected to be reflected in paleoceanographic proxies. Application of the lower confidence interval of modern culture ε_p dependence on log($CO_{2[aq]}$) of 3.5, would imply 3 halvings of CO_2, with a correspondingly lower magnitude of change in temperature.

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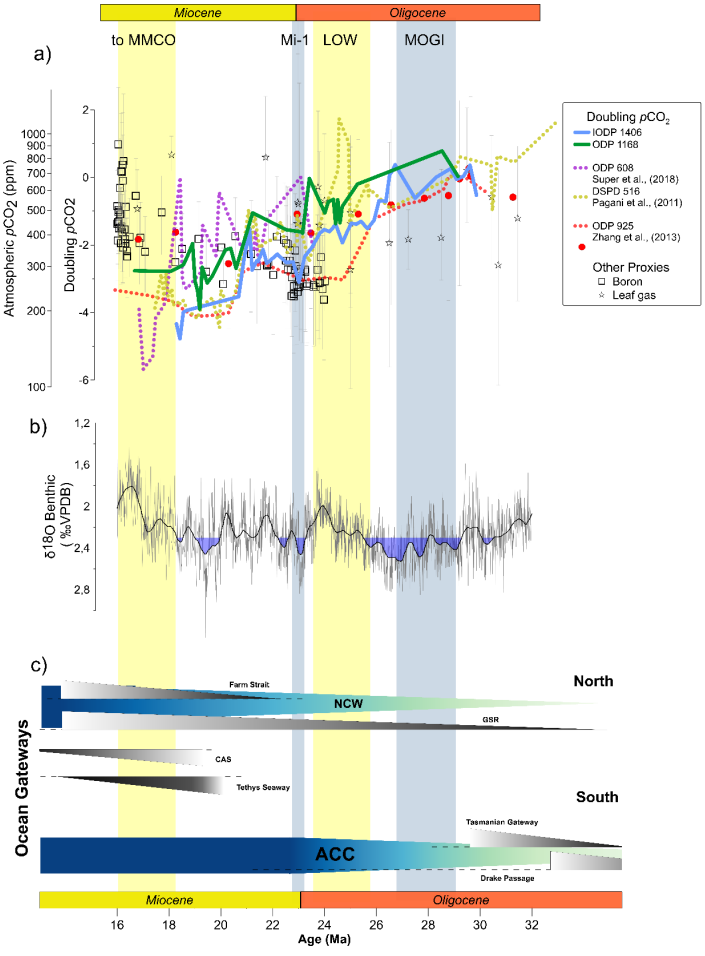

Figure 8: Implications of CO_2 as main climate driver. a) Shows pCO_2 doubling compared to previous estimates compiled in CenCO2PIP Consortium, (2023) (Erdei et al., 2012; Greenop et al., 2019; Liang et al., 2022a; Liang et al., 2022b; Londoño et al., 2018; Moraweck et al., 2019; Reichgelt et al., 2020; Roth-Nebelsick et al., 2014; Sosdian et al., 2018; Steinthorsdottir et al., 2021; Sun et al., 2017; Tesfamichael et al., 2017; Zhang et al., 2013). Only long term records from alkenone derived CO_2 are recalculated. b) Benthic $\delta^{18}O$ global compilation (Westerhold et al., 2020). c) Schematic representation of main paleoceanographic and paleogeographic changes over the studied time interval for the Northern and Southern Hemisphere. ACC: Antarctic Circumpolar Current. NCW: Northern Component Water.

The late Oligocene climate and CO_2 paradox has been discussed based on previously published lower resolution ε_p record from Site 925 (O'Brien et al., 2020). Our new results from two additional sites confirm the steep CO_2 decline through the late Oligocene warming and underscore the paradox. On a global scale, biomarker SST estimates do not show evidence for systematic cooling during the CO_2 decline (Guitián et al., 2019; Liu et al., 2018; O'Brien et al., 2020). If the interpretation of ε_p as a CO_2 decline is correct, it suggests a very different set of feedbacks and climate sensitivity during this time, or widespread regional heat transport effects on regional temperatures or significant misinterpretation of measured biomarker temperature signals. During this time the inferred CO_2 decline also coincides with sequence stratigraphic evidence for ice margin retreat in Antarctica (Levy et al., 2019; Salabarnada et al., 2018), and sea level transgressions inferred from estimates of deep sea $\delta^{18}O_{sw}$ and Mg/Ca records (Miller et al., 2020), suggesting a substantially different relationship between ice expansion and CO_2 than characterized the late Neogene.

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For the late Oligocene to early Miocene, the Southern Ocean Site 1168 is the only surface ocean temperature record which exhibits a long-term decline in SST coincident with the record of a large magnitude pCO_2 decline and decline in radiative forcing from the greenhouse effect. This long term cooling is despite the equatorward drift of the site over this time interval (Guitián and Stoll, 2021). Potentially, the ODP Site 1168 temperature trend reflects global temperature during the CO_2 decline, and whereas the long term alkenone temperature record at Newfoundland Ridge Site 1406 and Site 1404 (Liu et al. 2018) is affected by variations in the heat transport from the Gulf Stream that overwhelms the signal of radiative greenhouse forcing. While there is no evidence of a concomitant long term cooling in the benthic $\delta^{18}O$ series (e.g. Westerhold et al. (2020)), the ε_p minimum at 19 Ma coincides with a local maximum in benthic $\delta^{18}O$.

A decoupling was at one time proposed for the late Miocene based on apparent negligible pCO_2 change and substantial cooling of SST (LaRiviere et al., 2012). Revisions of the alkenone carbon fractionation to CO_2 calibration approaches for low pCO_2 periods have refined the record from the last 15 Ma, revealing clear pCO_2-SST covariation (Rae et al., 2021; Stoll et al., 2019). However, the Oligocene paradox is not easily resolvable from updated calibration of the ε_p-CO_2 relationship because the late Oligocene divergence arises from an inverse correlation between ε_p and SST reconstructions. Therefore, continued re-evaluation of SST records and interrogation of biogeochemical cycles potentially affecting the growth and physiology of alkenone producers, are needed to reconcile climate sensitivity to CO_2 in the Oligocene to early Miocene.

5 Conclusions

The new long term alkenone ε_p records from the Oligocene to early Miocene at North Atlantic Site IODP 1406 and Southern Ocean Site ODP 1168 reveal a significant 8 to 10 ‰ shift. The new records resolve abrupt 3 ‰ declines from 27 to 24.5 Ma and 24 to 22.5 Ma. The long term trend is comparable with previous lower resolution analysis when they are recalculated with the same methodology.

In addition to CO_2, ε_p may be modified by changes in cellular surface area to volume ratio and growth rate regulated by light, temperature and nutrients. However, our assessment of these effects using records of coccolith size and alkenone temperature estimates for exact time intervals of ε_p determination, shows that size and temperature effects have a negligible impact in the long term declining trend. The similarity of ε_p in widely separated sites experiencing contrasting temperature histories strongly suggests a global CO_2 decline as the most likely cause of the declining ε_p. At the same time, our high-resolution sampling reveals significant orbital scale variability in ε_p and underscores the potential for aliasing in low resolution records. Higher resolution ε_p time series, and more precise age models on legacy ε_p records to facilitate more confident comparisons of trends among sites, will provide a better characterization of the key long term trends.

Our results highlight the paradox of complex relationships between CO_2 indicators and SST at both the orbital and multi-million year timescales. The higher resolution sampling between 28.7 to 29.7 Ma shows that orbital ε_p maxima do not coincide with orbital minima in ice volume and/or warmer deep ocean temperature. Similarly, through the late Oligocene warming, CO_2 decline contrasts with evidence for Antarctic ice retreat and evidence of stable or warming SST. The transition from late Oligocene to early Miocene, reaching minimum CO_2 around 19 Ma, is coincident with significant cooling only in the Southern Ocean Site 1168, but not the North Atlantic site which may be more affected by changes in ocean heat transport.

Data availability

Data presented in this paper is stored at Zenodo public repository (https://doi.org/10.5281/zenodo.13908062)

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Author contribution

Study was conceived by HMS and PJP. Analysis completed by JG, SRP, RSW and LA. Interpretation by JG and HMS. Writing of original draft by JG and HMS with support of PJP.

Competing interests

The contact author has declared that none of the authors has any competing interests.

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