Natural variation of pelagic carbonate production during Cenozoic warm periods

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Epigraphs

"The future depends on what we do in the present"

Mahatma Gandhi

"The smallest action will always be better than the greatest intention"

Mahatma Gandhi

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Main symbols and Acronyms

AABW : Antarctic Bottom Water
AAIW : Antarctic intermediate water
AMOC : Atlantic meridional overturning circulation
BT : Blackman–Tukey
$CaCO_3$ AR : Carbonate accumulation rate
CBT : Cross Blackman–Tukey
DIC : Dissolved inorganic carbon
$\delta^{13}C$: stable carbon isotopes ratio: delta value for the relative abundance of 13C in a sample (‰) (Goosse, 2015),
as : $\delta^{13}C = \left[\frac{(13C/12C)sample}{(13C/12C)standard} - 1\right] \times 1000$
$\delta^{18}O$: stable oxygen isotopes ratio: delta value for the relative abundance of 18O in a sample (‰) (Goosse, 2015),
as : $\delta^{18}O = \left[\frac{(18O/16O)sample}{(18O/16O)standard} - 1\right] \times 1000$
E+T-P : eccentricity + eccentric - precession
Ecc : eccentricity (currently 0.0167)
G-IG : Glacial - Interglacial
ITCZ : Intertropical convergence zone
ky, My: kilo year, million year
LNADW : Lower North Atlantic Deep Water
MCO : Miocene climate optimum
Mis : Marine isotope stage
MPT: Mid-Pleistocene transition (900 ka ago)
MTM : Multi-Taper method
NADW : North Atlantic Deep Water
Nb [specimens] AR : number of specimens accumulation rate
NCW : Northern Component Water
NHG: Northern Hemisphere glaciations
Obl : obliquity (ε_{obl}), currently 23.45°
Ω (Omega) : saturation state (here of calcite)
pCO_2 : partial pressure of CO_2
PF : Planktonic foraminifera
ppm: parts per million
Pre : precession
psu : Practical salinity unit
PWP : Pliocene warm period
SA : Spectral analysis
SSS : Sea surface salinity
SST : Sea surface temperature
WF : Whole foraminifera shell
WT : Wavelet transform

Abstract (English)

Coccolithophore algae and planktonic foraminifera are the main producers of pelagic calcite. The export flux of their mineralised skeletons contributes significantly to the drawdown of carbon from the surface to the deep ocean and long-term (ka to Ma) carbon reservoir, and represent the main part of the inorganic carbon buried in the seafloor sediments. Compared to the organic carbon production and export from the upper ocean (the biological pump), many aspects of the orbital (ka) and geological (Ma) scale variability in pelagic calcification and inorganic carbon production (carbonate counter pump) remains less understood. The biological carbon uptake, called biological compensation, have been shown by model calculation to have a huge potential to affect the capacity of the ocean to absorb (anthropogenic) carbon dioxide, and so equilibrate the global carbon budget and hence climate. Since the pelagic calcite flux is made of two fundamentally different components, understanding of the process of biological compensation requires knowledge of variability of the relative contribution of planktonic foraminifera shells and coccoliths to the total pelagic calcite flux. The different response of the two groups could enhance or reduce the changes in total pelagic carbonate production. The capacity of the ocean to store inorganic carbon is directly related to the ion concentration in it (and so alkalinity), directly modulated by but also modulating the pelagic carbonate production. The aspects of the pelagic carbonate production that have changed through time (e.g. variability in shell/plate flux or size) and the mechanisms explaining the observed carbonate flux variability within the two main carbonate producers remain, despite their importance, largely unconstrained. Here I use marine sediments deposited in the equatorial Atlantic Ocean (Ceará Rise) to estimate the variability in pelagic carbonate production, during warm climates intervals ranging from the Neogene to the Quaternary. A re-evaluation of published records of pelagic carbonate production at this location revealed a systematic increase in sedimentation rate since the late Miocene, but no clear trend in carbonate accumulation rate. However, the records showed a large orbital scale variability in carbonate accumulation. In order to evaluate the observed orbital and long geological time scale variability of the pelagic carbonate production, I generated new high-resolution records of carbonate accumulation rate at ODP Site 927 across two Quaternary interglacials (MIS 5 and MIS 9), the Pliocene warm period (MIS KM5) and the Miocene climate optimum (MCO). Subsequently, I used different techniques to quantify the changes in the relative contribution of the two main pelagic carbonate producers to the total pelagic carbonate production within and between the chosen time intervals. Finally, automated image recognition techniques were applied, for both the planktonic foraminifera and the coccoliths, to investigate the parameters that have changed in calcite production in the two groups (e.g. abundance, size, or calcification). As expected from the published long-term records, the new data revealed orbital variability in each of the studied intervals, with a magnitude similar or even higher than the long geological time scale changes among the studied intervals. The pre-Quaternary record, not affected by dissolution, reveals that pelagic carbonate burial followed Earth obliquity (41 ka) and eccentricity (100 ka). Since preservation has been excluded to be driving the changes in carbonate accumulation rates (good fossils preservation, low foraminifera fragmentation index and no correlation between the carbonate accumulation rate and fragmentation index), these periodicities must reflect an orbital modulation of the pelagic biogenic carbonate production. I find that the relative contribution of the planktonic foraminifera compared to coccoliths to the total pelagic carbonate production remains relatively constant on long geological time scales, and shows a high orbital time scale variability (factor of two). The nature of this variability has changed from the Miocene to the Quaternary, but since we do not observe any correlation between the carbonate accumulation rate and the relative contribution of the foraminifera fraction to the total

carbonate accumulation rate, the changes of the relative contribution of the two groups are not driving the changes in total pelagic carbonate production. Looking for the explanation of the changes observed within the two groups, I find that the main driver of the pelagic carbonate changes, at all orbital frequencies as well as between the Miocene and the Pliocene, and for both the planktonic foraminifera and the coccoliths were changes in population growth: at all time scales, the pelagic carbonate production was mainly driven by changes in the number of specimens produced, whilst individual size and calcification were much less important. In fact, the data reveal an inverse relationship between carbonate accumulation and individual size, likely reflecting a shift in the composition of the communities for both the planktonic foraminifera and the coccoliths, with bigger populations made of smaller specimens and smaller populations made of bigger specimens. This observation is valid for both the orbital scale with the different dominant orbital periodicities we observe and the longer geological time scale. I conclude that at the studied location, pelagic carbonate production since the Miocene was driven by population growth of both main calcite producers. The observed dominant periodicities in carbonate accumulation rate indicate that the two groups responded to local changes in factors affecting their productivity, like light, temperature and nutrient delivery through upwelling rather than to global climate modulations, with a magnitude of change similar to that which resulted in long term shifts in carbonate accumulation rate. On both time scales, the observed changes in carbonate accumulation were large enough to affect the marine inorganic carbon cycle and thus the ocean’s capacity to absorb inorganic carbon.

Abstract (German)

Coccolithophore Algen und planktische Foraminiferen sind die Hauptproduzenten von pelagischem Kalzit. Der Exportfluss ihrer mineralisierten Skelette trägt wesentlich zur Absenkung des Kohlenstoffs von der Oberfläche in die Tiefsee und in das langfristige (ka bis Ma) Kohlenstoffreservoir bei und macht den größten Teil des anorganischen Kohlenstoffs aus, der in den Sedimenten des Meeresbodens gebunden ist. Verglichen mit der Produktion und dem Export von organischem Kohlenstoff aus dem oberen Ozean (der biologischen Pumpe) sind viele Aspekte der orbitalen (ka) und geologischen (Ma) Variabilität der pelagischen Kalzifizierung und der Produktion von anorganischem Kohlenstoff (Karbonat-Gegenpumpe) noch weniger bekannt. Modellrechnungen haben gezeigt, dass die biologische Kohlenstoffaufnahme, die sogenannte biologische Kompensation, ein enormes Potenzial hat, die Fähigkeit des Ozeans zur Aufnahme von (anthropogenem) Kohlenstoffdioxid zu beeinflussen und so den globalen Kohlenstoffhaushalt und damit das Klima ins Gleichgewicht zu bringen. Da sich der pelagische Kalzitfluss aus zwei grundlegend unterschiedlichen Komponenten zusammensetzt, erfordert das Verständnis des Prozesses der biologischen Kompensation die Kenntnis der Variabilität des relativen Beitrags von planktischen Foraminiferenschalen und Coccolithen zum gesamten pelagischen Kalzitfluss. Die unterschiedliche Reaktion der beiden Gruppen könnte die Veränderungen in der pelagischen Gesamtkarbonatproduktion verstärken oder verringern. Die Fähigkeit des Ozeans, anorganischen Kohlenstoff zu speichern, steht in direktem Zusammenhang mit der Ionenkonzentration (und damit der Alkalinität), die direkt von der pelagischen Karbonatproduktion abhängt, diese aber auch beeinflusst. Die Aspekte der pelagischen Karbonatproduktion, die sich im Laufe der Zeit verändert haben (z. B. die Variabilität des Schalen-/Plattenflusses oder der Größe), und die Mechanismen, die die beobachtete Variabilität des Karbonatflusses innerhalb der beiden Hauptkarbonatproduzenten erklären, sind trotz ihrer Bedeutung noch weitgehend ungeklärt. Hier verwende ich Meeressedimente, die im äquatorialen Atlantik (Ceará-Rise) abgelagert wurden, um die Variabilität der pelagischen Karbonatproduktion während warmer Klimazonen vom Neogen bis zum Quartär abzuschätzen. Eine Neubewertung der veröffentlichten Aufzeichnungen über die pelagische Karbonatproduktion an diesem Ort ergab einen systematischen Anstieg der Sedimentationsrate seit dem späten Miozän, aber keinen eindeutigen Trend in der Karbonatakkumulationsrate. Die Aufzeichnungen zeigten jedoch eine große orbitale Variabilität in der Karbonatakkumulation. Um die beobachtete orbitale und langzeitliche Variabilität der pelagischen Karbonatproduktion zu bewerten, habe ich an der ODP-Stelle 927 neue hochauflösende Aufzeichnungen der Karbonatakkumulationsrate über zwei quartäre Interglaziale (MIS 5 und MIS 9), die pliozäne Warmzeit (MIS KM5) und das miozäne Klimaoptimum (MCO) erstellt. Anschließend setzte ich verschiedene Techniken ein, um die Veränderungen des relativen Anteils der beiden wichtigsten pelagischen Karbonatproduzenten an der gesamten pelagischen Karbonatproduktion innerhalb und zwischen den gewählten Zeitintervallen zu quantifizieren. Schließlich wurden automatisierte Bilderkennungstechniken sowohl für die planktischen Foraminiferen als auch für die Coccolithen angewandt, um die Parameter zu untersuchen, die sich bei der Kalzitproduktion in den beiden Gruppen verändert haben (z. B. Häufigkeit, Größe oder Kalzifizierung). Wie aus den veröffentlichten Langzeitaufzeichnungen zu erwarten war, zeigten die neuen Daten eine orbitale Variabilität in jedem der untersuchten Intervalle, die ähnlich groß oder sogar größer war als die Veränderungen auf der langen geologischen Zeitskala zwischen den untersuchten Intervallen. Die Aufzeichnungen aus der Zeit vor dem Quartär, die nicht von der Auflösung betroffen sind, zeigen, dass die Ablagerung pelagischer Karbonate der Achsenneigung (41 ka) und der Exzentrizität (100 ka) folgte. Da ausgeschlossen wurde, dass die Erhaltung die

Veränderungen der Karbonatakkumulationsraten vorantreibt (gute Fossilerhaltung, niedriger Fragmentierungsindex der Foraminiferen und keine Korrelation zwischen der Karbonatakkumulationsrate und dem Fragmentierungsindex), müssen diese Periodizitäten eine orbitale Veränderung der pelagischen biogenen Karbonatproduktion widerspiegeln. Ich stelle fest, dass der relative Beitrag der planktischen Foraminiferen im Vergleich zu den Coccolithen zur gesamten pelagischen Karbonatproduktion auf langen geologischen Zeitskalen relativ konstant bleibt und eine hohe orbitale Zeitskalenvariabilität (Faktor zwei) aufweist. Die Art dieser Variabilität hat sich vom Miozän bis zum Quartär verändert, aber da wir keine Korrelation zwischen der Karbonatakkumulationsrate und dem relativen Beitrag der Foraminiferenfraktion zur Gesamtkarbonatakkumulationsrate beobachten, sind die Veränderungen des relativen Beitrags der beiden Gruppen nicht die treibende Kraft für die Veränderungen der pelagischen Gesamtkarbonatproduktion. Auf der Suche nach einer Erklärung für die beobachteten Veränderungen innerhalb der beiden Gruppen stelle ich fest, dass die Haupttriebkraft für die Veränderungen der pelagischen Karbonatproduktion bei allen Orbitalfrequenzen sowie zwischen dem Miozän und dem Pliozän und sowohl für die planktischen Foraminiferen als auch für die Coccolithen Veränderungen des Populationswachstums waren: Auf allen Zeitskalen wurde die pelagische Karbonatproduktion hauptsächlich durch Veränderungen der Anzahl der produzierten Exemplare angetrieben, während die individuelle Größe und die Kalzifizierung viel weniger wichtig waren. Tatsächlich zeigen die Daten eine umgekehrte Beziehung zwischen Karbonatakkumulation und individueller Größe, was wahrscheinlich eine Verschiebung in der Zusammensetzung der Gemeinschaften sowohl bei den planktischen Foraminiferen als auch bei den Coccolithen widerspiegelt, wobei größere Populationen aus kleineren Exemplaren und kleinere Populationen aus größeren Exemplaren bestehen. Diese Beobachtung gilt sowohl für die orbitale Skala mit den von uns beobachteten unterschiedlichen dominanten orbitalen Periodizitäten als auch für die längere geologische Zeitskala.

Ich schließe daraus, dass die pelagische Karbonatproduktion am untersuchten Standort seit dem Miozän durch das Populationswachstum der beiden wichtigsten Kalzitproduzenten angetrieben wurde. Die beobachteten dominanten Periodizitäten in der Karbonatakkumulationsrate deuten darauf hin, dass die beiden Gruppen eher auf lokale Veränderungen von Faktoren reagierten, die ihre Produktivität beeinflussen, wie Licht, Temperatur und Nährstoffzufuhr durch Auftrieb, als auf globale Klimaveränderungen, und zwar mit einem ähnlichen Ausmaß an Veränderungen, wie sie zu langfristigen Verschiebungen in der Karbonatakkumulationsrate führten. Auf beiden Zeitskalen waren die beobachteten Veränderungen der Karbonatakkumulation groß genug, um den marinen anorganischen Kohlenstoffkreislauf und damit die Fähigkeit des Ozeans zur Aufnahme von anorganischem Kohlenstoff zu beeinflussen.

Abstract (French)

Les coccolithophores et les foraminifères planctoniques sont les principaux producteurs de calcite pélagiques. Le flux d'export de leurs squelettes minéralisés contribue de manière significative au déplacement du carbone de l'Océan de surface vers les abysses et vers le réservoir de carbone à plus long terme (ka à Ma), et ils représentent la majeure partie du carbone inorganique enfoui dans les sédiments des fonds océaniques. Contrairement à la production et l'export de carbone organique depuis la surface des Océans (la pompe biologique), de nombreux aspects de la variabilité de la calcification pélagique et de la production de carbone inorganique (la contre pompe à carbonate) aux échelles orbitale (ka) et géologique (Ma) restent peu comprises. L'assimilation du carbone via des processus biologiques (la compensation biologique), a été démontrée, via des calculs de modélisation, avoir un grand potentiel à affecter la capacité de l'océan à absorber le dioxyde de carbone (anthropogénique), et donc, à équilibrer le budget de carbone global et ainsi le climat. Puisque le flux pélagique de calcite est constitué de deux composantes complètements différentes, comprendre les processus de la compensation biologique requiert des connaissances sur la variabilité de la contribution relative des foraminifères planctoniques et des coccolithes à la production de carbonate pélagique total. Une réponse différente des deux groupes pourrait accentuer ou réduire les changements de production de carbonate pélagique total. La capacité de l'Océan à stocker le carbone inorganique est directement liée à sa concentration en ions (et donc à son alcalinité), directement modulée, mais aussi modulant, la production de carbonate pélagique. Les aspects de la production de carbonate pélagique, ayant changé au cours du temps, (e.g. la variabilité du flux de tests / placolithes ou leur taille) et les mécanismes expliquant la variabilité du flux de carbonate observé entre les deux principaux organismes producteurs de carbonate restent, en dépit de leur importance, largement incompris. Ici, j'utilise des sédiments marins déposé dans l'Océan Atlantique équatorial (Ceará Rise) afin d'estimer la variabilité de la production pélagique de carbonate, durant les intervalles climatiques chauds allant du Néogène au Quaternaire. Une réévaluation d'enregistrements de production de carbonate pélagique publiés à cette location a révélé une augmentation systématique du taux de sédimentation depuis la fin du Miocène, mais aucune tendance claire dans le taux d'accumulation de carbonate. De plus, les enregistrements montrent une importante variabilité orbitale dans le taux d'accumulation. Afin d'évaluer la variabilité de la production pélagique de carbonate aux échelles orbitale et géologique, j'ai généré de nouveaux enregistrements à haute résolution des taux d'accumulation de carbonate au Site ODP 927 au travers de deux interglaciaires du Quaternaire (MIS 5 et MIS 9), de l'intervalle chaud du Pliocène (MIS KM5) et de l'optimum climatique du Miocène (MCO). Par la suite, j'ai utilisé différentes techniques afin de quantifier les changements dans la contribution relative des deux principaux producteurs de carbonate pélagique à la production de carbonate pélagique totale, au sein et entre les intervalles de temps choisis. Enfin, des techniques de reconnaissance d'image automatique ont été utilisées, pour les foraminifères planctoniques ainsi que pour les coccolithes, pour investiguer les paramètres ayant changé dans la production de calcite au sein des deux groupes (e.g. abondance, taille ou calcification). Comme attendu d'après les enregistrements long-terme existants, les nouvelles données révèlent une variabilité orbitale dans chacun des intervalles étudiés, d'une magnitude similaire ou même supérieure de celle trouvée dans les changements à l'échelle de temps géologique entre les intervalles étudiés. L'enregistrements pré-Quaternaire, non affecté par la dissolution, révèle que l'enfouissement de carbonate pélagique a suivi l'obliquité (41 ka) et l'excentricité (100 ka) de l'orbite terrestre. Comme la préservation a été exclue d'être un contrôle des changements de taux d'accumulation de carbonate (la préservation des fossiles est bonne, l'indice de fragmentation des foraminifères est bas, et il n'y a pas de corrélation

entre le taux d'accumulation de carbonate et l'indice de fragmentation des foraminifères), ces périodicités reflètent probablement des modulations orbitales du taux de production de carbonate biogénique pélagique. Je trouve que la contribution relative des foraminifères planctoniques, comparée à celle coccolithes, à la production de carbonate pélagique totale reste relativement constante à l'échelle géologique, et montre une grande variabilité a l'échelle de temps orbitale (d'un facteur deux). La nature de cette variabilité a changé du Miocène au Quaternaire, mais comme nous n'observons aucune corrélation entre le taux d'accumulation de carbonate et la contribution relative des foraminifères au taux d'accumulation de carbonate total, les changements de la contribution relative des deux groupes ne sont pas à l'origine des changements de production de carbonate pélagique total. Cherchant l'explication des changements observés au sein des deux groupes, je trouve que le principal mécanisme dirigeant les changements du carbonate pélagique, pour toutes les périodicités orbitales, entre le Miocène et le Pliocène, à la fois pour les foraminifères planctoniques et pour les coccolithes, est la modulation de la taille des populations : pour toutes les échelles de temps, la production de carbonate pélagique est principalement dirigée par des changements du nombre de spécimens, alors que leur taille ou leur degré de calcification restent bien moins importants. En effet, les données révèlent une relation inverse entre le taux d'accumulation de carbonate et la taille des spécimens, reflétant probablement un changement des communautés pour les foraminifères planctoniques ainsi que pour les coccolithes, avec de plus grandes populations constituées de plus petits spécimens et de plus petites populations constituées de plus grands spécimens. Cette observation est valable pour l'échelle orbitale, avec les différentes périodicités dominantes que nous observons, ainsi que pour l'échelle géologique plus longue. Je conclus qu'à la location étudiée, la production de carbonate pélagique depuis le Miocène est dirigée par la croissance des populations des deux principaux producteurs de calcite. Les périodicités dominantes observées dans le taux d'accumulation de carbonate indiquent que les deux groupes ont répondu à des changements locaux de facteurs affectant leur productivité, comme la lumière, la température ou les apports de nutriments via les upwellings, eux-mêmes modulés par les cycles orbitaux, plutôt qu'aux modulations climatiques globales, avec une magnitude de changement similaire à celle qui a résulté aux changements sur le long terme du taux d'accumulation de carbonate. Pour les deux échelles de temps, les changements observés de l'accumulation de carbonate ont été suffisamment importants pour affecter le cycle du carbone inorganique marin et par conséquent, la capacité de l'Océan à absorber le carbone inorganique.

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Own contribution to the manuscripts

This PhD project has been prepared and the main scientific question designed by the candidate (PC) with the advice of the PhD committee members (MK, HP, TB and KB). The choice of the samples (and geographic location of this study) as well as the main questions corresponding to each chapter have been defined by the candidate jointly with MK. The whole project is based on the same 261 samples, collected by PC in the Bremen core repository (in 2019), on cores previously collected in the equatorial Atlantic Ocean (ODP Leg 154, in 1994).

The first study's question (**chapter II**) and protocol has been defined and prepared by the candidate with the help from all the co-authors. The PhD candidate has sampled all the cores at Bremen core ODP/IODP repository and prepared the samples that have been given to BK for carbonate content LECO analysis. The candidate has prepared a compilation of the previously published carbonate content and calculated the accumulation rates for the five Ceará Rise sites, with the help of TW for the attribution of the most recent composite depths and corresponding ages to the different samples (in order to have a consistency, as the data were coming from different publications, and therefore, where not presented using the same age model). With the advice and help of TW, the candidate has re-tuned the age model for the three periods of interest, to have the most accurate and high-resolution age model possible. The candidate picked benthic foraminifera on the 50 samples from the oldest studied interval and stable isotopes analyses have been run by HK on them. The analyses (i.e. calculation of carbonate content and accumulation rate, spectral analysis, corrections of the stable isotopes records), interpretation as well as the drafting of the first manuscript were carried out by PC, with the supervision of MK and TW. As this manuscript is under review process for publication, the manuscript has also been modified after the two reviewers' comments.

For the second study (**chapter III**), the candidate defined the protocol and carried out the laboratory processing of samples, including the washing and sieving of the samples and preparation of coccolithophores microscopic slides using quantitative random settling protocol. After this, the candidate proceeded to the coarse fraction analysis, and the coccoliths slides (small fraction analysis) using the SYRACO device have been processed by LB at Cerege (France). The results analysis and interpretation have been carried out by PC for both the foraminifera and the coccoliths fraction. The final analysis (e.g. calculation of the carbonate accumulation rate for all the fractions, spectral analysis, quantification of change, figures) have been processed by the candidate. The drafting of the manuscript has been done by PC and reviewed by MK.

For the third study (**chapter IV**), the candidate defined the protocol (and created new microscopic slides for the coarse fraction analysis) and carried out the laboratory processing (Keyence pictures of the coarse fraction, and processing of the analysis on these pictures). The fine fraction analysis (coccoliths sizes measurements and counting) have been done at the same time as the ones for the second study by LB. The size data analysis, calculation of the shape and lobateness parameters, calculation and analysis of the number of specimens, spectral analysis (both Wavelet transform and Blackman-Tukey), interpretations and all the resulting figures have been done by the candidate (PC) with the advices of MK. The drafting of the manuscript has been done by PC and reviewed by MK.

Chapter I. Introduction

I.1 The Ocean as a carbon reservoir, state of the art and research gaps

I.1.i General introduction

The ocean, covering more than 70 % of the Earth surface (Goosse, 2015), represents one of the major anthropogenic carbon sink, with the export of around 25% of the (anthropogenic) carbon from the atmosphere to the deep ocean (Sabine et al., 2004; Khatiwala et al., 2009; Landschützer et al., 2014; Friedlingstein et al., 2019, 2020; DeVries, 2022), crucial in the climate system, as we know that the CO_2 is the major greenhouse gas today (0.0395 % of the air composition in 2013) and the atmospheric CO_2 concentration keeps increasing due to the anthropogenic activities (currently around 100 ppm above the pre-industrial pCO_2 values, Denman et al., 2007). The amount of anthropogenic CO_2 absorbed by the ocean has been estimated around 2 Pg-C y^{-1} for 2000 (Mikaloff Fletcher et al., 2006; Takahashi et al., 2009). The atmospheric pCO_2 increased from 278 ppm to 395 ppm between 1750 and 2013 to 407 ppm in 2018 (Siegenthaler, 2005; Joos and Spahni, 2008; Friedlingstein et al., 2019; Goosse, 2015), responsible for climate warming, modifying the ecosystems, the environment, the heat transport and repartition over our planet and the climate system as a whole (Ciais et al., 2013). The increasing pCO_2 related to anthropogenic activities has been the main driver of the SST increase, with at least 67% of it forced by human activities (Santer et al., 2006). The CO_2 transfer from the atmosphere to the surface ocean occurs when the CO_2 concentration in the atmosphere is not in equilibrium with the CO_2 concentration of the surface ocean, which creates a flux (Goosse, 2015; Gruber et al., 2009). The CO_2 flux between the atmosphere and the surface ocean is not constant through the time (on time scales going from years to million years, and depends on many parameters, e.g. the temperature, the salinity, the atmospheric pCO_2 pressure, the ocean pCO_2 pressure, the wind speed, the physical properties of the surface ocean or nutrients delivery (DeVries, 2022; Marinov et al., 2008; Lefèvre et al., 2014; Andrié et al., 1986; Fung et al., 2005; Takahashi et al., 2009). A warming and freshening of the surface ocean reduce the CO_2 solubility, increases the stratification and leads to a weakening of the Atlantic meridional overturning circulation (AMOC), reducing the carbon export. Increasing stratification also reduces nutrients delivery and so reduces the biological productivity (Fung et al., 2005). There is also a geographical variability, with a higher CO_2 flux on the Southern Ocean than at low latitudes (Milliman, 1993; Khatiwala et al., 2009). If global oceans are net CO_2 sinks, contributing to the reduction of the atmospheric pCO_2, the sink areas are concentrated in the high latitudes while tropical oceans are generally CO_2 sources (Takahashi et al., 2009; Landschützer et al., 2014; Ibánhez et al., 2016; Gruber et al., 2009), with low seasonal variability of the CO_2 flux (Feely et al., 2009).

In the Atlantic Ocean, it has been shown that the climatic conditions and the biological production are impacting the relationship between the surface ocean pCO_2 and the oceanic circulation (Boot et al., 2022). If some have found that a change of the strength of the AMOC only (towards a weakening, according to the predictions) alone, would not have a strong impact on the atmospheric pCO_2 (Boot et al., 2022), other studies are highlighting the influence of the intermediate and deep ocean circulation in the nutrients delivery, and so, productivity and atmospheric pCO_2, and that variability in surface nutrient concentration or export production alone are not enough to understand the atmospheric pCO_2 modulations and carbon cycle (Marinov et al., 2008).

Between 2009 and 2018, fossil CO_2 emissions due to anthropogenic activities accounted for about 9.5 GtC yr^{-1} and the ocean absorbed around 2.5 GtC yr^{-1} for the same time interval, and both the emissions and absorption by the ocean are in an increasing trend (Khatiwala et al., 2009; Friedlingstein et al., 2019; DeVries, 2022; Landschützer et al., 2014; Bennington et al., 2022). The average atmosphere to surface ocean carbon flux is estimated around 0.4 tC month^{-1} km^{-2} (Takahashi et al., 2009). The atmospheric pCO_2 and the inorganic carbon stocked in the ocean are closely related to each other (Marinov et al., 2008). The pelagic carbonate production is strongly influencing and modulating the pCO_2 concentrations but is also influenced and modulated by it, and the relationship linking those two parameters is still under debate (Boot et al., 2022).

The transfer of CO_2 from the atmosphere to the surface ocean is lowering the average ocean pH (so increasing acidity), estimated at - 0.1 since 1750 according to Denman et al. (2007) and the Working Group I (WGI) contribution to the Sixth Assessment Report (AR6) of the Intergovernmental Panel on Climate Change (IPCC) (2021). This phenomenon may negatively impact the carbonate system in the ocean, from short (reduced calcification of calcifiers organisms) to longer time scales (affecting the carbonate sediment) (Denman et al., 2007). Bolton et al. (2016) demonstrated that the sea surface pCO_2 changes are modulating the pelagic carbonate production (and so, the temperature, which is itself driving the CO_2 solubility in the surface waters). The biological production increases the ocean uptake via the reduction of pCO_2 concentration in the surface ocean (Fung et al., 2005). The seasonal phytoplankton blooms related to insolation increase contribute to make the surface ocean a carbon sink (Takahashi et al., 2009). At their death, the pelagic calcifiers are settling to the deep ocean, and so, exporting carbon from the surface ocean to the seafloor, having a strong influence on the modulation of the atmospheric pCO_2 (Boyd et al., 2019; Sutherland et al., 2022).

Some models are estimating that an increase of temperature would lead to the increase of anthropogenic CO_2 remaining in the atmosphere, and so, contribute to an enhancement of the temperature increase (positive feedback), estimated between 20 and 224 ppm by 2100 (Denman et al., 2007). Because marine organisms carbonate production accounted for around 5.3 GT yr^{-1} and around 2.4 GT yr^{-1} of it is produced by pelagic calcifiers (Milliman, 1993), and because the biogenic calcium carbonate production is at the origin of around 90% of the carbon currently buried in the seafloor (Sarmiento and Gruber, 2006; Feely, 2004; Toyofuku et al., 2017), better understanding its behaviour under higher temperature and higher pCO_2 conditions is crucial in the ongoing climate change.

If we tend more and more to understand better the mechanisms at work today, their behaviour in a changing climate and especially under warmer and warmer conditions (and increasing atmospheric pCO_2 due to anthropogenic emissions) remains poorly understood. However, these mechanisms are key knowledge to better constrain our models and so, realistically estimate the ongoing conditions in the actual context of climate warming. In this study, we have made the choice to focus on the pelagic carbonate production at the surface ocean, responsible for ¼ carbon export per year (Sabine et al., 2004; Khatiwala et al., 2009; Landschützer et al., 2014; Friedlingstein et al., 2019, 2020; DeVries, 2022). This pelagic carbonate production, especially during warm periods, is a key parameter to estimate the climate and efficiency of the ocean as a (anthropogenic) carbon sink, a precious information that can be derived from marine sediment records, archives of the past climate history, that are collected via coring the ocean's floor.

There are two steps in the understanding of the pelagic carbonate production processes: understanding how it varies and what does vary in the organisms (within the pelagic carbonate producers, what makes this changes and make our results look how they do and "why" we observe what we observe), and the second step is understanding the environmental, orbital and climate forcing on them that makes them change that way and why it induce the observed response. We here focus on the first part, indispensable to better constrain our model for prediction of the direction of the pelagic carbonate production and possible direction and timings of their influence on the global climate for the coming years to hundred years. To do so, we have chosen a marine sediment core in the Equatorial Atlantic Ocean, where the resolution is very good, with low dissolution, and a very well constrained age model. The equatorial location allows as well a record which is not impacted by large temperature changes through the time. This sediment core is covering a large time interval in the Cenozoic (From Early Miocene to Quaternary), allowing us to work on different warming intervals in recent Earth History, at different time scales and under different pCO_2 conditions and oceanic currents system, in order to better understand what happened in the past and to better envisage the different scenarios that await us in the future.

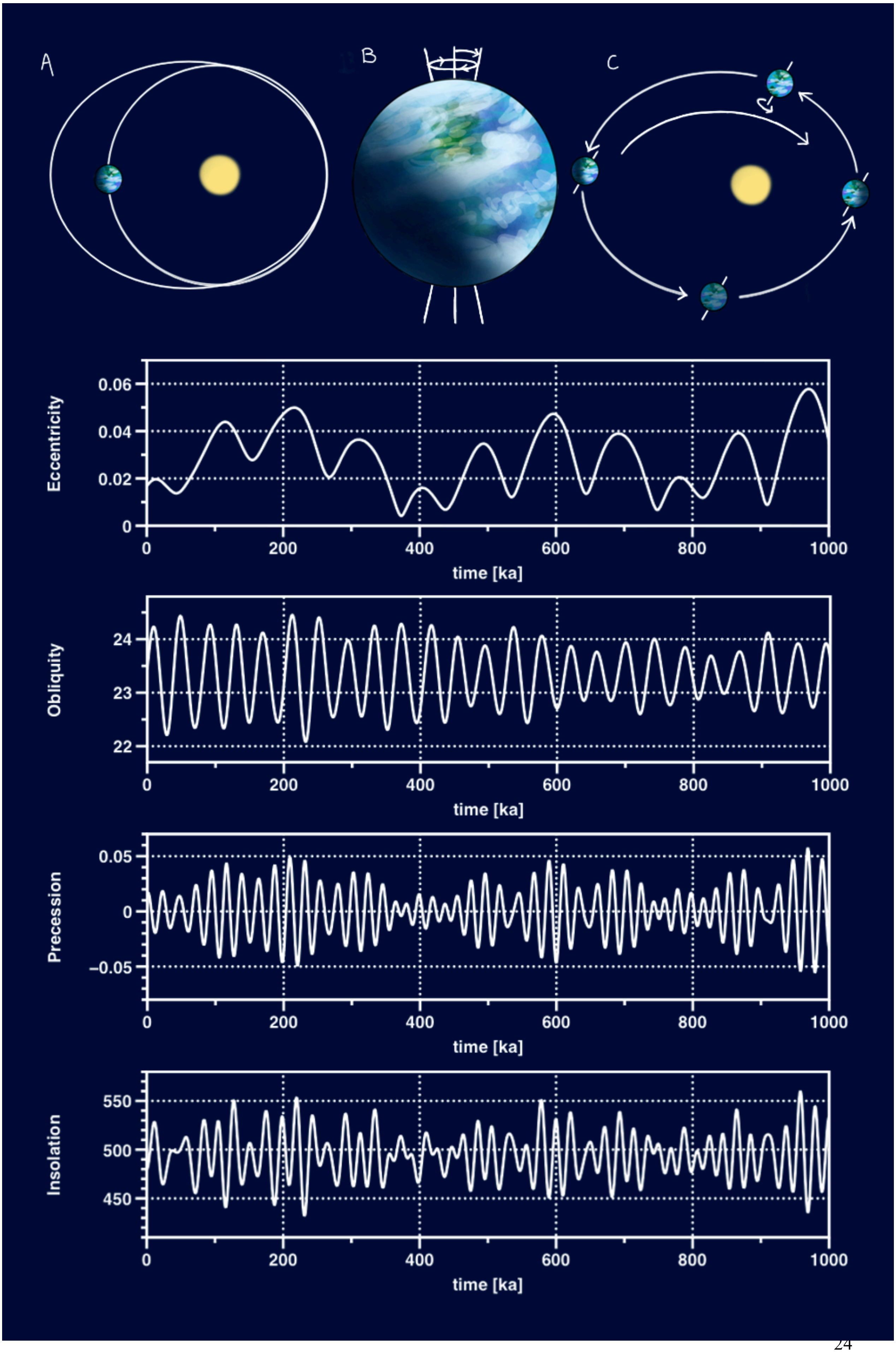
As some studies have already shown the influence of the orbital forcing (and low latitude insolation on the pelagic carbonate production (e.g. Beaufort et al., 1997, 2022), we are here investing the pelagic carbonate production at orbital (ka) and geological (Ma) time scales.

I.1.ii Climate and Ocean system

Section 1. Orbital forcing

The Earth is moving around the sun, following an elliptical trajectory. This trajectory is characterised by different parameters, changing through the time periodically (Figure 1) and influencing the quantity of solar energy arriving at the Earth's surface. This modulation of the Earth insolation is having a strong influence on the climate and environmental conditions on Earth, in the atmosphere, on the continents and in the Oceans (Hays et al., 1976). Milankovitch, in his astronomical theory of climate (1941) was the first to mention the existence of cycles in the different parameters describing the orbital trajectory of the planets around the sun. It is today admitted that there are three parameters, following different periodicities: the eccentricity, the obliquity and the precession (Figure 1).

The eccentricity is defined by how round is the orbit of the Earth around the sun. This parameter is changing with the dominant periodicities of 95, 100, 123 and 404 ka. An eccentricity nearly at zero means that the Earth's orbital trajectory is almost circular, and in these conditions, the mean annual insolation is the smallest. When the eccentricity increases, the mean annual energy received at the Earth surface increases (at all latitudes). The obliquity is defining how tilted the Earth axis. This parameter is changing with the dominant periodicities of 40, 41 and 54 ka, from an angle of 22° to an angle of 24.5°. When the obliquity increases, the annual mean insolation at the equator slightly decreases. Finally, the precession, which is the Earth distance to the sun at the summer solstice, is changing with the dominant periodicities of 19, 22 and 24 ka. This has a strong influence on the seasonality, and the contrast between the seasons. When the precession increases (and even more when the eccentricity is high too), this is impacting the isolation at all latitudes, influencing the seasonal contrast, and determining what is the earth position relat ive to the sun at the boreal summer and winter. A higher precession means a lower insolation (Goosse, 2015; Berger and Loutre, 2004). The tropical condition and insolation are important in the global climate modulations at orbital and suborbital time scales (Beaufort et al., 1997; Berger et al., 2006).


A
B
C
Eccentricity
0.06
0.04
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0
0
200
400
600
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1000
time [ka]
Obliquity
24
23
22
0
200
400
600
800
1000
time [ka]
Precession
0.05
0
−0.05
0
200
400
600
800
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time [ka]
Insolation
550
500
450
0
200
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600
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time [ka]

Figure 1. schematic representation of the three orbital parameters: A) the eccentricity, B) the obliquity and C) the precession (modified after Goosse, 2015; Hay et al., 1997; Berger and Yin, 2012) and their periodic signals over the last 1000 ka (Laskar et al., 2004). Proportions are not taken in account.

Section 2. Marine inorganic carbon cycle

The atmospheric concentration in CO_2 is an important factor influencing the climate (I.1.i). In the climate system, the pCO_2 in the atmosphere and the ocean are closely related, as there are exchanges between the atmosphere and the surface ocean. The zone between 40 and 60° latitude in both hemispheres is where the major pCO_2 uptake takes place (Takahashi et al., 2002). We here concentrate on the - oceanic - inorganic carbon cycle (Figure 2). With the increase of pCO_2 in the atmosphere (especially anthropogenic CO_2 release), more CO_2 is transferred to the surface ocean, and with it, the speciation of different ions, with the release of hydrogen positive ions, is modifying the chemistry of the surface ocean and making it more acidic (Goosse, 2015). The pCO_2 at the sea surface is depending on the atmospheric pCO_2 and the temperature and so the ocean as a carbon sink as well (Feely, 2004; Landschützer et al., 2014; Honjo et al., 2014; Gao et al., 2017; Takahashi et al., 2009). The changes in dissolved pCO_2 have an influence on the ion's concentration in the surface ocean and its acidity. A higher concentration in CO_2 dissolved in the ocean also means higher concentration in carbonate $[CO_3^{2-}]$ and bicarbonate $[HCO_3^-]$ ions. These ions are entering into the equation of the carbonate precipitation by the marine organisms (the pelagic calcifiers) living at the surface ocean. This is the carbonate uptake or carbonate biological compensation (by opposition to the dissolution or chemical compensation). These pelagic calcifiers are both consuming CO_2 by incorporating carbon in their carbonate shells and releasing CO_2 via the carbonate counter-pump. By these processes, they strongly influence the surface ocean chemistry (e.g. DIC and Alkalinity, Figure 2). Alkalinity is of importance in the CO_2 uptake from the atmosphere to the surface ocean, the carbonate production and the ocean buffering in a changing climate context (Middelburg et al., 2020), modifying the carbonate compensation depth (Boudreau et al., 2018). According to Boudreau et al. (2019), the ocean cooling over the last 15 Ma might be at the origin of the increase of DIC and alkalinity observed for that time interval. Meanwhile, warmer climates and increasing atmospheric pCO_2 might increase weathering rates and ocean alkalinity, with higher marine calcification (Si and Rosenthal, 2019; Sutherland et al., 2022). At their death, these pelagic calcifiers sink to the ocean floor (this is the carbon export) and are affected by dissolution, here again, influencing the ocean chemistry (alkalinity, DIC and CO_2 concentration). The sinking processes are taking days to weeks, depending on the particles' sizes, the currents, the water depth or if they are single particles (often planktonic foraminifera) or aggregated ballast (often coccoliths) (Guidi et al., 2009, 2015; Laws et al., 2000; Le Moigne et al., 2014; Legendre et al., 2018). The carbonate ooze accumulates on the seafloor, the most recent ones above the oldest, making this sediment a good archive of the past climate, environments and oceanic conditions. The level of carbonate saturation in the seawater is defined as Ω (Figure 2). When $\Omega>1$, the ocean is saturated so there is no dissolution. When $\Omega<1$, the ocean is undersaturated and we start to observe dissolution. The saturation horizon is defined as $\Omega=1$. The carbonate compensation depth (CCD) is the limit at which all the carbonate is dissolved. Between the saturation horizon and the CCD is the Lysocline (also called transition zone). These conditions are strongly influenced by the currents and ocean configuration. According to Lea, (2000), the tropical conditions are both playing an important role on and being strongly affected by the climate modulations (Goosse, 2015). The oceanic ion concentration is affected by the ocean structure and currents distribution.

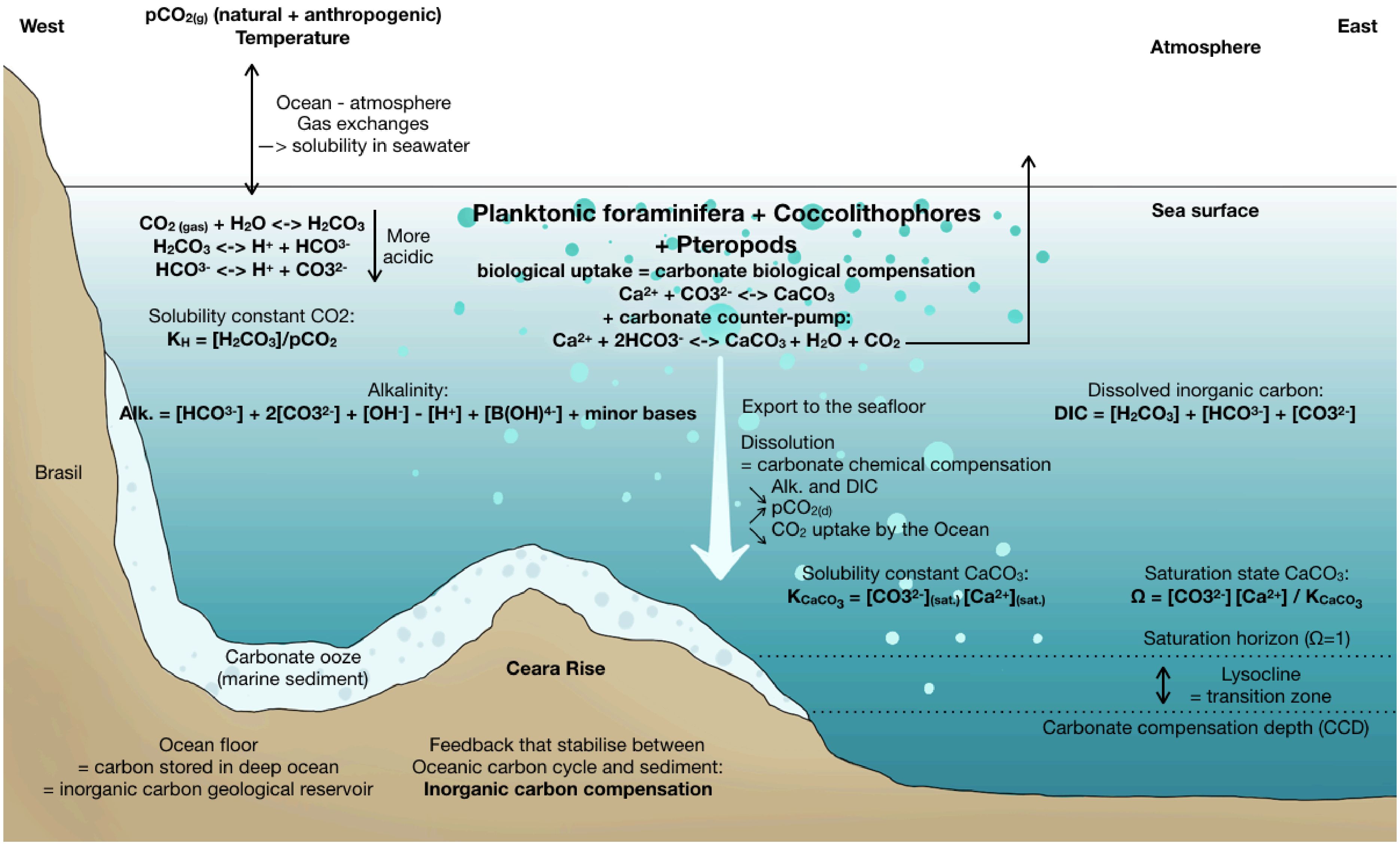

Figure 2. Marine inorganic carbon cycle: the example of the equatorial Atlantic Ocean (Goosse, 2015; Boudreau et al., 2018; Middelburg et al., 2020).

Section 3. The Ocean - general aspects and zoom on the Atlantic

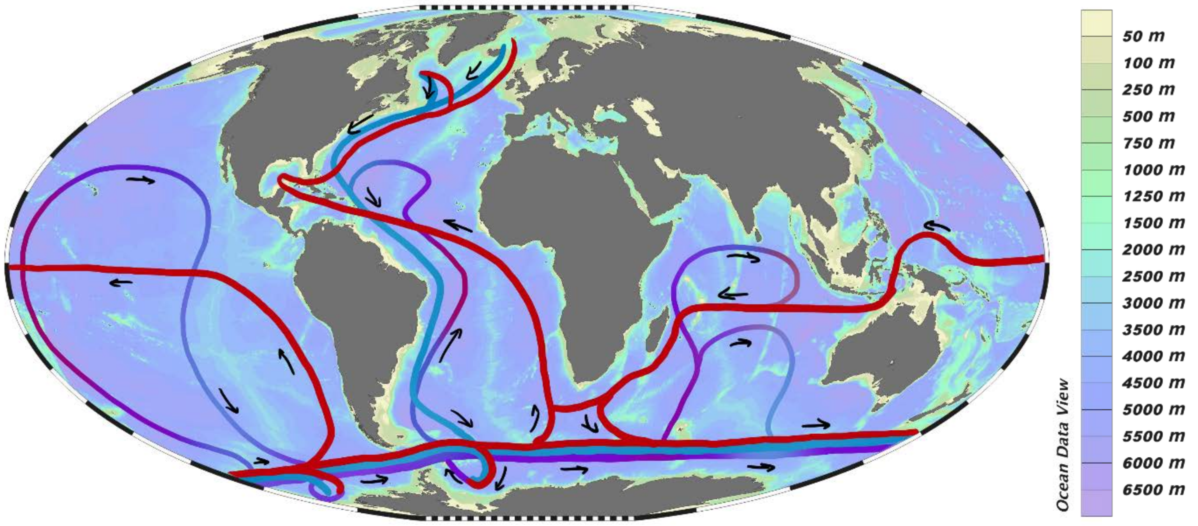

Figure 3. World ocean thermo-haline currents circulation, modified after (Rahmstorf, 2002), ocean data view (Schlitzer, 2018).

Salinity and temperature are not the same everywhere in the ocean, both in surface and in the depth structure, creating oceanic currents (Figure 3) with different properties (e.g. salinity, temperature, nutrient content or ion concentrations) that have a strong influence in the marine productivity (e.g. upwellings delivering nutrients) or the deep ocean circulation (e.g. presence or absence of deep currents undersaturated in carbonate, (Curry et al., 1995; Gröger et al., 2003b; Frenz et al., 2006).

From Neogene to present, the continental configuration at the Earth's surface remains similar (Dowsett et al., 2009) and so the currents dynamics too. The main tectonic change that has affected the Atlantic Ocean is the closure of the Panama Isthmus, between 13 Ma and 2.6 Ma (Bartoli et al., 2005; Lunt et al., 2008; O'Dea et al., 2016). This affected the oceanic circulation, currents position and exchange between the different oceans as well as ocean atmosphere feedback mechanisms, and so, climate in general since the late Miocene-early Pliocene (Haug and Tiedemann, 1998; Lear et al., 2003; Maier-Reimer and Mikolajewicz, 1990; Billups et al., 1999; Haug et al., 2001). A change in the ocean circulation system was initiated around 4.6 Ma ago (Haug and Tiedemann, 1998). Lunt et al. (2008) found an enhanced AMOC after the Panama Isthmus was closed and it may also have played a role in the initiation of the proto-NADW at the very end of the Miocene-beginning of the Pliocene (Lear et al., 2003). The closure of the Panama Isthmus causes a decrease of the water exchanges between the Atlantic and the Pacific Ocean and the intensification of the Northern hemisphere glaciation (NHG) (appearance of perennial ice caps in the North hemisphere) (Bartoli et al., 2005; Lunt et al., 2008a).

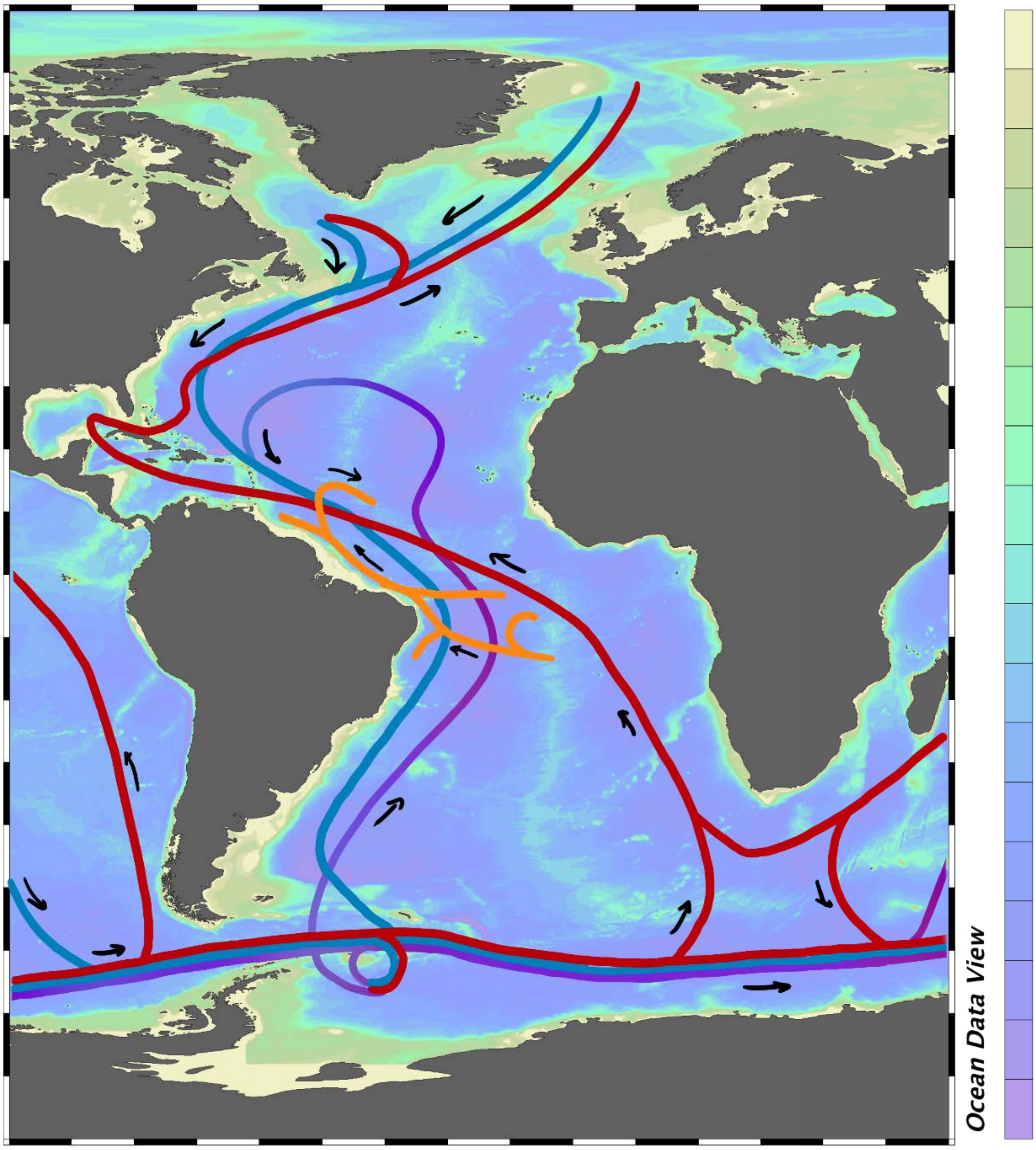

Figure 4. overturning oceanic circulation- Atlantic - AMOC (modified after Rühlemann et al., 2001; Rahmstorf, 2002), ocean data view (Schlitzer, 2018).

The ocean's structure (Figure 4) (and upwellings areas, Lessa et al., 2017) have an influence on the nutrient supply on the surface and so productivity but also on the sinking processes and carbonate preservation in the deep ocean (Cavaleiro et al., 2018; Beaufort et al., 2022; Zondervan, 2007). On the western equatorial Atlantic, the main currents are the NADW (purple), the AABW (blue), the North Brazil current (orange) (Rühlemann et al., 2001; Gröger et al., 2003b; Herrford et al., 2017), the south equatorial current, the north equatorial counter current, the equatorial undercurrent (Araujo et al., 2019).

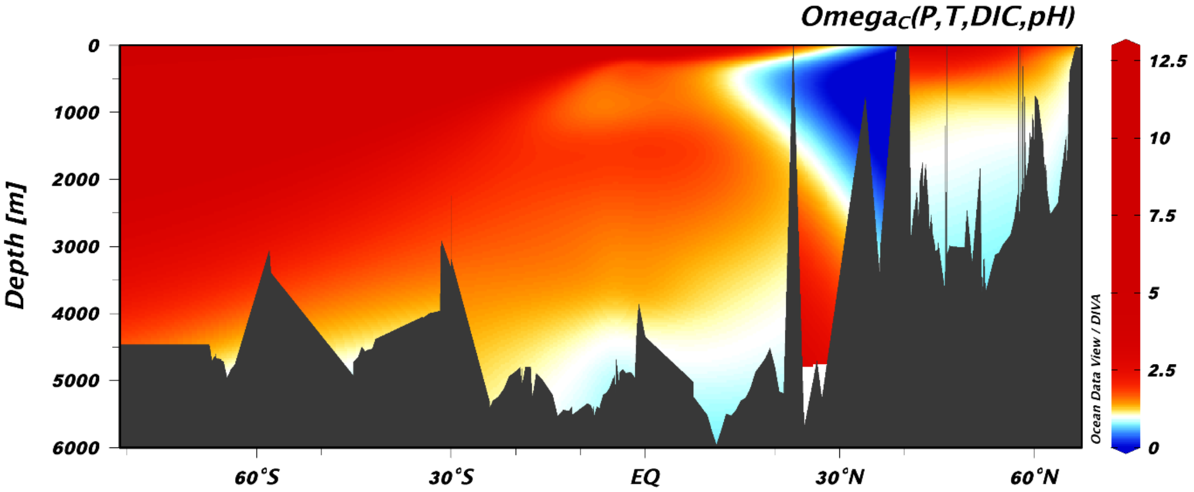

Figure 5. Transect North-South of the Atlantic Ocean, saturation state Ω calcite (present day), ocean data view (Schlitzer, 2018).

In the depth structure, the current's position and so physical properties of the water masses are known to have changed (e.g. mixing zone between NADW and AABW, deepening of the CCD due to alkalinity change; Si and Rosenthal, 2019; Herrford et al., 2017; Billups et al., 1997; Maier-Reimer and Mikolajewicz, 1990; Gröger et al., 2003b, a). These currents are also under the influence of the G-IG cycles and orbital cycles during the Cenozoic (Kleiven et al., 2003; Rühlemann et al., 2004, 1999). In the Atlantic Ocean, the saturation horizon (Ω calcite = 1, Figure 5) corresponds to the interface between the NADW and the AABW (Curry et al., 1995).

Through the Cenozoic and Quaternary, not all the setting up of the modern conditions took place at the same time in the Atlantic Ocean structure (Figure 6c). During the Late Eocene - Early Miocene (23-17 Ma), the proto-AABW appeared with the enhanced glaciation in the Southern Ocean and increase of ice volume in the Antarctic (Lear et al., 2004; Pekar and DeConto, 2006; Billups et al., 2002). The ice volume on Antarctica has been estimated similar to the present day one, with cold Southern Component Deep Water and unrestricted circumpolar flow, and decreases later during the MCO, with the increasing bottom water temperatures (4 to 8°C) fluctuating at eccentricity paced, suggesting an orbital forcing behind since the Early Miocene (Pekar and DeConto, 2006; Billups et al., 2002; Lear et al., 2004).

With the Antarctic ice sheet becoming permanent, the AABW became more stable. The closure of the Panama Isthmus (I.1.ii Section 3) triggered a reorganisation of the deep currents system in the Atlantic (Haug and Tiedemann, 1998) and the decreasing atmospheric pCO_2 at that time contributes to an increase of the temperature gradient from low to high northern latitudes, and suggested to be (one of) the cause for the initiation of northern hemisphere glaciations (NHG): the Early NHG, and later, the NHG (Lear et al., 2003; Raymo et al., 1992; Bartoli et al., 2005; Lunt et al., 2008; Haug and Tiedemann, 1998; O'Dea et al., 2016). The initiation of the NHG (and the setting up of permanent ice sheets in the Northern Hemisphere) has been estimated at 2.7 Ma ago, with an intensification until 1.8 Ma (Raymo, 1994; Tiedemann et al., 1994).

With the increasing presence of ice at the northern hemisphere high latitudes, and enhanced G-IG cycles, added to a decrease of the exchanges between the Atlantic and the Pacific Ocean due to the closure of the Panama Isthmus, the proto NADW set up at the very end of the Miocene, beginning of the Pliocene (around 5.3 Ma) (Lear et al., 2003).

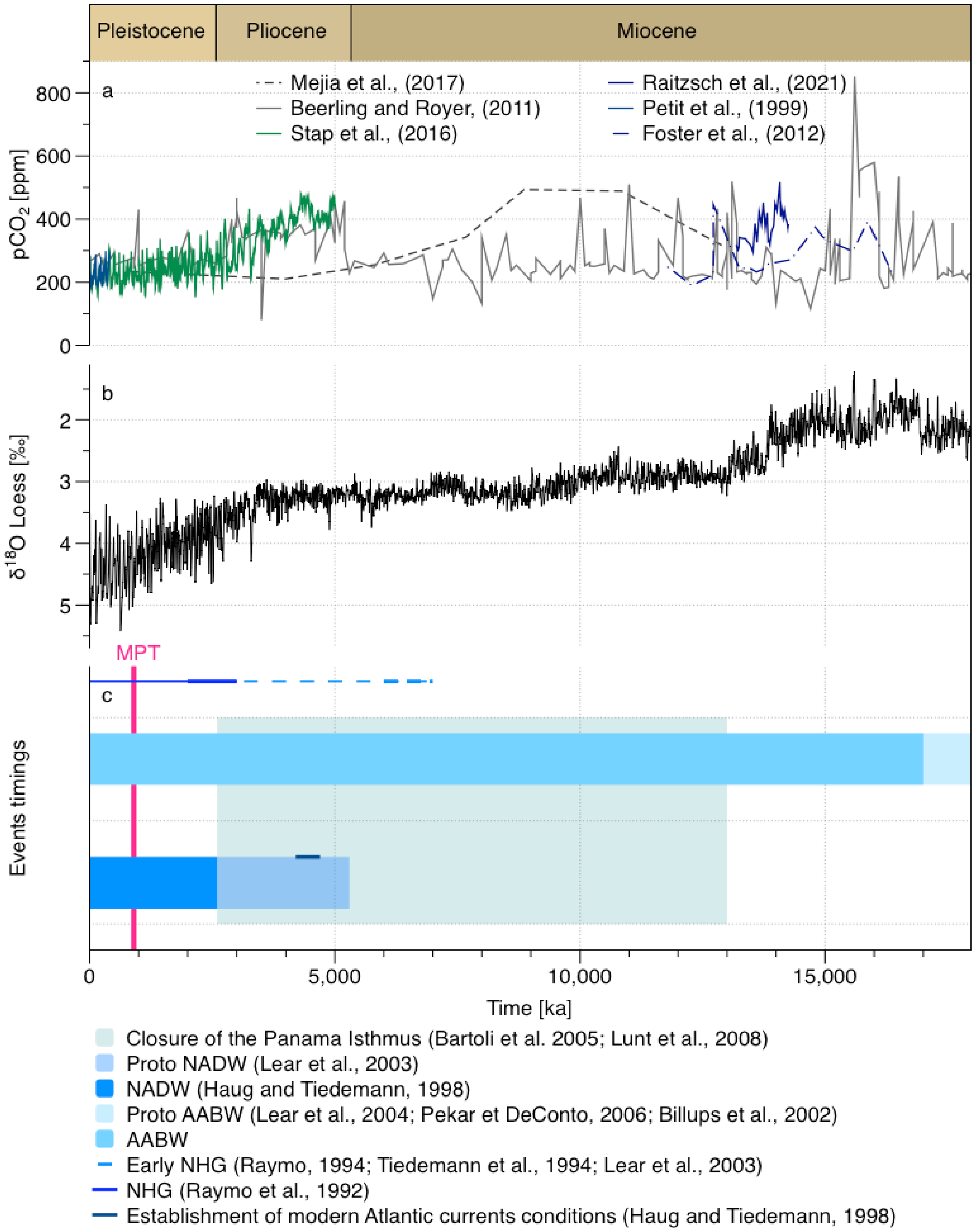

Figure 6. a) pCO$_2$ (Mejia et al., 2017; Beerling and Royer, 2011; Stap et al., 2016; Raitzsch et al., 2021; Petit et al., 1999; Foster et al., 2012); b) d^{18}O Loess and c) Timings of the major events in the Atlantic current setting up over the last 18000 ka.

Some studies (e.g. Haug and Tiedemann, 1998) estimated that the modern conditions in the current system in the Atlantic Ocean have been reached around 4.6 Ma (Figure 6). At the end of the Pliocene-beginning of the Pleistocene, the NADW is setted up and we observe the presence of an enhanced AMOC (similar or even higher than today) (Haug and Tiedemann, 1998). The warm Pliocene is marked by a well ventilated deep Atlantic Ocean, and after the Plio-Pleistocene transition, the conditions remains the same during the interglacials, but there is a decrease in NADW below 4000 mbsl during the glacials in the western equatorial Atlantic Ocean (Bell et al., 2015). Adkins et al. (2013) suggested that with the increasing NADW after the MPT and the presence of cold and salty AABW, the deep ocean became more stratified than the modern one, which increases the ocean's capacity to absorb CO_2, and so, contribute to further cooling. On the contrary, enhanced deep water ventilation brings back carbon to the surface ocean, and so contributes to the increase of atmospheric pCO_2 (Vervoort et al., 2021).

The NCW (precursor of the modern NADW) setted up in the middle Eocene (Vahlenkamp et al., 2018a, b) and the NADW started later, during the Pliocene (Haug and Tiedemann, 1998). With the Plio-Pleistocene transition (and the onset of 100 ka G-IG cycles), Gröger et al. (2003b) observed a reduction of the LNADW circulation. In this area, Gröger et al. (2003b) also noted the role of the North Brazil Current and NADW during the warm periods, with the presence of ADW during the cold periods (low $[CO_3^{2-}]$, causing dissolution). During the warmer intervals, the NADW was warmer and AABW remains at lower latitudes (Dowsett et al., 2009).

Section 4. Ceará Rise, Equatorial Atlantic Ocean _ Oceanic conditions

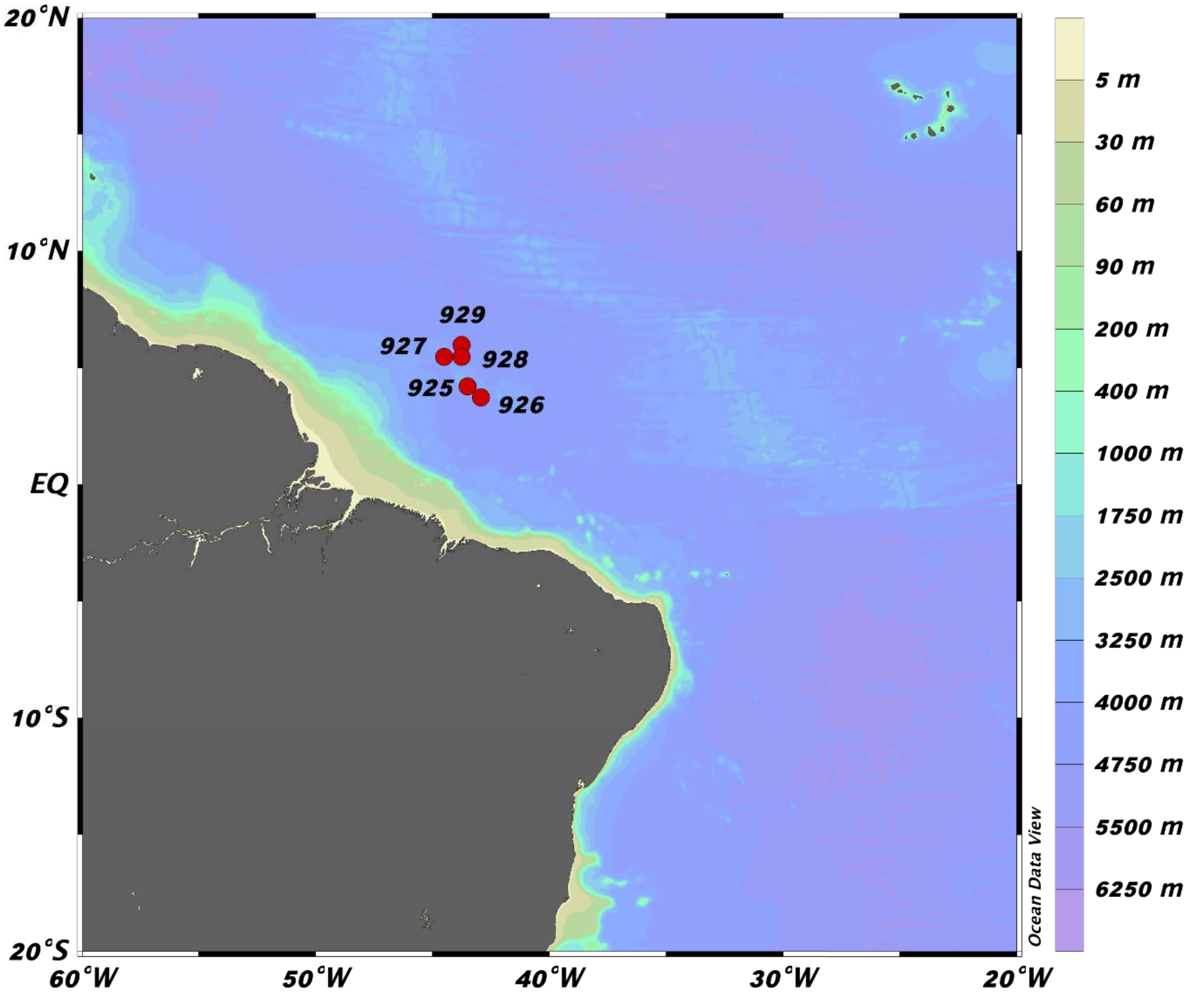

Figure 7. Map of the site location, ocean data view (Schlitzer, 2018).

We have made the choice to work at the Ceará Rise, equatorial Atlantic Ocean, using marine sediment collected during the ODP Leg 154 (Figure 7), ranging from present to the Eocene, and rich in carbonate sediment (Shackleton et al., 1999; Bickert et al., 1997; Shackleton and Crowhurst, 1997) The Ceará Rise is an aseismic ridge that formed during the late Cretaceous, about 80 Ma ago (Curry et al., 1995). The present temperature in the deep ocean at Ceará Rise location is around 2°C. In the current conditions, the NADW is present between 2000 and 4000 mbsl from 35°N to 50°S, warmer and more saline than the deeper AABW. They represent respectively ⅓ and ⅔ of the ocean currents volume (Johnson, 2008). In the western tropical Atlantic Ocean, the average depth of the seafloor is 4500 mbsl, and the Ceará Rise has a maximum thickness of 1900 m of lithogenic and biogenic sediments, making the culminant point of it at about 2600 mbsl (Curry et al., 1995), well above today's regional lysocline depth (Frenz et al., 2006; Gröger et al., 2003b, a; Curry et al., 1995; Cullen and Curry, 1997). The Ceará Rise sites are located at the interface between the modern NADW and AABW, also corresponding to the Lysocline depth (I.1.ii Section 3), and the sites above the Lysocline depths (sites 925 and 927) are presenting well preserved carbonate sediments (Curry et al., 1995; Cullen and Curry 1997). This location, far from large temperature changes known at the high latitudes (Herbert et al., 2016), is presenting well preserved carbonate sediments, ideal for the study of the calcifiers organisms' productivity (so the observations we are doing are driven by changes in productivity and not changes in dissolution). At this location, the sedimentation rate is high enough to have an orbital to sub-suborbital sampling resolution, for both the Neogene and the Quaternary. Some studies are suggesting that due to the topography of the Ceará Rise and the strong NADW, the AABW doesn't reach the western part of the Ceará Rise (Rhein et al., 1998). As mentioned by Paul et al. (2000), and taking in account the accumulation of sediments and the subsidence, the depth at this location is assumed to remained relatively constant in the Cenozoic and Quaternary, meaning that the location of this site relatively to the lysocline depth is mainly explained by changes of the lysocline depth itself.

The lysocline depth (I.1.ii Section 2) at this site has changed through the time, with the changing currents and the onset of the cold and corrosive AABW (Curry et al., 1995; Gröger et al., 2003b; Frenz et al., 2006), especially during Quaternary cold intervals, making the lysocline depth shallower, and so, causing the dissolution of the deep-sea sediment at that depth. The stronger the AMOC, the deeper the lysocline (if there is a strong input of NADW waters, it makes the depth of the lysocline (interface between AABW and NADW) deeper. During the Pliocene, the lysocline depth remains very similar to today or even deeper, at a time when the AMOC was relatively strong (or even stronger than today, supported by Raymo et al., 1996; Billups et al., 1997; Bell et al., 2015 or Haug and Tiedemann, 1998 results), and so, site 927 was continuously above the lysocline depth, making the preservation really good during this time interval (Frenz et al., 2006). Preiss Damler et al. (2013) and King et al. (1997) found a shallower Lysocline during the late Miocene than during the Pliocene, but still below site 927 depth (4000 mbsl) they also found a shoalling of the Lysocline from 14 to 11.5 Ma, meaning that the Lysocline was deeper before that date. This is supported by results from Van Andel et al. (1975) who found a deep CCD in all oceans during the early Miocene.

As the lysocline depth remains relatively constant and deep (except during the cold intervals of the Quaternary), the Ceará Rise, and especially the Site 927 location therefore stays above the regional lysocline (figure 5, Ω calcite remains above 1 between the lysocline depth -4200 mbsl- and the surface) along the last 20 Ma, preventing the carbonate sediment to be affected dissolution, and making it a good location to study the pelagic carbonate production, as the carbonate accumulation rate mainly reflects changes in pelagic carbonate production (Brummer and van Eijden, 1992; Bassinot et al., 1997).

Concerning the sea surface conditions, it has been shown that the least temperature change over time from Miocene to present (on a long geological time scale) occurred in the tropics for all the oceans (Herbert et al., 2016). Additionally, Curry et al., (1995) has mentioned that the low variability of the surface temperature at the Site 927 location is ideal to work on global temperature climate modulations, rather than local temperature and climate changes and they also observed upwelling conditions. Today, in the Ceará Rise location, the total alkalinity and the inorganic carbon concentration in the water are strongly related to the SSS (Bonou et al., 2016). The surface conditions and especially the salinity, are driven by the position of the intertropical convergence zone (ITCZ), equatorial area where the atmospheric gyres cause precipitation, and so, a decrease of the SSS. It has been shown that with the increase of temperature gradient from low to high latitudes (i.e. glacials intervals and boreal winter), modifying the sea surface currents system and enhancing the trade winds, the ITCZ moves to a southward position (Broccoli et al., 2006; Schmidt and Spero, 2011), modifying the sea surface conditions of temperature and salinity, and so, the Alkalinity and inorganic carbon concentrations.

Section 5. Ceará Rise, Equatorial Atlantic Ocean _ Sea surface conditions and CO_2 flux to the surface ocean

It is admitted that in the tropical oceans, the average flux of CO_2 is from the ocean to the atmosphere, making the tropical ocean a source of CO_2 (Takahashi et al., 2009; Landschützer et al., 2014; Araujo et al., 2019), partly due to the presence of an upwelling in this area, delivering CO_2 and nutrients rich waters (the total alkalinity and inorganic carbon concentrations are the highest in the CO_2-rich waters delivered by the equatorial upwelling, Bonou et al., 2016). As a consequence, a change of the equatorial upwelling or of the ocean circulation in this area would strongly impact the flux of CO_2 in the tropical Atlantic Ocean (Lefèvre et al., 2014). However, Bonou et al. (2016) demonstrated that the total alkalinity and the quantity of inorganic carbon are strongly related to the SSS conditions in this area, and the SST variability is not influencing the total alkalinity and inorganic carbon concentration. Lefevre et al. (2010) results also showed a strong link between the salinity and total alkalinity, DIC and CO_2 flux. The flux of CO_2 is not homogeneous either in space or time: due to the Amazon river discharge and the seasonal precipitations related to the presence of the ITCZ (two sources of fresh waters, undersaturated in CO_2) the area close to the Amazon fan is also a CO_2 sink (Ibánhez et al., 2015; Ternon et al., 2000; Körtzinger, 2003; Cooley et al., 2007; Lefévre et al., 2010; Bonou et al., 2016). In this area, the surface waters are also undersaturated in CO_2 due to the intense primary production related to the Amazon discharge, providing nutrients (Ibánhez et al., 2015; Ternon et al., 2000; Körtzinger, 2003; Cooley et al., 2007; Lefévre et al., 2010; Araujo et al., 2019). According to Ibánhez et al. (2015), the DIC drawdown in the Amazon plume is estimated to be about 154 µmol kg^{-1}. The carbon uptake from the atmosphere to the surface ocean related to biological activities in the Amazon plume is estimated at 15 ± 6 Tg C yr^{-1} (Cooley et al., 2007). As the CO_2 flux depends on the pCO_2 atmospheric as well, an increase of the atmospheric pCO_2 may lead to a decrease of the flux from the ocean to the atmosphere in the tropical Atlantic Ocean, outside of the Amazon fan area (Araujo et al., 2019).

A change of sea surface temperature and/or precipitation would affect the CO_2 flux (Lefèvre et al., 2014; Ibánhez et al., 2015; Lefévre et al., 2010; Araujo et al., 2019). In the Ceará Rise region, the SST values over the year are oscillating between 26.2 °C and 29.1°C, with a total alkalinity between 1031 and 2372 µmol kg^{-1}, and a pCO_2 around 355 ± 52 µatm and a sea air CO_2 flux of -0.2 ± 2.0 mmol m^{-2} d^{-1} (Araujo et al., 2019).

Because of the difference of CO_2 saturation of the different water masses and ocean currents, the CO_2 uptake by the ocean is also dependent on the ocean circulation (e.g. NBC highly saturated in CO_2 while the NEC is less, modifying the CO_2 absorption by the surface ocean) (Ibánhez et al., 2015). The mean annual flux of CO_2 in the tropical Atlantic has been estimated by several studies: 1.05 mmol m^{-2} d^{-1} (Andrié et al., 1986), between 81.1 ± 1.1 and 81.5 ± 1.1 Tg C yr^{-1} (Ibánhez et la., 2016), average: +0.3 ± 1.7 mmol m$^{−2}$ d$^{−1}$; range: −1.2 to +2.0 mmol m$^{−2}$ d$^{−1}$ (Araujo et al., 2019), 0.014 ± 0.005 Pg C yr^{-1} (corresponding average CO_2 flux density of 1.35 mmol m^{-2} d^{-1} (Körtzinger, 2003), -1.7 ± 0.4 Pg C y^{-1} (Gruber et al., 2009), between 0.11 Pg C y^{-1} (year 2000) (Takahashi et al., 2009) and 0.10 ± 0.06 Pg C y^{-1} (year 2010) (Landschützer et al., 2014) (Ibánhez et al., 2015), depending on the season, a sink of CO_2 0.40 mmol m^{-2} d^{-1} and a source of CO_2 1.32 mmol m^{-2} d^{-1} (Lefèvre et al., 2014), 7.61 ± 1.01 to 7.85 ± 1.02 Tg C yr^{-1} for the Amazon plume and 81.1 ± 1.1 to 81.5 ± 1.1 Tg C yr^{-1} for the tropical Atlantic (Ibánhez et la., 2016).

Section 6. Response and feedbacks notions

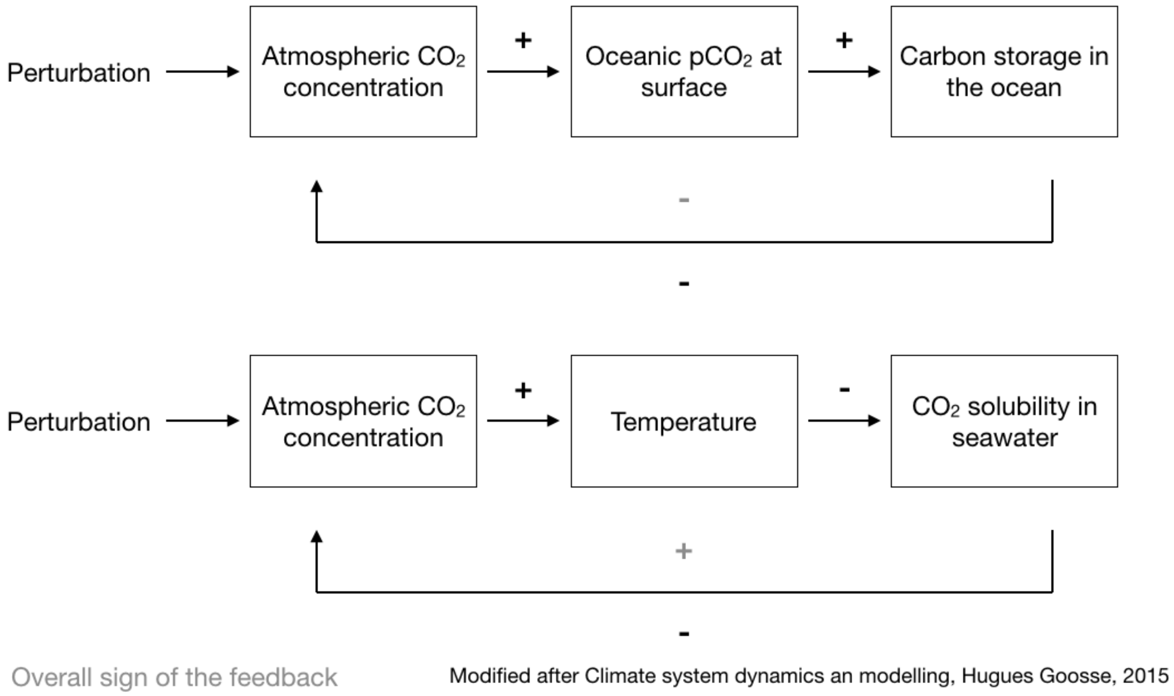

Figure 8. Schematic representation with arrows on a graphic for what influences what and how (modified after Goosse, 2015).

Response: change of one parameter following a perturbation

Feedback: when the response is influencing back the original parameter can be positive (enhance the original parameter) or negative (attenuate the original parameter). The context in the one the forcing takes place has a strong importance, and is influencing the climate system response (De Vleeschouwer et al., 2020).

In the climate and ocean system, there are known feedbacks that are acting on the response of the oceans conditions to the changing climate, and these feedbacks are influencing the climate, to enhance or attenuate the changing trend (Figure 8).

Here we focus on the feedbacks acting on the ocean system and at orbital to geological time scale. For example, in the ocean, the thermohaline circulation, depending on the temperature and the salinity of the water masses, the weaker the thermohaline circulation, the less the water is saline at high latitude, making the thermohaline circulation even weaker (Goosse, 2015).

In the case of the (oceanic) carbon cycle, the carbonate production processes (Figures 2 and 9) are influenced by the atmospheric pCO_2. In that situation, any increase of the atmospheric CO_2 concentration (e.g. anthropogenic emissions) represents a perturbation of the system and has an influence on ocean atmosphere interface equilibrium, and so, the surface water pCO_2.

With an increase of the atmospheric pCO_2, the surface ocean pCO_2 is increasing too, changing the ions concentrations and speciations of the molecules in the surface ocean, and modifying their equilibrium. The increasing ions concentration in the surface ocean reduces the efficiency of the surface ocean to absorb CO_2 (as it reduces the CO_2 solubility). Additionally, there is no need for any climate change to induce a change in the concentration of CO_2 in the atmosphere, as the pelagic carbonate producers are incorporating carbon in their shells, which is exported to the seafloor at their depth, making the ocean a carbon sink. By reducing the surface water concentrations in CO_2, it increases the capacity of the ocean to absorb CO_2 (increased CO_2 solubility and exchanges from the atmosphere towards the surface ocean).

On a long time scale (from years to thousand years), the “calcium carbonate compensation” (Figures 2 and 9) describes another feedback. Indeed, the ocean saturation in carbonate and bicarbonate ions is driving the oceans' solubility of calcite. This saturation state, describe as alkalinity is varying in the water profile and changing depending on the water masses and currents (e.g. the deep currents, that hasn’t seen the surface for a long time are undersaturated in ions, and so, more less saturated (which makes them corrosive). The position of the lysocline is not constant, and defines the areas of the ocean where the carbonate is preserved in the seafloor, and the changes of the lysocline depth are making the alkalinity more stable in the ocean.

“Using a simplified ocean box model with both constant and variable calcification, we show that even modest drops in calcification can lead to appreciable long-term alkalinity build-up in the oceans and, thus, create overdeepening [...] Chemical carbonate compensation implicitly assumes that the production of $CaCO_3$ remains the same. But what if it doesn’t? Evidence has accumulated that calcifiers respond to changes in the chemistry of their surrounding waters, both at the physiological and ecological levels. [...] Calcification is the primary mechanism for alkalinity removal from the oceans. If this rate falls, alkalinity will build up in the surface ocean on the time scale of the delivery of alkalinity to the oceans; likewise, if calcifiers increase their rates, surface alkalinity will fall. Ocean surface waters that become enriched/depleted in alkalinity due to falling/rising calcification will reach the deep sea due to deep convection, thus raising/lowering the alkalinity of deep waters [...]. These are the elements of what we term ‘biological carbonate compensation’.” (Boudreau et al., 2018).

The pelagic carbonate production is influencing the concentration of ions in the water, and so, the alkalinity of it. If, via a decrease of pelagic carbonate production, the alkalinity increases, the lysocline and saturation horizon are deeper, allowing a better preservation of the carbonate sediment in the seafloor, making the CO_2 solubility higher, and so, higher efficiency of the carbon export from the surface ocean to the seafloor (capacity of the ocean to be a CO_2 sink is higher, higher capacity of the ocean to absorb CO_2) (Boudreau et al., 2018; Sarmiento and Gruber, 2006).

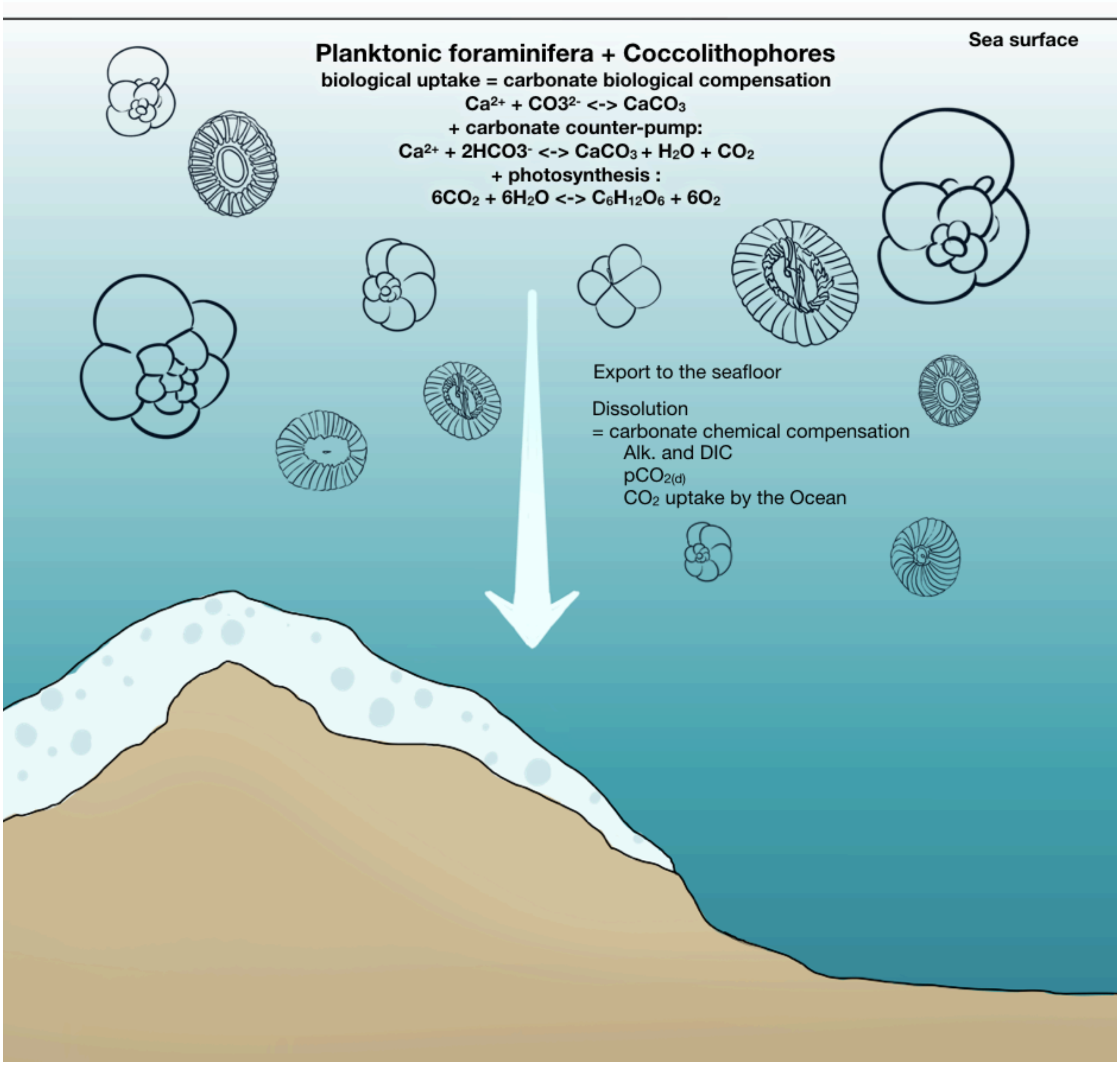

Figure 9. Schematic representation of the carbonate Biological compensation: Zoom on Figure 2 (Boudreau et al., 2018; Boscolo-Galazzo et al., 2018; Middelburg et al., 2020; Goosse, 2015).

I.1.iii. Looking for possible analogues to the actual climate warming: looking at the past warm periods in the Neogene and Quaternary

We are currently under global warming conditions due to the intensive release of anthropogenic greenhouse gases in the atmosphere (Pörtner et al., 2014). But to better understand what does it means in terms of climate conditions and how the environment is changing in such a period, from short to long geological time scales, it is interesting to have a look at previous warm periods and climate perturbations in Neogene and Quaternary (for similar world configuration). The chosen intervals for this study needed to be known as potential analogues for the current climate warming, and the samples had to be at a resolution good enough to cover both the orbital and the geological time scales, to be located in the Equatorial Atlantic Ocean, well preserved and well documented in the literature.

We here focus on four warm intervals (Figure 10), corresponding to our criteria and known to be good analogues to the current conditions or even + 1-2 °C as suggested by some model predictions (Pörtner et al., 2014).

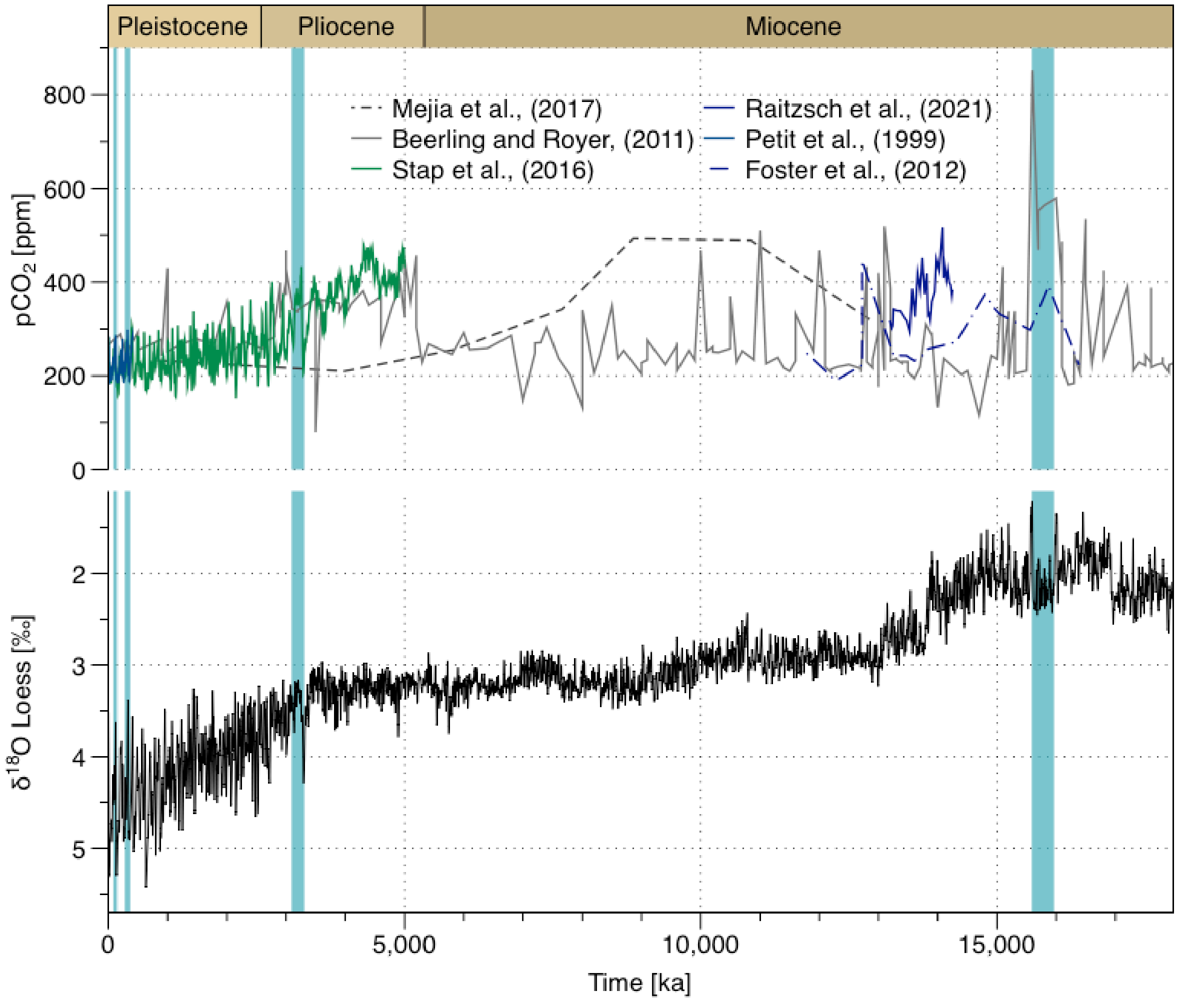

Figure 10. Position of the the four warm periods studied in this thesis (blue shadows) along global benthic δ ^{18}O (Westerhold et al., 2020) and pCO$_2$ records (Mejia et al., 2017; Beerling and Royer, 2011; Stap et al., 2016; Raitzsch et al., 2021; Petit et al., 1999; Foster et al., 2012) for the last 18000 ka.

Section 1. Pleistocene MIS 5 and 9

The last 800 ka are characterised by strong 100 ka eccentricity paced G-IG cycles.

The MIS 5 (130 ka ago) is a particularly warm and long interglacial over the past 500 ka, with an abrupt transition from the previous glacial period (Howard, 1997; Müller and Kukla, 2004; Sirocko et al., 2005) and drastic changes in the ocean circulation and conditions (Rühlemann et al., 2001). Due to warmer polar temperatures (3-5°C), a global surface temperature 1.5 to 2 °C warmer than today (Drury et al., 2016; Clark and Huybers, 2009; Kopp et al., 2009; Schwab et al., 2013), a bottom water temperature change around 4.5°C (Dwyer et al., 1995), and higher sea level (around 6.6 m) than today (Clark and Huybers, 2009; Kopp et al., 2009), this interval is considered as a good analogue to the Holocene or + 1 or 2 °C scenarios as suggested by model predictions (Clark and Huybers, 2009; Kopp et al., 2009; Howard, 1997; Kukla, 1997; Pörtner et al., 2014).

The MIS 9 (330 ka ago), with higher sea surface temperature (and more stratified) and higher Antarctica temperatures (Ayling et al., 2006; Marino et al., 2014) has been shown to be a good analogue for actual conditions or warmer scenarios (Leonhardt et al., 2015; Past Interglacials Working Group of PAGES, 2016; Voelker et al., 2010). The atmospheric greenhouse gas concentration during this time period is known to be high (pCO_2 around 300 ppm and pCH_4 around 25 ppb) making it one of the warmest interglacials (Past Interglacials Working Group of PAGES, 2016; Marino et al., 2014; Voelker et al., 2010).

Section 2. Pliocene warm period (PWP) MIS KM5

This interval, ranging from 3264 ka to 3025 ka corresponds to a warm (negative oxygen excursion, global temperature 2 to 3°C higher than pre-industrial values and deep water temperatures 1.5°C higher), high pCO_2 (330 to 425 ppm) time period, with a higher sea level than today (21 to 23 m) (Dwyer et al., 1995; Dowsett et al., 1996; Sloan et al., 1996; Haywood and Valdes, 2004; Brierley and Kingsford, 2009; Haywood et al., 2000; Lunt et al., 2010, 2008; Naish et al., 2009; Pollard and DeConto, 2009; Pagani et al., 2010; Seki et al., 2010; Haywood et al., 2013; Willeit et al., 2015). Added to similar orbital forcing and insolation conditions than what we are currently experiencing (Haywood et al., 2013), this makes it a good analogue for future climate predictions (Ravelo et al., 2004; Ravelo and Wara, 2004; Li et al., 2011; Lunt et al., 2010) and key period to study the climate system (Lunt et al., 2010).

The Pliocene is characterised by 41 ka obliquity paced G-IG cycles (Lisiecki and Raymo, 2005). If the Antarctic ice sheet has been in place for a long time, it is not the case of the Arctic one, which is still small and unstable at this time period (Willeit et al., 2015).

Section 3. Miocene climatic optimum (MCO)

The MCO (from 17 Ma to 14.7 Ma) corresponds to a strong carbon cycle re-organisation and climate transition, visible in the climate record as a strong carbon-isotope excursion between 17.1 and 12.7 Ma with dominant periodicities observed in the climate ($\delta^{18}O$ and $\delta^{13}C$ records) of 100 and 400 ka before 14.7 Ma, 41 ka between 14.7 and 13.9 Ma and 100 ka again after 13.9 Ma (Holbourn et al., 2007, 2015). By contrast to the Late Pleistocene eccentricity paced G-IG cycles, the Miocene ones are more symmetric (Holbourn et al., 2015, 2014, 2018). It is characterised by an abrupt warming (the deep-water temperature increased by about 5°C, Holbourn et al., 2015), with a low global ice volume, as only the Antarctic ice sheets are present but smaller and more dynamic than present day, and the onset of the Arctic one has not occurred yet (De Vleeschouwer et al., 2017; Zachos et al., 2008; Foster et al., 2012; Kamikuri and Moore, 2017). Due to this low ice cover, some studies are suggesting a direct answer of the ocean carbon reservoir to the orbital forcing (Zachos, 2001). This period is characterised as warmer than today (the Tropical Atlantic SST was 28 to 30 °C, Zhang et al., 2013 and the global temperature 3 to 8°C warmer than present, Pound et al., 2012; You et al., 2009) with a large sea level amplitude change (Haq et al., 1987). The atmospheric pCO_2 peaked between 460 and 564 ppm (Kurschner et al., 2008) but with overall levels relatively low (between 350 and 400 ppm, Foster et al., 2012) and this rapid increase of pCO_2 is suggested to be at the origin of the sharp warming and carbon cycle re-organisation (Holbourn et al., 2015). These conditions make it a good analogue to actual climate warming conditions and even future predicted climates (Pound et al., 2012; You et al., 2009; Foster et al., 2012; Zachos et al., 2008).

I.1.iv. Microfossils as a memory of past climates, oceanic conditions and productivity

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To study the palaeoclimates, palaeoenvironments, and their variability, we rarely have the access to a direct evaluation and measurement of the variable we want to study. In this situation, we use an indirect record of different measurable observations/parameters preserved in various archives. This indirect parameter is called a "proxy". The interpretation of the proxy record relies on the assumed link between the observed variable and the climate/environment.

The $CaCO_3$ production in the surface ocean is mainly found into two different forms: calcite (planktonic foraminifera and coccolithophores) and aragonite (pteropods). Because of the high sensitivity of aragonite to dissolution, we are here focusing on planktonic foraminifera and coccolithophores, the two major components of the sediment at Ceará Rise site. In general, the marine plankton is highly affected by the temperature and ocean condition modulations (Boscolo-Galazzo et al., 2018).

Section 1. Planktonic foraminifera

Planktonic foraminifera are marine protozoan, and diverse group of Rhizaria that first appeared in the mid-Jurassic and present in all the oceans at all latitudes since the mid-Cretaceous (Caron and Homewood, 1983). They produce a carbonate test, so they are well preserved in the marine sediment. Their presence in all the oceans and their sensitivity to environmental conditions changes makes them good proxies for the oceans' conditions and chemistry and climate. Planktonic foraminifera are measuring around 50 to 1000 µm and are living several months (depending on the species and the seasons). After their death, they sink to the seafloor (days to weeks depending how deep is the site, the currents, and the particles/agglomerate sizes, volume, shape, Schiebel and Hemleben, 2017).

Section 2. Coccoliths

The coccoliths are minute plates of calcite, produced by unicellular marine protists, the coccolithophores. The coccolithophores are growing $CaCO_3$ crystals, with the ones the cell is covered with. A large number of species has been described from their appearance to present, with important taxonomy variability (Young et al., 2005). On orbital to sub-orbital time scales, they represent an important factor of pCO_2 change (Cavaleiro et al., 2018). They are good environmental proxy, as they are present everywhere, in all the oceans, at all the latitudes since the Jurassic (De Vargas et al., 2007) and are sensitive to environment changes (Stolz and Baumann, 2010), responding on ecological to geological time scale (De Vargas et al., 2007). Their size has varied through the time between 3.6 and 10.6 µm length (Aubry et al., 2005) and they are well preserved in the sediment, making them a good archive for past climate and environments.

Coccolithophores growth rate (and calcification) is modulated by the environmental conditions, sensitive to the temperature (faster growth rate and increased calcification with increasing temperature), pCO_2 and PO_4 concentrations (Krumhardt et al., 2017). Their development is better under optimum conditions (Krumhardt et al., 2017; Beaufort et al., 2011). According to Krumhardt et al. (2017) the light intensity is impacting differently the different species of coccolithophores (and their PIC/POC ratios).

I.1.v. Research gaps, missing elements and unknown areas

Although the different elements of the carbon cycle have been intensively studied in the last decades, there are still some grey areas in what we know about this cycle and the mechanisms governing its functioning, especially when it comes to the role of the pelagic carbonate production.

First, the potentially large role of biological compensation (I.1.ii. Section 6) on the marine carbon budget, a process empirically poorly supported, has recently been highlighted (Sarmiento and Gruber, 2006; Boudreau et al., 2018, 2019; Middelburg et al., 2020; Boscolo-Galazzo et al., 2018). Due to the relatively new interest in these processes, the mechanisms behind the carbon budget modulation related to the changes in pelagic carbonate production and how the carbon cycle modulations are impacting the pelagic carbonate production remains to be studied.

Second, within the pelagic carbonate flux that is buried in the seafloor sediments, there are two major components: the planktonic foraminifera and the coccoliths, and recent studies show that what the composition of the sediments is does matters (Si and Rosenthal, 2019) but there are too little data on how this really varied in the orbital and geological time scales. Additionally, very little is known on the relative proportion of these two components changes with the environmental conditions' modulations, particularly in a context of climate warming.

Only very few studies have focused on making the distinction between the two main pelagic carbonate producers (e.g. Si and Rosenthal., 2019) and when they did, it wasn't particularly on warm periods, or they did not look at the two proxies on the same samples to avoid small gaps or age model bias.

Finally, to model the involved processes, we need to know what affects the carbonate flux within each group, the reasons why the carbonate flux of each of the two main components of the carbonate flux is changing. Kiss et al. (2021) recently shown that on very short time scale, in recent sediment, the planktonic foraminifera calcite flux is changing because of the number of shells rather that their sizes, weight or taxonomy, but we do not know if the trends were similar on longer time scales. Furthermore, we are here involving both the planktonic foraminifera and the coccoliths rather than focusing on one of the two groups only, to have a larger picture of the mechanisms at work.

I.2 Thesis objectives and outline

I.2.i Research questions

The ocean plays a major role in the (inorganic) carbon cycle (Figure 2) and the pelagic carbonate production by the pelagic carbonate calcifiers is an important part of it. Climate warming, oceanic changes and modification of the processes involved in the inorganic carbon cycle could induce major change in the ocean capacity to absorb CO_2. In the actual context of climate warming, understanding how these pelagic calcifiers have responded in past climate warming episodes of recent Earth history could give precious information to understand the processes driving the changes and to make better decisions to preserve our oceans and environment. I here focus on the pelagic carbonate production processes from Early Miocene to Quaternary and aim to better understand how and why it has changed, on both long geological and shorter orbital time scale.

In my PhD project, I aim to understand how pelagic carbonate production is changing in a warming context, and I focus on the two main pelagic carbonate calcifiers: the planktonic foraminifera and the coccoliths.

I.2.ii Outline of manuscripts

To answer, I first focused on the pelagic carbonate production in general, then I differentiate the planktonic foraminifera and the coccoliths contribution to the total pelagic carbonate flux, and finally, I looked for the reasons for these observed changes within the two groups. As I wanted to use the same approach for both the planktonic foraminifera and the coccoliths, the pelagic carbonate production is here estimated by burial and not any other indirect productivity measure (e.g. trace element or species composition).

The sampling plan and the samples used are the same along the three chapters. After defining the site location: at equatorial latitude, so the pelagic carbonate production could not respond to high temperature variability, high preservation, so the observed changes in carbonate accumulation rates are due to production changes and not dissolution changes, high sedimentation rate, to be able to sample at orbital resolution and well constrained age model, so the carbonate accumulation rates are not driven by artificial sedimentation rates shifts (I.1.ii. Section 4).

As previous studies have shown an orbital imprint on the pelagic carbonate production record (e.g. Beaufort et al., 1997, 2022), I was expecting an orbital signal on our record too (I.1.i), so we samples at a resolution high enough to observe them (I am sampling at even depth and not even time, to make sure that I am not creating an artificial cyclic modulation, by a sampling in pace with the periodicity of the expected cycles). For the two Quaternary interglacial intervals, I made sure I was covering the warm period plus the flanking glacial to interglacial warming event. Concerning the Pliocene and Miocene, I sampled in order to cover at least two eccentricity cycles. The sampling has been done based on the Wilkens et al., (2017) age model for the samples ranging from 0 to 14 Ma and based on Shackleton et al., (1999) age model for the samples between 14 and 16.5 Ma. I sampled every 5 cm in the Quaternary (corresponding approximately to a 1 ka resolution) and every 10 cm in the Neogene (corresponding approximately to a 4 ka resolution). At the end, I sampled 60 samples for the MIS 5, 79 samples for the MIS 9, 72 samples for the MIS KM5 and 50 samples for the MCO. After the revision of the age model (II.3.ii), those samples cover 62.74 ka for the MIS 5 (ranging from 87.5 ka to 150.2 ka), 93.90 ka for the MIS 9 (ranging from 276.4 ka to 370.3 ka), 211.55 ka for the MIS KM5 (ranging from 3095.5 ka to 3307 ka) and 374.99 ka for the MCO (ranging from 15589.3 ka to 15964.3 ka).

Based on those samples, our main question has been divided into three sub questions as follows.

Section 1. Manuscript 1 - Question1

I wanted to understand how the pelagic carbonate production is changing as a whole, in a warming context, what is causing this change and what are the forcings behind it (Figure 11).

In this chapter, I aim to determine and quantify the pelagic carbonate production. As it has already been shown that there is a link between the pelagic carbonate productivity and the orbital cycles (e.g. Beaufort et al., 1997, 2022) and that the tropical areas are playing an important role in the regulation of the global climate (e.g. Lea, 2000) (I.1.ii. Section 5), I wanted to better understand these links in tropical areas. To do so, I selected four warm periods in recent Earth History, known to be potential analogues for the ongoing climate change and even for future climate warming scenarios (I.1.iii.). I chose to work at the Ceará Rise site (tropical Atlantic Ocean). The

$CaCO_3$ AR records of the 5 sites of the Leg 154 are presented and compared, justifying the choice of the site 927 for high resolution carbonate production records. I produced a high-resolution carbonate accumulation rate record, at Ceará Rise, tropical Atlantic Ocean, and analysed it at both orbital and geological time scales (within and between the chosen time intervals presented in this chapter). Additionally, I ran spectral analysis on those records and compared it to actual orbital cyclicities.

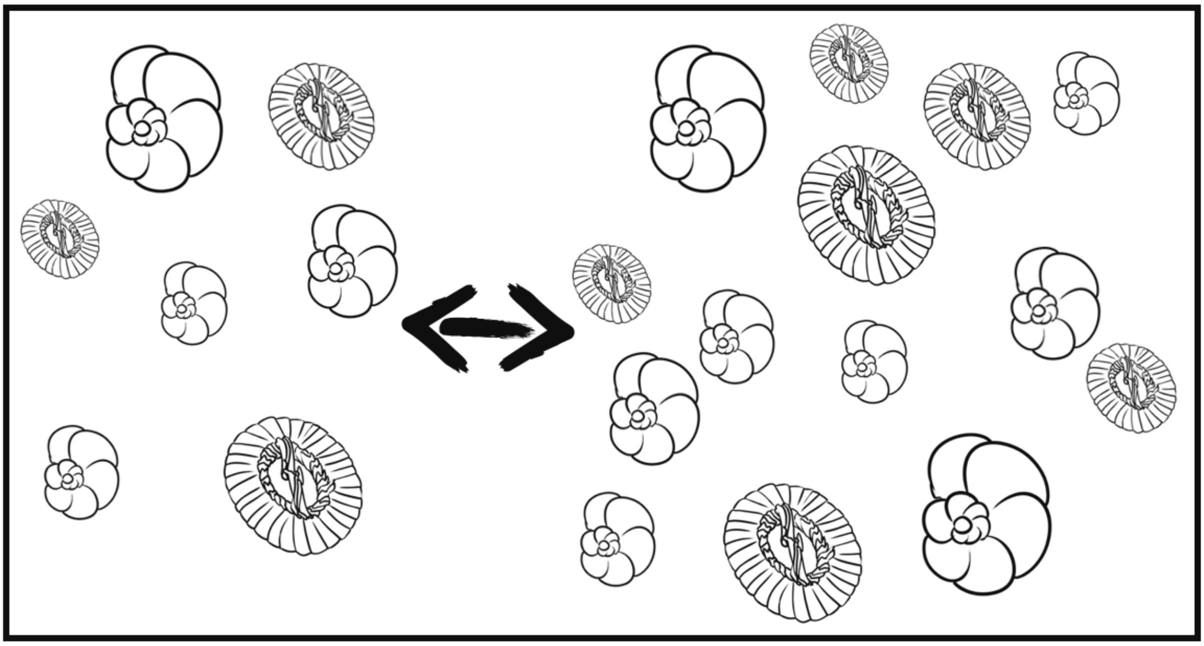


Figure 11. Schematic representation of the question of the first manuscript (chapter #II): What are the variations of the pelagic carbonate production through the time and how is it related to the orbital modulation?

Section 2. Manuscript 2 - Question2

I wanted to disentangle the relative contribution of the two mains pelagic calcifiers (planktonic foraminifera and coccoliths) to the total carbonate flux (Figure 12). I also wanted to understand their responses to the changing conditions in a context of climate warming, at different time scales, under different temperature and pCO_2 conditions. To do so, I have analysed the same samples as in the chapter #2 and separated them in different size fractions, in order to quantify the proportion of the two calcifiers in it. The coccoliths AR has been estimated with two independent methods, one similar to Si and Rosenthal (2019), assuming that the coccoliths carbonate contribution to the bulk is the bulk $CaCO_3$ AR minus the coarse fraction contribution to it, and the second one, using SYRACO optical microscopy automated measurements. In this chapter I am showing that if they have similar response, this response isn't the same amplitude for the two pelagic carbonate producers, making their relative contribution to the total carbonate flux to change. The proportion of planktonic foraminifera and coccoliths is changing with the orbital cycles and with higher amplitude on orbital time scale than on long geological time scale. Additionally, I ran spectral analysis on all the different records I obtained and the results are presented in this chapter.

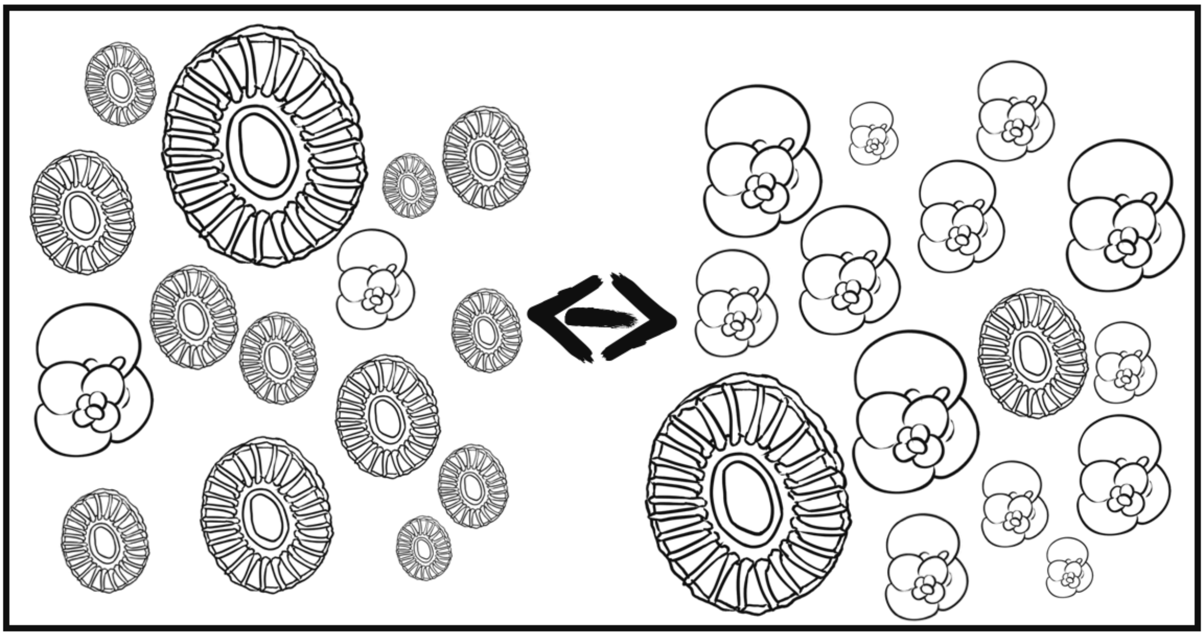
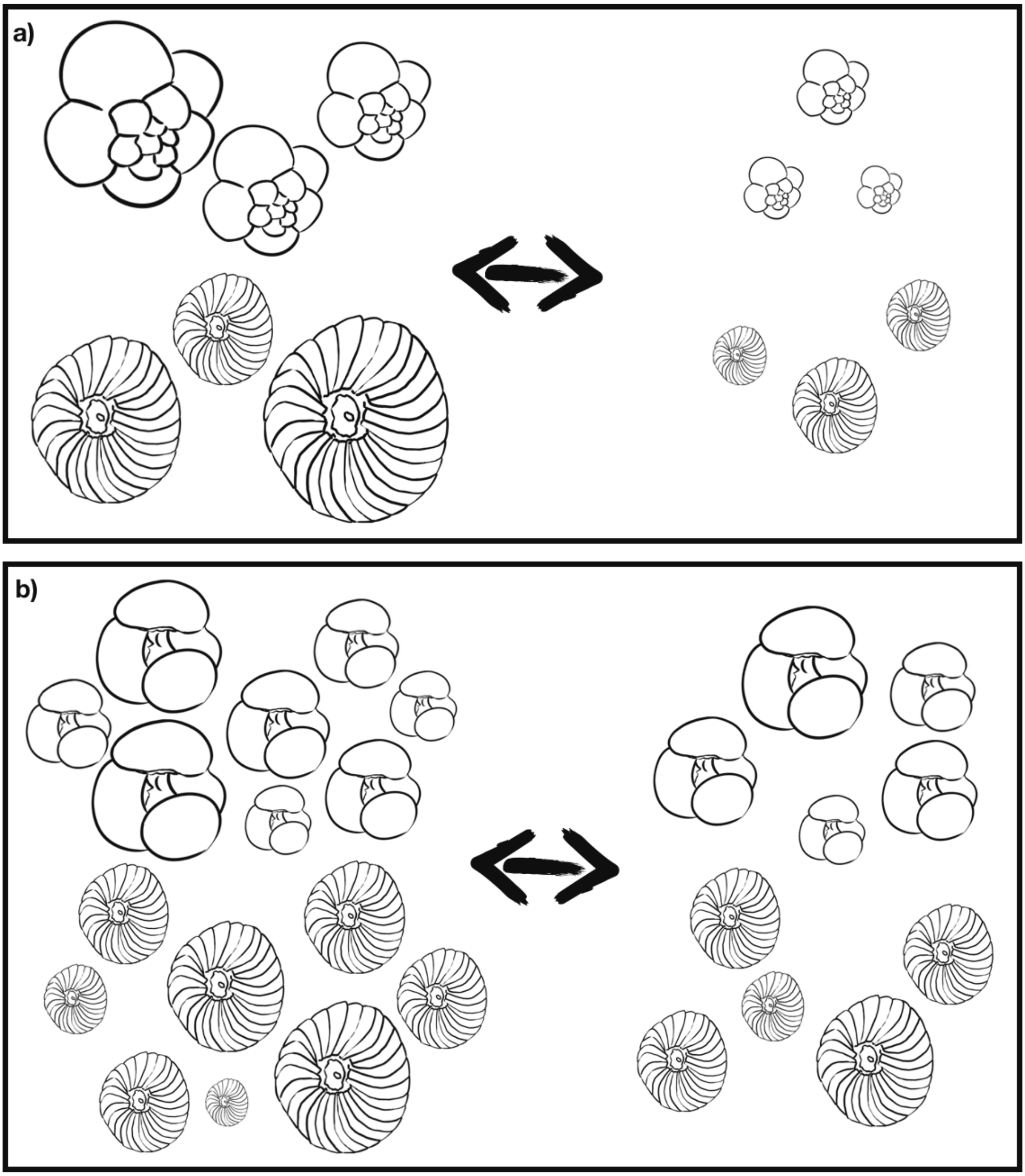


Figure 12. Schematic representation of the question of the second manuscript (chapter #III): How is changing the relative contribution of the two main carbonate producers to the total pelagic carbonate production through the time?

Section 3. Manuscript 3 - Question3

I wanted to explain the carbonate flux changes for both the planktonic foraminifera and the coccoliths (Figure 13): what is changing the contribution of both and are the two main pelagic carbonate producers increasing/decreasing their productivity for the same reasons? Is their size (Figure 13a), their number of specimens (Figure 13b), their shape (and taxonomy) (Figure 13c) or how heavily calcified they are (Figure 13d) which is changing? What are the timings of these changes, and are they both responding the same way at the same time or not? To do so, I have counted and measured a significant number of specimens for both the planktonic foraminifera and the coccoliths using the Keyence automated device for the planktonic foraminifera and the SYRACO automated device for the coccoliths. The results are compared to the carbonate accumulation rates measured in the two previous chapters. Spectral analyses have been run on the obtained records, the results are presented in this chapter.


a)
b)

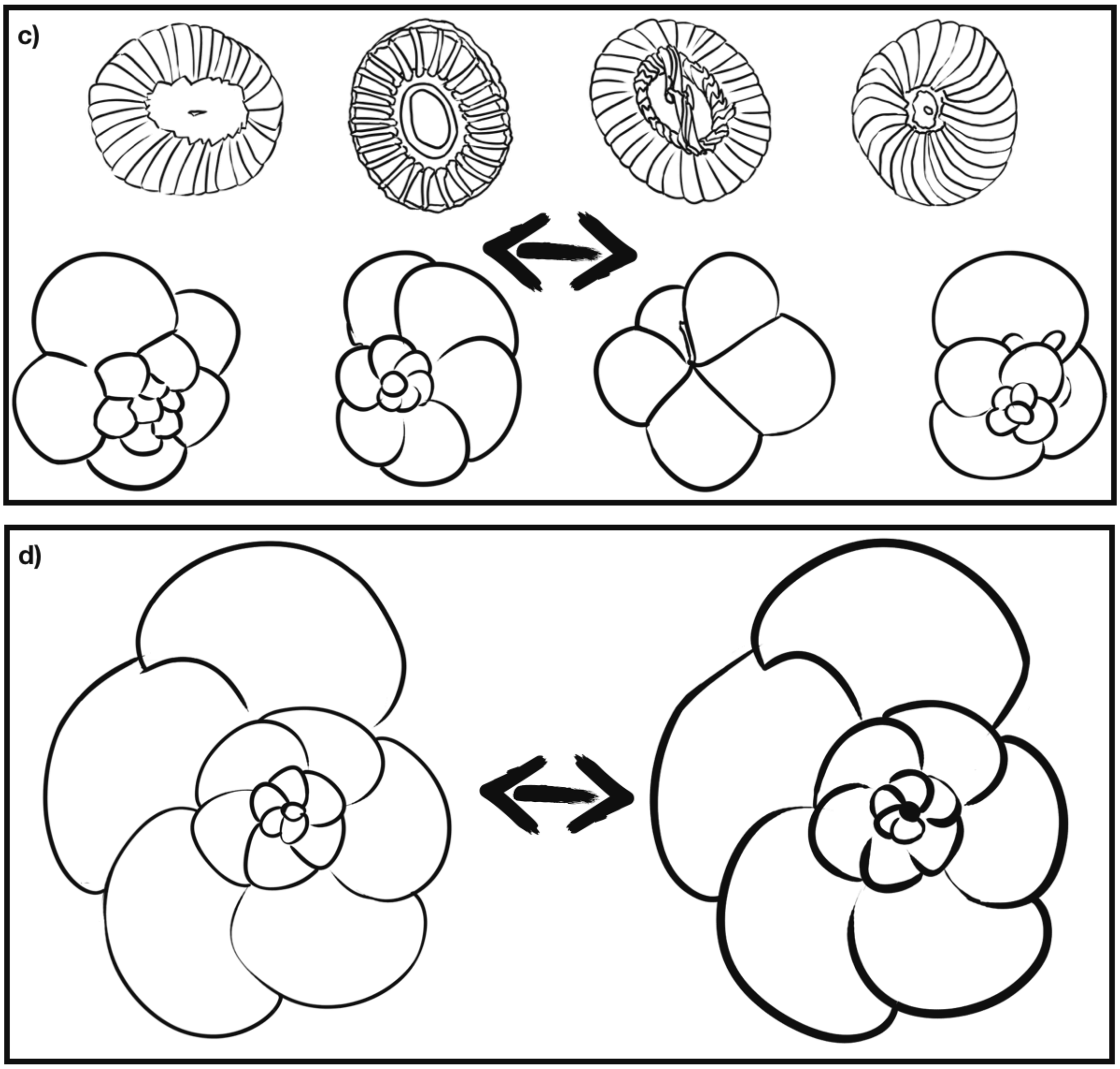


Figure 13. Schematic representation of the question of the third manuscript (chapter #IV): What is the reason behind the observed changes in the carbonate production within the two mains pelagic calcifiers? Are they both changing the same way/for the same reasons/following the same orbital periodicity? Is it a) their sizes, b) their number of specimens, c) their shapes (and taxonomy) or d) how heavily calcified they are?

I.3 Bibliography

Adkins, J. F.: The role of deep ocean circulation in setting glacial climates, Paleoceanography, 28, 539–561, https://doi.org/10.1002/palo.20046, 2013.

Andrié, C., Oudot, C., Genthon, C., and Merlivat, L.: CO_2 fluxes in the tropical Atlantic during FOCAL cruises, J. Geophys. Res., 91, 11741, https://doi.org/10.1029/JC091iC10p11741, 1986.

Araujo, M., Noriega, C., Medeiros, C., Lefèvre, N., Ibánhez, J. S. P., Flores Montes, M., Silva, A. C. da, and Santos, M. de L.: On the variability in the CO_2 system and water productivity in the western tropical Atlantic off North and Northeast Brazil, Journal of Marine Systems, 189, 62–77, https://doi.org/10.1016/j.jmarsys.2018.09.008, 2019.

Aubry, M.-P., Bord, D., Beaufort, L., Kahn, A., and Boyd, S.: Trends in size changes in the coccolithophorids, calcareous nannoplankton, during the Mesozoic: A pilot study, Micropaleontology, 51, 309–318, https://doi.org/10.2113/gsmicropal.51.4.309, 2005.

Ayling, B. F., McCulloch, M. T., Gagan, M. K., Stirling, C. H., Andersen, M. B., and Blake, S. G.: Sr/Ca and $\delta^{18}O$ seasonality in a Porites coral from the MIS 9 (339–303 ka) interglacial, Earth and Planetary Science Letters, 248, 462–475, https://doi.org/10.1016/j.epsl.2006.06.009, 2006.

Bartoli, G., Sarnthein, M., Weinelt, M., Erlenkeuser, H., Garbe-Schönberg, D., and Lea, D. W.: Final closure of Panama and the onset of northern hemisphere glaciation, Earth and Planetary Science Letters, 237, 33–44, https://doi.org/10.1016/j.epsl.2005.06.020, 2005.

Bassinot, F. C., Beaufort, L., Vincent, E., and Labeyrie, L.: Changes in the dynamics of western equatorial Atlantic surface currents and biogenic productivity at the “mid-Pleistocene revolution” (~930 ka), in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 269–284, https://doi.org/10.2973/odp.proc.sr.154.108.1997, 1997.

Beaufort, L., Lancelot, Y., Camberlin, P., Cayre, O., Vincent, E., Bassinot, F., and Labeyrie, L.: Insolation cycles as a major control of equatorial Indian Ocean primary production, Science, 278, 1451–1454, 1997.

Beaufort, L., Probert, I., de Garidel-Thoron, T., Bendif, E. M., Ruiz-Pino, D., Metzl, N., Goyet, C., Buchet, N., Coupel, P., Grelaud, M., Rost, B., Rickaby, R. E. M., and de Vargas, C.: Sensitivity of coccolithophores to carbonate chemistry and ocean acidification, Nature, 476, 80–83, https://doi.org/10.1038/nature10295, 2011.

Beaufort, L., Bolton, C. T., Sarr, A.-C., Suchéras-Marx, B., Rosenthal, Y., Donnadieu, Y., Barbarin, N., Bova, S., Cornuault, P., Gally, Y., Gray, E., Mazur, J.-C., and Tetard, M.: Cyclic evolution of phytoplankton forced by changes in tropical seasonality, Nature, 601, 79–84, https://doi.org/10.1038/s41586-021-04195-7, 2022.

Beerling, D. J. and Royer, D. L.: Reconstructions of atmospheric carbon dioxide concentrations over the past 65 million years are heading towards consensus. It is time for systematic testing of the proxies, against measurements and against each other., NATURE GEOSCIENCE, 4, 418–420, https://doi.org/10.1038/ngeo1186, 2011.

Bell, D. B., Jung, S. J. A., and Kroon, D.: The Plio-Pleistocene development of Atlantic deep-water circulation and its influence on climate trends, Quaternary Science Reviews, 123, 265–282, https://doi.org/10.1016/j.quascirev.2015.06.026, 2015.

Bennington, V., Gloege, L., and McKinley, G. A.: Variability in the Global Ocean Carbon Sink From 1959 to 2020 by Correcting Models With Observations, Geophysical Research Letters, 49, https://doi.org/10.1029/2022GL098632, 2022.

Berger, A. and Loutre, M. F.: Théorie astronomique des paléoclimats, Comptes Rendus Geoscience, 336, 701–709, https://doi.org/10.1016/j.crte.2004.02.006, 2004.

Berger, A. and Yin, Q.: Astronomical Theory and Orbital Forcing, in: The SAGE Handbook of Environmental Change: Volume 1, SAGE Publications Ltd, 1 Oliver’s Yard, 55 City Road, London EC1Y 1SP United Kingdom, 405–425, https://doi.org/10.4135/9781446253045.n19, 2012.

Berger, A., Loutre, M. F., and Melice, J. L.: Equatorial insolation: from precession harmonics to eccentricity frequencies, Clim. Past, 6, 2006.

Bickert, T., Cordes, R., and Wefer, G.: Late Pliocene to mid-Pleistocene (2.6–1.0 m.y.) carbonate dissolution in the western equatorial Atlantic: results of Leg 154, Ceara Rise, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 229–237, https://doi.org/10.2973/odp.proc.sr.154.109.1997, 1997.

Billups, K., Ravelo, A. C., and Zachos, J. C.: Early Pliocene deep-water circulation: stable isotope evidence for enhanced northern component deep water., in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 319–330, https://doi.org/10.2973/odp.proc.sr.154.115.1997, 1997.

Billups, K., Ravelo, A. C., Zachos, J. C., and Norris, R. D.: Link between oceanic heat transport, thermohaline circulation, and the Intertropical Convergence Zone in the early Pliocene Atlantic, Geology, 27, 319–322, https://doi.org/10.1130/0091-7613(1999)027<0319:LBOHTT>2.3.CO;2, 1999.

Billups, K., Channell, J. E. T., and Zachos, J.: Late Oligocene to early Miocene geochronology and paleoceanography from the subantarctic South Atlantic, Paleoceanography, 17, 4-1-4–11, https://doi.org/10.1029/2000PA000568, 2002.

Bolton, C. T., Hernández-Sánchez, M. T., Fuertes, M.-Á., González-Lemos, S., Abrevaya, L., Mendez-Vicente, A., Flores, J.-A., Probert, I., Giosan, L., Johnson, J., and Stoll, H. M.: Decrease in coccolithophore calcification and CO_2 since the middle Miocene, Nature Communications, 7, 10284, https://doi.org/10.1038/ncomms10284, 2016.

Bonou, F. K., Noriega, C., Lefèvre, N., and Araujo, M.: Distribution of CO_2 parameters in the Western Tropical Atlantic Ocean, Dynamics of Atmospheres and Oceans, 73, 47–60, https://doi.org/10.1016/j.dynatmoce.2015.12.001, 2016.

Boot, A., von der Heydt, A. S., and Dijkstra, H. A.: Effect of the Atlantic Meridional Overturning Circulation on atmospheric $p\mathrm{CO}_2$ variations, Earth System Dynamics, 13, 1041–1058, https://doi.org/10.5194/esd-13-1041-2022, 2022.

Boscolo-Galazzo, F., Crichton, K. A., Barker, S., and Pearson, P. N.: Temperature dependency of metabolic rates in the upper ocean: A positive feedback to global climate change?, Global and Planetary Change, 170, 201–212, https://doi.org/10.1016/j.gloplacha.2018.08.017, 2018.

Boudreau, B. P., Middelburg, J. J., and Luo, Y.: The role of calcification in carbonate compensation, Nature Geoscience, 11, 894–900, https://doi.org/10.1038/s41561-018-0259-5, 2018.

Boudreau, B. P., Middelburg, J. J., Sluijs, A., and van der Ploeg, R.: Secular variations in the carbonate chemistry of the oceans over the Cenozoic, Earth and Planetary Science Letters, 512, 194–206, https://doi.org/10.1016/j.epsl.2019.02.004, 2019.

Boyd, P. W., Claustre, H., Levy, M., Siegel, D. A., and Weber, T.: Multi-faceted particle pumps drive carbon sequestration in the ocean, Nature, 568, 327–335, https://doi.org/10.1038/s41586-019-1098-2, 2019.

Brierley, A. S. and Kingsford, M. J.: Impacts of Climate Change on Marine Organisms and Ecosystems, Current Biology, 19, R602–R614, https://doi.org/10.1016/j.cub.2009.05.046, 2009.

Broccoli, A. J., Dahl, K. A., and Stouffer, R. J.: Response of the ITCZ to Northern Hemisphere cooling, Geophysical Research Letter, 33, n/a-n/a, https://doi.org/10.1029/2005GL024546, 2006.

Brummer, G. J. A. and van Eijden, A. J. M.: “Blue-ocean” paleoproductivity estimates from pelagic carbonate mass accumulation rates, Marine Micropaleontology, 19, 99–117, https://doi.org/10.1016/0377-8398(92)90023-D, 1992.

Caron, M. and Homewood, P.: Evolution of early planktic foraminifers, Marine Micropaleontology, 7, 453–462, https://doi.org/10.1016/0377-8398(83)90010-5, 1983.

Cavaleiro, C., Voelker, A. H. L., Stoll, H., Baumann, K.-H., Kulhanek, D. K., Naafs, B. D. A., Stein, R., Grützner, J., Ventura, C., and Kucera, M.: Insolation forcing of coccolithophore productivity in the North Atlantic during the Middle Pleistocene, Quaternary Science Reviews, 191, 318–336, https://doi.org/10.1016/j.quascirev.2018.05.027, 2018.

Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., Chhabra, A., DeFries, R., Galloway, J., and Heimann, M.: Carbon and other biogeochemical cycles, in: Climate change 2013: the physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, 465–570, 2013.

Clark, P. U. and Huybers, P.: Interglacial and future sea level: Global change, Nature, 462, 856–857, https://doi.org/10.1038/462856a, 2009.

Cooley, S. R., Coles, V. J., Subramaniam, A., and Yager, P. L.: Seasonal variations in the Amazon plume-related atmospheric carbon sink, Global Biogeochemical Cycles, 21, n/a-n/a, https://doi.org/10.1029/2006GB002831, 2007.

Cullen, J. L. and Curry, W. B.: Variations in planktonic foraminifer faunas and carbonate preservation at Site 927: evidence for changing surface water conditions in the western tropical Atlantic Ocean during the middle Pleistocene, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 207–228, https://doi.org/10.2973/odp.proc.sr.154.111.1997, 1997.

Curry, W. B., Shackleton, N. J., Richter, C., and et al. (Eds.): Proceedings of the Ocean Drilling Program, 154 Initial Reports, Ocean Drilling Program, https://doi.org/10.2973/odp.proc.ir.154.1995, 1995.

De Vargas, C., Aubry, M.-P., Probert, I., and Young, J.: Origin and Evolution of Coccolithophores: From Coastal Hunters to Oceanic Farmers, in: Evolution of Primary Producers in the Sea, Elsevier, 251–285, https://doi.org/10.1016/B978-012370518-1/50013-8, 2007.

De Vleeschouwer, D., Vahlenkamp, M., Crucifix, M., and Pälike, H.: Alternating Southern and Northern Hemisphere climate response to astronomical forcing during the past 35 m.y., Geology, 45, 375–378, https://doi.org/10.1130/G38663.1, 2017.

De Vleeschouwer, D., Drury, A. J., Vahlenkamp, M., Rochholz, F., Liebrand, D., and Pälike, H.: High-latitude biomes and rock weathering mediate climate–carbon cycle feedbacks on eccentricity timescales, Nature Communication, 11, 5013, https://doi.org/10.1038/s41467-020-18733-w, 2020.

Denman, K. L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickinson, R. E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., Archer, D., Arora, V., Austin, J., Baker, D., Berry, J. A., Betts, R., Bonan, G., Bousquet, P., Canadell, J., Christian, J., Clark, D. A., Dameris, M., Dentener, F., Easterling, D., Eyring, V., Feichter, J., Friedlingstein, P., Fung, I., Fuzzi, S., Gong, S., Gruber, N., Guenther, A., Gurney, K., Henderson-Sellers, A., House, J., Jones, A., Jones, C., Kärcher, B., Kawamiya, M., Lassey, K., Leck, C., Lee-Taylor, J., Malhi, Y., Masarie, K., McFiggans, G., Menon, S., Miller, J. B., Peylin, P., Pitman, A., Quaas, J., Raupach, M., Rayner, P., Rehder, G., Riebesell, U., Rödenbeck, C., Rotstayn, L., Roulet, N., Sabine, C., Schultz, M. G., Schulz, M., Schwartz, S. E., Steffen, W., Stevenson, D., Tian, Y., Trenberth, K. E., Noije, T. V., Wild, O., Zhang, T., Zhou, L., Boonpragob, K., Heimann, M., and Molina, M.: Couplings Between Changes in the Climate System and Biogeochemistry, 90, 2007.

DeVries, T.: Atmospheric CO_2 and Sea Surface Temperature Variability Cannot Explain Recent Decadal Variability of the Ocean CO_2 Sink, Geophysical Research Letters, 49, https://doi.org/10.1029/2021GL096018, 2022.

Dowsett, H., Barron, J., and Poore, R.: Middle Pliocene sea surface temperatures: a global reconstruction, Marine Micropaleontology, 27, 13–25, 1996.

Dowsett, H. J., Robinson, M. M., and Foley, K. M.: Pliocene three-dimensional global ocean temperature reconstruction, Climate of the Past, 15, 2009.

Drury, A. J., John, C. M., and Shevenell, A. E.: Evaluating climatic response to external radiative forcing during the late Miocene to early Pliocene: New perspectives from eastern equatorial Pacific (IODP U1338) and North Atlantic (ODP 982) locations: Late Miocene-Early Pliocene Variability, Paleoceanography, 31, 167–184, https://doi.org/10.1002/2015PA002881, 2016.

Dwyer, G. S., Cronin, T. M., Baker, P. A., Raymo, M. E., Buzas, J. S., and Correge, T.: North Atlantic Deepwater Temperature Change During Late Pliocene and Late Quaternary Climatic Cycles, Science, 270, 1347–1351, https://doi.org/10.1126/science.270.5240.1347, 1995.

Feely, R. A.: Impact of Anthropogenic CO_2 on the $CaCO_3$ System in the Oceans, Science, 305, 362–366, https://doi.org/10.1126/science.1097329, 2004.

Feely, R. A., Doney, S. T. C., and Cooley, S. A. R.: Ocean acidification: Present conditions and future changes in a high CO_2 world, Oceanography, 22, 36–47, 2009.

Foster, G. L., Lear, C. H., and Rae, J. W. B.: The evolution of pCO_2, ice volume and climate during the middle Miocene, Earth and Planetary Science Letters, 341–344, 243–254, https://doi.org/10.1016/j.epsl.2012.06.007, 2012.

Frenz, M., Henrich, R., and Zychla, B.: Carbonate preservation patterns at the Ceará Rise – Evidence for the Pliocene super conveyor, Marine Geology, 232, 173–180, https://doi.org/10.1016/j.margeo.2006.07.006, 2006.

Friedlingstein, P., Jones, M. W., O'Sullivan, M., Andrew, R. M., Hauck, J., Peters, G. P., Peters, W., Pongratz, J., Sitch, S., Le Quéré, C., Bakker, D. C. E., Canadell, J. G., Ciais, P., Jackson, R. B., Anthoni, P., Barbero, L., Bastos, A., Bastrikov, V., Becker, M., Bopp, L., Buitenhuis, E., Chandra, N., Chevallier, F., Chini, L. P., Currie, K. I., Feely, R. A., Gehlen, M., Gilfillan, D., Gkritzalis, T., Goll, D. S., Gruber, N., Gutekunst, S., Harris, I., Haverd, V., Houghton, R. A., Hurtt, G., Ilyina, T., Jain, A. K., Joetzjer, E., Kaplan, J. O., Kato, E., Klein Goldewijk, K., Korsbakken, J. I., Landschützer, P., Lauvset, S. K., Lefèvre, N., Lenton, A., Lienert, S., Lombardozzi, D., Marland, G., McGuire, P. C., Melton, J. R., Metzl, N., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S.-I., Neill, C., Omar, A. M., Ono, T., Peregon, A., Pierrot, D., Poulter, B., Rehder, G., Resplandy, L., Robertson, E., Rödenbeck, C., Séférian, R., Schwinger, J., Smith, N., Tans, P. P., Tian, H., Tilbrook, B., Tubiello, F. N., van der Werf, G. R., Wiltshire, A. J., and Zaehle, S.: Global Carbon Budget 2019, Earth System Science Data, 11, 1783–1838, https://doi.org/10.5194/essd-11-1783-2019, 2019.

Foster, G. L., Lear, C. H., and Rae, J. W. B.: The evolution of pCO_2, ice volume and climate during the middle Miocene, Earth and Planetary Science Letters, 341–344, 243–254, https://doi.org/10.1016/j.epsl.2012.06.007, 2012.

Friedlingstein, P., O'Sullivan, M., Jones, M. W., Andrew, R. M., Hauck, J., Olsen, A., Peters, G. P., Peters, W., Pongratz, J., Sitch, S., Le Quéré, C., Canadell, J. G., Ciais, P., Jackson, R. B., Alin, S., Aragão, L. E. O. C., Arneth, A., Arora, V., Bates, N. R., Becker, M., Benoit-Cattin, A., Bittig, H. C., Bopp, L., Bultan, S., Chandra, N., Chevallier, F., Chini, L. P., Evans, W., Florentie, L., Forster, P. M., Gasser, T., Gehlen, M., Gilfillan, D., Gkritzalis, T., Gregor, L., Gruber, N., Harris, I., Hartung, K., Haverd, V., Houghton, R. A., Ilyina, T., Jain, A. K., Joetzjer, E., Kadono, K., Kato, E., Kitidis, V., Korsbakken, J. I., Landschützer, P., Lefèvre, N., Lenton, A., Lienert, S., Liu, Z., Lombardozzi, D., Marland, G., Metzl, N., Munro, D. R., Nabel, J. E. M. S., Nakaoka, S.-I., Niwa, Y., O'Brien, K., Ono, T., Palmer, P. I., Pierrot, D., Poulter, B., Resplandy, L., Robertson, E., Rödenbeck, C., Schwinger, J., Séférian, R., Skjelvan, I., Smith, A. J. P., Sutton, A. J., Tanhua, T., Tans, P. P., Tian, H., Tilbrook, B., van der Werf, G., Vuichard, N., Walker, A. P., Wanninkhof, R., Watson, A. J., Willis, D., Wiltshire, A. J., Yuan, W., Yue, X., and Zaehle, S.: Global Carbon Budget 2020, Earth System Science Data, 12, 3269–3340, https://doi.org/10.5194/essd-12-3269-2020, 2020.

Fung, I. Y., Doney, S. C., Lindsay, K., and John, J.: Evolution of carbon sinks in a changing climate, Proceedings of the National Academy of Sciences U.S.A., 102, 11201–11206, https://doi.org/10.1073/pnas.0504949102, 2005.

Gao, K., Zhang, Y., and Häder, D.-P.: Individual and interactive effects of ocean acidification, global warming, and UV radiation on phytoplankton, Journal of Applied Phycology, 30, 743–759, https://doi.org/10.1007/s10811-017-1329-6, 2017.

Goosse, H.: Climate system dynamics and modeling, Cambridge University Press, New York, NY, 358 pp., 2015.

Gröger, M., Henrich, R., and Bickert, T.: Glacial–interglacial variability in lower North Atlantic deep water: inference from silt grain-size analysis and carbonate preservation in the western equatorial Atlantic, Marine Geology, 201, 321–332, https://doi.org/10.1016/S0025-3227(03)00263-9, 2003a.

Gröger, M., Henrich, R., and Bickert, T.: Variability of silt grain size and planktonic foraminiferal preservation in Plio/Pleistocene sediments from the western equatorial Atlantic and Caribbean, Marine Geology, 201, 307–320, https://doi.org/10.1016/S0025-3227(03)00264-0, 2003b.

Gruber, N., Gloor, M., Mikaloff Fletcher, S. E., Doney, S. C., Dutkiewicz, S., Follows, M. J., Gerber, M., Jacobson, A. R., Joos, F., Lindsay, K., Menemenlis, D., Mouchet, A., Müller, S. A., Sarmiento, J. L., and Takahashi, T.: Oceanic sources, sinks, and transport of atmospheric CO_2, Global Biogeochemical Cycles, 23, n/a-n/a, https://doi.org/10.1029/2008GB003349, 2009.

Guidi, L., Stemmann, L., Jackson, G. A., Ibanez, F., Claustre, H., Legendre, L., Picheral, M., and Gorskya, G.: Effects of phytoplankton community on production, size, and export of large aggregates: A world-ocean analysis, American Society of Limnology and Oceanography, 54, 1951–1963, https://doi.org/10.4319/lo.2009.54.6.1951, 2009.

Guidi, L., Legendre, L., Reygondeau, G., Uitz, J., Stemmann, L., and Henson, S. A.: A new look at ocean carbon remineralization for estimating deepwater sequestration, Global Biogeochemical Cycles, 29, 1044–1059, https://doi.org/10.1002/2014GB005063, 2015.

Haq, B. U., Hardenbol, J., and Vail, P. R.: Chronology of Fluctuating Sea Levels Since the Triassic, Science, 235, 1156–1167, https://doi.org/10.1126/science.235.4793.1156, 1987.

Haug, G. H. and Tiedemann, R.: Effect of the formation of the Isthmus of Panama on Atlantic Ocean thermohaline circulation, Nature, 393, 673–676, https://doi.org/10.1038/31447, 1998.

Haug, G. H., Tiedemann, R., Zahn, R., and Ravelo, A. C.: Role of Panama uplift on oceanic freshwater balance, Geology, 29, 3, p 207-210, 2001.

Hay, W. W., DeConto, R. M., and Wold, C. N.: Climate: Is the past the key to the future?, Geologische Rundschau, 86, 471–491, 1997.

Hays, J. D., Imbrie, J., and Shackleton, N. J.: Variations in the Earth's Orbit: Pacemaker of the Ice Ages, Science, 194, 4270, 13, 1976.

Haywood, A. M. and Valdes, P. J.: Modelling Pliocene warmth: contribution of atmosphere, oceans and cryosphere, Earth and Planetary Science Letters, 218, 363–377, https://doi.org/10.1016/S0012-821X(03)00685-X, 2004.

Haywood, A. M., Valdes, P. J., and Sellwood, B. W.: Global scale palaeoclimate reconstruction of the middle Pliocene climate using the UKMO GCM: initial results, Global and Planetary Change, 25, 239–256, https://doi.org/10.1016/S0921-8181(00)00028-X, 2000.

Haywood, A. M., Dolan, A. M., Pickering, S. J., Dowsett, H. J., McClymont, E. L., Prescott, C. L., Salzmann, U., Hill, D. J., Hunter, S. J., Lunt, D. J., Pope, J. O., and Valdes, P. J.: On the identification of a Pliocene time slice for data-model comparison, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 371, 20120515–20120515, https://doi.org/10.1098/rsta.2012.0515, 2013.

Herbert, T. D., Lawrence, K. T., Tzanova, A., Peterson, L. C., Caballero-Gill, R., and Kelly, C. S.: Late Miocene global cooling and the rise of modern ecosystems, Nature Geoscience, 9, 843–847, https://doi.org/10.1038/ngeo2813, 2016.

Herrford, J., Brandt, P., and Zenk, W.: Property changes of deep and bottom waters in the Western Tropical Atlantic, Deep Sea Research Part I: Oceanographic Research Papers, 124, 103–125, https://doi.org/10.1016/j.dsr.2017.04.007, 2017.

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 and Planetary Science Letters, 261, 534–550, https://doi.org/10.1016/j.epsl.2007.07.026, 2007.

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, 19–22, https://doi.org/10.1130/G34890.1, 2014.

Holbourn, A., Kuhnt, W., Kochhann, K. G. D., Andersen, N., and Sebastian Meier, K. J.: Global perturbation of the carbon cycle at the onset of the Miocene Climatic Optimum, Geology, 43, 123–126, https://doi.org/10.1130/G36317.1, 2015.

Holbourn, A. E., Kuhnt, W., Clemens, S. C., Kochhann, K. G. D., Jöhnck, J., Lübbers, J., and Andersen, N.: Late Miocene climate cooling and intensification of southeast Asian winter monsoon, Nature Communication, 9, 1584, https://doi.org/10.1038/s41467-018-03950-1, 2018.

Honjo, S., Eglinton, T., Taylor, C., Ulmer, K., Sievert, S., Bracher, A., German, C., Edgcomb, V., Francois, R., Iglesias-Rodriguez, M. D., Van Mooy, B., and Rapeta, D.: Understanding the Role of the Biological Pump in the Global Carbon Cycle: An Imperative for Ocean Science, oceanography, 27, 10–16, https://doi.org/10.5670/oceanog.2014.78, 2014.

Howard, W. R.: A warm future in the past, Nature, 388, 418–419, https://doi.org/10.1038/41201, 1997.

Ibánhez, J. S. P., Diverrès, D., Araujo, M., and Lefèvre, N.: Seasonal and interannual variability of sea-air CO_2 fluxes in the tropical Atlantic affected by the Amazon River plume, Global Biogeochemical Cycles, 29, 1640–1655, https://doi.org/10.1002/2015GB005110, 2015.

Ibánhez, J. S. P., Araujo, M., and Lefèvre, N.: The overlooked tropical oceanic CO_2 sink: Overlooked Tropical Oceanic CO_2 Sink, Geophysical Research Letters, 43, 3804–3812, https://doi.org/10.1002/2016GL068020, 2016.

Intergovernmental Panel On Climate Change: Climate Change 2021 – The Physical Science Basis: Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, 1st ed., Cambridge University Press, https://doi.org/10.1017/9781009157896, 2021.

Johnson, G. C.: Quantifying Antarctic Bottom Water and North Atlantic Deep Water volumes, J. Geophys. Res., 113, C05027, https://doi.org/10.1029/2007JC004477, 2008.

Joos, F. and Spahni, R.: Rates of change in natural and anthropogenic radiative forcing over the past 20,000 years, Proc. Natl. Acad. Sci. U.S.A., 105, 1425–1430, https://doi.org/10.1073/pnas.0707386105, 2008.

Kamikuri, S. and Moore, T. C.: Reconstruction of oceanic circulation patterns in the tropical Pacific across the early/middle Miocene boundary as inferred from radiolarian assemblages, Palaeogeography, Palaeoclimatology, Palaeoecology, 487, 136–148, https://doi.org/10.1016/j.palaeo.2017.08.028, 2017.

Khatiwala, S., Primeau, F., and Hall, T.: Reconstruction of the history of anthropogenic CO_2 concentrations in the ocean, Nature, 462, 346–349, https://doi.org/10.1038/nature08526, 2009.

King, T. A., Ellis, W. G., Murray, D. W., and Shackleton, N. J.: Miocene evolution of carbonate sedimentation at the Ceara Rise: a multivariate date/proxy approach, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 349–365, https://doi.org/10.2973/odp.proc.sr.154.116.1997, 1997.

Kiss, P., Jonkers, L., Hudáčková, N., Reuter, R. T., Donner, B., Fischer, G., and Kucera, M.: Determinants of Planktonic Foraminifera Calcite Flux: Implications for the Prediction of Intra- and Inter- Annual Pelagic Carbonate Budgets, Global Biogeochemical Cycles, 35, https://doi.org/10.1029/2020GB006748, 2021.

Kleiven, H. F., Jansen, E., Curry, W. B., Hodell, D. A., and Venz, K.: Atlantic Ocean thermohaline circulation changes on orbital to suborbital timescales during the mid-Pleistocene, Paleoceanography, 18, 13, https://doi.org/10.1029/2001PA000629, 2003.

Kopp, R. E., Simons, F. J., Mitrovica, J. X., Maloof, A. C., and Oppenheimer, M.: Probabilistic assessment of sea level during the last interglacial stage, Nature, 462, 6, https://doi.org/10.1038/nature08686, 2009.

Körtzinger, A.: A significant CO_2 sink in the tropical Atlantic Ocean associated with the Amazon River plume, Geophysical Research Letters, 30, 24, 2287, https://doi.org/10.1029/2003GL018841, 2003.

Krumhardt, K. M., Lovenduski, N. S., Iglesias-Rodriguez, M. D., and Kleypas, J. A.: Coccolithophore growth and calcification in a changing ocean, Progress in Oceanography, 159, 276–295, https://doi.org/10.1016/j.pocean.2017.10.007, 2017.

Kukla, G.: How long and how stable was the last interglacial?, Quaternary Science Reviews, 16, 605–612, https://doi.org/10.1016/S0277-3791(96)00114-X, 1997.

Kurschner, W. M., Kvacek, Z., and Dilcher, D. L.: The impact of Miocene atmospheric carbon dioxide fluctuations on climate and the evolution of terrestrial ecosystems, Proceedings of the National Academy of Sciences, 105, 449–453, https://doi.org/10.1073/pnas.0708588105, 2008.

Landschützer, P., Gruber, N., Bakker, D. C. E., and Schuster, U.: Recent variability of the global ocean carbon sink, Global Biogeochemical Cycles, 28, 927–949, https://doi.org/10.1002/2014GB004853, 2014.

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, Astronomy & Astrophysics, 428, 261–285, https://doi.org/10.1051/0004-6361:20041335, 2004.

Laws, E. A., Falkowski, P. G., Smith, W. O., Ducklow, H., and McCarthy, J. J.: Temperature effects on export production in the open ocean, Global Biogeochemical Cycles, 14, 1231–1246, https://doi.org/10.1029/1999GB001229, 2000.

Le Moigne, F. A. C., Pabortsava, K., Marcinko, C. L. J., Martin, P., and Sanders, R. J.: Where is mineral ballast important for surface export of particulate organic carbon in the ocean?, Geophysical Research Letters, 41, 8460–8468, https://doi.org/10.1002/2014GL061678, 2014.

Lea, D. W.: Climate Impact of Late Quaternary Equatorial Pacific Sea Surface Temperature Variations, Science, 289, 1719–1724, https://doi.org/10.1126/science.289.5485.1719, 2000.

Lear, C. H., Rosenthal, Y., and Wright, J. D.: The closing of a seaway: ocean water masses and global climate change, Earth and Planetary Science Letters, 210, 425–436, https://doi.org/10.1016/S0012-821X(03)00164-X, 2003.

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, 4, PA4015, https://doi.org/10.1029/2004PA001039, 2004.

Lefévre, N., Diverrés, D., and Gallois, F.: Origin of CO_2 undersaturation in the western tropical Atlantic, Tellus B: Chemical and Physical Meteorology, 62, 595–607, https://doi.org/10.1111/j.1600-0889.2010.00475.x, 2010.

Lefèvre, N., Urbano, D. F., Gallois, F., and Diverrès, D.: Impact of physical processes on the seasonal distribution of the fugacity of CO_2 in the western tropical Atlantic, Journal of Geophysical Research: Oceans, 119, 646–663, https://doi.org/10.1002/2013JC009248, 2014.

Legendre, L., Rivkin, R. B., Jiao, N., and Handling editor: Howard Browman: Advanced experimental approaches to marine water-column biogeochemical processes, ICES Journal of Marine Science, 75, 30–42, https://doi.org/10.1093/icesjms/fsx146, 2018.

Leonhardt, A., A. L. Toledo, F., and Carlos Coimbra, J.: The Mid-Brunhes event in the southwestern Atlantic Ocean: coccolithophore assemblages during the Mis 11-9, Revista Brasileira De Paleontologia, 18, 343–354, https://doi.org/10.4072/rbp.2015.3.01, 2015.

Lessa, D. V. O., Santos, T. P., Venancio, I. M., and Albuquerque, A. L. S.: Offshore expansion of the Brazilian coastal upwelling zones during Marine Isotope Stage 5, Global and Planetary Change, 158, 13–20, https://doi.org/10.1016/j.gloplacha.2017.09.006, 2017.

Li, L., Li, Q., Tian, J., Wang, P., Wang, H., and Liu, Z.: A 4-Ma record of thermal evolution in the tropical western Pacific and its implications on climate change, Earth and Planetary Science Letters, 309, 10–20, https://doi.org/10.1016/j.epsl.2011.04.016, 2011.

Lisiecki, L. E. and Raymo, M. E.: A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}O$ records, Paleoceanography, 20, PA1003, https://doi.org/10.1029/2004PA001071, 2005.

Lunt, D. J., Foster, G. L., Haywood, A. M., and Stone, E. J.: Late Pliocene Greenland glaciation controlled by a decline in atmospheric CO_2 levels, Nature, 454, 1102–1105, https://doi.org/10.1038/nature07223, 2008.

Lunt, D. J., Haywood, A. M., Schmidt, G. A., Salzmann, U., Valdes, P. J., and Dowsett, H. J.: Earth system sensitivity inferred from Pliocene modelling and data, Nature Geosciences, 3, 60–64, https://doi.org/10.1038/ngeo706, 2010.

Maier-Reimer, E. and Mikolajewicz, U.: Ocean general circulation model sensitivity experiment with an open central American Isthmus, Paleoceanography, 5, 349–366, 1990.

Marino, M., Maiorano, P., Tarantino, F., Voelker, A., Capotondi, L., Girone, A., Lirer, F., Flores, J.-A., and Naafs, B. D. A.: Coccolithophores as proxy of seawater changes at orbital-to-millennial scale during middle Pleistocene Marine Isotope Stages 14-9 in North Atlantic core MD01-2446, Paleoceanography, 29, 518–532, https://doi.org/10.1002/2013PA002574, 2014.

Marinov, I., Gnanadesikan, A., Sarmiento, J. L., Toggweiler, J. R., Follows, M., and Mignone, B. K.: Impact of oceanic circulation on biological carbon storage in the ocean and atmospheric pCO_2, Global Biogeochemical Cycles, 22, GB3007, https://doi.org/10.1029/2007GB002958, 2008.

Mejía, L. M., Méndez-Vicente, A., Abrevaya, L., Lawrence, K. T., Ladlow, C., Bolton, C., Cacho, I., and Stoll, H.: A diatom record of CO_2 decline since the late Miocene, Earth and Planetary Science Letters, 479, 18–33, https://doi.org/10.1016/j.epsl.2017.08.034, 2017.

Middelburg, J. J., Soetaert, K., and Hagens, M.: Ocean Alkalinity, Buffering and Biogeochemical Processes, Reviews of Geophysics, 58, https://doi.org/10.1029/2019RG000681, 2020.

Mikaloff Fletcher, S. E., Gruber, N., Jacobson, A. R., Doney, S. C., Dutkiewicz, S., Gerber, M., Follows, M., Joos, F., Lindsay, K., Menemenlis, D., Mouchet, A., Müller, S. A., and Sarmiento, J. L.: Inverse estimates of anthropogenic CO_2 uptake, transport, and storage by the ocean, Global Biogeochemical Cycles, 20, GB2002, https://doi.org/10.1029/2005GB002530, 2006.

Milankovitch, M.: Canon of insolation and the iceage problem, Koniglich Serbische Akademice Beograd, Special Publication, 132, 1941.

Milliman, J. D.: Production and accumulation of calcium carbonate in the ocean: budget of a nonsteady state, Global Biogeochemical Cycles, 7, 927–957, 1993.

Müller, U. C. and Kukla, G. J.: North Atlantic Current and European environments during the declining stage of the last interglacial, Geology, 32, 1009, https://doi.org/10.1130/G20901.1, 2004.

Naish, T., Powell, R., Levy, R., Wilson, G., Scherer, R., Talarico, F., Krissek, L., Niessen, F., Pompilio, M., Wilson, T., Carter, L., DeConto, R., Huybers, P., McKay, R., Pollard, D., Ross, J., Winter, D., Barrett, P., Browne, G., Cody, R., Cowan, E., Crampton, J., Dunbar, G., Dunbar, N., Florindo, F., Gebhardt, C., Graham, I., Hannah, M., Hansaraj, D., Harwood, D., Helling, D., Henrys, S., Hinnov, L., Kuhn, G., Kyle, P., Läufer, A., Maffioli, P., Magens, D., Mandernack, K., McIntosh, W., Millan, C., Morin, R., Ohneiser, C., Paulsen, T., Persico, D., Raine, I., Reed, J., Riesselman, C., Sagnotti, L., Schmitt, D., Sjunneskog, C., Strong, P., Taviani, M., Vogel, S., Wilch, T., and Williams, T.: Obliquity-paced Pliocene West Antarctic ice sheet oscillations, Nature, 458, 322–328, https://doi.org/10.1038/nature07867, 2009.

O'Dea, A., Lessios, H. A., Coates, A. G., Eytan, R. I., Restrepo-Moreno, S. A., Cione, A. L., Collins, L. S., de Queiroz, A., Farris, D. W., Norris, R. D., Stallard, R. F., Woodburne, M. O., Aguilera, O., Aubry, M.-P., Berggren, W. A., Budd, A. F., Cozzuol, M. A., Coppard, S. E., Duque-Caro, H., Finnegan, S., Gasparini, G. M., Grossman, E. L., Johnson, K. G., Keigwin, L. D., Knowlton, N., Leigh, E. G., Leonard-Pingel, J. S., Marko, P. B., Pyenson, N. D., Rachello-Dolmen, P. G., Soibelzon, E., Soibelzon, L., Todd, J. A., Vermeij, G. J., and Jackson, J. B. C.: Formation of the Isthmus of Panama, Science Advances, 2, 11, https://doi.org/10.1126/sciadv.1600883, 2016.

Pagani, M., Liu, Z., LaRiviere, J., and Ravelo, A. C.: High Earth-system climate sensitivity determined from Pliocene carbon dioxide concentrations, Nature Geosciences, 3, 27–30, https://doi.org/10.1038/ngeo724, 2010.

Past Interglacials Working Group of PAGES: Interglacials of the last 800,000 years, Reviews of Geophysics, 54, 1, 162–219, https://doi.org/10.1002/2015RG000482, 2016.

Paul, H. A., Zachos, J. C., Flower, B. P., and Tripati, A.: Orbitally induced climate and geochemical variability across the Oligocene/Miocene boundary, Paleoceanography, 15, 471–485, https://doi.org/10.1029/1999PA000443, 2000.

Pekar, S. F. and DeConto, R. M.: High-resolution ice-volume estimates for the early Miocene: Evidence for a dynamic ice sheet in Antarctica, Palaeogeography, Palaeoclimatology, Palaeoecology, 231, 101–109, https://doi.org/10.1016/j.palaeo.2005.07.027, 2006.

Petit, J. R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V. M., Legrand, M., Lipenkov, V. Y., Lorius, C., PÉpin, L., Ritz, C., Saltzman, E., and Stievenard, M.: Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, Nature, 399, 429–436, https://doi.org/10.1038/20859, 1999.

Pollard, D. and DeConto, R. M.: Modelling West Antarctic ice sheet growth and collapse through the past five million years, Nature, 458, 329–332, https://doi.org/10.1038/nature07809, 2009.

Pörtner, H. O., Karl, D. M., Boyd, P. W., Cheung, W. W. L., Lluch-Cota, S. E., Nojiri, Y., Schmidt, D. N., and Zavialov, P. O.: Part A: Global and Sectoral Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Field, C.B., V.R. Barros, D.J. Dokken, K.J. Mach, M.D. Mastrandrea, T.E. Bilir, M. Chatterjee, K.L. Ebi, Y.O. Estrada, R.C. Genova, B. Girma, E.S. Kissel, A.N. Levy, S. MacCracken, P.R. Mastrandrea, and L.L. White (eds.)]., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, Climate Change 2014: Impacts, Adaptation, and Vulnerability, 411–484, 2014.

Pound, M. J., Haywood, A. M., Salzmann, U., and Riding, J. B.: Global vegetation dynamics and latitudinal temperature gradients during the Mid to Late Miocene (15.97–5.33Ma), Earth-Science Reviews, 112, 1–22, https://doi.org/10.1016/j.earscirev.2012.02.005, 2012.

Preiss-Daimler, I. V., Henrich, R., and Bickert, T.: The final Miocene carbonate crash in the Atlantic: Assessing carbonate accumulation, preservation and production, Marine Geology, 343, 39–46, https://doi.org/10.1016/j.margeo.2013.06.010, 2013.

Rahmstorf, S.: Ocean circulation and climate during the past 120,000 years, Nature, 419, 207–214, https://doi.org/10.1038/nature01090, 2002.

Raitzsch, M., Bijma, J., Bickert, T., Schulz, M., Holbourn, A., and Kučera, M.: Atmospheric carbon dioxide variations across the middle Miocene climate transition, Climate of the Past, 17, 703–719, https://doi.org/10.5194/cp-17-703-2021, 2021.

Ravelo, A. C. and Wara, M. W.: The Role of the Tropical Oceans on Global Climate During a Warm Period and a Major Climate Transition, Oceanography, 17, 32–41, https://doi.org/10.5670/oceanog.2004.28, 2004.

Ravelo, A. C., Andreasen, D. H., Lyle, M., Olivarez Lyle, A., and Wara, M. W.: Regional climate shifts caused by gradual global cooling in the Pliocene epoch, Nature, 429, 263–267, https://doi.org/10.1038/nature02567, 2004.

Raymo, M. E.: The initiation of Northern Hemisphere glaciation, Annual Review of Earth and Planetary Sciences, 22, 353–383, 1994.

Raymo, M. E., Hodell, D., and Jansen, E.: Response of deep ocean circulation to initiation of northern hemisphere glaciation (3-2 MA), Paleoceanography, 7, 645–672, https://doi.org/10.1029/92PA01609, 1992.

Raymo, M. E., Grant, B., Horowitz, M., and Rau, G. H.: Mid-Pliocene warmth: stronger greenhouse and stronger conveyor, Marine Micropaleontology, 27, 313–326, 1996.

Rhein, M., Stramma, L., and Krahmann, G.: The spreading of Antarctic bottom water in the tropical Atlantic, Deep Sea Research Part I: Oceanographic Research Papers, 45, 507–527, https://doi.org/10.1016/S0967-0637(97)00030-7, 1998.

Rühlemann, C., Mulitza, S., Müller, P. J., Wefer, G., and Zahn, R.: Warming of the tropical Atlantic Ocean and slowdown of thermohaline circulation during the last deglaciation, Nature, 402, 511–514, https://doi.org/10.1038/990069, 1999.

Rühlemann, C., Diekmann, B., Mulitza, S., and Frank, M.: Late Quaternary changes of western equatorial Atlantic surface circulation and Amazon lowland climate recorded in Ceará Rise deep-sea sediments, Paleoceanography, 16, 293–305, https://doi.org/10.1029/1999PA000474, 2001.

Rühlemann, C., Mulitza, S., Lohmann, G., Paul, A., Prange, M., and Wefer, G.: Intermediate depth warming in the tropical Atlantic related to weakened thermohaline circulation: Combining paleoclimate data and modeling results for the last deglaciation, Paleoceanography, 19, PA1025, https://doi.org/10.1029/2003PA000948, 2004.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-H., Kozyr, A., Ono, T., and Rios, A. F.: The Oceanic Sink for Anthropogenic CO_2, Science, 305, 367–371, https://doi.org/10.1126/science.1097403, 2004.

Santer, B. D., Wigley, T. M. L., Gleckler, P. J., Bonfils, C., Wehner, M. F., AchutaRao, K., Barnett, T. P., Boyle, J. S., Brüggemann, W., Fiorino, M., Gillett, N., Hansen, J. E., Jones, P. D., Klein, S. A., Meehl, G. A., Raper, S. C. B., Reynolds, R. W., Taylor, K. E., and Washington, W. M.: Forced and unforced ocean temperature changes in Atlantic and Pacific tropical cyclogenesis regions, Proceedings of the National Academy of Sciences U.S.A., 103, 13905–13910, https://doi.org/10.1073/pnas.0602861103, 2006.

Sarmiento, J. L. and Gruber, N.: Ocean biogeochemical dynamics, Princeton University Press, Princeton, 503 pp., 2006.

Schiebel, R. and Hemleben, C.: Planktic Foraminifers in the Modern Ocean, Springer Berlin Heidelberg, Berlin, Heidelberg, https://doi.org/10.1007/978-3-662-50297-6, 2017.

Schlitzer, R.: Ocean Data View, 2018.

Schmidt, M. W. and Spero, H. J.: Meridional shifts in the marine ITCZ and the tropical hydrologic cycle over the last three glacial cycles, Paleoceanography, 26, PA1206, https://doi.org/10.1029/2010PA001976, 2011.

Schwab, C., Kinkel, H., Weinelt, M., and Repschläger, J.: A coccolithophore based view on paleoenvironmental changes in the open ocean mid-latitude North Atlantic between 130 and 48 ka BP with special emphasis on MIS 5e, Quaternary Science Reviews, 81, 35–47, https://doi.org/10.1016/j.quascirev.2013.09.021, 2013.

Seki, O., Foster, G. L., Schmidt, D. N., Mackensen, A., Kawamura, K., and Pancost, R. D.: Alkenone and boron-based Pliocene pCO2 records, Earth and Planetary Science Letters, 292, 201–211, https://doi.org/10.1016/j.epsl.2010.01.037, 2010.

Shackleton, N. J. and Crowhurst, S.: Sediment fluxes based on an orbitally tuned time scale 5 Ma to 14 Ma, Site 926, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 69–82, https://doi.org/10.2973/odp.proc.sr.154.102.1997, 1997.

Shackleton, N. J., Crowhurst, S. J., Weedon, G. P., and Laskar, J.: Astronomical calibration of Oligocene--Miocene time, Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences, 357, 1907–1929, https://doi.org/10.1098/rsta.1999.0407, 1999.

Si, W. and Rosenthal, Y.: Reduced continental weathering and marine calcification linked to late Neogene decline in atmospheric CO_2, Nature Geosciences, 12, 833–838, https://doi.org/10.1038/s41561-019-0450-3, 2019.

Siegenthaler, U.: Stable Carbon Cycle-Climate Relationship During the Late Pleistocene, Science, 310, 1313–1317, https://doi.org/10.1126/science.1120130, 2005.

Sirocko, F., Seelos, K., Schaber, K., Rein, B., Dreher, F., Diehl, M., Lehne, R., Jäger, K., Krbetschek, M., and Degering, D.: A late Eemian aridity pulse in central Europe during the last glacial inception, Nature, 436, 833–836, https://doi.org/10.1038/nature03905, 2005.

Sloan, L. C., Crowley, T. J., and Pollard, D.: Modeling of middle Pliocene climate with the NCAR GENESIS general circulation model, Marine Micropaleontology, 27, 51–61, 1996.

Stap, L. B., de Boer, B., Ziegler, M., Bintanja, R., Lourens, L. J., and van de Wal, R. S. W.: CO_2 over the past 5 million years: Continuous simulation and new δ^{11}B-based proxy data, Earth and Planetary Science Letters, 439, 1–10, https://doi.org/10.1016/j.epsl.2016.01.022, 2016.

Stolz, K. and Baumann, K.-H.: Changes in palaeoceanography and palaeoecology during Marine Isotope Stage (MIS) 5 in the eastern North Atlantic (ODP Site 980) deduced from calcareous nannoplankton observations, Palaeogeography, Palaeoclimatology, Palaeoecology, 292, 295–305, https://doi.org/10.1016/j.palaeo.2010.04.002, 2010.

Sutherland, R., Dos Santos, Z., Agnini, C., Alegret, L., Lam, A. R., Westerhold, T., Drake, M. K., Harper, D. T., Dallanave, E., Newsam, C., Cramwinckel, M. J., Dickens, G. R., Collot, J., Etienne, S. J. G., Bordenave, A., Stratford, W. R., Zhou, X., Li, H., and Asatryan, G.: Neogene Mass Accumulation Rate of Carbonate Sediment Across Northern Zealandia, Tasman Sea, Southwest Pacific, Paleoceanography and Paleoclimatology, 37, https://doi.org/10.1029/2021PA004294, 2022.

Takahashi, T., Sutherland, S. C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, R., Feely, R. A., Sabine, C., Olafsson, J., and Nojiri, Y.: Global sea–air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects, Deep Sea Research Part II: Topical Studies in Oceanography, 49, 1601–1622, https://doi.org/10.1016/S0967-0645(02)00003-6, 2002.

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., Hoppema, M., Olafsson, J., Arnarson, 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 pCO_2, and net sea–air CO_2 flux over the global oceans, Deep Sea Research Part II: Topical Studies in Oceanography, 56, 554–577, https://doi.org/10.1016/j.dsr2.2008.12.009, 2009.

Ternon, J. F., Oudot, C., Dessier, A., and Diverres, D.: A seasonal tropical sink for atmospheric CO_2 in the Atlantic ocean: the role of the Amazon River discharge, Marine Chemistry, 68, 183–201, https://doi.org/10.1016/S0304-4203(99)00077-8, 2000.

Tiedemann, R., Sarnthein, M., and Shackleton, N. J.: Astronomic timescale for the Pliocene Atlantic δ^{18}O and dust flux records of Ocean Drilling Program Site 659, Paleoceanography, 9, 619–638, https://doi.org/10.1029/94PA00208, 1994.

Toyofuku, T., Matsuo, M. Y., de Nooijer, L. J., Nagai, Y., Kawada, S., Fujita, K., Reichart, G.-J., Nomaki, H., Tsuchiya, M., Sakaguchi, H., and Kitazato, H.: Proton pumping accompanies calcification in foraminifera, Nature Communication, 8, 14145, https://doi.org/10.1038/ncomms14145, 2017.

Vahlenkamp, M., Niezgodzki, I., De Vleeschouwer, D., Bickert, T., Harper, D., Kirtland Turner, S., Lohmann, G., Sexton, P., Zachos, J., and Pälike, H.: Astronomically paced changes in deep-water circulation in the western North Atlantic during the middle Eocene, Earth and Planetary Science Letters, 484, 329–340, https://doi.org/10.1016/j.epsl.2017.12.016, 2018a.

Vahlenkamp, M., Niezgodzki, I., De Vleeschouwer, D., Lohmann, G., Bickert, T., and Pälike, H.: Ocean and climate response to North Atlantic seaway changes at the onset of long-term Eocene cooling, Earth and Planetary Science Letters, 498, 185–195, https://doi.org/10.1016/j.epsl.2018.06.031, 2018b.

Van Andel, T. H.: Mesozoic/cenozoic calcite compensation depth and the global distribution of calcareous sediments, Earth and Planetary Science Letters, 26, 187–194, https://doi.org/10.1016/0012-821X(75)90086-2, 1975.

Vervoort, P., Kirtland Turner, S., Rochholz, F., and Ridgwell, A.: Earth System Model Analysis of How Astronomical Forcing Is Imprinted Onto the Marine Geological Record: The Role of the Inorganic (Carbonate) Carbon Cycle and Feedbacks, Paleoceanography Paleoclimatology, 36, https://doi.org/10.1029/2020PA004090, 2021.

Voelker, A. H. L., Rodrigues, T., Billups, K., Oppo, D., McManus, J., Stein, R., Hefter, J., and Grimalt, J. O.: Variations in mid-latitude North Atlantic surface water properties during the mid-Brunhes (MIS 9–14) and their implications for the thermohaline circulation, Climate of the Past, 6, 531–552, https://doi.org/10.5194/cp-6-531-2010, 2010.

Westerhold, T., Marwan, N., Drury, A. J., Liebrand, D., Agnini, C., Anagnostou, E., Barnet, J. S. K., Bohaty, S. M., De Vleeschouwer, D., Florindo, F., Frederichs, T., Hodell, D. A., Holbourn, A. E., Kroon, D., Lauretano, V., Littler, K., Lourens, L. J., Lyle, M., Pälike, H., Röhl, U., Tian, J., Wilkens, R. H., Wilson, P. A., and Zachos, J. C.: An astronomically dated record of Earth's climate and its predictability over the last 66 million years, Science, 369, 1383–1387, https://doi.org/10.1126/science.aba6853, 2020.

Wilkens, R. H., Westerhold, T., Drury, A. J., Lyle, M., Gorgas, T., and Tian, J.: Revisiting the Ceara Rise, equatorial Atlantic Ocean: isotope stratigraphy of ODP Leg 154 from 0 to 5 Ma, Climate of the Past, 13, 779–793, https://doi.org/10.5194/cp-13-779-2017, 2017.

Willeit, M., Ganopolski, A., Calov, R., Robinson, A., and Maslin, M.: The role of CO_2 decline for the onset of Northern Hemisphere glaciation, Quaternary Science Reviews, 119, 22–34, https://doi.org/10.1016/j.quascirev.2015.04.015, 2015.

You, Y., Huber, M., Muller, R. D., Poulsen, C. J., and Ribbe, J.: Simulation of the Middle Miocene Climate Optimum, Geophysical Research Letters, 36, 5, https://doi.org/10.1029/2008GL036571, 2009.

Young, J. R., Geisen, M., and Probert, I.: A review of selected aspects of coccolithophore biology with implications for paleobiodiversity estimation, Micropaleontology, 51, 267–288, https://doi.org/10.2113/gsmicropal.51.4.267, 2005.

Zachos, J.: Trends, Rhythms, and Aberrations in Global Climate 65 Ma to Present, Science, 292, 686–693, https://doi.org/10.1126/science.1059412, 2001.

Zachos, J. C., Dickens, G. R., and Zeebe, R. E.: An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics, Nature, 451, 279–283, https://doi.org/10.1038/nature06588, 2008.

Zhang, Y. G., Pagani, M., Liu, Z., Bohaty, S. M., and DeConto, R.: A 40-million-year history of atmospheric CO_2, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 371, 20130096, https://doi.org/10.1098/rsta.2013.0096, 2013.

Zondervan, I.: The effects of light, macronutrients, trace metals and CO_2 on the production of calcium carbonate and organic carbon in coccolithophores—A review, Deep Sea Research Part II: Topical Studies in Oceanography, 54, 521–537, https://doi.org/10.1016/j.dsr2.2006.12.004, 2007.

Chapter II. Nature and origin of variations in pelagic carbonate production in the tropical ocean since the mid-Miocene (ODP Site 927)

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Abstract

Marine plankton is an important component of the global carbon cycle. Whereas the production and seafloor export of organic carbon produced by the plankton, the biological pump, has received much attention, the long-term variability in plankton calcification, controlling the carbonate counter pump, remains less well understood. However, it has been shown that changes in pelagic calcification (biological compensation) could affect the ocean's buffering capacity and thus regulate global carbon budget on geological timescales. Here we use Neogene pelagic sediments deposited on the Ceara Rise in the tropical Atlantic to characterize the variability in pelagic carbonate production with a focus on warm climates. A re-evaluation of published records of carbonate accumulation at the Ceara Rise reveals a systematic increase in sedimentation rates since the late Miocene, but the carbonate accumulation rate does not show a clear trend. Instead, we observe substantial orbital timescale variability in carbonate accumulation, combined with a trend towards less carbonate on average at sites located below 4 km, likely due to the effect of carbonate dissolution. To evaluate long-term changes against possible orbital-scale variability, we generated new high-resolution records of carbonate accumulation rate at Ocean Drilling Program (ODP) Site 927 across two Quaternary interglacials (MIS 5 and MIS 9), the Pliocene warm period (MIS KM5) and the Miocene Climatic Optimum (MCO). We observe that the highest carbonate accumulation rates occurred during the Pliocene but that each of the studied intervals was characterized by large-magnitude orbital variability. Prominent variations in carbonate accumulation prior to the Quaternary preservation cycles appear to follow Earth obliquity and eccentricity. These results imply that pelagic carbonate accumulation in the tropical ocean, buffered from large temperature changes, varied on orbital timescales. The magnitude of the orbital-scale variability was similar or even higher than the long-term mean differences among the studied intervals. Since preservation can be excluded as a driver of these changes prior to the Quaternary, the observed variations must reflect changes in the export flux of pelagic biogenic carbonate. We conclude that the overall carbonate production by pelagic calcifiers responded to local changes in light, temperature and nutrients delivered by upwelling, which followed long orbital cycles, as well as to long-term shifts in climate and/or ocean chemistry. The inferred changes on both timescales were sufficiently large such that when extrapolated on a global scale, they could have played a role in the regulation of the carbon cycle and global climate evolution during the transition from the Miocene warm climates into the Quaternary icehouse.

Chapter II. Nature and origin of variations in pelagic carbonate production in the tropical ocean since the Mid Miocene (ODP Site 927)

II.1 Introduction

The ocean plays a key role in the climate system as one of the major sinks for anthropogenic atmospheric CO_2 (Landschützer et al., 2014). Most of the excess atmospheric carbon (CO_2) is absorbed by the ocean as dissolved CO_2 which becomes part of the seawater carbonate system and can be sequestered by the metabolic activity of marine organisms. A large part of the carbon sequestration is due to carbon fixation into organic matter by photosynthesis (Henson et al., 2012; Passow and Carlson, 2012; Sarmiento et al., 2004). However, next to the sequestration of CO_2 by photosynthesis and export via the biological pump, marine organisms also participate in the global carbon cycle by carbonate biomineralization. Milliman (1993) estimated that today's marine carbonate production by organisms amounts to 5.3 GT yr^{-1} of which about a half is accounted for by pelagic calcifiers (2.4 GT yr^{-1}). Since aragonite and high-Mg calcite are unstable and largely dissolve before deposition, the geologically relevant aspect of the pelagic biogenic carbonate production is mediated mainly by low-Mg calcite, that may be variable but is mostly dominated by both planktic foraminifera and coccolithophores (Boudreau et al., 2018). The carbonate biomineralization, also termed the carbonate counter-pump, leads in the short term (ka) to the release of CO_2 from seawater because it consumes alkalinity, but on long, geological timescales (Ma), it sequesters carbon from the dissolved volatile ocean-atmosphere reservoir into the more inert sedimentary reservoir. Manipulative experiments, ocean chemistry profiles and numerical models all indicate that pelagic carbonate production is affected by a range of environmental parameters, such as temperature, nutrient availability or pCO_2 (Feely, 2004; Gehlen et al., 2007). Therefore, a change in any of these parameters could impact the pelagic carbonate production, resulting in a process that Boudreau et al. (2018) termed biological compensation. In contrast to chemical compensation, where changes in ocean carbonate chemistry are compensated by dissolution of seafloor carbonate deposits, biological compensation refers to changes in ocean carbonate chemistry due to globally relevant shifts in carbonate biomineralization. For example, a decrease in global oceanic biomineralization would lead to an increase of alkalinity, which would cause an increase CO_2 solubility and therefore lead to an increased capacity of the ocean to take up CO_2 (Boudreau et al., 2018; Sarmiento and Gruber, 2006). Using a modelling approach, Boudreau et al. (2018) showed that a global carbonate productivity change by only 10 % would be sufficient for the process of biological compensation to affect the marine carbon cycle on timescales from years to millions of years.

For the process of biological compensation to play an important role in the global carbon cycle, it must be demonstrated that sufficiently large changes in global carbonate biomineralization occurred in the geological past. However, measuring changes in global biogenic carbonate production is difficult, because productivity and biomineralization vary in space, and changes observed in individual records could be compensated by complementary shifts elsewhere in the ocean (Drury et al., 2020). In most parts of the ocean, climate change causes plankton assemblages to migrate, with biogeographic provinces expanding and contracting in pace with orbital cycles (Yasuhara et al., 2020). These processes should result mainly in the spatial reorganization of pelagic carbonate production and as long as the forcing is cyclic, the effects should cancel out over time.

Beyond orbital timescales, understanding of changes in carbonate production are complicated by the confounding effects of biological and chemical compensation on carbonate content of deep-sea sediments (Boudreau et al., 2018). Nevertheless, the few existing continuous records indicate the presence of long-term shifts in carbonate production by a factor of 2 or more manifested, for example, as the late Miocene carbonate maximum (Lyle et al., 2019; Drury et al., 2020; Liebrand et al., 2016). Although there is abundant evidence for local changes in pelagic calcification and carbonate production, their spatial extent remains unknown, making it difficult to judge whether the local shifts may have resulted in globally significant biogeochemical response (Lyle et al., 2019; Drury et al., 2020).

Here we have investigated pelagic carbonate accumulation, as a proxy for production, in an equatorial location, where the plankton could not respond to the climate cycles by migration and where long-term changes in temperature, a key parameter likely affecting biomineralization, were buffered compared to higher latitudes. Low-magnitude tropical sea surface temperature (SST) variability in the Atlantic in the Pliocene and in the Miocene was reported by Herbert et al. (2016) and Curry et al. (1995). Since orbitally driven environmental change still affected the tropics, the Cenozoic tropical plankton represents a natural experiment where the tropical calcifying community responded to a number of orbital cycles and long-term changes in ocean chemistry, reflecting changing atmospheric CO_2. Whilst these records cannot provide a direct answer to how much pelagic carbonate production changed globally, they can provide a first-order constraint on the amount of change in pelagic calcification that could occur due to changes in the constitution and/or abundance of the calcifiers on different timescales. We specifically decided to target intervals with warmer global climate states, providing potential analogues to gauge the amount of change in tropical pelagic carbonate production under a global warming scenario (Fig. 2), and the tropical Atlantic location allows us to complement records from the Pacific and South Atlantic (Lyle et al., 2019; Drury et al., 2020; Pälike et al., 2006a) to assess the spatial coherence of long term trends and the amount and nature of short-term variability.

Next to analysing long-term changes in carbonate accumulation, the existence of persistent orbital variability implies that new data will be required, characterizing the short-term response of the tropical pelagic carbonate production system. To this end, in the present study the changes in carbonate production through time have been studied in four intervals, occurring during four warm periods of the late Cenozoic: the marine isotopic stage (MIS) 5 (87.5 to 150.2 ka), the MIS 9 (276.4 to 370.3 ka), the MIS KM5 (3095.5 to 3307 ka) and the Miocene Climatic Optimum (MCO) (15589.3 to 15964.3 ka).

This approach allows us to evaluate long-term changes in pelagic carbonate production since the Mid-Miocene and at the same time to characterize the orbital-scale variability and determine if the orbital periodicity forcing carbonate production changed from the Miocene to present.

II.1.i Time intervals

The MIS 5, as the last warmest and longest interglacial of the past 500 ka (Howard, 1997), with an abrupt glacial-interglacial transition (Howard, 1997; Müller and Kukla, 2004; Sirocko et al., 2005) is considered to be a good analogue for the actual warm Holocene (Howard, 1997; Kukla, 1997) and even a partial analogue for + 1 - 2°C scenarios because of polar temperatures 3 to 5°C warmer than today and a sea level about 6.6 m higher than today (Clark and Huybers, 2009; Kopp et al., 2009). During this interglacial, Chalk et al. (2019) observed a change in the current circulation in the Atlantic Ocean, with an enhanced Antarctic Bottom Water (AABW) below 3400 m.b.s.l. and well-ventilated, high pH, and $[CO_3^{2-}]$ water mass around 2200 m.b.s.l. They also highlighted a correlation between the $[CO_3^{2-}]$ and the pCO_2 in the West Atlantic during cold intervals, with an increase of the volume of the high dissolved inorganic carbon (DIC), low $[CO_3^{2-}]$ deep-water masses in the North Atlantic.

The MIS 9 in the equatorial Atlantic presents well-preserved sediment at a period known to be under high obliquity with a unique insolation signal. Stable oxygen isotope values are low during this period (low ice volume). It is

one of the interglacials showing the highest pCO_2 (around 300 ppm) and pCH_4 (around 25 ppb) conditions in the late Pleistocene. This period is also one of the warmest, stablest and shortest interglacials, with a weak surface water ventilation (Past Interglacials Working Group of PAGES, 2016; Marino et al., 2014; Voelker et al., 2010).
The Pliocene warm period (PWP) MIS KM5 corresponds to a period with a similar orbital forcing to present day and an insolation distribution close to the modern one (Haywood et al., 2013). This interval (3.264 ka - 3.025 ka) is also described as a negative oxygen isotope slope and a sea level 21 - 23 m above the present-day one (Lunt et al., 2010, 2008b; Naish et al., 2009; Pollard and DeConto, 2009) with a well-ventilated deep Atlantic Ocean (Bell et al., 2015). The temperature is 3°C higher than pre-industrial values (Haywood et al., 2000; Lunt et al., 2010) and the CO_2 concentration is close to the present value, i.e. 330 - 425 ppmv during the warm interglacials (Pagani et al., 2010; Seki et al., 2010), making it a good analogue for future climate (Ravelo and Wara, 2004) and an important period to understand the climate system (Lunt et al., 2010). Furthermore, this period is also described as being wetter than today (Leroy and Dupont, 1994; Dodson and Macphail, 2004) but the latitudinal distribution of the rainforest was close to the present day distribution (Salzmann et al., 2011).

The MCO corresponds to a period with an eccentricity-modulated precession $\delta^{18}O$ signal and low global ice volume, featuring a Northern Hemisphere that is free of continental ice sheets, important 100 and 400 ka orbital variability, and an Antarctic ice sheet that is smaller but more dynamic than today (De Vleeschouwer et al., 2017; Holbourn et al., 2007). Haq et al. (1987) highlighted the large sea level amplitude from 16 to 14 Ma, and the annual global temperature was 3 to 8°C higher than today (Pound et al., 2012; You et al., 2009). The climate during the MCO is known to be correlated with atmospheric CO_2 concentration changes (Foster et al., 2012), with CO_2 concentration being generally lower than at present (Foster et al., 2012; Ruddiman, 2010; Zachos et al., 2008; Zachos, 2001b, a), but peaking at 16 Ma between 460 and 564 ppmv (Kürschner et al., 2008). Even if a decline in $\delta^{18}O$ and $\delta^{13}C$ at 16.9 Ma was suspected to be linked to increase of carbonate dissolution, a sign of strong changes in the carbon cycle (Holbourn et al., 2015), carbonate production appears to have been the main control of the $CaCO_3$ record (Liebrand et al., 2016).

II.2 Material and Methods

II.2.i Site location

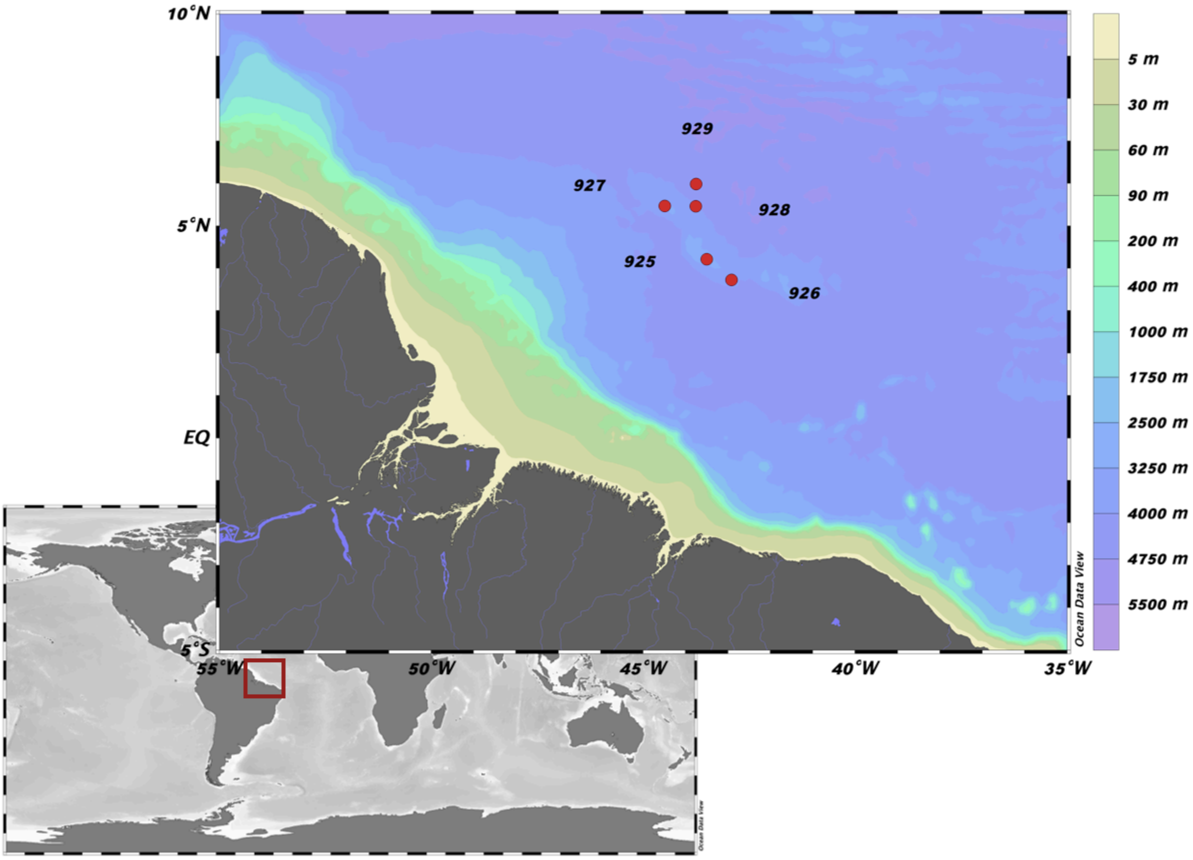

Figure 1. Location of the material of this study at the Ceará Rise, ODP Leg 154 (ocean Data View, Schlitzer, 2018).

Ceara Rise, located in the equatorial Atlantic Ocean, represents an ideal location to quantify the variability in tropical Atlantic pelagic carbonate production since the Miocene. This aseismic ridge rises several kilometres above the surrounding abyssal plain, well above the modern regional lysocline, located between 4100 and 4200 mbsl (Frenz et al., 2006; Gröger et al., 2003a, b; Curry et al., 1995; Cullen and Curry, 1997; Bickert et al., 1997). The ridge is bathed by the shallower North Atlantic deep water (NADW) and the deeper Antarctic bottom water (AABW) (Rühlemann et al., 2001; Gröger et al., 2003b; Herrford et al., 2017), and the interface of the two water masses corresponds to the regional lysocline depth. Around the ridge, the average depth of the seafloor is at 4500 mbsl but the Ceara Rise ridge rises by as much as 1900 m above the surrounding abyssal plain, with its top reaching the depth of 2600 mbsl (Curry et al., 1995). This provides an opportunity to sample pelagic sediments that are largely unaffected by dissolution and their accumulation therefore mainly reflects changes in pelagic carbonate production as suggested by Brummer and van Eijden, (1992). The Ceara Rise (Fig.1) has been visited by Ocean Drilling Program (ODP) Leg 154 (Curry et al., 1995), recovering a transect of sediment sequences ranging into the Eocene that are rich in carbonate and show prominent cycles due to variable input of clastic material from the Amazon fan (Shackleton et al., 1999; Bickert et al., 1997; Shackleton and Crowhurst, 1997). The cycles are reflected in sediment physical properties, such as colour or magnetic susceptibility, and because of the very good recovery and repeated coring at the same sites, continuous spliced records could be produced that facilitated the development of orbitally tuned age models (Shackleton et al., 1999; Zeeden et al., 2013; Wilkens et al., 2017; Shackleton and Crowhurst, 1997), a prerequisite for the quantification of carbonate accumulation. Since all high-resolution Neogene records of carbonate accumulation (Drury et al., 2020; Lyle et al., 2019), including those from the Ceara Rise (Curry et al., 1995; King et al., 1997) show a large orbital-scale variability, hinting at prominent orbital-scale variability in pelagic carbonate production, next to a compilation and re-evaluation of existing carbonate records, the selected time slices had to be newly sampled and analysed at higher resolution.

II.2.ii Compilation of existing carbonate data from ODP Leg 154

The combination of the availability of high-resolution age models and good carbonate preservation make the Ceara Rise a model region to study pelagic carbonate production and preservation. We compiled existing data on carbonate content ($CaCO_3$ %) at all the Leg 154 sites since the Miocene (Curry et al., 1995; Frenz et al., 2006; King et al., 1997) and used those to calculate carbonate accumulation rates ($CaCO_3$ AR). The few other existing datasets on carbonate content from the Ceara Rise sites (e.g., Tiedemann and Franz, 1997) could not be used because some of the information needed to calculate accumulation rates or the original samples ID and depths was not available.

The carbonate content data were combined with dry bulk density (DBD) and sedimentation rate (SR) to calculate the $CaCO_3$ AR as Eq. (1).

(1) $CaCO_3$ AR = ($CaCO_3$ % / 100) x DBD x SR

Following the approach by Lyle (2003), we first derived for each site a calibration between the gamma-ray attenuation (GRA) bulk density and DBD using data from Curry et al. (1995). The resulting site-specific calibrations (Fig. S1) were then applied on GRA bulk density values, which were extracted from Curry et al. (1995), and interpolated to the position of the analysed samples using linear interpolation. This yielded DBD values between 0.40 g cm^{-3} and 1.64 g cm^{-3}. For two samples, the calibration returned negative DBD (at 129.62 mcd and 135.47 mcd) due to two anomalous GRA values below 1. In these cases, we used the DBD of the nearest point instead.

II.2.iii Context and sampling plan

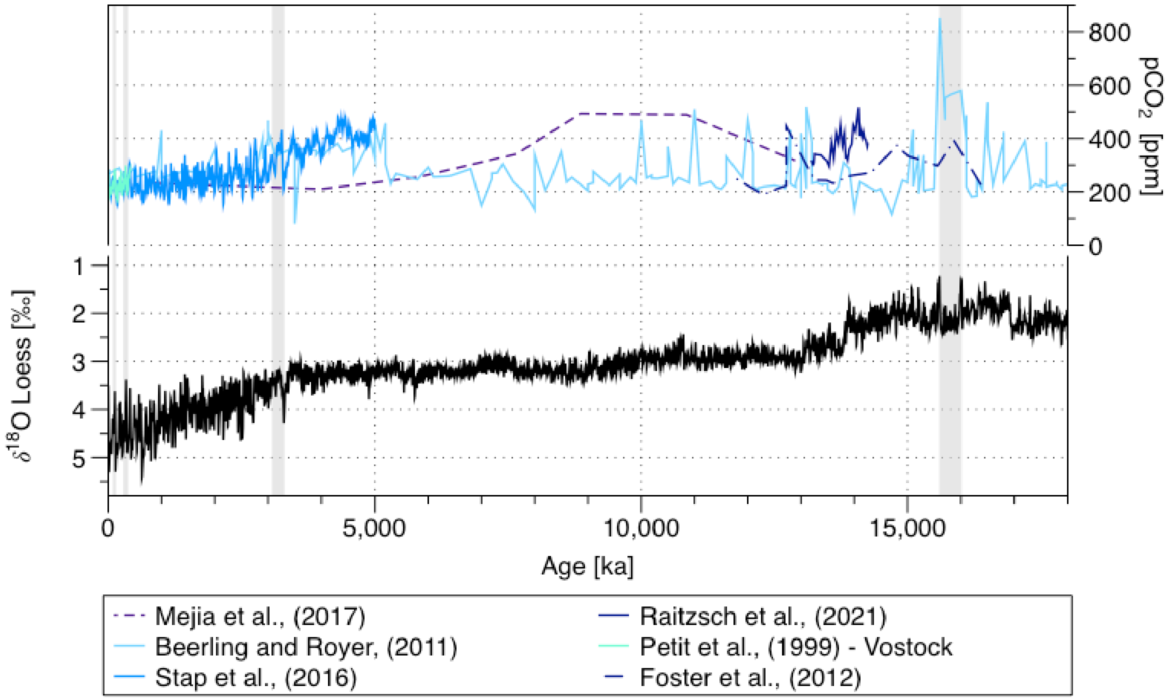

Figure 2. Oxygen stable isotopes ($\delta^{18}O$) shown as a smoothed record (Loess) (Westerhold et al., 2020) and pCO_2 (Mejía et al., 2017; Beerling and Royer, 2011; Stap et al., 2016; Raitzsch et al., 2021; Foster et al., 2012; Petit et al., 1999) over the last 18000 ka and sampled intervals (shadows).

We sampled the record at Site 927 at high resolution for the four periods of interest (Fig. 2), making sure that for each interval both the interglacial and the flanking glacial in the Quaternary and at least two full eccentricity cycles during the Pliocene and Miocene have been covered. These four intervals are covering a large range of global temperature and CO_2 values (Fig. 2). We selected Site 927 because it is one of the two shallow sites of Leg 154, located well above the lysocline at present (Frenz et al., 2005; Curry et al., 1995; Bickert et al., 1997), and because numerous palaeoceanographic datasets and carbonate measurements exist for this site (e.g. (Pälike et al., 2006a; Bickert et al., 1997; Frenz et al., 2006; Gröger et al., 2003b; King et al., 1997; Curry and Cullen, 1997). The site appears generally less affected by slumps or turbidites than the four others, which were not observed in the four studied intervals (sampled out of the slumps and turbidites reported lithostratigraphic units) (Curry et al., 1995). The sampling was guided by the Wilkens et al. (2017) age model for the samples from 0 to 14 Ma, and by the Shackleton et al. (1999) age model for the samples from 14 to 16.5 Ma. Considering the typical mixing depth of 5 - 10 cm in deep sea sediments, we sampled at 5 cm in the Quaternary and 10 cm in the Neogene, which in both cases provides sub-orbital resolution. The resolution was higher in the Quaternary, because the peak interglacial warmth periods are short (<10 ka for MIS 5e; Stolz and Baumann, 2010; Müller and Kukla, 2004; Sirocko et al., 2005) and we wanted to cover these by multiple samples. In total, we collected and analysed 139 samples for the two Quaternary intervals, 72 samples for the Pliocene and 50 samples for the Miocene.

II.2.iv Stable isotopes analyses

We performed stable isotopes analyses ($\delta^{18}O$ and $\delta^{13}C$) at Bremen university, using a ThermoFisher Scientific MAT 253plus gas isotope ratio mass spectrometer with Kiel IV automated carbonate preparation device. This gives $\delta^{18}O$ values with a standard deviation of house standard (Solnhofen limestone) over measurement period of 0.07 ‰ and $\delta^{13}C$ values with standard deviation of house standard (Solnhofen limestone) over measurement period of 0.03 ‰. The sediment samples were washed and sieved at 63 µm using tap water and dried overnight in the oven at 50°C. Then, they have been dry-sieved at 150 µm for benthic foraminifera picking. All the Miocene samples have been picked, only 3 samples did not have enough material to run the stable isotopes analyses. For some of the samples we had enough material to analyse two or three replicates using different species known to be relevant markers for $\delta^{18}O$ seawater: *Cibicidoides mundulus*, *Cibicidoides wuellerstorfi* and *Oridorsalis umbonatus* (Katz et al., 2003; Rathmann and Kuhnert, 2008). We did not mix the species in one single measurement. For the species-specific $\delta^{18}O$ and $\delta^{13}C$ values correction, we used the calibration given in the supplement table S3 from Westerhold et al. (2020).

II.2.v Age model

Section 1. For the existing data compilation

Because the orbitally tuned age models as well as the splices for the individual sites have been recently revised (Wilkens et al., 2017), we re-evaluated the composite depth of all samples and assigned new ages to them based on Wilkens et al. (2017) and used the new ages to derive sedimentation rates (SR).

Section 2. For the four high-resolution intervals of core 927

The existing most recent age model for Site 927 is based on a directly tuned age model from Site 926 that has been point-to-point correlated with the composite record from Site 927 using core images, magnetic susceptibility, greyscale values and stable isotopes (Wilkens et al., 2017; Zeeden et al., 2013). For the determination of $CaCO_3$ AR during the four target intervals, this age model requires adjustments because it provides too low resolution and is not tuned below core 927A-30H, section 6, 70 cm (303.60 rmcd), corresponding to 926A-28H, section 3, 18 cm (277.82 rmcd). Thus, to estimate $CaCO_3$ AR for the three studied intervals, we developed modified age models, where SRs have been constrained directly by astronomical tuning of sediment properties in the studied cores.

II.2.vi Carbonate analyses

To determine the $CaCO_3$ AR for the newly sampled intervals, we performed carbonate content analyses on the bulk sediment using a LECO CS744 elemental analyser at Bremen University. The analysis was performed by heating 0.1 g of homogenized material in a ceramic dish and measuring the resulting CO_2 in IR cells. The carbonate content has been calculated as the difference between the total carbon content and the organic carbon content, measured in a second sample that was pre-treated with hydrochloric acid to remove carbonates. Both measurements have an accuracy of 0.001 mg (1 ppm) or 0.5 % relative standard deviation (RSD). The inorganic carbon was then converted to carbonate content using the molecular mass of calcium carbonate. Dry bulk density for all the newly analysed samples at Site 927 was determined from GRA bulk density as described above (Sect. 2.2.) and combined with the carbonate content and SR from the modified age models to calculate the $CaCO_3$ AR.

II.3 results

II.3.i Long-term trends in carbonate accumulation rates

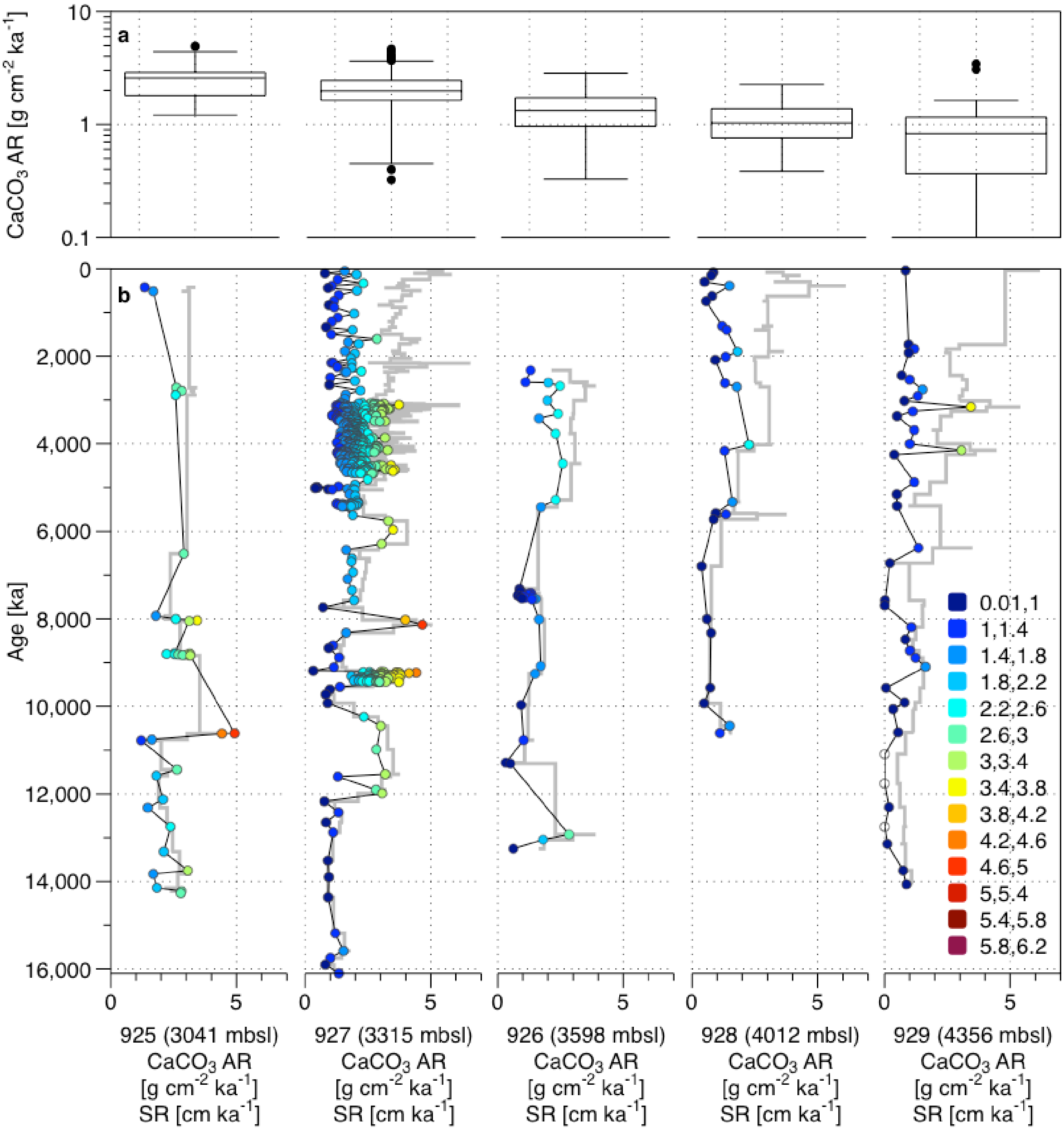

Figure 3. a) Box plots of the $CaCO_3$ AR for the five cores and b) $CaCO_3$ AR and SR (grey line) through the time for the Sites 925, 926, 927, 928 and 929 (black line and dots) for the five cores of the Leg 154. The $CaCO_3$ AR are calculated from existing carbonate content data for all Leg 154 sites (Curry et al., 1995; Frenz et al., 2006; King et al., 1997). The colour shade corresponds to the values of $CaCO_3$ AR.

Using existing carbonate content data for all Leg 154 sites (Curry et al., 1995; Frenz et al., 2006; King et al., 1997), combined with new age models (Wilkens et al., 2017), for each site, records of $CaCO_3$ AR since the mid-Miocene were calculated (Fig. 3). Curry et al. (1995) noted the occasional presence of slumps or hiatuses in the sediment sequences, especially at Site 928 and Site 929. Here we used the age models for the entire sediment package, ignoring the presence of these events. This is because the slumps only represent a small fraction of the sediment sequence and therefore are unlikely to affect the overall trends.

The mean $CaCO_3$ AR varies considerably among the sites, reflecting their depth and therefore likely the amount of dissolution. ODP Sites 925 and 927 (present depth 3041 mbsl and 3315 mbsl) show consistently higher $CaCO_3$ AR (between 1.5 and 3 g cm^{-2} ka^{-1}) than the three remaining sites, located below 3400 mbsl (around 1 g cm^{-2} ka^{-1}). Curry and Cullen (1997) show an effect of distance from the Amazon Fan on sediment composition on Ceara Rise for the late Quaternary, but this change is only manifested by differences in the AR of terrigenous (non-carbonate) sediments. This is seen in patterns of carbonate content of the sediment (their Figure 2) but not in changes in carbonate accumulation. Also, there is little evidence that the Amazon discharge plume reaches far enough offshore to induce changes in productivity over the plateau. At present, the discharge is strongly deflected northwards and stimulates productivity mainly along a narrow coastal strip (Gouveia et al., 2019). The same authors note that some of the Amazon discharge may be deflected into the North Brazil Current, but this affects productivity only little and mainly north off the Ceara Rise. To visualize long-term trends, we subtracted at each site the mean values of $CaCO_3$ AR and SR (Fig. 4). All sites show a prominent trend of increasing SR, beginning in the late Miocene (8 Ma ago) (Fig. 4), which is known to reflect increasing amount of clastic material transported from the Amazon Fan (Curry et al., 1995; Pälike et al., 2006b; Bickert et al., 1997; Harris et al., 1997; Shackleton and Crowhurst, 1997). The $CaCO_3$ AR, on the contrary, shows a less obvious temporal trend on a long timescale (Fig. 4), indicating that the increase in SR is compensated by decreased carbonate content in the sediment. Instead, the $CaCO_3$ AR record at all Ceara Rise sites show a pervasive short-term (likely orbital) variability, with substantial magnitude (Curry et al., 1995).

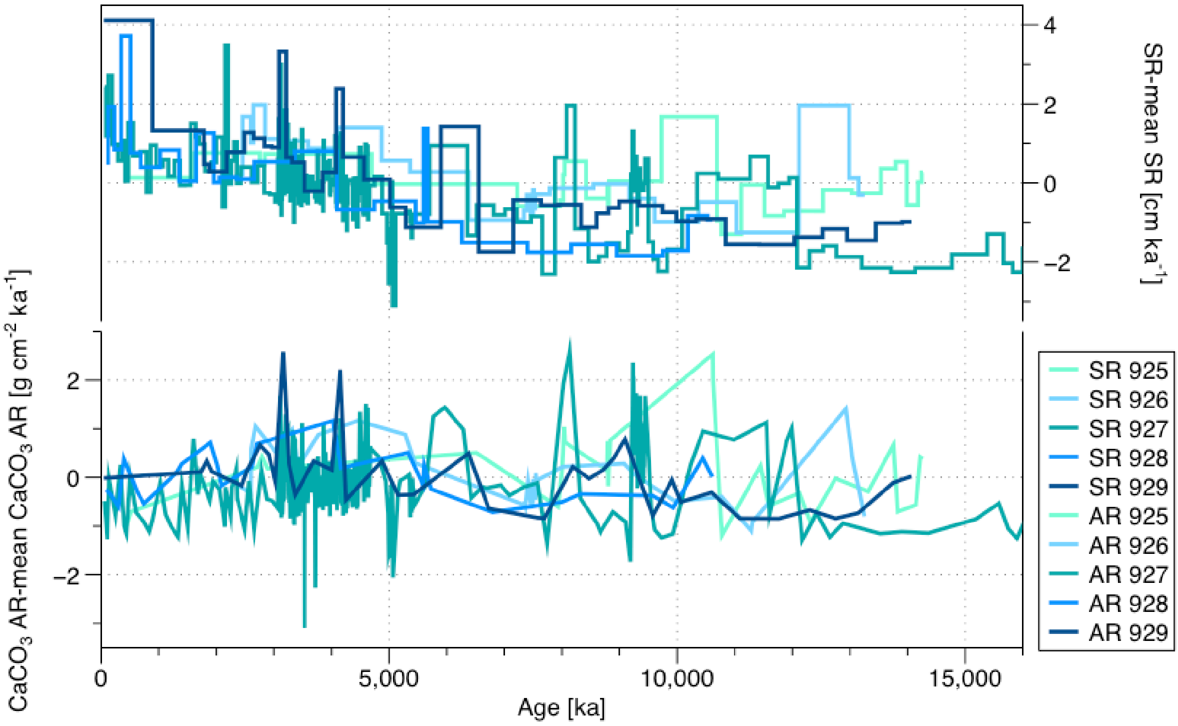

Figure 4. a) SR from which the average SR has been subtracted and b) $CaCO_3$ AR from which the average $CaCO_3$ AR has been subtracted, both for the five sites of Leg 154 over the last 16 Ma.

II.3.ii Age models for target intervals at ODP Site 927

Section 1. Pleistocene

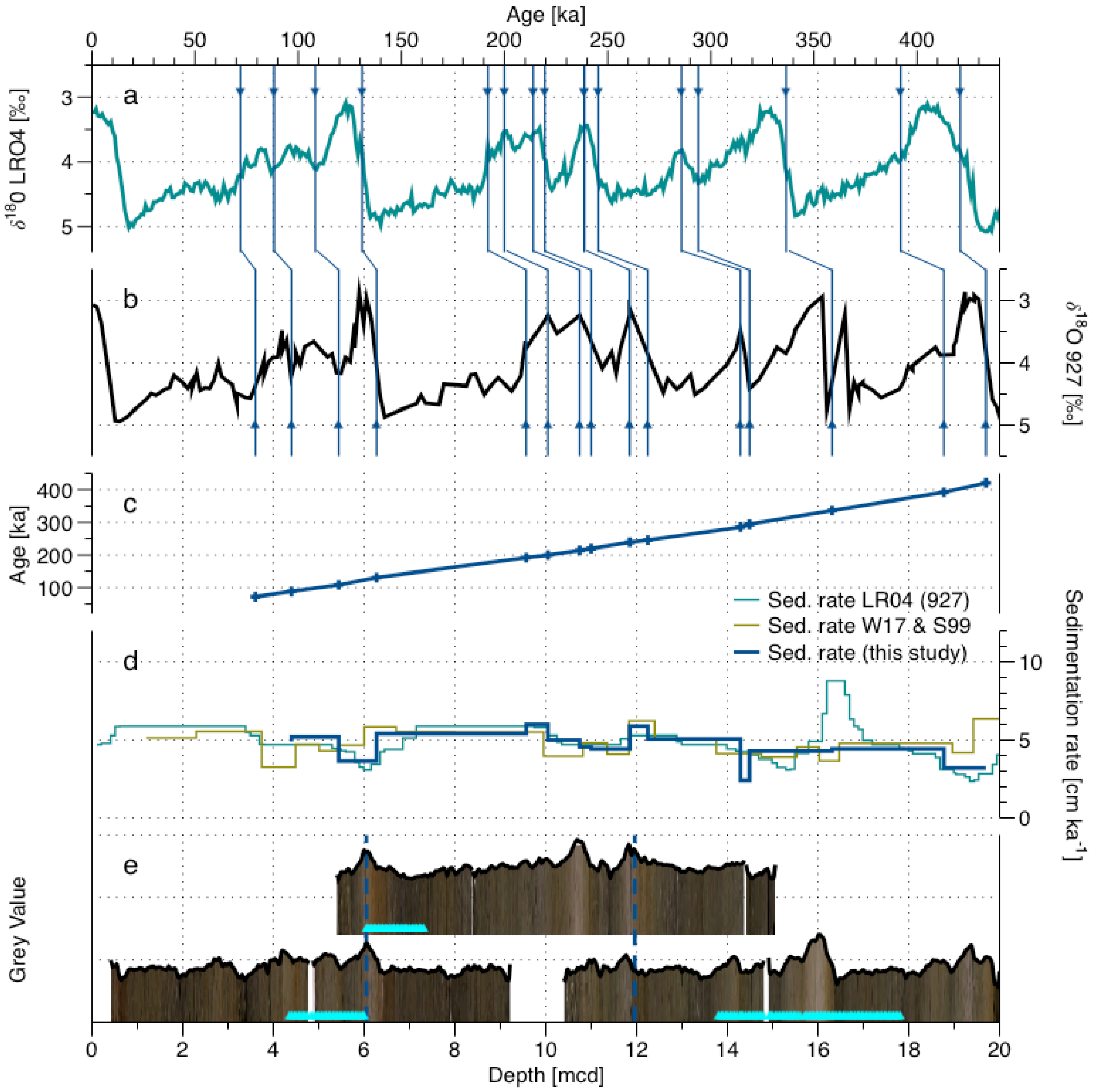

Figure 5. Depth - age correlation for the Late Pleistocene, cores 927A 1H, 927B 2H and 927A 2H – following the splice –, with a) the Lisiecki and Raymo, (2005) δ ^{18}O stack; b) the local δ ^{18}O record (Wilkens et al., 2017, modified from Bickert et al., 2004); c) the age - depth record with control points; d) the SR from Wilkens et al. (2017) (green), the SR using the LRO4 depths and ages for site 927 (blue-green) and the SR defined in this study (blue); e) the core images (Wilkens et al., 2017) and grey value record for the three cores of the spliced used, the position of the switch from one core to the other in the splice (dashed lines) and the position of the samples used in the present study in the cores (light blue triangles).

The Pleistocene interval in the studied core has a high-resolution age model based on benthic oxygen isotope data (Bickert et al., 2004) that were incorporated in the benthic stack of Lisiecki and Raymo (2005) who had added a constant 4-5 ka lag to take into account the delay in the δ ^{18}O data (ice volume inertia) with respect to the insolation forcing (Lisiecki and Raymo, 2005). However, Wilkens et al. (2017) revised the splice for this site (the way individual core segments are aligned), which means the age model in Lisiecki and Raymo (2005) has to be validated. To this end, we first checked the new alignment of the individual cores by generating high-resolution sediment colour (grey value) curves from the core images presented by Wilkens et al. (2017) (Fig. 5e). The grey value curve was extracted using the ImageJ software and calculated from RGB images using the NTSC formula (Rasband, 1997) with values averaged across the entire core width perpendicular to the core axis and the resulting noisy curve was smoothed as first component of the singular spectrum analysis (SSA) obtained with Analyseries software (Paillard et al., 1996). This curve was used to compare the overlapping parts of the cores spanning the last 400 ka, validating the alignment by Wilkens et al. (2017), which we thus adopt without modification. For the age model, we carried out a manual tuning of the 927 δ^{18}O data (Bickert et al., 2004) using the new composite depth by Wilkens et al. (2017) to the LR04 stack (Lisiecki and Raymo, 2005). Because the benthic stable oxygen record reflects mainly global sea level change (Bickert et al., 2004), the tuning was based on the identification of all unambiguously recognizable δ^{18}O maxima and times of fastest sea-level change (Fig. 5a). By the fastest sea level change (coinciding with the fastest ice volume change), we mean the inflection points of the d18O curve (327.55 mcd to 15605 ka and 331.5 mcd to 15930 ka). The resulting SRs are indeed more similar to those inferred from the age model by Wilkens et al. (2017) than those implied by the age model for the site as implemented in the LR04 stack (Lisiecki and Raymo, 2005).

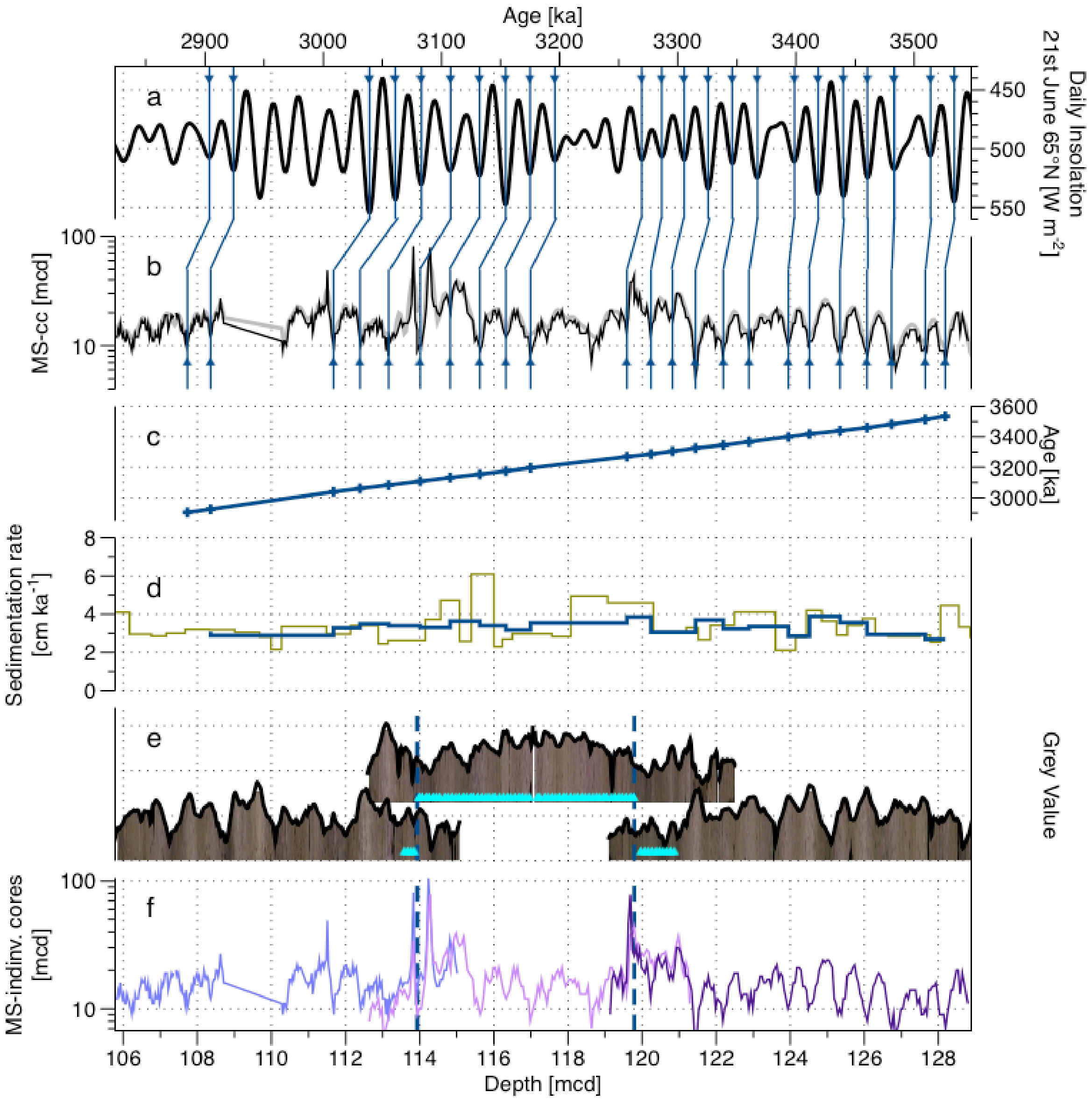

Figure 6. Depth - age correlation for the Pliocene interval across cores 154 927C 11H, 154 927A 12H and 154 927B 13H. a) the daily Insolation 21st of June at 65°N record (Laskar et al., 2004); b) the MS record (black) and MS smoothed record (grey) according to the splice presented in this study; c) the age - depth record with control points; d) the SR from Wilkens et al. (2017) age model (green) and from this study (blue); e) the core images for the cores of the splice from the ones the samples are from (Wilkens et al., 2017) and the grey value record extracted from it, plus step from one core to the other in the splice (dashed lines) and position of the samples used in this study in the cores (light blue triangles); f) MS record for the individual cores (Curry et al., 1995; Wilkens et al., 2017) and steps from one core to the other in the splice (dashed lines).

For the Pliocene interval, the first step has been to validate the core alignment. First, we generated a grey value curve (Sect. 3.2.1) but noted that this signal is weaker and shows many idiosyncratic features among the overlapping parts of the cores from the individual holes. Therefore, we decided to carry out the tuning on the magnetic susceptibility (MS) signal as done by Shackleton et al. (1999), which was also measured in all cores

(Curry et al., 1995). MS shows a distinct signal in this part of the sediment sequence, which can be used for tuning (like it has been used at Site 926), but for this it must be in alignment across the individual core segments. The alignment revealed that the existing splice by Wilkens et al. (2017) has to be adjusted for the purpose of tuning in this interval (Fig. S2.) by a shift of the core 927 C 11 H by 2 cm shallower, a shift of the core A 12 H by 15 cm deeper and a shift of the core B 13 H 9 cm deeper in the splice compared to the spliced MS record of Wilkens et al. (2017). Otherwise, the construction of the spliced record remained the same, retaining the same depths where the signal from one core switches to a signal from the adjacent core. These depths are indicated by dashed lines across the overlapping sections of the cores (Fig. 6d). The spliced MS signal (Fig. 6b) has then been tuned to the daily insolation on 21st of June at 65°N. This is because this representation of orbital forcing of global climate shows the best pattern of influence from both obliquity and precession (Laskar et al., 2004) (Fig. 6a) and has been used for tuning at the studied location in previous studies (e.g. Zeeden et al., 2013), who also provide arguments for why the MS and insolation are co-varying without lag. The tuning of the MS signal to an orbital target is possible because the existing age model of Wilkens et al. (2017) is sufficiently precise to provide a specific tuning target age interval, as confirmed by similar modulation of the insolation target and of the spliced MS record. The tuning has been done by correlating recognizable 23 MS minima to insolation maxima for this interval, using the Analyseries software (Paillard et al., 1996), assuming the signals are in antiphase without lag (Wilkens et al., 2017; Zeeden et al., 2013, 2015). As MS minima are easier to identify than the MS maxima, we prefer here to work with MS minima and insolation maxima instead of MS maxima and insolation minima as in Zeeden et al. (2013).

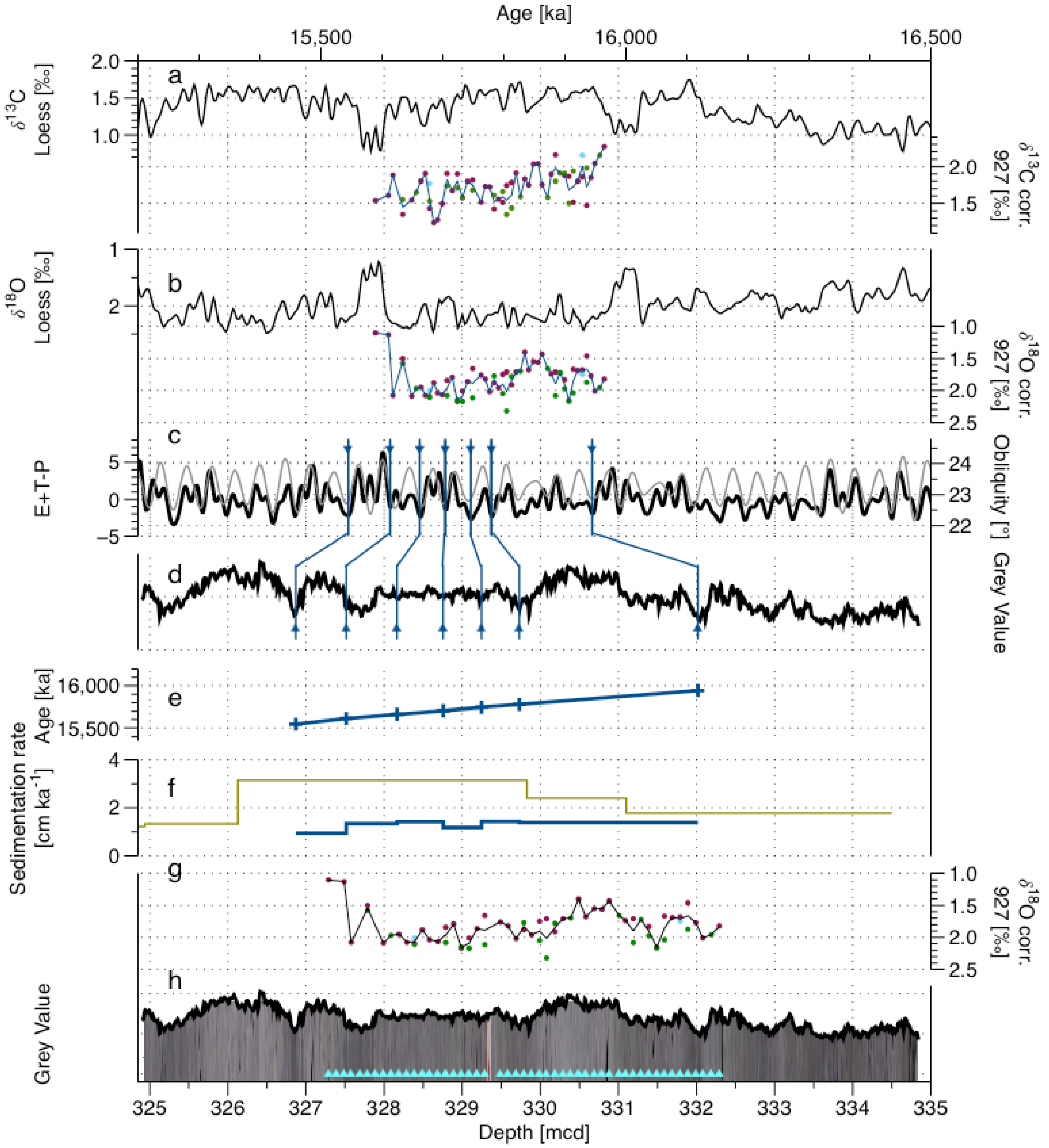

Figure 7. Depth - age correlation for the Mid-Miocene, core 154 927 A33H. a) δ^{13}C loess smooth composite record (from sites U1337 and U1338, Westerhold et al., 2020) and δ^{13}C corrected measured in Miocene samples from this study (*O.umbonatus* in pink, *C. mundulus* in green and *C. wuellerstorfi* in blue, the line corresponds to the average value); b) δ^{18}O loess smoothed composite record (from sites U1337 and U1338, Westerhold et al. (2020) and δ^{18}O corrected measured in Miocene samples from this study (*O.umbonatus* in pink, *C. mundulus* in green and *C. wuellerstorfi* in blue, the line corresponds to the average value); c) Obliquity (grey) and E+T-P (black) records (Laskar et al., 2004); d) SSA of the grey value record extracted from the core image -corrected from the light bias- e) age - depth and control points; f) SR from Shackleton et al. (1999) age model (green), from nannofossils events (Curry et al., 1995; Pälike et al., 2010; Wilkens et al., 2017) (dark blue) and from this study (blue); g) δ^{18}O corrected measured on Miocene samples from this study against depth (*O.umbonatus* in pink, *C.*

mundulus in green and *C. wuellerstorfi* in blue, the line corresponds to the average value); h) core image (Wilkens et al., 2017), smoothed grey value record and position of the samples for this study in the core (light blue triangles).

The existing age model for the Miocene interval by Shackleton et al. (1999) is based on a combination of orbital tuning and biostratigraphy. It presents a distinct shift in the SR around 330 mcd (Fig. 7c), dominating the $CaCO_3$ AR record for the studied period. There does not seem to be any distinct shift in the physical properties at that depth (Curry et al., 1995), and we therefore felt compelled to test the possibility that the singular change in SR does not correctly represent the changes in the sedimentation at this site. Since the studied interval is within one core segment, we tested whether a "nested" tuned age model can be developed, allowing a more precise estimation of the variability in the SR. As in this part of the sediment sequence the MS was not the dominant signal, we have made the choice to work with both the sediment colour and the stable isotopes to have two independent markers for this age model (analyses run for the purpose of this study; see Sect. 3.2.1. and 2.4.).

To have an independent estimation of the SR, we also evaluated the biostratigraphy from the shipboard data (Curry et al., 1995) with revised mcd (Wilkens et al., 2017) and revised biomarker ages GTS 2020 (Raffi et al., 2020). Three biostratigraphic markers have been evaluated: last appearance datum (LAD) of *Sphenolithus heteromorphus*, LAD *Helicosphaera ampliaperta* and LAD abundant *Discoaster deflandrei*. The combination of these markers gives us two SR options. Using LAD *H. ampliaperta* (the less reliable marker according to Raffi et al., 2020), in combination with LAD *D. deflandrei*, gives an SR of 1.65 cm ka^{-1}. Alternatively, considering LAD *S. heteromorphus*, which is recorded in the core further from the studied interval but is considered more reliable according to Raffi et al. (2020), in combination with LAD *D. deflandrei*, gives an SR of 1.11 cm ka^{-1}.

A sediment colour proxy was generated for the studied core (Sect. 3.2.1) (Fig. 7d). Due to the light appearance of the sediment composing this core and the way the pictures have been taken onboard (on the different 1.5 metres sections with a centred camera and centred white source of light), there is a strong 1.5 metres induced light cyclicity in the original light images (Curry et al., 1995; Wilkens et al., 2017). To reduce this bias, the core images were adjusted for the edge effect using the lighting correction function inside the Code for Ocean Drilling Data (CODD, Wilkens et al., 2017) (Fig. 7d). For the identification of the cyclicity in the core, we carried out spectral analyses on the corrected grey value curve using the multitaper method (MTM) (carried out using astrochron package on R, Meyers, 2014 ; R 4.1.2., R Core Team, 2021) (Fig. S6). This revealed three broad but distinct peaks for the frequencies 0.48 (period: 2.08 m), 0.7 (period: 1.43 m) and 1.4 (period: 0.71 m). Applying the two alternatives, biostratigraphy-derived SR reveals that the most distinct 71 cm cycles could represent obliquity when the SR of 1.65 cm ka^{-1} is applied. Finally, we used the $\delta^{18}O$ record to define the exact temporal window of the sampled interval and confirm the assumed cyclicity by matching the isotopic signal to the Westerhold et al. (2020) stable isotopes loess smoothed record $\delta^{18}O$ curve as a target. The new isotopic curve reveals a prominent minimum, which corresponds to the 15.6 Ma event, but the older 16.0 Ma isotopic minimum (also seen in carbon isotopic record of the target) is not recorded, indicating that the sampled interval spans less than 400 ka and confirming that the average SR must be >1.2 cm ka^{-1}. Overall, the new oxygen and carbon stable isotope signals show similar trends and absolute values as the global stack and representative individual records (Fig. S3), but the resolution of the new record is slightly lower. It does seem to record stable oxygen isotopic maxima at 15720 and 15900 ka that are also seen in the other records, but the absolute values appear lighter by about 0.5 ‰, and the shape of the corrected average record between these maxima appears to display a stronger eccentricity component.

The new stable carbon isotope record also shows similar absolute values and an overall decreasing trend as seen in the global stack (Fig. S3), but our corrected average signal is hard to compare to the stack in detail, and the representative records both show substantial divergence at orbital timescales. The new record does not show the stable carbon isotopic minimum at 15980 ka nor the increasing trend afterwards, indicating that it must have started later. The divergence at the beginning of our record by almost 1 ‰ from the stack has to be seen in the context of a similar departure seen in the record from Site U1338. Because the new isotopic curve does not allow sufficiently robust tuning within the target interval, after the alignment with the younger isotopic maximum we used the E+T-P signal as a target curve (taking in account the eccentricity, the obliquity and the precession) (Fig. 7a) (Laskar et al., 2004) to tune prominent light minima with E+T-P minima (and obliquity minima) (Shackleton et al., 1999; Zeeden et al., 2013) (Fig. 7a and b). This tuning has then been verified by plotting the stable isotope (both $\delta^{18}O$ and $\delta^{13}C$) record using the new given ages and comparing it to the existing stable isotopes loess smooth records from Westerhold et al. (2020) (Fig. S3.).

II.3.iii High-resolution records of carbonate content and carbonate accumulation rates at ODP Site 927

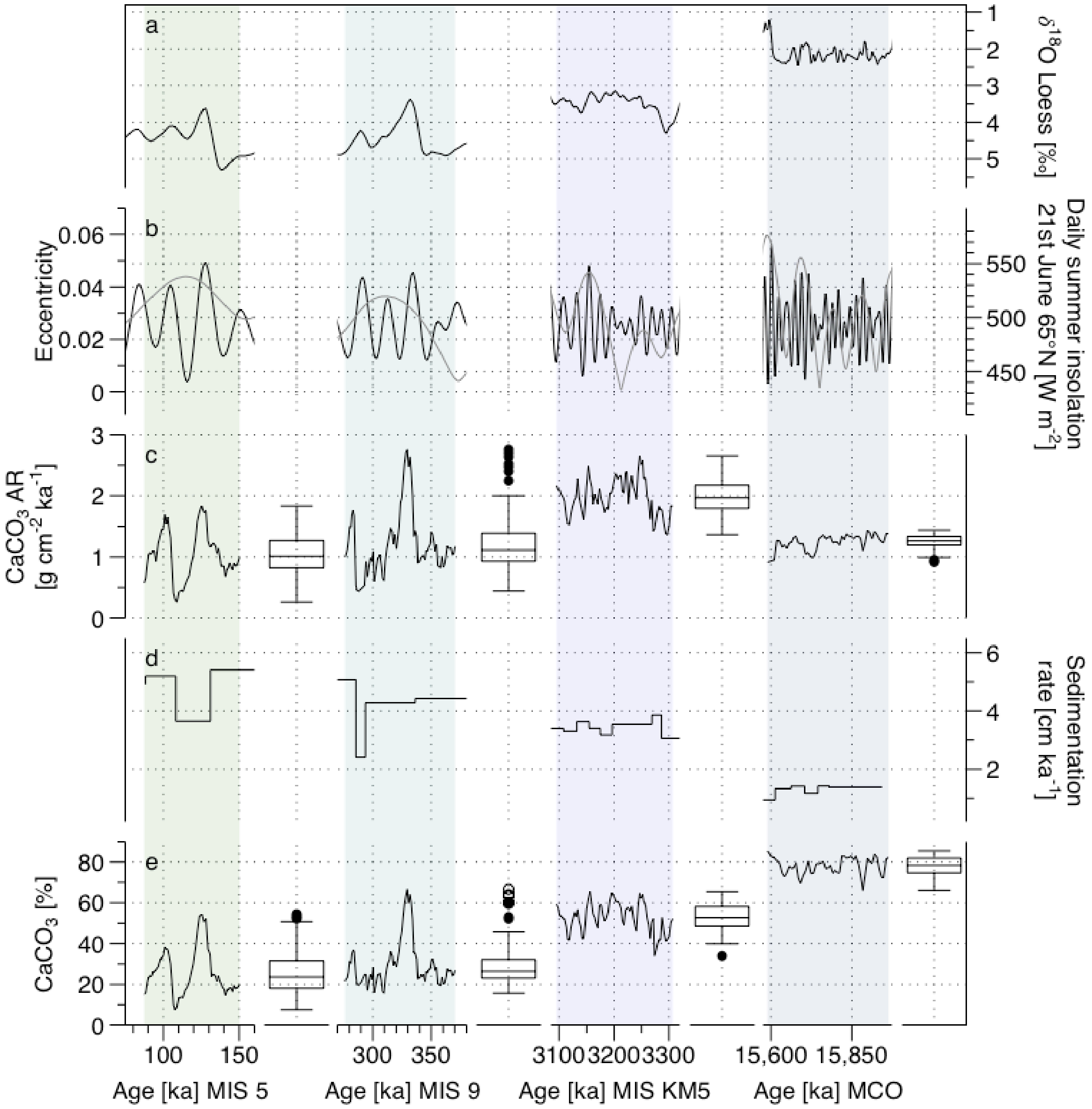

Figure 8. a) Quaternary and Pliocene benthic stable oxygen records from Site 927 and a global stack for the Miocene (Bickert et al., 2004; Westerhold et al., 2020); b) orbital parameters: eccentricity and daily summer insolation 21st of June at 65°N (Laskar et al., 2004); c) $CaCO_3$ AR and boxplot for each interval; d) SR and e) $CaCO_3$ % in the dried bulk sediment and boxplot for each interval.

The new carbonate content analyses are based on 261 measurements, yielding values comparable to existing low-resolution measurements, confirming decreasing carbonate content throughout the Neogene due to dilution by clastic sediments from Amazon fan (Curry et al., 1995; Bickert et al., 1997; Harris et al., 1997) and indicating particularly strong variations in the Quaternary (Fig. 8). In combination with the new high-resolution SR data (Fig. 8), these measurements provide records of sub-orbital variability in $CaCO_3$ AR across the four intervals, showing orbital-scale variability exceeding the differences in mean $CaCO_3$ AR among the intervals (Fig. 8).

The comparison between the highly resolved record for the four intervals of interest (Fig. 8c, 8d, and 8e) and the environmental parameters (Fig. 8a and 8b) highlights the good correlation - in terms of phase and amplitude - between the $CaCO_3$ AR (reflecting the pelagic carbonate production) and the insolation at 65°N signal for the two warm interglacials observed. For the MIS 5 and the MIS 9 warm interglacials, there is a strong correlation between the $CaCO_3$ % and $CaCO_3$ AR (r^2 of 0.86 and 0.93) (Fig. 8 and Fig. 9). At the same time, the SR is reaching high values (3 to 5 cm ka^{-1}), independently of $CaCO_3$ AR changes, indicating the role of another component than the pelagic carbonate production influencing the SR. In contrast, during the MIS KM5, the $CaCO_3$ AR is driven by both the carbonate content and the SR, and in the Miocene, the $CaCO_3$ AR appears to be dominantly driven by SR only (Fig. 9). Furthermore, the slope of the relationship between carbonate content and $CaCO_3$ AR appears to decrease with increasing age, indicating that the earlier in the record, the less the carbonate content is influencing the $CaCO_3$ AR.

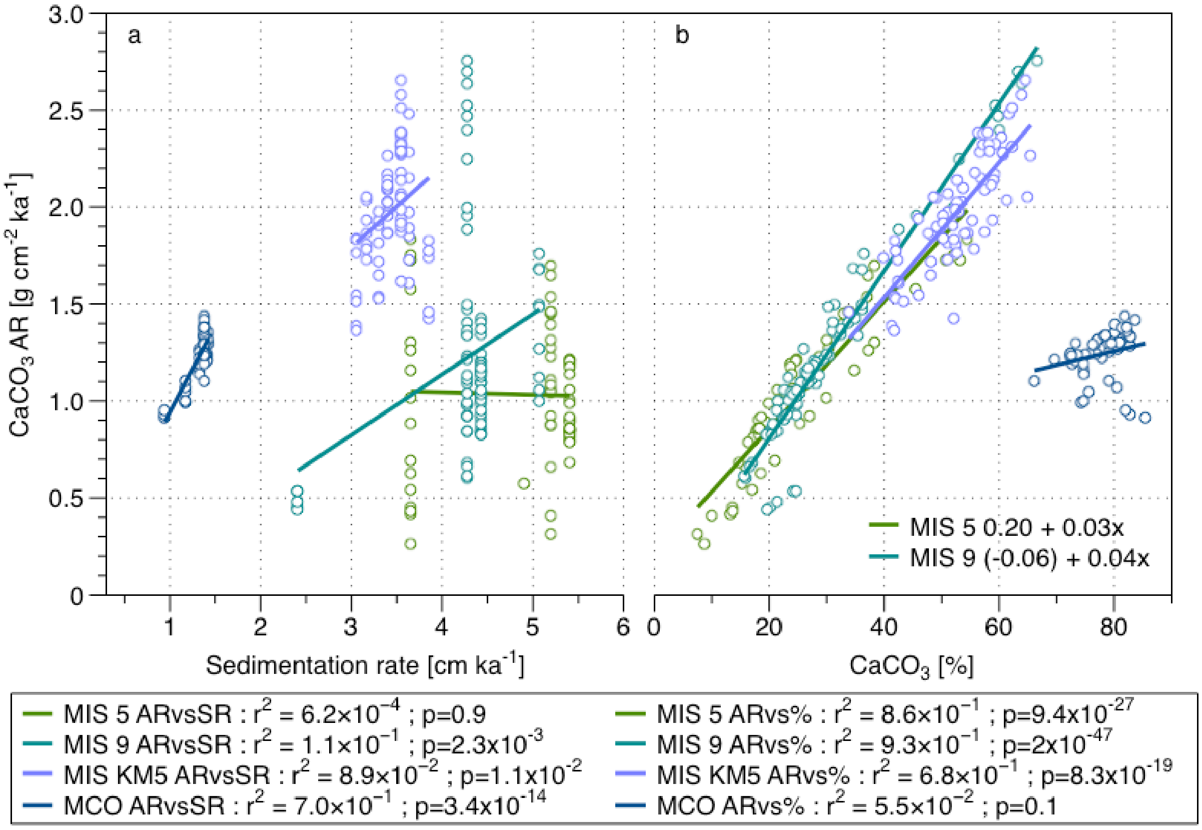

Figure 9. a) Relationship between the $CaCO_3$ AR and the SR and b) relationship between the $CaCO_3$ AR and the $CaCO_3$ % for the four periods of interest.

The presence of multiple $CaCO_3$ AR values for the same SR values, especially for the Quaternary intervals, is due to the few available values of SR, because the studied intervals are short and the tuning cannot be carried out on much higher resolution than orbital. This pattern likely affects the correlation analysis and in such a situation, it would have been appropriate to treat the $CaCO_3$ AR data as groups of observations, each representing a different mean SR, and test for differences using ANOVA. However, the number of observations for some of the intervals is too low, to run the test effectively. However, this limitation may have caused the apparently significant relationship between $CaCO_3$ AR and SR for MIS9, which we indeed consider likely to be an artefact.

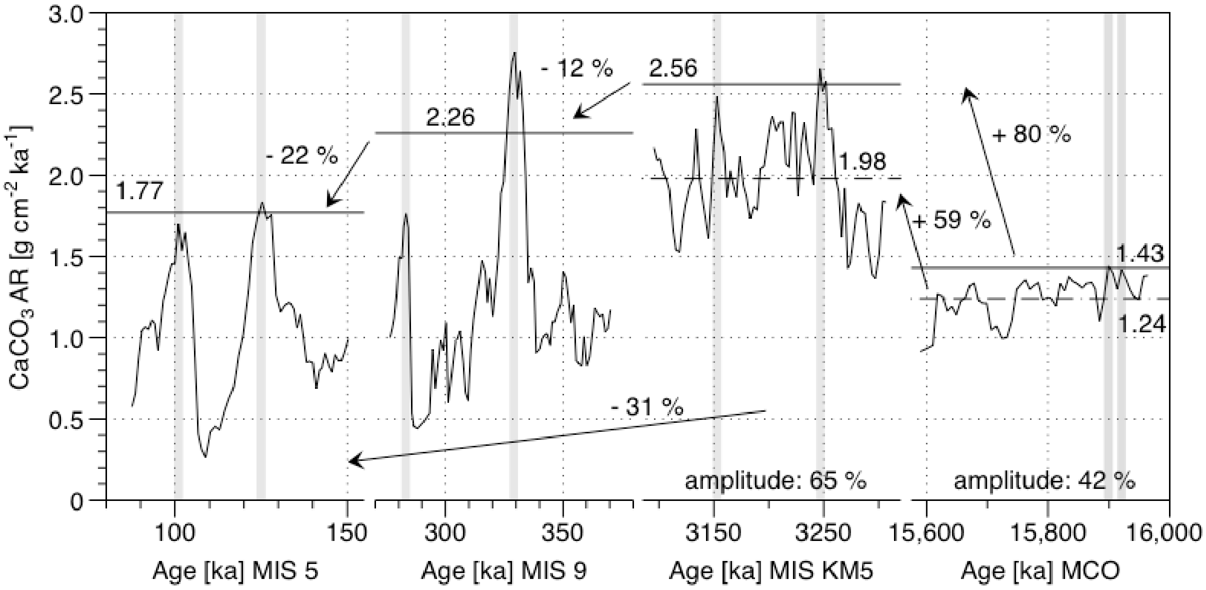

Figure 10. $CaCO_3$ AR for each period of interest, average value between two maxima per period (for Quaternary and Pliocene), average value taking in account maxima and minima for the Pliocene and the Miocene, and quantification of change within (amplitude)/between each of the periods of interest. The shaded areas are underlying the maxima values of $CaCO_3$ AR used for the quantification of change between the time intervals calculation.

When we look at the trend of the highest values reached on long geological timescale from the mid-Miocene to MIS 5 (Fig. 10), we observe a 31 % decrease in $CaCO_3$ AR from the Pliocene (highest value) to the Pleistocene MIS 5 (lowest value), excluding dissolution intervals in the Pleistocene. Taking into account the average value of the MCO and MIS KM5, we found an increase in the pelagic carbonate production of 59 % from Miocene to Pliocene MIS KM5. If we now take into account the maxima values for the Quaternary and Pliocene MIS KM5, we observe a decrease of 12 % from the Pliocene MIS KM5 to Pleistocene and a decrease of 22 % from Pleistocene MIS 9 to Pleistocene MIS 5.

Looking at the amplitude of the variability within the Pliocene and Miocene interval, we found higher values in the Pliocene (65 %) compared to the average of the period (1.98 g cm^{-2} ka^{-1}) than in the Miocene (42 %) compared to the average (1.24 g cm^{-2} ka^{-1}).

II.4 Discussion

II.4.i Carbonate preservation during the Quaternary

During the Pleistocene, the $CaCO_3$ AR at Site 927 was driven only by the carbonate content, indicating that the signal is affected by dissolution. This is confirmed by the presence of very low values of carbonate content and $CaCO_3$ AR during the cold intervals in the Pleistocene, in phase with the $\delta^{18}O$ and insolation signal, indicating a relationship to changes in deep-water circulation, confirming the conclusions by Bickert et al. (1997). As expected from the overall stratigraphy and palaeoceanography of the Ceara Rise sites (Curry et al., 1995; Frenz et al., 2006; King et al., 1997), the new carbonate content (Fig. 8e) and $CaCO_3$ AR (Fig. 8c) records from Site 927 show strong minima during cold intervals of the Quaternary (indicated by $\delta^{18}O$ record) which is consistent with the shoaling of the corrosive AABW (Miller et al., 2012; Harris et al., 1997), causing dissolution at shallower depth (Gröger et al., 2003a, b). In contrast, the maxima in $CaCO_3$ AR and carbonate content in the sediment during the Quaternary do not appear to be affected by dissolution. Therefore, whilst we cannot use the Quaternary variability in the $CaCO_3$ AR to estimate the orbital-scale variability in pelagic carbonate production, we can use the interglacial maxima (Fig. 10) to estimate pelagic carbonate production during the Quaternary, assuming that during the studied Pleistocene interglacials Site 927 was positioned above the lysocline, as is the case during the Holocene.

II.4.ii Carbonate preservation during the Pliocene and Miocene

Because the Ceara Rise sites became periodically affected by the more corrosive Antarctic bottom water only after the initiation of the North Hemisphere glaciation (Liebrand et al., 2016; Harris et al., 1997; Pälike et al., 2006a), the studied Pliocene and Miocene intervals should not be affected by dissolution. Paul et al. (2000) note that the exact subsidence history of the Ceara Rise is unknown but assume minimal subsidence since the early Miocene. Similarly, sea level differences among Quaternary interglacials and the Pliocene and Miocene were likely on the order of tens of metres. Therefore, the largest changes in palaeodepth would have been due to sediment cover, which would make the studied mid-Miocene interval about 300 m deeper compared to the present one (this depth is still above the present day lysocline depth of 4200 mbsl). Throughout the entire studied interval since the Miocene (Fig. 3), the shallowest cores (925 and 927) record higher $CaCO_3$ AR values than the deeper ones. This also indicates that these sites likely remained above the lysocline (Curry et al., 1995; Bickert et al., 1997; Frenz et al., 2006; Gröger et al., 2003a, b) and that the $CaCO_3$ AR signals recorded at these sites primarily record changes in pelagic carbonate production. To provide further support for the lack of dissolution control on the pre-Quaternary variation in $CaCO_3$ AR, for the Pliocene and Miocene interval we generated new data on the degree of fragmentation of planktonic foraminifera shells, a commonly accepted proxy for the extent of carbonate dissolution (Berger et al., 1982; Preiss-Daimler et al., 2013). The fragmentation data (Fig. S4) reveal good preservation (see also Fig. S7) of foraminiferal shells throughout the Pliocene and Miocene intervals, showing no correlation with $CaCO_3$ AR (Fig. S5), confirming that the $CaCO_3$ AR was not driven by dissolution at that time and therefore must reflect pelagic carbonate production changes.

II.4.iii Orbital variability in the Pliocene and Miocene

Assuming dissolution did not play a significant role in the observed variations in $CaCO_3$ AR in Pleistocene interglacials and prior to the Quaternary and that pelagic carbonate is the main component of the carbonate fraction of the sediment (Curry et al., 1995), we here observe the changes in the export flux of pelagic biogenic carbonate. Under the same assumption, the new record from Site 927 reveals that pelagic carbonate production (assessed by the pelagic $CaCO_3$ AR) in the equatorial ocean (avoiding large-amplitude temperature changes) has changed on a geological timescale by a factor of 2 and on orbital timescales by up to 50 %. The presence of orbital-scale variability in pelagic carbonate production is an interesting phenomenon that requires further analysis. First, we tested whether or not this variability is periodic, i.e. whether the underlying changes in pelagic carbonate production responded to orbital forcing. Such analysis is possible because the studied intervals have been tuned to the orbital target using parameters other than carbonate content (Fig. 6 and 7). Multitaper method (MTM) spectra derived with the astrochron package in R (Meyers, 2014, using R, 4.1.2., R Core Team, 2021) (Fig. 11) highlight significant periodicity close to the precession band for the MIS KM5 and periodicities in the obliquity and 100 ka eccentricity bands for the MCO. This implies that during both intervals, the pelagic production likely varied in response to orbitally driven environmental factors, such as insolation (light intensity for phytoplankton, Cavaleiro et al., 2018) or nutrient availability due to changes in upwelling (Cavaleiro et al., 2020). Interestingly, the dominant periodicities appear different between the Pliocene and Miocene. Next, we asked whether or not the observed periodicities in $CaCO_3$ AR are coherent with the actual insolation, obliquity and eccentricity signals. This is possible because the underlying age models have been tuned such that they should preserve the correct phase relationship with the orbital forcing (Fig. 6 and 7). To this end, we carried out cross Blackman-Tukey (BT) analyses using the Analyseries software 2.0 (Paillard et al., 1996). The results (Fig. 12) indicate a coherence with insolation in the precession band and with the 41 ka obliquity for the MIS KM5. In both cases, the coherence occurs in phase. In contrast, for the MCO we observe a coherence at 41 ka with the obliquity periodicity and at 100 ka with eccentricity, but in both cases the coherence is anti-phased. That the pelagic carbonate production is responding to an eccentricity-paced periodicity (Fig. 11 and 12) is interesting, as eccentricity was not the main driver of the Earth climate signal (Westerhold et al., 2020; De Vleeschouwer et al., 2020). The carbon cycle in the Miocene appears to show eccentricity pacing (Holbourn et al., 2007, 2018; De Vleeschouwer et al., 2020; Raitzsch et al., 2020), and our results indicate that pelagic carbonate productivity may play a role in modulation of this cyclicity. We also note that the discovery of eccentricity forcing pelagic carbonate production in the Miocene and a shift towards obliquity and precession forcing in the Pliocene is consistent with the observations from mid-latitudes by Drury et al. (2020), and the modelling study by Vervoort et al. (2021) provides potential mechanisms on how the eccentricity and obliquity frequencies in carbonate production may arise despite the dominance of the precession frequencies in the forcing.

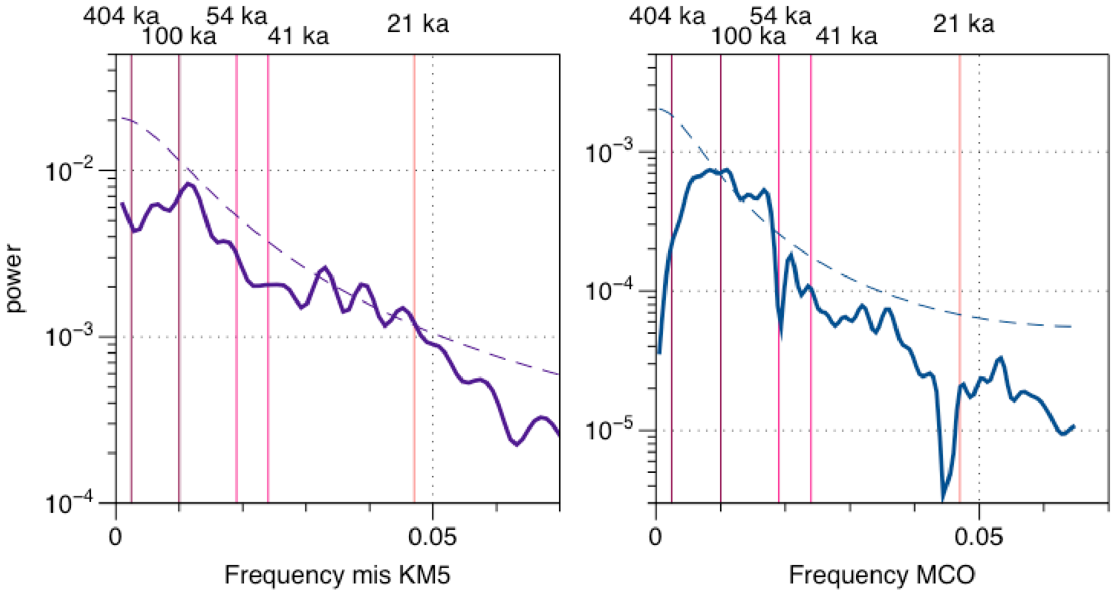

Figure 11. MTM spectral analysis of the $CaCO_3$ AR record through time (Meyers, 2014, R Core Team, 2021). The dashed lines represent the 95 % significance level. The pink shadows correspond to the orbital periodicities (eccentricity 404 ka and 100 ka, obliquity 54 ka and 41 ka and precession 21 ka).

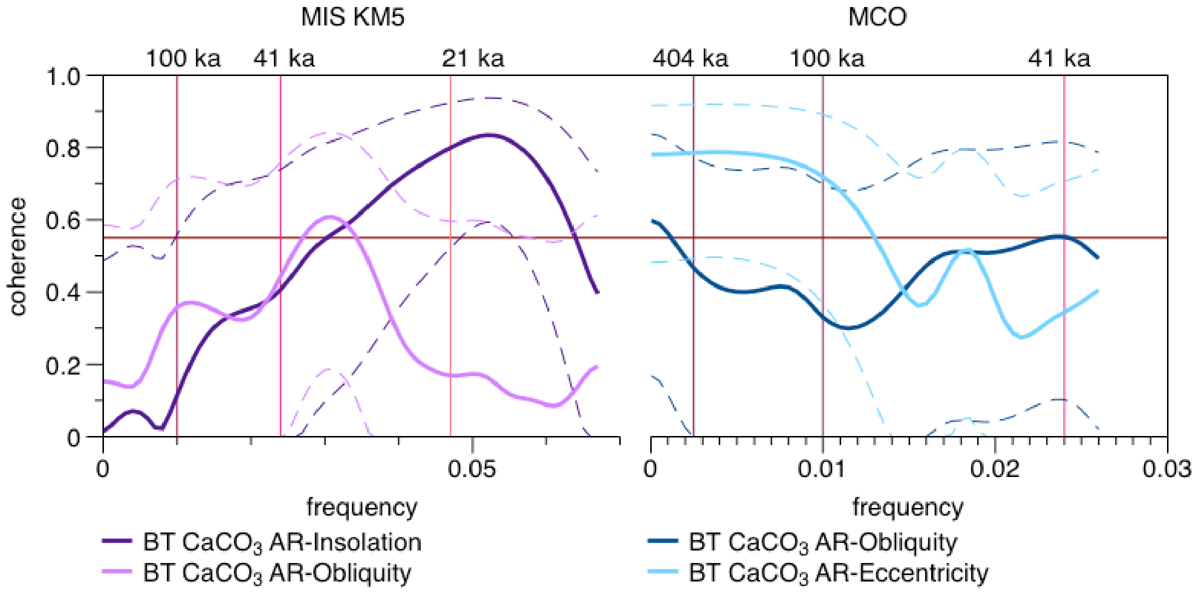

Figure 12. Coherence diagram BT cross correlation (Paillard et al., 1996) between the $CaCO_3$ AR and the orbital parameters (Laskar et al., 2004). The dashed curves show the 90% confidence intervals. The horizontal red line corresponds to the non-zero coherence at a significance level of 90 %. The pink vertical lines correspond to the orbital periodicities (eccentricity 404 ka and 100 ka, obliquity 54 ka and 41 ka and precession 21 ka).

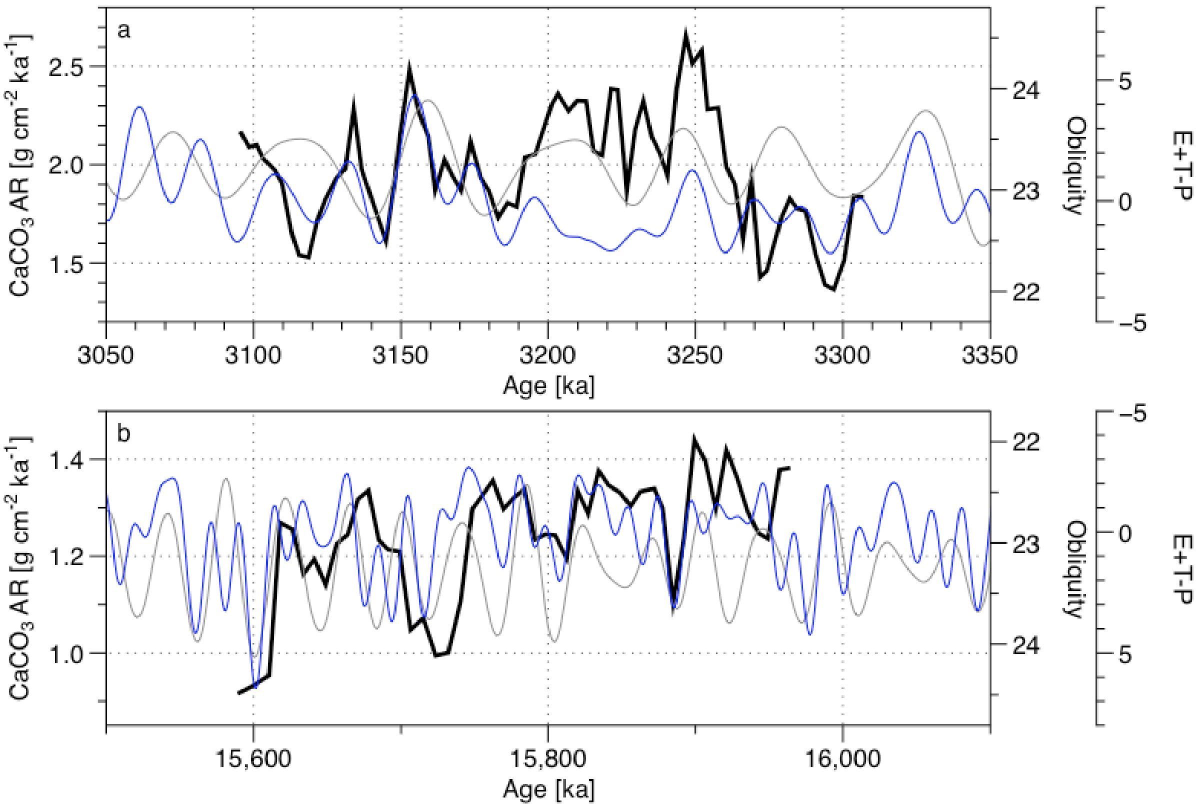

Figure 13. Comparison of the $CaCO_3$ AR (black) with both the obliquity (grey) and the E+T-P orbital records (blue) (Laskar et al., 2004) for a) the MIS KM5 and b) the MCO.

Finally, we consider the apparent shift in the phase in the relationship between orbital forcing and the $CaCO_3$ AR record between the Pliocene and Miocene. This relationship implied by the cross-spectral analysis is clearly visible in the raw data (Fig. 13) and we consider it unlikely that it is due to tuning artefacts. We note that the Miocene record ends with a strong and distinct minimum in the oxygen isotope record, which provides a strong constraint on the phase relationship between the youngest $CaCO_3$ AR and obliquity cycle. These show an opposite phase relationship to that observed during the Pliocene. This could be explained by a change in the carbonate production response to the insolation changes between the Pliocene and the Miocene. Indeed, the production of different pelagic calcifiers could be promoted by a decreased mean annual insolation at equatorial latitude (with high E+T-P and high obliquity) during the Pliocene compared to the Miocene, when the pelagic carbonate calcifiers appears to be promoted by a higher mean annual insolation at equatorial latitude (with low E+T-P and low obliquity). We can then expect a higher weight of the foraminifera (non-photosynthetic) in the carbonate production balance during the Pliocene and a higher weight of the coccolithophores (doing photosynthesis) in the carbonate production balance during the Miocene. This is coherent with the climate-carbon cycle changes occurring between the Miocene and the Pliocene, highlighted by De Vleeschouwer et al. (2020), who found changes in the phase relationship of $\delta^{18}O$ and $\delta^{13}C$ before and after 6 Ma.

II.4.iv Long-term trend (differences between periods)

Because of the observed changes in what appears to be carbonate production among the studied intervals and especially within the studied intervals, we conclude that tropical pelagic calcifiers responded to environmental or biotic forcing on orbital cycles, as well as to long-term shifts in climate and/or ocean chemistry. In other words, either the production, the community composition or the biomineralization of the tropical pelagic calcifiers may respond to local changes in light, temperature and nutrients delivered by upwelling, which followed orbital cycles, as well as to long-term shifts in climate and/or ocean chemistry. The inferred changes in pelagic carbonate production on both timescales are sufficiently large that when extrapolated on a global scale, they could have played a role in the regulation of the carbon cycle. For example, Boudreau et al. (2018) estimated that changes in global pelagic carbonate production on the order of 10 % would be sufficient to affect the marine carbon cycle on timescales from year to millions of years. Whereas the drivers of the orbital-scale variability could be plausibly attributed to changes in local oceanic parameters affecting primary production, the causes of the long-term shifts require another explanation.

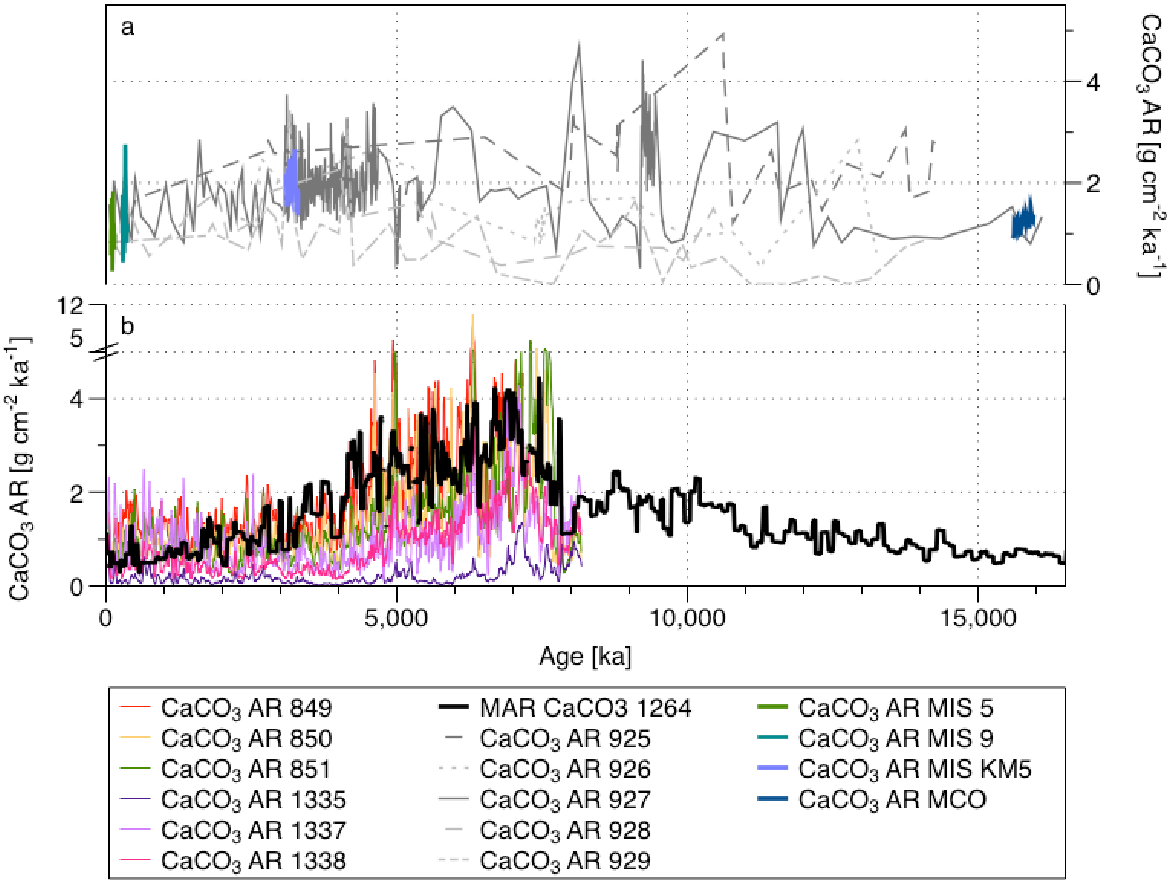

Figure 14. Comparison of the $CaCO_3$ AR at a) the 5 Ceará Rise sites (Sect. 3.1., in Grey) and $CaCO_3$ AR at high resolution (this study; in colours) and b) $CaCO_3$ AR record in the equatorial Pacific (colours) (Lyle et al., 2019) and South Atlantic Ocean (black) (Site 1264, Drury et al., 2020).

There are two studies presenting long continuous $CaCO_3$ AR records from the Miocene to the present (Fig. 14). Both records show an increasing $CaCO_3$ AR from the early Miocene to Pliocene and a decreasing $CaCO_3$ AR from the Pliocene to Quaternary and both records indicate the presence of high-amplitude variability on orbital scales throughout the last 16 Myr (Drury et al., 2020; Lyle et al., 2019). The observed $CaCO_3$ AR at the Ceara Rise appears coherent with both records (Fig. 14), as well as with the recent results by Sutherland et al. (2022) from the South Pacific. Our record shows similar absolute values to Lyle et al. (2019) and Drury et al. (2020) (a $CaCO_3$ AR between 0 and 5 g cm^{-2} ka^{-1}) and a similar overall trend, with its highest values being in the late Miocene-early Pliocene. Clearly, the overall trend of $CaCO_3$ AR at the Ceara Rise supports the existence of a late Miocene carbonate maximum also under tropical conditions. Interestingly, our observations from the Ceara Rise also support the conclusion from Sutherland et al. (2022) that there does not appear to be any strong relationship between pelagic carbonate production and global CO_2, other than the fact that the lowest $CaCO_3$ AR in both their and our records are observed during the MCO with presumably highest CO_2.

II.5 Conclusion

A compilation of $CaCO_3$ AR for the five sites of Leg 154 in the western equatorial Atlantic Ocean documents a distinct increase in SR from Miocene to Quaternary, but the $CaCO_3$ AR remained relatively stable. The two shallowest sites at the Ceara Rise (925 and 927) consistently record higher $CaCO_3$ AR, confirming observations of good carbonate preservation during Quaternary interglacials and throughout the Pliocene and Miocene. This means that the observed changes in $CaCO_3$ AR at these sites should reflect changes in pelagic carbonate production.

To analyse long-term and orbital-scale patterns of pelagic carbonate production variability, we generated new data for four periods at Site 927.

We found that $CaCO_3$ AR, as a proxy for pelagic carbonate production in the tropical Atlantic, exhibited both long-term changes and a pervasive orbital-scale variability. We observe a 31 % decrease in $CaCO_3$ AR from the Pliocene MIS KM5 to the Pleistocene interglacial MIS 5, but 59 % higher values for the Pliocene warm period than for the Miocene climatic optimum. On the orbital timescale, the Quaternary signals are overprinted by precession and insolation forcing on deep-water circulation, causing dissolution. However, concerning the Pliocene Warm Period and the Miocene Climatic Optimum, we observe a persistent variability in $CaCO_3$ AR with an amplitude exceeding that of the long-term mean shifts. We show that the $CaCO_3$ AR at low latitude varied in phase with insolation (precession) cycles during the Pliocene, whereas the Miocene signal is dominated by 100 ka eccentricity cycles, which are exactly anti-phased with the carbonate signal.

We conclude that the low-latitude pelagic carbonate production responded strongly to orbital-driven local tropical processes, rather than to secular changes in the global climate or ocean chemistry (like global CO_2). The Ceara Rise records are consistent with the existence of a late Miocene to Pliocene global carbonate production optimum, but the magnitude of the long-term change appears smaller than outside the tropics. Instead, orbital-scale variability dominates the record and the inferred magnitude of production changes are potentially sufficient to affect the global carbon cycle through the process of biological compensation (Boudreau et al., 2018).

Our results imply that in the context of the ongoing and projected global change, pelagic carbonate production may be an important variable in the parametrization of the global marine carbon cycle, especially with regard to the long-term (millennial-scale) fate of anthropogenic carbon injection. To parametrize the pelagic carbonate production, it remains to be shown whether it changes due to changes in production (population sizes), biomineralization (amount of carbonate produced per individual) or community composition (shift to more or less calcified taxa).

II.6 Data availability

All data sets are available on Pangaea (https://doi.org/10.1594/PANGAEA.945848, Cornuault et al., 2022a, https://doi.org/10.1594/PANGAEA.945773, Cornuault et al., 2022b, https://doi.org/10.1594/PANGAEA.945812, Cornuault et al., 2022c, https://doi.org/10.1594/PANGAEA.945789, Cornuault et al., 2022d, https://doi.org/10.1594/PANGAEA.945707, Cornuault et al., 2022e).

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II.8 Bibliography

Beerling, D. J. and Royer, D. L.: Reconstructions of atmospheric carbon dioxide concentrations over the past 65 million years are heading towards consensus. It is time for systematic testing of the proxies, against measurements and against each other., Nature Geoscience, 4, 418-420, https://doi.org/10.1038/ngeo1186, 2011.

Bell, D. B., Jung, S. J. A., and Kroon, D.: The Plio-Pleistocene development of Atlantic deep-water circulation and its influence on climate trends, Quaternary Science Reviews, 123, 265–282, https://doi.org/10.1016/j.quascirev.2015.06.026, 2015.

Berger, W. H., Bonneau, M. C., and Parker, F. L.: Foraminifera on the deep-sea floor - lysocline and dissolution rate, Oceanologica Acta (0399-1784) (Gauthier-Villars), Vol. 5, 249–258, 1982.

Bickert, T., Cordes, R., and Wefer, G.: Late Pliocene to mid-Pleistocene (2.6–1.0 m.y.) carbonate dissolution in the western equatorial Atlantic: results of Leg 154, Ceara Rise, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 229–237, https://doi.org/10.2973/odp.proc.sr.154.109.1997, 1997.

Bickert, T., Haug, G. H., and Tiedemann, R.: Late Neogene benthic stable isotope record of Ocean Drilling Program Site 999: Implications for Caribbean paleoceanography, organic carbon burial, and the Messinian Salinity Crisis, Paleoceanography, 19, PA1023, https://doi.org/10.1029/2002PA000799, 2004.

Boudreau, B. P., Middelburg, J. J., and Luo, Y.: The role of calcification in carbonate compensation, Nature Geoscience, 11, 894–900, https://doi.org/10.1038/s41561-018-0259-5, 2018.

Brummer, G. J. A. and van Eijden, A. J. M.: “Blue-ocean” paleoproductivity estimates from pelagic carbonate mass accumulation rates, Marine Micropaleontology, 19, 99–117, https://doi.org/10.1016/0377-8398(92)90023-D, 1992.

Cavaleiro, C., Voelker, A. H. L., Stoll, H., Baumann, K.-H., Kulhanek, D. K., Naafs, B. D. A., Stein, R., Grützner, J., Ventura, C., and Kucera, M.: Insolation forcing of coccolithophore productivity in the North Atlantic during the Middle Pleistocene, Quaternary Science Reviews, 191, 318–336, https://doi.org/10.1016/j.quascirev.2018.05.027, 2018.

Cavaleiro, C., Voelker, A. H. L., Stoll, H., Baumann, K.-H., and Kucera, M.: Coccolithophore productivity at the western Iberian Margin during the Middle Pleistocene (310–455 ka) – evidence from coccolith Sr⁄Ca data, Climate of the Past, 16, 2017–2037, https://doi.org/10.5194/cp-16-2017-2020, 2020.

Chalk, T. B., Foster, G. L., and Wilson, P. A.: Dynamic storage of glacial CO_2 in the Atlantic Ocean revealed by boron [CO_3^{2-}] and pH records, Earth and Planetary Science Letters, 510, 1–11, https://doi.org/10.1016/j.epsl.2018.12.022, 2019.

Clark, P. U. and Huybers, P.: Interglacial and future sea level: Global change, Nature, 462, 856–857, https://doi.org/10.1038/462856a, 2009.

Cullen, J. L. and Curry, W. B.: Variations in planktonic foraminifer faunas and carbonate preservation at Site 927: evidence for changing surface water conditions in the western tropical Atlantic Ocean during the middle Pleistocene, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 207–228, https://doi.org/10.2973/odp.proc.sr.154.111.1997, 1997.

Curry, W. B. and Cullen, J. L.: Carbonate production and dissolution in the western equatorial Atlantic during the last 1 M.y, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, Ocean Drilling Program, 189–199, https://doi.org/10.2973/odp.proc.sr.154.112.1997, 1997.

Curry, W. B., Shackleton, N. J., Richter, C., and et al. (Eds.): Proceedings of the Ocean Drilling Program, 154 Initial Reports, Ocean Drilling Program, https://doi.org/10.2973/odp.proc.ir.154.1995, 1995.

De Vleeschouwer, D., Vahlenkamp, M., Crucifix, M., and Pälike, H.: Alternating Southern and Northern Hemisphere climate response to astronomical forcing during the past 35 m.y., Geology, 45, 375–378, https://doi.org/10.1130/G38663.1, 2017.

De Vleeschouwer, D., Drury, A. J., Vahlenkamp, M., Rochholz, F., Liebrand, D., and Pälike, H.: High-latitude biomes and rock weathering mediate climate–carbon cycle feedbacks on eccentricity timescales, Nature Communications, 11, 5013, https://doi.org/10.1038/s41467-020-18733-w, 2020.

Dodson, J. and Macphail, M. K.: Palynological evidence for aridity events and vegetation change during the Middle Pliocene, a warm period in Southwestern Australia, Global and Planetary Change, 41, 285–307, https://doi.org/10.1016/j.gloplacha.2004.01.013, 2004.

Drury, A. J., Liebrand, D., Westerhold, T., Beddow, H. M., Hodell, D. A., Rohlfs, N., Wilkens, R. H., Lyle, M., Bell, D. B., Kroon, D., Pälike, H., and Lourens, L. J.: Climate, cryosphere and carbon cycle controls on Southeast Atlantic orbital-scale carbonate deposition since the Oligocene (30–0 Ma), Clim. Past, 17, 2091–2117, https://doi.org/10.5194/cp-17-2091-2021, 2021.

Feely, R. A.: Impact of Anthropogenic CO_2 on the $CaCO_3$ System in the Oceans, Science, 305, 362–366, https://doi.org/10.1126/science.1097329, 2004.

Foster, G. L., Lear, C. H., and Rae, J. W. B.: The evolution of pCO_2, ice volume and climate during the middle Miocene, Earth and Planetary Science Letters, 341–344, 243–254, https://doi.org/10.1016/j.epsl.2012.06.007, 2012.

Frenz, M., Baumann, K.-H., Boeckel, B., Hoppner, R., and Henrich, R.: Quantification of Foraminifer and Coccolith Carbonate in South Atlantic Surface Sediments by Means of Carbonate Grain-Size Distributions, Journal of Sedimentary Research, 75, 464–475, https://doi.org/10.2110/jsr.2005.036, 2005.

Frenz, M., Henrich, R., and Zychla, B.: Carbonate preservation patterns at the Ceará Rise – Evidence for the Pliocene super conveyor, Marine Geology, 232, 173–180, https://doi.org/10.1016/j.margeo.2006.07.006, 2006.

Gehlen, M., Gangstø, R., Schneider, B., Bopp, L., Aumont, O., and Ethe, C.: The fate of pelagic $CaCO_3$ production in a high CO_2 ocean: a model study, Biogeosciences, 505-519, https://doi.org/10.5194/bg-4-505-2007, 2007.

Gouveia, N. A., Gherardi, D. F. M., and Aragão, L. E. O. C.: The Role of the Amazon River Plume on the Intensification of the Hydrological Cycle, Geophysical Research Letters, 9, 2019.

Gröger, M., Henrich, R., and Bickert, T.: Glacial–interglacial variability in lower North Atlantic deep water: inference from silt grain-size analysis and carbonate preservation in the western equatorial Atlantic, Marine Geology, 201, 321–332, https://doi.org/10.1016/S0025-3227(03)00263-9, 2003a.

Gröger, M., Henrich, R., and Bickert, T.: Variability of silt grain size and planktonic foraminiferal preservation in Plio/Pleistocene sediments from the western equatorial Atlantic and Caribbean, Marine Geology, 201, 307–320, https://doi.org/10.1016/S0025-3227(03)00264-0, 2003b.

Haq, B. U., Hardenbol, J., and Vail, P. R.: Chronology of Fluctuating Sea Levels Since the Triassic, Science, 235, 1156–1167, https://doi.org/10.1126/science.235.4793.1156, 1987.

Harris, S. E., Mix, A. C., and King, T.: Biogenic and terrigenous sedimentation at Ceara Rise, western tropical Atlantic, supports Pliocene–Pleistocene deep-water linkage between hemispheres, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 331–345, https://doi.org/10.2973/odp.proc.sr.154.114.1997, 1997.

Haywood, A. M., Valdes, P. J., and Sellwood, B. W.: Global scale palaeoclimate reconstruction of the middle Pliocene climate using the UKMO GCM: initial results, Global and Planetary Change, 25, 239–256, https://doi.org/10.1016/S0921-8181(00)00028-X, 2000.

Haywood, A. M., Dolan, A. M., Pickering, S. J., Dowsett, H. J., McClymont, E. L., Prescott, C. L., Salzmann, U., Hill, D. J., Hunter, S. J., Lunt, D. J., Pope, J. O., and Valdes, P. J.: On the identification of a Pliocene time slice for data-model comparison, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 371, 20120515–20120515, https://doi.org/10.1098/rsta.2012.0515, 2013.

Henson, S. A., Sanders, R., and Madsen, E.: Global patterns in efficiency of particulate organic carbon export and transfer to the deep ocean, Global Biogeochemical Cycles, 26, GB1028, https://doi.org/10.1029/2011GB004099, 2012.

Herbert, T. D., Lawrence, K. T., Tzanova, A., Peterson, L. C., Caballero-Gill, R., and Kelly, C. S.: Late Miocene global cooling and the rise of modern ecosystems, Nature Geoscience, 9, 843–847, https://doi.org/10.1038/ngeo2813, 2016.

Herrford, J., Brandt, P., and Zenk, W.: Property changes of deep and bottom waters in the Western Tropical Atlantic, Deep Sea Research Part I: Oceanographic Research Papers, 124, 103–125, https://doi.org/10.1016/j.dsr.2017.04.007, 2017.

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 and Planetary Science Letters, 261, 534–550, https://doi.org/10.1016/j.epsl.2007.07.026, 2007.

Holbourn, A., Kuhnt, W., Kochhann, K. G. D., Andersen, N., and Sebastian Meier, K. J.: Global perturbation of the carbon cycle at the onset of the Miocene Climatic Optimum, Geology, 43, 123–126, https://doi.org/10.1130/G36317.1, 2015.

Holbourn, A. E., Kuhnt, W., Clemens, S. C., Kochhann, K. G. D., Jöhnck, J., Lübbers, J., and Andersen, N.: Late Miocene climate cooling and intensification of southeast Asian winter monsoon, Nat Commun, 9, 1584, https://doi.org/10.1038/s41467-018-03950-1, 2018.

Howard, W. R.: A warm future in the past, Nature, 388, 418–419, https://doi.org/10.1038/41201, 1997.

Katz, M. E., Katz, D. R., Wright, J. D., Miller, K. G., Pak, D. K., Shackleton, N. J., and Thomas, E.: Early Cenozoic benthic foraminiferal isotopes: Species reliability and interspecies correction factors, Paleoceanography, 18, 1024, https://doi.org/10.1029/2002PA000798, 2003.

King, T. A., Ellis, W. G., Murray, D. W., and Shackleton, N. J.: Miocene evolution of carbonate sedimentation at the Ceara Rise: a multivariate date/proxy approach, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 349–365, https://doi.org/10.2973/odp.proc.sr.154.116.1997, 1997.

Kopp, R. E., Simons, F. J., Mitrovica, J. X., Maloof, A. C., and Oppenheimer, M.: Probabilistic assessment of sea level during the last interglacial stage, Nature, 462, 6, https://doi.org/10.1038/nature08686, 2009.

Kukla, G.: How long and how stable was the last interglacial?, Quaternary Science Reviews, 16, 605–612, https://doi.org/10.1016/S0277-3791(96)00114-X, 1997.

Kurschner, W. M., Kvacek, Z., and Dilcher, D. L.: The impact of Miocene atmospheric carbon dioxide fluctuations on climate and the evolution of terrestrial ecosystems, Proceedings of the National Academy of Sciences, 105, 449–453, https://doi.org/10.1073/pnas.0708588105, 2008.

Landschützer, P., Gruber, N., Bakker, D. C. E., and Schuster, U.: Recent variability of the global ocean carbon sink, Global Biogeochemical Cycles, 28, 927–949, https://doi.org/10.1002/2014GB004853, 2014.

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, Astronomy & Astrophysics, 428, 261–285, https://doi.org/10.1051/0004-6361:20041335, 2004.

Leroy, S. and Dupont, L.: Development of vegetation and continental aridity in northwestern Africa during the Late Pliocene: the pollen record of ODP site 658, Palaeogeography, Palaeoclimatology, Palaeoecology, 109, 295–316, https://doi.org/10.1016/0031-0182(94)90181-3, 1994.

Liebrand, D., Beddow, H. M., Lourens, L. J., Pälike, H., Raffi, I., Bohaty, S. M., Hilgen, F. J., Saes, M. J. M., Wilson, P. A., van Dijk, A. E., Hodell, D. A., Kroon, D., Huck, C. E., and Batenburg, S. J.: Cyclostratigraphy and eccentricity tuning of the early Oligocene through early Miocene (30.1–17.1 Ma): *Cibicides mundulus* stable oxygen and carbon isotope records from Walvis Ridge Site 1264, Earth and Planetary Science Letters, 450, 392–405, https://doi.org/10.1016/j.epsl.2016.06.007, 2016.

Lisiecki, L. E. and Raymo, M. E.: A Pliocene-Pleistocene stack of 57 globally distributed benthic δ^{18}O records, Paleoceanography, 20, PA1003, https://doi.org/10.1029/2004PA001071, 2005.

Lunt, D. J., Foster, G. L., Haywood, A. M., and Stone, E. J.: Late Pliocene Greenland glaciation controlled by a decline in atmospheric CO_2 levels, Nature, 454, 1102–1105, https://doi.org/10.1038/nature07223, 2008.

Lunt, D. J., Haywood, A. M., Schmidt, G. A., Salzmann, U., Valdes, P. J., and Dowsett, H. J.: Earth system sensitivity inferred from Pliocene modelling and data, Nature Geoscience, 3, 60–64, https://doi.org/10.1038/ngeo706, 2010.

Lyle, M.: Neogene carbonate burial in the Pacific Ocean, Paleoceanography, 18, 3, 1059, https://doi.org/10.1029/2002PA000777, 2003.

Lyle, M., Drury, A. J., Tian, J., Wilkens, R., and Westerhold, T.: Late Miocene to Holocene high-resolution eastern equatorial Pacific carbonate records: stratigraphy linked by dissolution and paleoproductivity, Climate of the Past, 15, 1715–1739, https://doi.org/10.5194/cp-15-1715-2019, 2019.

Marino, M., Maiorano, P., Tarantino, F., Voelker, A., Capotondi, L., Girone, A., Lirer, F., Flores, J.-A., and Naafs, B. D. A.: Coccolithophores as proxy of seawater changes at orbital-to-millennial scale during middle Pleistocene Marine Isotope Stages 14-9 in North Atlantic core MD01-2446, Paleoceanography, 29, 518–532, https://doi.org/10.1002/2013PA002574, 2014.

Mejía, L. M., Méndez-Vicente, A., Abrevaya, L., Lawrence, K. T., Ladlow, C., Bolton, C., Cacho, I., and Stoll, H.: A diatom record of CO_2 decline since the late Miocene, Earth and Planetary Science Letters, 479, 18–33, https://doi.org/10.1016/j.epsl.2017.08.034, 2017.

Meyers, S. R.: Astrochron: An R package for astrochronology., 2014.

Miller, K. G., Wright, J. D., Browning, J. V., Kulpecz, A., Kominz, M., Naish, T. R., Cramer, B. S., Rosenthal, Y., Peltier, W. R., and Sosdian, S.: High tide of the warm Pliocene: Implications of global sea level for Antarctic deglaciation, Geology, 40, 407–410, https://doi.org/10.1130/G32869.1, 2012.

Milliman, J. D.: Production and accumulation of calcium carbonate in the ocean: budget of a nonsteady state, Global Biogeochemical Cycles, 7, 4, 927-957, 1993.

Müller, U. C. and Kukla, G. J.: North Atlantic Current and European environments during the declining stage of the last interglacial, Geology, 32, 1009, https://doi.org/10.1130/G20901.1, 2004.

Naish, T., Powell, R., Levy, R., Wilson, G., Scherer, R., Talarico, F., Krissek, L., Niessen, F., Pompilio, M., Wilson, T., Carter, L., DeConto, R., Huybers, P., McKay, R., Pollard, D., Ross, J., Winter, D., Barrett, P., Browne, G., Cody, R., Cowan, E., Crampton, J., Dunbar, G., Dunbar, N., Florindo, F., Gebhardt, C., Graham, I., Hannah, M., Hansaraj, D., Harwood, D., Helling, D., Henrys, S., Hinnov, L., Kuhn, G., Kyle, P., Läufer, A., Maffioli, P., Magens, D., Mandernack, K., McIntosh, W., Millan, C., Morin, R., Ohneiser, C., Paulsen, T., Persico, D., Raine, I., Reed, J., Riesselman, C., Sagnotti, L., Schmitt, D., Sjunneskog, C., Strong, P., Taviani, M., Vogel, S., Wilch, T., and Williams, T.: Obliquity-paced Pliocene West Antarctic ice sheet oscillations, Nature, 458, 322–328, https://doi.org/10.1038/nature07867, 2009.

Pagani, M., Liu, Z., LaRiviere, J., and Ravelo, A. C.: High Earth-system climate sensitivity determined from Pliocene carbon dioxide concentrations, Nature Geoscience, 3, 27–30, https://doi.org/10.1038/ngeo724, 2010.

Paillard, D., Labeyrie, L., and Yiou, P.: Macintosh Program performs time-series analysis, Eos Trans. AGU, 77, 379–379, https://doi.org/10.1029/96EO00259, 1996.

Pälike, H., Frazier, J., and Zachos, J. C.: Extended orbitally forced palaeoclimatic records from the equatorial Atlantic Ceara Rise, Quaternary Science Reviews, 25, 3138–3149, https://doi.org/10.1016/j.quascirev.2006.02.011, 2006a.

Pälike, H., Norris, R. D., Herrle, J. O., Wilson, P. A., Coxall, H. K., Lear, C. H., Shackleton, N. J., Tripati, A. K., and Wade, B. S.: The Heartbeat of the Oligocene Climate System, Science, 314, 1894–1898, https://doi.org/10.1126/science.1133822, 2006b.

Pälike, H., Lyle, M., Nishi, H., Raffi, I., Gamage, K., Klaus, A., and Expedition 320/321 Scientists (Eds.): Proceedings of the Integrated Ocean Drilling Program, 320/321, International Ocean Discovery Program, https://doi.org/10.2204/iodp.proc.320321.2010, 2010.

Passow, U. and Carlson, C.: The biological pump in a high CO_2 world, Marine Ecology Progress Series, 470, 249–271, https://doi.org/10.3354/meps09985, 2012.

Past Interglacials Working Group of PAGES: Interglacials of the last 800,000 years, Reviews of Geophysics, 54, 162–219, https://doi.org/10.1002/2015RG000482, 2016.

Paul, H. A., Zachos, J. C., Flower, B. P., and Tripati, A.: Orbitally induced climate and geochemical variability across the Oligocene/Miocene boundary, Paleoceanography, 15, 471–485, https://doi.org/10.1029/1999PA000443, 2000.

Petit, J. R., Jouzel, J., Raynaud, D., Barkov, N. I., Barnola, J.-M., Basile, I., Bender, M., Chappellaz, J., Davis, M., Delaygue, G., Delmotte, M., Kotlyakov, V. M., Legrand, M., Lipenkov, V. Y., Lorius, C., PÉpin, L., Ritz, C., Saltzman, E., and Stievenard, M.: Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, Nature, 399, 429–436, https://doi.org/10.1038/20859, 1999.

Pollard, D. and DeConto, R. M.: Modelling West Antarctic ice sheet growth and collapse through the past five million years, Nature, 458, 329–332, https://doi.org/10.1038/nature07809, 2009.

Pound, M. J., Haywood, A. M., Salzmann, U., and Riding, J. B.: Global vegetation dynamics and latitudinal temperature gradients during the Mid to Late Miocene (15.97–5.33Ma), Earth-Science Reviews, 112, 1–22, https://doi.org/10.1016/j.earscirev.2012.02.005, 2012.

Preiss-Daimler, I. V., Henrich, R., and Bickert, T.: The final Miocene carbonate crash in the Atlantic: Assessing carbonate accumulation, preservation and production, Marine Geology, 343, 39–46, https://doi.org/10.1016/j.margeo.2013.06.010, 2013.

R Core Team: R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria., 2021.

Raffi, I., Wade, B. S., Pälike, H., Beu, A. G., Cooper, R., Crundwell, M. P., Krijgsman, W., Moore, T., Raine, I., Sardella, R., and Vernyhorova, Y. V.: The Neogene Period, in: Geologic Time Scale 2020, Elsevier, 1141–1215, https://doi.org/10.1016/B978-0-12-824360-2.00029-2, 2020.

Raitzsch, M., Bijma, J., Bickert, T., Schulz, M., Holbourn, A., and Kučera, M.: Eccentricity-paced atmospheric carbon-dioxide variations across the middle Miocene climate transition, Climate of the Past, https://doi.org/10.5194/cp-2020-96, 2020.

Raitzsch, M., Bijma, J., Bickert, T., Schulz, M., Holbourn, A., and Kučera, M.: Atmospheric carbon dioxide variations across the middle Miocene climate transition, Climate of the Past, 17, 703–719, https://doi.org/10.5194/cp-17-703-2021, 2021.

Rasband, W. S.: ImageJ, 1997.

Rathmann, S. and Kuhnert, H.: Carbonate ion effect on Mg/Ca, Sr/Ca and stable isotopes on the benthic foraminifera *Oridorsalis umbonatus* off Namibia, Marine Micropaleontology, 66, 120–133, https://doi.org/10.1016/j.marmicro.2007.08.001, 2008.

Ravelo, A. C. and Wara, M. W.: The Role of the Tropical Oceans on Global Climate During a Warm Period and a Major Climate Transition, Oceanography, 17, 32–41, https://doi.org/10.5670/oceanog.2004.28, 2004.

Ruddiman, W. F.: A Paleoclimatic Enigma?, Science, 328, 838–839, https://doi.org/10.1126/science.1188292, 2010.

Rühlemann, C., Diekmann, B., Mulitza, S., and Frank, M.: Late Quaternary changes of western equatorial Atlantic surface circulation and Amazon lowland climate recorded in Ceará Rise deep-sea sediments, Paleoceanography, 16, 293–305, https://doi.org/10.1029/1999PA000474, 2001.

Salzmann, U., Williams, M., Haywood, A. M., Johnson, A. L. A., Kender, S., and Zalasiewicz, J.: Climate and environment of a Pliocene warm world, Palaeogeography, Palaeoclimatology, Palaeoecology, 309, 1–8, https://doi.org/10.1016/j.palaeo.2011.05.044, 2011.

Sarmiento, J. L. and Gruber, N.: Ocean biogeochemical dynamics, Princeton University Press, Princeton, 503 pp., 2006.

Sarmiento, J. L., Gruber, N., Brzezinski, M. A., and Dunne, J. P.: High-latitude controls of thermocline nutrients and low latitude biological productivity, Nature, 427, 56–60, https://doi.org/10.1038/nature02127, 2004.

Schlitzer, R.: Ocean Data View, 2018.

Seki, O., Foster, G. L., Schmidt, D. N., Mackensen, A., Kawamura, K., and Pancost, R. D.: Alkenone and boron-based Pliocene pCO_2 records, Earth and Planetary Science Letters, 292, 201–211, https://doi.org/10.1016/j.epsl.2010.01.037, 2010.

Shackleton, N. J. and Crowhurst, S.: Sediment fluxes based on an orbitally tuned time scale 5 Ma to 14 Ma, Site 926, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 69–82, https://doi.org/10.2973/odp.proc.sr.154.102.1997, 1997.

Shackleton, N. J., Crowhurst, S. J., Weedon, G. P., and Laskar, J.: Astronomical calibration of Oligocene--Miocene time, Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences, 357, 1907–1929, https://doi.org/10.1098/rsta.1999.0407, 1999.

Sirocko, F., Seelos, K., Schaber, K., Rein, B., Dreher, F., Diehl, M., Lehne, R., Jäger, K., Krbetschek, M., and Degering, D.: A late Eemian aridity pulse in central Europe during the last glacial inception, Nature, 436, 833–836, https://doi.org/10.1038/nature03905, 2005.

Stap, L. B., de Boer, B., Ziegler, M., Bintanja, R., Lourens, L. J., and van de Wal, R. S. W.: CO_2 over the past 5 million years: Continuous simulation and new δ^{11}B-based proxy data, Earth and Planetary Science Letters, 439, 1–10, https://doi.org/10.1016/j.epsl.2016.01.022, 2016.

Stolz, K. and Baumann, K.-H.: Changes in palaeoceanography and palaeoecology during Marine Isotope Stage (MIS) 5 in the eastern North Atlantic (ODP Site 980) deduced from calcareous nannoplankton observations, Palaeogeography, Palaeoclimatology, Palaeoecology, 292, 295-305, https://doi.org/10.1016/j.palaeo.2010.04.002, 2010.

Sutherland, R., Dos Santos, Z., Agnini, C., Alegret, L., Lam, A. R., Westerhold, T., Drake, M. K., Harper, D. T., Dallanave, E., Newsam, C., Cramwinckel, M. J., Dickens, G. R., Collot, J., Etienne, S. J. G., Bordenave, A., Stratford, W. R., Zhou, X., Li, H., and Asatryan, G.: Neogene Mass Accumulation Rate of Carbonate Sediment Across Northern Zealandia, Tasman Sea, Southwest Pacific, Paleoceanography and Paleoclimatology, 37, 2, https://doi.org/10.1029/2021PA004294, 2022.

Tiedemann, R. and Franz, S. O.: Deep-water circulation, chemistry, and terrigenous sediment supply in the equatorial Atlantic during the Pliocene, 3.3–2.6 Ma and 5–4.5 Ma, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 299–318, https://doi.org/10.2973/odp.proc.sr.154.120.1997, 1997.

Vervoort, P., Kirtland Turner, S., Rochholz, F., and Ridgwell, A.: Earth System Model Analysis of How Astronomical Forcing Is Imprinted Onto the Marine Geological Record: The Role of the Inorganic (Carbonate) Carbon Cycle and Feedbacks, Paleoceanography and Paleoclimatology, 36, 10, 20, https://doi.org/10.1029/2020PA004090, 2021.

Voelker, A. H. L., Rodrigues, T., Billups, K., Oppo, D., McManus, J., Stein, R., Hefter, J., and Grimalt, J. O.: Variations in mid-latitude North Atlantic surface water properties during the mid-Brunhes (MIS 9–14) and their implications for the thermohaline circulation, Climate of the Past, 6, 531–552, https://doi.org/10.5194/cp-6-531-2010, 2010.

Westerhold, T., Marwan, N., Drury, A. J., Liebrand, D., Agnini, C., Anagnostou, E., Barnet, J. S. K., Bohaty, S. M., De Vleeschouwer, D., Florindo, F., Frederichs, T., Hodell, D. A., Holbourn, A. E., Kroon, D., Lauretano, V., Littler, K., Lourens, L. J., Lyle, M., Pälike, H., Röhl, U., Tian, J., Wilkens, R. H., Wilson, P. A., and Zachos, J. C.: An astronomically dated record of Earth's climate and its predictability over the last 66 million years, Science, 369, 1383–1387, https://doi.org/10.1126/science.aba6853, 2020.

Wilkens, R. H., Westerhold, T., Drury, A. J., Lyle, M., Gorgas, T., and Tian, J.: Revisiting the Ceara Rise, equatorial Atlantic Ocean: isotope stratigraphy of ODP Leg 154 from 0 to 5 Ma, Climate of the Past, 13, 779–793, https://doi.org/10.5194/cp-13-779-2017, 2017.

Yasuhara, M., Wei, C.-L., Kucera, M., Costello, M. J., Tittensor, D. P., Kiessling, W., Bonebrake, T. C., Tabor, C. R., Feng, R., Baselga, A., Kretschmer, K., Kusumoto, B., and Kubota, Y.: Past and future decline of tropical pelagic biodiversity, Proceedings of the National Academy of Sciences USA, 117, 23, 12891–12896, https://doi.org/10.1073/pnas.1916923117, 2020.

You, Y., Huber, M., Muller, R. D., Poulsen, C. J., and Ribbe, J.: Simulation of the Middle Miocene Climate Optimum, Geophysical Research Letters, 36, L04702, 5, https://doi.org/10.1029/2008GL036571, 2009.

Zachos, J.: Trends, Rhythms, and Aberrations in Global Climate 65 Ma to Present, Science, 292, 686–693, https://doi.org/10.1126/science.1059412, 2001a.

Zachos, J. C.: Climate Response to Orbital Forcing Across the Oligocene-Miocene Boundary, Science, 292, 274–278, https://doi.org/10.1126/science.1058288, 2001b.

Zachos, J. C., Dickens, G. R., and Zeebe, R. E.: An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics, Nature, 451, 279–283, https://doi.org/10.1038/nature06588, 2008.

Zeeden, C., Hilgen, F., Westerhold, T., Lourens, L., Röhl, U., and Bickert, T.: Revised Miocene splice, astronomical tuning and calcareous plankton biochronology of ODP Site 926 between 5 and 14.4Ma, Palaeogeography, Palaeoclimatology, Palaeoecology, 369, 430–451, https://doi.org/10.1016/j.palaeo.2012.11.009, 2013.

Zeeden, C., Meyers, S. R., Lourens, L. J., and Hilgen, F. J.: Testing astronomically tuned age models, Paleoceanography, 30, 369–383, https://doi.org/10.1002/2014PA002762, 2015.

II.9 Appendix/supplements

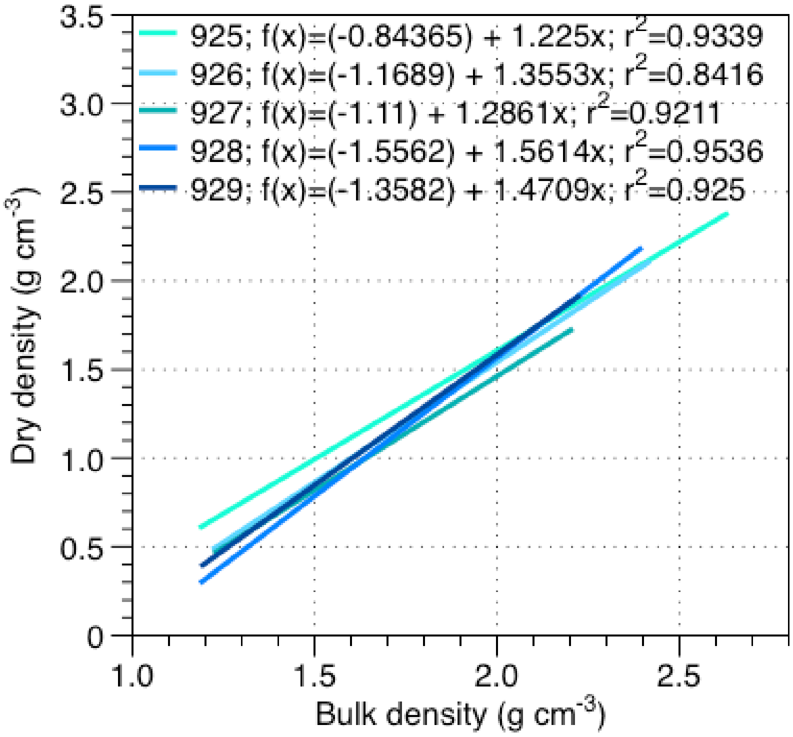

Figure S1. Regression curves for the gamma-ray attenuation (GRA) bulk density and DBD using data from Curry et al. (1995) for the five cores of the Leg 154.

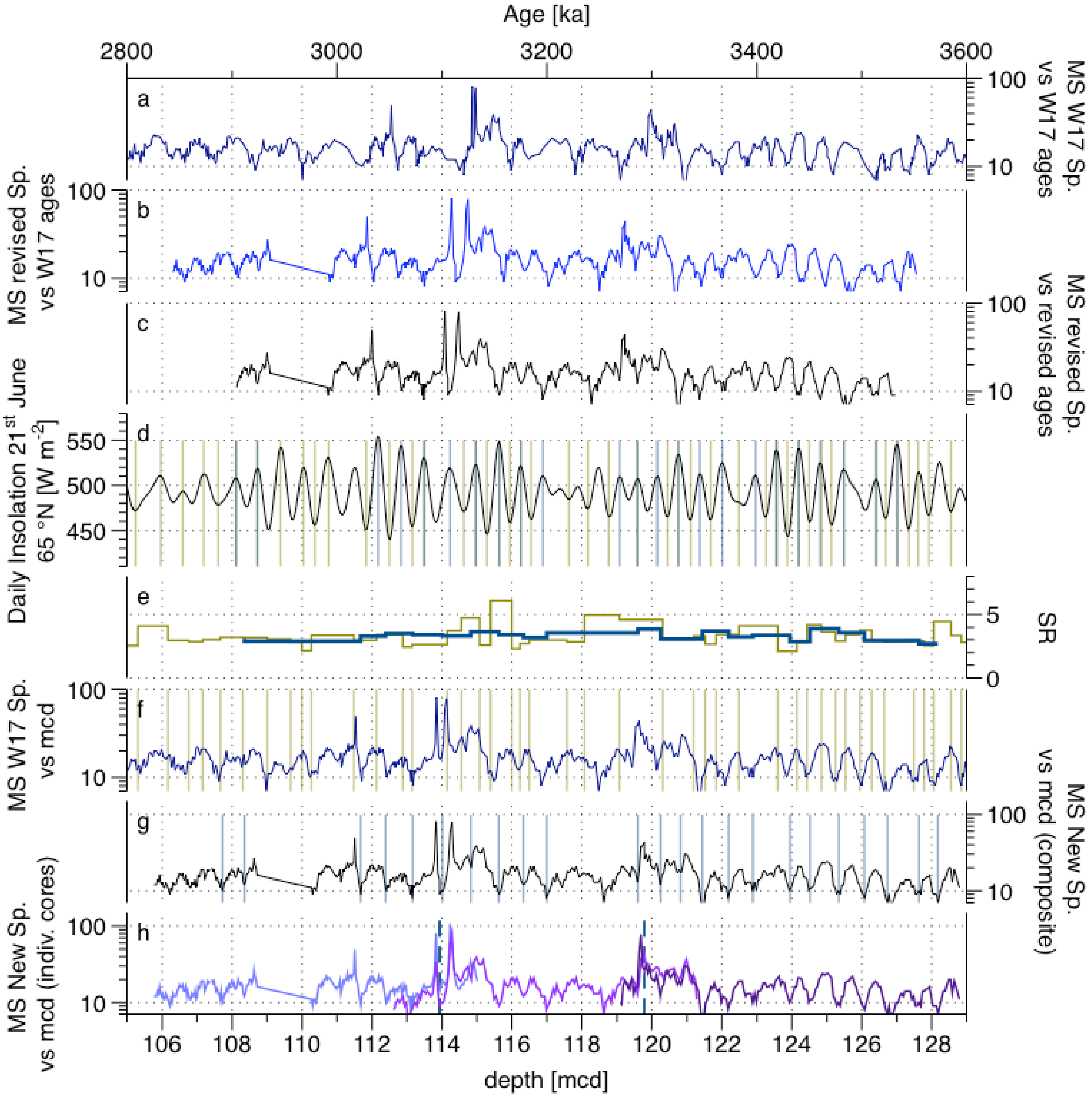

Figure S2. Comparison of the magnetic susceptibility (MS) records according to the different composite depths and age-model options for the Pliocene interval of this study. a) MS record versus age (Wilkens et al., 2017); b) MS record following the revised splice (Sect. 3.2.2) versus Wilkens et al. (2017) ages; c) MS record following the revised splice (Sect. 3.2.2.) versus revised age model ages (Sect. 3.2.2.); d) daily summer insolation 21st of June, 65°N (Laskar et al., 2004), the green lines correspond to the control points ages of Wilkens et al. (2017) age model and the blue lines correspond to the control points ages of the revised age model (Sect. 3.2.2.); e) comparison between the sedimentation rate of Wilkens et al. (2017) age model and the sedimentation rate of the revised age model (Sect. 3.2.2.); f) MS record versus depth (Wilkens et al., 2017), the green lines correspond to the control points composite depth of Wilkens et al. (2017)age model; g) MS record versus revised composite depth (Sect. 3.2.2.), the blue line correspond to the control points composite depths of the revised age model (Sect. 3.2.2.); h) Individual cores MS records versus revised composite depth (Sect. 3.2.2.), the blue dash lines correspond to the depths we switch from one individual core section to the other in the composite splice.

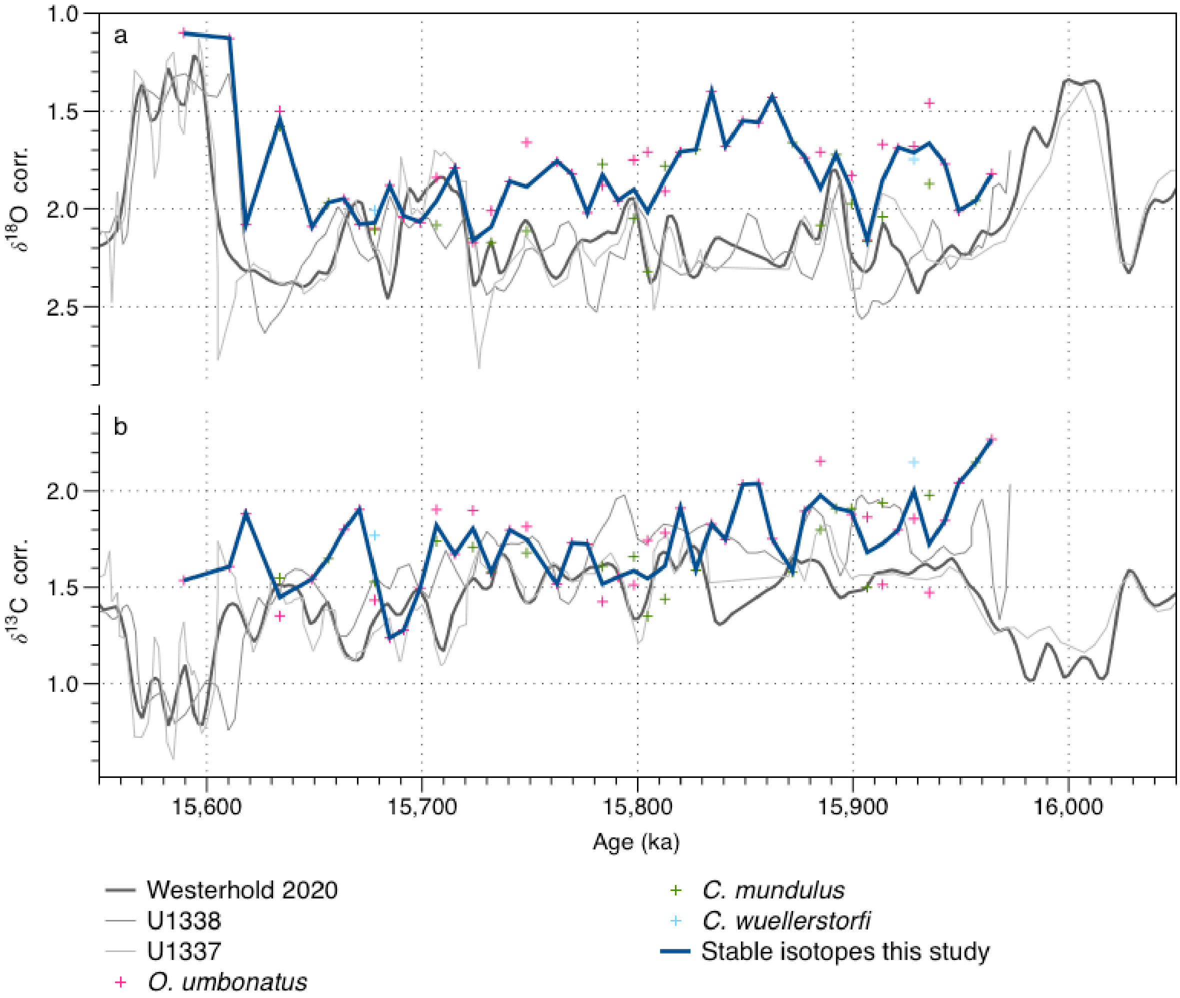

Figure S3. Stable isotopes analyses species-specific corrected and average record from this study compared to the stable isotopes loess smooth record (Westerhold et al., 2020) and stable isotopes record of sites U1338 and U1337 (Lyle et al., 2019) for both a) the δ ^{18}O and b) the δ ^{13}C.

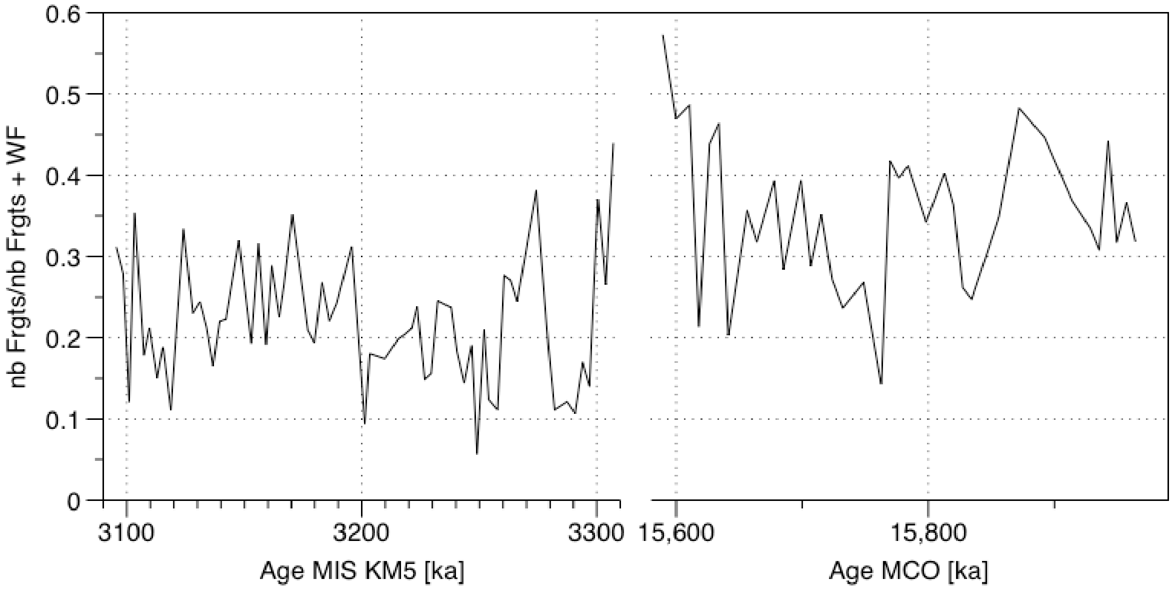

Figure S4. Fragmentation index (nb Frgts/nb Frgts + WF) in the <63 µm size fraction for both the Pliocene (MIS KM5) and the Miocene (MCO) intervals. Rarely above 0.40, a proof that there is no dissolution during these two time intervals, and particularly for this size fraction.

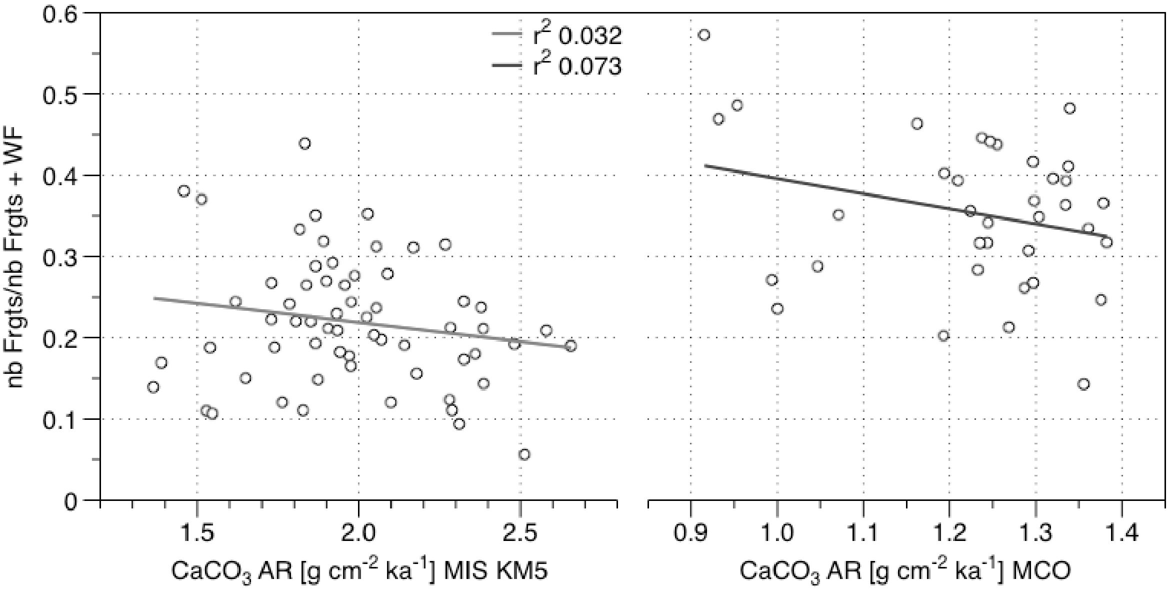

Figure S5. Correlation plots between the $CaCO_3$ AR and the fragmentation index (nb Frgts/nb Frgts + WF) in the <63 µm size fraction for both the Pliocene (MIS KM5) and the Miocene (MCO) intervals. The r^2 are really small and not significant for the two time intervals represented.

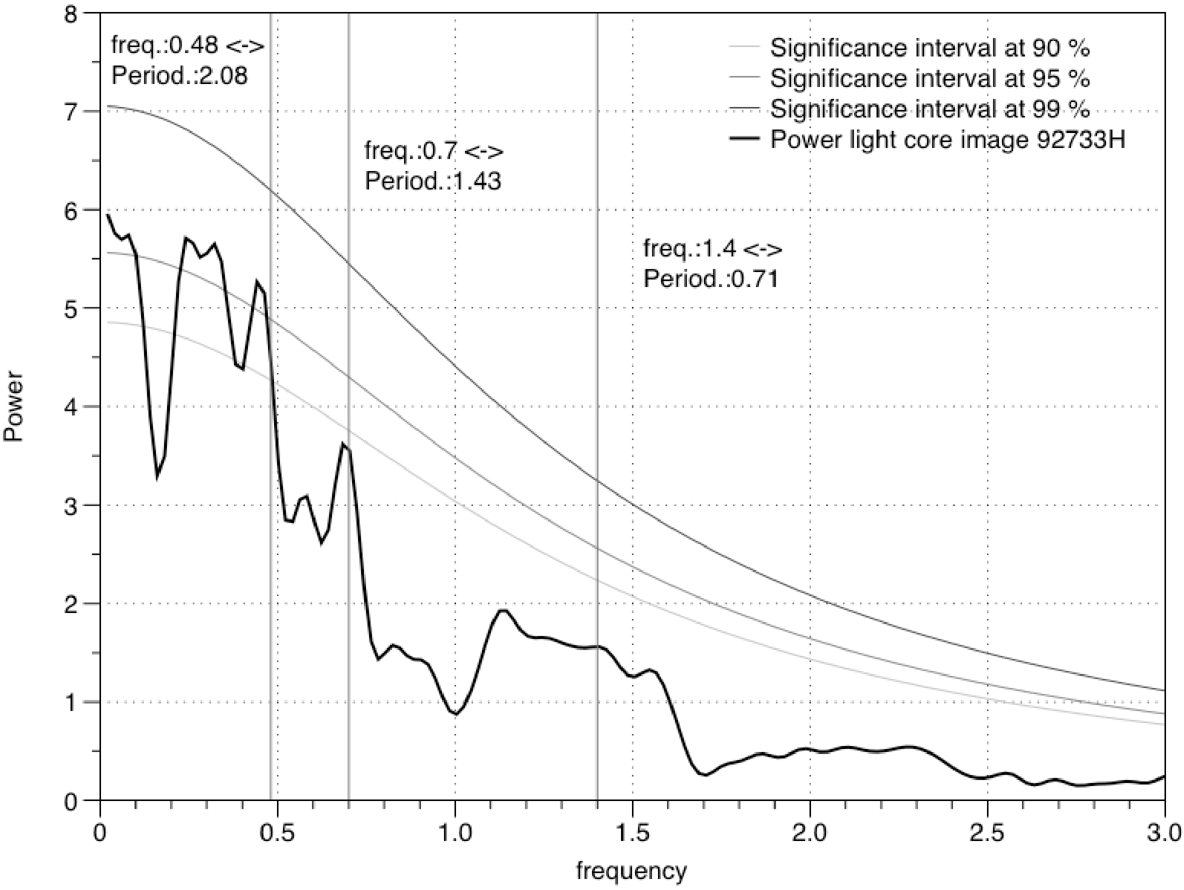

Figure S6. MTM spectral analyses of the light curve of delighted core image 927 33H versus depth (mcd).

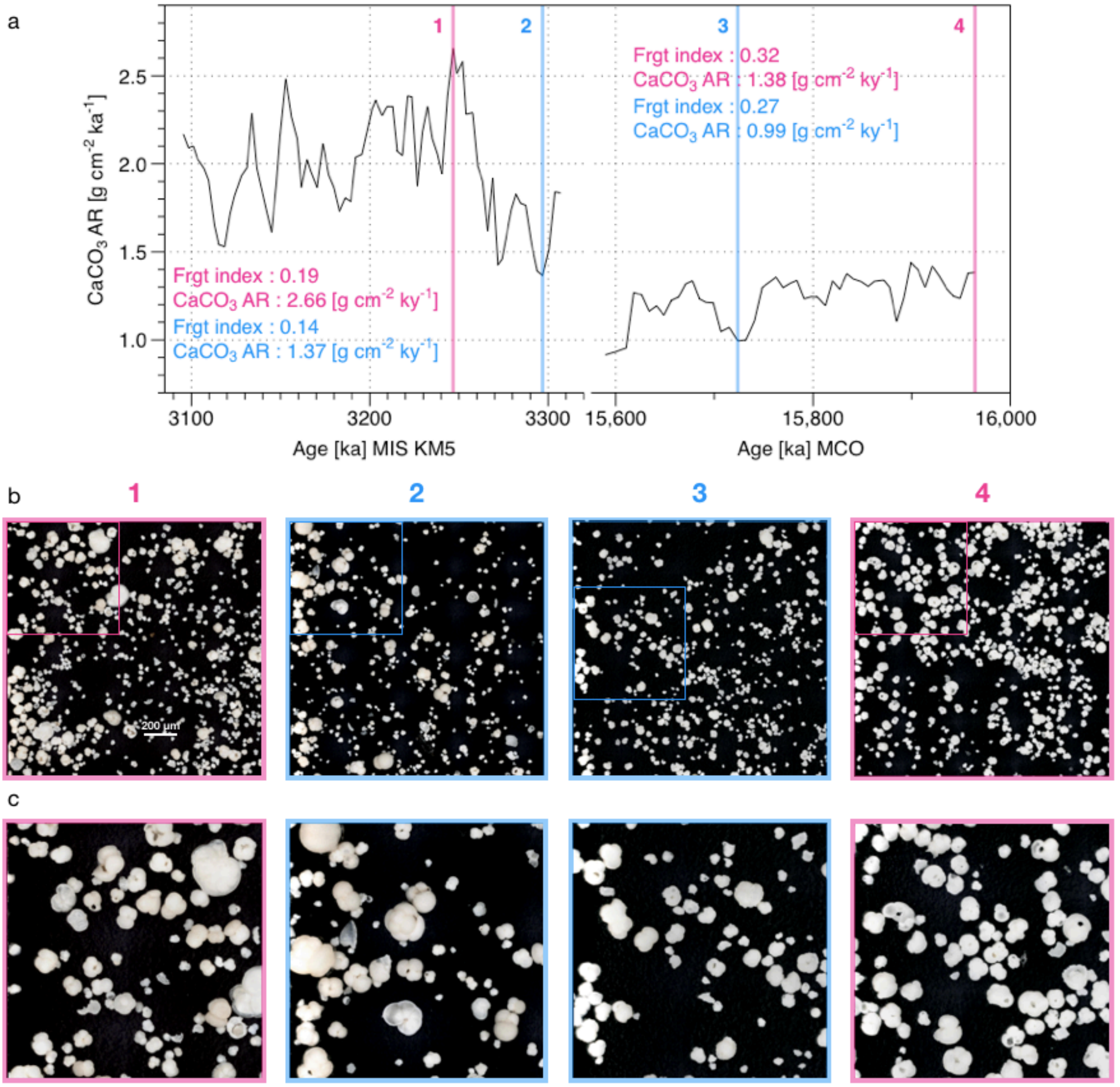

Figure S7. Pictures of the >63 µm size fraction of the samples with high (pink) and low (blue) $CaCO_3$ AR for both the Pliocene and the Miocene intervals (b) and zoom on those pictures (c). The fragmentation index values and the $CaCO_3$ AR of the chosen samples are given with a text colour corresponding to the lines highlighting the position of the samples on the curves (a).

Chapter III. Orbital-scale variability in the contribution of foraminifera and coccolithophores to pelagic carbonate production

(manuscript in preparation)

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Abstract

Throughout the Cenozoic, calcareous nannoplankton and planktonic foraminifera were the main producers of pelagic carbonate preserved on the seafloor. While past variability in pelagic carbonate production has been previously studied, relatively little is known about the variability in the contribution of the two components. This is important because the different responses of the two groups could amplify or reduce the fluctuations in total carbonate production. Here we present new data from the tropical Atlantic that allow us to quantify changes in the relative contribution of the two groups on orbital scales and between periods of different climate states since the Miocene. We find that the contribution of the planktonic foraminifera and the coccolithophores to the deposited pelagic carbonate remained similar (within 30%) on long time scales, but varied by up to a factor of two on orbital time scales. We show that the nature of the variability has changed fundamentally since the Miocene. The contribution of planktonic foraminifera did not correlate with the total pelagic carbonate production, neither in the Pliocene, where the dominant cyclicity was in the precession band and in phase, nor in the Miocene, when the predominant cyclicity was in the eccentricity band and in antiphase. Collectively, these results reveal a previously unnoted significant variability in tropical pelagic carbonate productivity between foraminifera and coccolithophores, suggesting that these calcifiers reacted fundamentally differently to orbital forcing in the tropical ocean.

III.1 Introduction

The biomineralisation of carbonate by pelagic calcifiers (planktonic foraminifera and calcareous nannofossils) is a key element of the marine carbon cycle, facilitating the long-term removal of carbon into the sedimentary reservoir (Landschützer et al., 2014). This reservoir interacts with the marine carbon cycle in various ways, such as chemical compensation, where sedimentary carbonate dissolution can compensate changes in ocean carbonate chemistry, and biological compensation, which refers to changes in the amount of carbonate biomineralisation, removing dissolved carbonate and bicarbonate, thereby lowering oceanic alkalinity (Boudreau et al., 2018). Remarkably, modelling studies show that a change in carbonate production of only 10% on short (ka) to geological time scales would be sufficient to affect the marine carbon cycle. A global decrease in carbonate biomineralisation would lead to a higher alkalinity and, thus, to a higher capacity of the ocean to absorb dissolved CO_2 (Boudreau et al., 2018). Both biological and chemical compensation depend not only on the total amount of oceanic biomineralisation, but also on the composition of the deposited carbonate (Si and Rosenthal, 2019). This is because the main components of the pelagic calcite flux to the seafloor, planktonic foraminifera and calcareous nannoplanktons, produce skeletons of very different sizes and shapes and thus different sinking behaviour and susceptibility to dissolution. Calcareous nannoplanktons are up to two orders of magnitude smaller than foraminifera shells, but can sink rapidly as they are often concentrated in faecal pellets (Ziveri et al., 2007; Richardson and Jackson, 2007; Fischer and Karakaş, 2009). The shells of foraminifera are composed of mesocrystalline material with a large surface-to-volume ratio, making their shells more susceptible to dissolution (Honjo and Erez, 1978; Frenz et al., 2005).

While total pelagic calcite production and burial and its changes on geological time scales have been intensively studied locally and globally, the relative contribution of planktonic foraminifera and coccolithophores to the burial flux remains less well constrained. Estimates of the current contribution of coccoliths to the biogenic calcite exported from the photic zone in the modern ocean vary between 20 and 80 % (Baumann et al., 2004; Frenz et al., 2006; Schiebel, 2002; Ramaswamy and Gaye, 2006; Frenz et al., 2005), and there is strong evidence that the composition of the pelagic carbonate flux varied on geological time scales (Chiu and Broecker, 2008; Si and Rosenthal, 2019). There are three factors that can influence the bulk composition of pelagic carbonate arriving to the seafloor: the population size of the producers, their mean cell size, and their investment in biomineralisation relative to cell size. Because coccolithophores and planktonic foraminifera follow different lifestyles, have different metabolisms, and have different environmental preferences, they may respond differently to environmental change with respect to each of the three factors, resulting in differences in the pelagic calcite flux composition (Langer, 2008; Gehlen et al., 2007; Si and Rosenthal, 2019). Si and Rosenthal (2019) show a long geological time scale shift towards more foraminifera and proportionally less coccoliths towards the Quaternary and explain it to be due to long-term weathering alkalinity change towards a decrease related to the pCO_2 modulation. In our study presented here, we investigate these variations at orbital time scale. To understand to what degree the composition of pelagic carbonate flux varied in the past and to qualify and quantify the changes in the differential contribution of the two mains pelagic calcifiers to the total pelagic carbonate production, estimated from carbonate accumulation rate ($CaCO_3$ AR) (Brummer and van Eijden, 1992; Liebrand et al., 2016), we generated new data for Leg 154 ODP Site 927, Ceará Rise. Here we know that carbonate preservation was good during Quaternary interglacials and throughout the Neogene (Curry et al., 1995) and where the site remained in a tropical setting throughout while at the same time we recorded orbital cyclicity of sediment properties, allowing tuned age model and quantification of flux with high resolution. Pelagic carbonate production varies on both orbital and geological timescales (e.g. Si and Rosenthal, 2019; Beaufort et al., 1997, 2022), thus we sampled at a resolution allowing us to resolve orbital cycles. In all cases, we determined the contribution of coccoliths and foraminifera to the same samples and used two independent methods to estimate the coccoliths fraction. This study focuses on four time intervals known to be potential analogs for today’s climate warming conditions: the marine isotopic stage (MIS) 5 (87.5 to 150.2 ka, Clark and Huybers, 2009; Kopp et al., 2009), the MIS 9 (276.4 to 370.3 ka, Past Interglacials Working Group of PAGES, 2016; Voelker et al., 2010), the Pliocene warm period (PWP, MIS KM5, 3095.5 to 3307 ka, Ravelo et al., 2004) and the Miocene climatic optimum (MCO, 15.6 to 16 Ma, Pound et al., 2012; You et al., 2009; Foster et al., 2012; Zachos et al., 2008).

III.2 Material and Methods

ODP Site 927 on the Ceará Rise in the western tropical Atlantic Ocean (5°27.77'N, 44°28.84'W, 3315 metres below sea level (m.b.s.l.)) is located above the modern regional lysocline (4200 mbsl, Frenz et al., 2006; Curry et al., 1995; Cullen and Curry, 1997). However, the depth of the lysocline has varied in the past, and some of the shoaling episodes has resulted in the site being affected by carbonate dissolution. Such episodes are known from the glacial periods of the late Quaternary and are related to the restructuring of the Atlantic Meridional Overturning Circulation (AMOC) and an increased influence of the more corrosive Antarctic bottom waters (Gröger et al., 2003b). During the studied intervals of the Pliocene and Miocene, no such events occurred at this site. The corresponding sediments from these intervals are rich in carbonate, show no relationship between carbonate content and carbonate flux, and the preservation of planktonic foraminifera shells is always good, indicating deposition above the regional lysocline (Curry et al., 1995; Gröger et al., 2003b). The location of this site is far from the high-latitude climate changes and large-scale temperature variations at different time scales. From this site, we already have a set of samples corresponding to these four time intervals, of which we already know the carbonate content and have a high resolution tuned age model (Cornuault et al., 2023). Thanks to their good state of preservation, their high carbonate content and their orbital resolution, the samples allow us to study both the planktonic foraminifera and the coccoliths in the same samples, preventing a possible bias on the relative changes between the two groups in respect to timing (and potential lags) of their response.

III.2.i Coccolithophores and foraminifera samples preparation

To quantify the coccolithophore $CaCO_3$ contained in the <32 μm fraction, we prepared microscope slides using a quantitative protocol to determine the amount of sediment <32 μm on the slide and the amount of carbonate <32 μm it contained. We produced a random and even distribution of the material on the slide. The protocol for random settling used in this study for the four periods of interest is very close to the one presented by Beaufort et al. (2014). In this protocol, a very tiny quantity of sediment is disaggregated in water in a vial and poured in a receiver containing a 12mm x 12 mm coverslip, over a <32 μm mesh metal sieve. This is left for settling over 4h, after which the water is gently drained out from the top and the receiver with the coverslip is put in the oven overnight to dry. The coverslips are weighted before and after so we know exactly the amount of material on each of them. We then mount them on slides using NOA74 glue, mounting 8 samples per slide for automated analysis. The exception to Beaufort et al. (2014) protocol is that we used ~ 0.1 mm3 of bulk sediment in 1 mL of Volvic water in a 15 mL centrifugation falcon instead of the quantities they mention. The tube is placed in a vortex for approximately 30 seconds at medium speed and then in an ultrasonic bath for around 8 seconds at medium power to obtain a very homogenous solution. The lamella are placed in the bottom of the settling supports developed by Tetard M. and the obtained solution is poured over a 32 μm mesh metal sieve, itself above a glass funnel and the receiver in which the settling will be done. All the supports containing the lamellae are placed in the oven at 50 °C for 24 h.

Concerning the foraminifera size fraction analysis, as we considered most of the foraminifera to be above 63 μm, and that there is not so much material other than foraminifera above 63 μm (Si and Rosenthal, 2019). The bulk sediment samples were disaggregated in tap water in centrifugation 15 mL falcons placed in rotating carousel overnight and washed and sieved at 63 μm (the quantity of foraminifera fragments below 63 μm is not significant, Chiu and Broecker, 2008). Because at this location the carbonate is mainly composed of foraminifera and coccoliths (Curry et al., 1995), we suppose that the coarse fraction is composed of 100 % of foraminifera calcium carbonate. The dry bulk sediment (DBS) and coarse fraction of the sediment are weighed in order to calculate the proportion of the coarse fraction relative to the dry bulk sediment: Coarse fraction (>63 µm) % = (>63 µm (g) / DBS (g))*100

III.2.ii Contribution of the small and coarse fraction to the total carbonate

To characterise the contribution of the planktonic foraminifera and the coccoliths to the total carbonate, we have used two different and independent approaches. First, we assumed that the majority of the foraminifera shells and the coccoliths can be separated by size. Specifically, following Si and Rosenthal (2019), we assumed that the >63 µm size fraction is composed at 100 % of foraminifera $CaCO_3$ (Si and Rosenthal, 2019). Second, to explore the effect of the simplification of using 63 µm as a size threshold, we generated an independent record of coccolith fraction $CaCO_3$ AR (based on automated image analysis of the <32 µm size fraction of the sediment).

For the first approach, knowing the bulk carbonate content (Cornuault et al., 2023) and the coarse fraction carbonate over the dry bulk sediment (see above), we can calculate the percentage of the contribution of the <63 µm size fraction to the total carbonate content and so $CaCO_3$ AR. Following the direct approach by Si and Rosenthal (2019), we can also calculate the contribution of the coccoliths, considering that $CaCO_3$ AR cocco = $CaCO_3$ AR bulk - $CaCO_3$ AR foram. For each of the class sizes, using the sedimentation rate (SR) values and the dry bulk density (DBD), we can then derive the $CaCO_3$ AR: $CaCO_3$ AR = ($CaCO_3$ % / 100) x DBD x SR as a pelagic carbonate production proxy (Liebrand et al., 2016).

However, because the <63 µm size fraction may contain non-coccoliths carbonate particles, we used an independent method to estimate the small fraction carbonate content, using automated microscope analysis. The resulting output is not directly comparable to the first data results, but gives an alternate estimation of how the carbonate contribution of the small fraction has changed through the time from Miocene to present and within each time interval (Figures 3, S2 and S3).

These automated microscope analyses are processed using SYRACO device that automatically takes optical microscope pictures at analyzed polarized light (Beaufort et al., 2014; Beaufort and Dollfus, 2004) and provides an estimation of the weight of calcite per coccolith analysed and the total mass of calcite contained on the analysed field of view (FOV). Knowing the number of FOV analysed and the number of FOV on the whole lamella, we can calculate the quantity of carbonate in the small fraction on the whole lamella. As we know the quantity of bulk carbonate on the slide, we can then calculate the carbonate content of the small fraction, as the ratio between the carbonate mass estimated by SYRACO and the mass of bulk sediment.

III.2.iii Spectral analysis

To see whether these changes are orbitally driven or not, we performed a Wavelet Transform (WT) spectral analysis (WaveletComp 1.1 package on R, Roesch and Schmidbauer, 2018) using R (4.1.2., R Core Team, 2021) for all parameters for the Pliocene and the Miocene intervals (not for the Quaternary, as these two time intervals are marked by strong precession-paced dissolution cycles, Harris et al., 1997). Additionally, to observe the actual relationship between the change in the relative contribution of the two size fractions and the environmental conditions at orbital time scale, we compared our results to an E+T-P record (Laskar et al., 2004) that reflects the different orbital parameters.

III.3 results

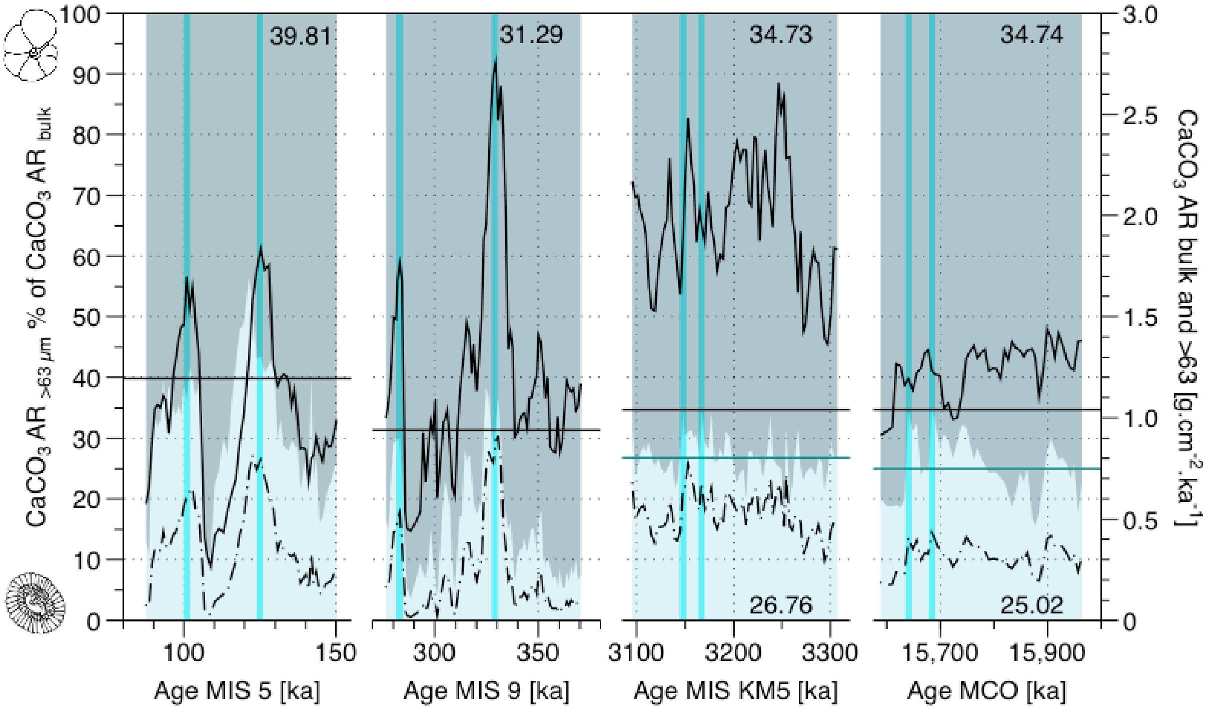

Figure 1. Quantification of variability of the >63 µm carbonate contribution to the total $CaCO_3$ AR between / within the time intervals from MCO to MIS 5 (filling) and $CaCO_3$ AR of the total (black plain line) and >63 µm size fractions (black dash line). The two values used for the calculation of the average value of contribution of the coarse to the total $CaCO_3$ AR are the ones highlighted by the vertical blue lines (for the Quaternary, they corresponds to the samples having the highest total $CaCO_3$ AR, to avoid the samples possibly affected by dissolution, and for the MIS KM5 and MCO, they correspond to the highest values of the contribution of the coarse fraction to the total $CaCO_3$ AR). The average values of the contribution of the coarse fraction to the bulk carbonate accumulation rate taking in account the two highest points of the intervals are materialised by the horizontal black lines. For the MIS KM5 and MCO, the blue horizontal lines represent the average value of the contribution of the coarse fraction to the bulk for the whole interval (all the values corresponding to the horizontal lines are written on the panels).

The estimated contribution of foraminifera to the sedimentary carbonate based on particle size fractionation varies between 3.5 % and 56.4 % (Figure 1). The largest variations are observed in the Quaternary, which is related to the different susceptibility of foraminifera and coccoliths to carbonate dissolution, which affected the Ceará Rise sediments during Quaternary glacials. However, a variability on orbital scales was also present during the Pliocene and Miocene (Figure 1) and is also evident in the record of coccolith fraction accumulation obtained by the SYRACO method (Figure 2). In contrast to the strong and consistent variability on orbital time scales, the peak values of foraminifera fraction contribution for the four intervals studied were remarkably similar, ranging between 31.3 % for MIS 9 and 39.8 % for MIS 5 (Figure 1).

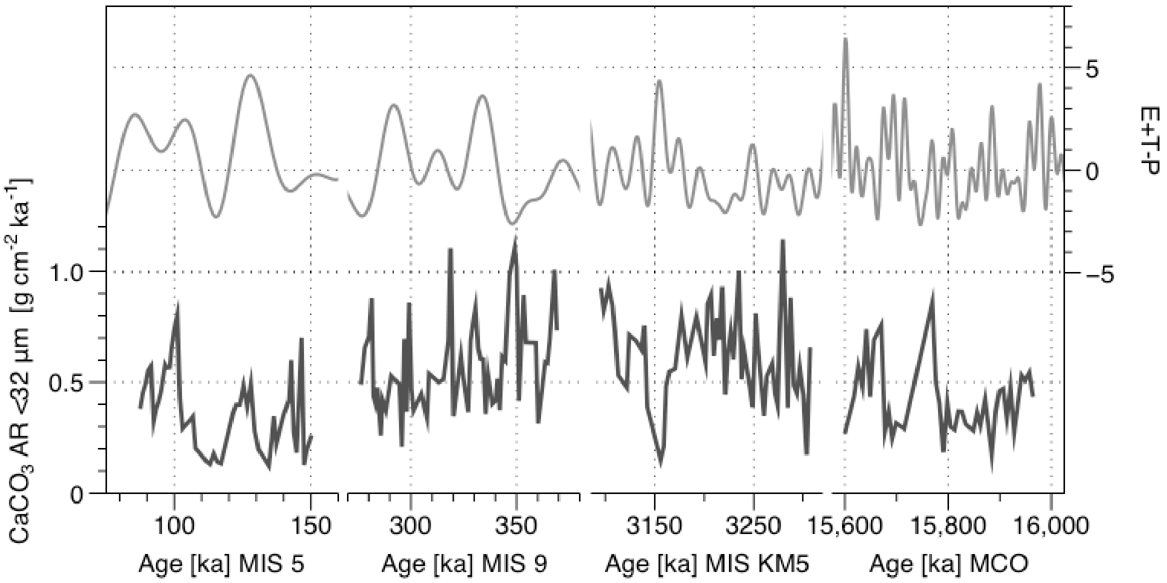

Figure 2. $CaCO_3$ AR <32 µm from MCO to MIS 5 -SYRACO- compared with E+T-P (Laskar et al., 2004).

This is consistent with the effect of dissolution on sediment composition during Quaternary glacials, and the strong positive correlation between foraminifera fraction contribution to the total $CaCO_3$ AR and bulk carbonate flux in the Quaternary intervals (Figure 3). In contrast, the composition of the carbonate flux shows no relationship with bulk carbonate flux during Pliocene and Miocene (Figure 3).

During the Neogene, the contribution of the coarse fraction (foraminifera) to the $CaCO_3$ AR bulk and the $CaCO_3$ AR bulk do not co-vary, and they are in phase during the MIS KM5 and in antiphase during the MCO (Fig 1). Moreover, for the Miocene, the $CaCO_3$ AR bulk is showing lower amplitude changes than the contribution of the coarse fraction to it, whereas for the Pliocene, it is the reverse (Figure 1). During the Quaternary, the contribution of the coarse fraction (Figure 1 and 2) is driven by foraminifera dissolution (more sensitive than coccoliths, Frenz et al., 2005; Gröger et al., 2003a) due to deep ocean circulation changes (Curry et al., 1995; Harris et al., 1997). On a long geological time scale, we observe a 37 % increase from the Miocene to the Pleistocene (taking in account maxima values average) but very similar average values between the Miocene and the Pleistocene (Figure 2).

The variability within time intervals is larger than between the time intervals and the orbital scale variability within each time interval is the larger component of variability (63 % and 78 % amplitude, respectively for the Pliocene and the Miocene).

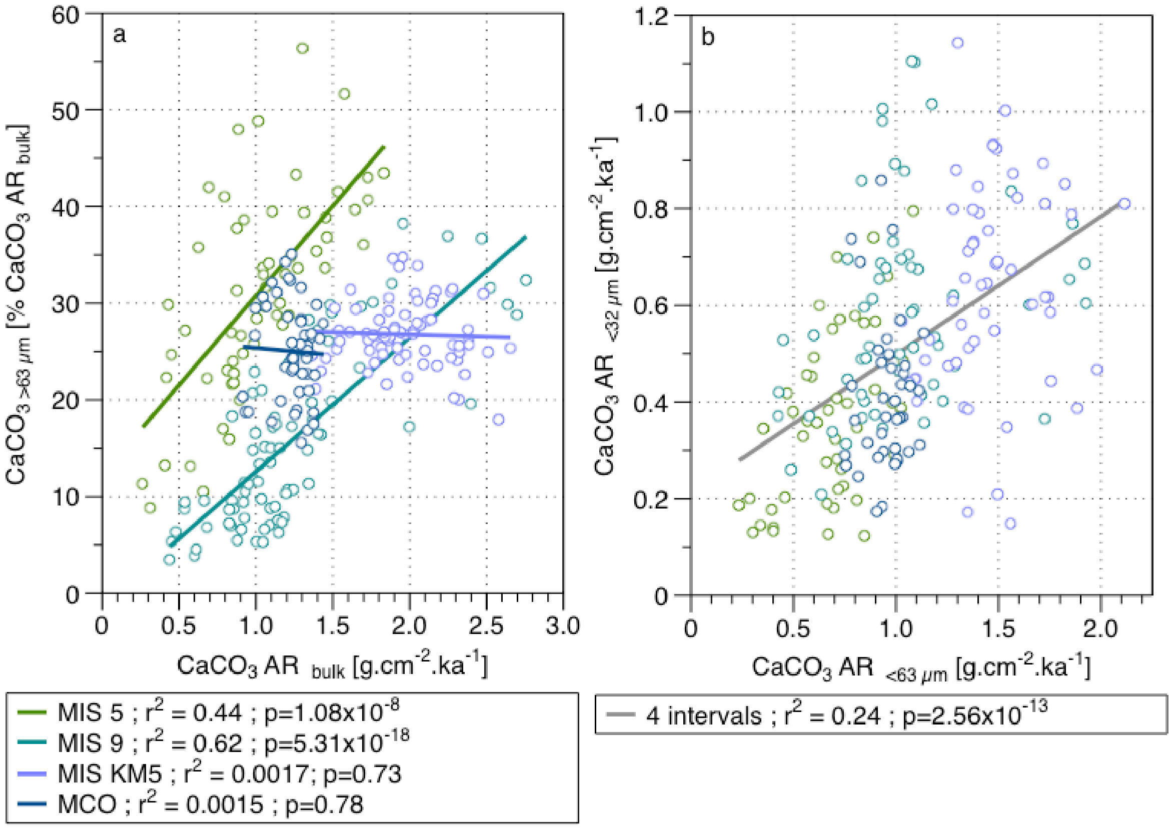

Figure 3. a) Contribution of the >63 µm fraction to the total CaCO$_3$ AR vs bulk CaCO$_3$ AR and b) <32 µm CaCO$_3$ AR (SYRACO) vs <63 µm CaCO$_3$ AR.

To test whether the relative contribution of the two size fraction is related to the total CaCO$_3$ AR or not, we plotted the contribution of the coarse fraction to the bulk CaCO$_3$ AR vs the CaCO$_3$ AR bulk (Figure 3a). Additionally, to test if our simplification is correct, we plotted the CaCO$_3$ AR <32 µm estimated using SYRACO device over the CaCO$_3$ AR <63 µm estimated using Si and Rosenthal (2019) approach. Since this is the same parameter estimated with two different methods, we do not make the distinction between the four intervals for this second correlation panel, as it should be varying the same way (Figure 3b).

There is no correlation between the coarse fraction contribution to the total CaCO$_3$ AR and the bulk CaCO$_3$ AR (almost horizontal regression curves) so the relative contribution of the two pelagic calcifiers isn't driving the total bulk CaCO$_3$AR (Figure 3a). Furthermore, for the four intervals, we observe a good positive correlation between the CaCO$_3$ AR estimation of the small fraction of the two methods for the four intervals (r^2 = 0.24) and not so many points above the 1 to 1 line, as expected (Figure 3b).

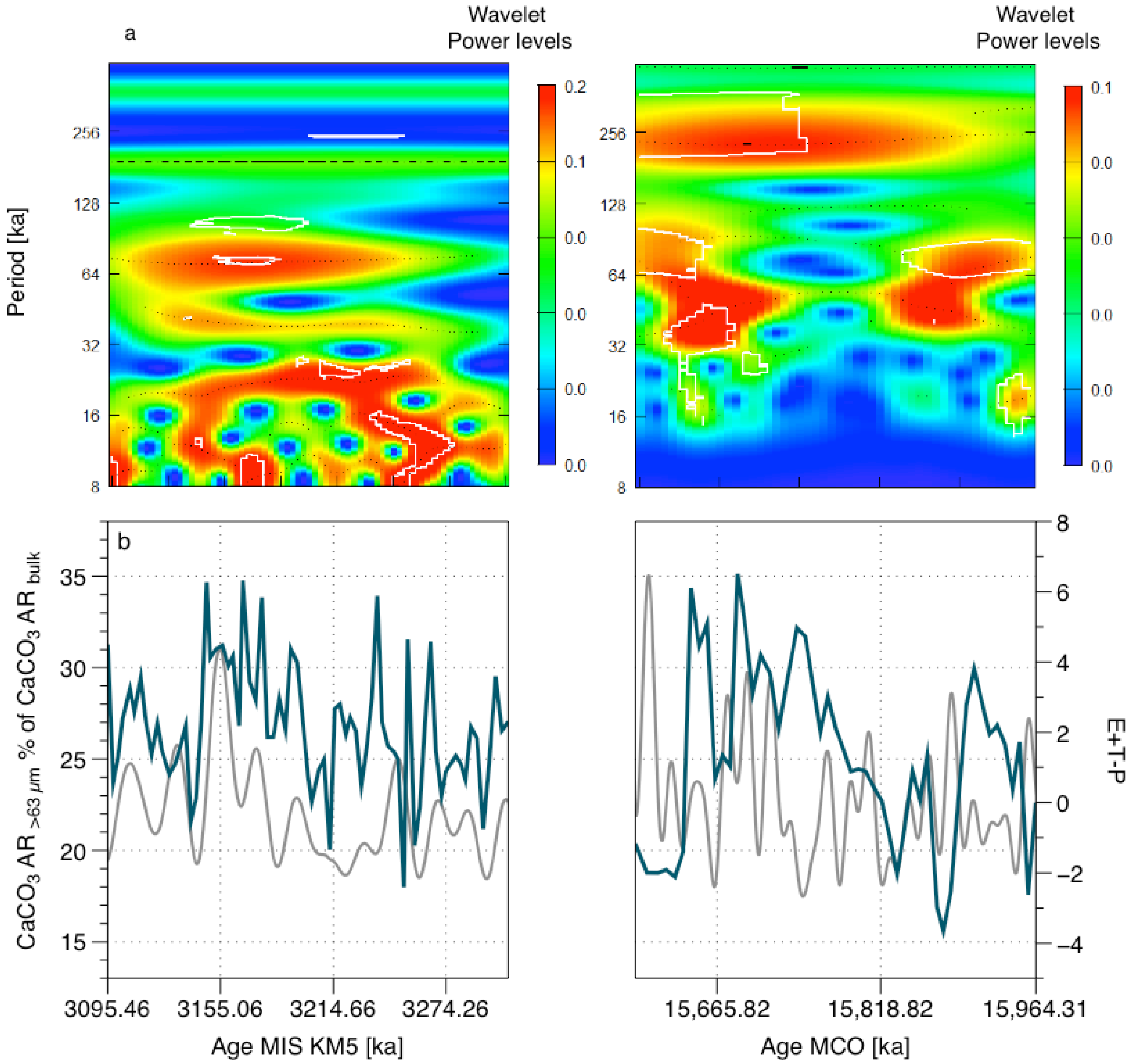

Figure 4. a) Wavelet transform coarse fraction percentage of bulk $CaCO_3$ AR for both MIS KM5 and MCO, significance value on the figure = 0.1, b) coarse fraction contribution to bulk $CaCO_3$ AR and the actual E+T-P (Laskar et al., 2004).

For the MIS KM5, we observe a clear and continuous precession imprint around 20 ka periodicity from 3100 ka to 3270 ka which seems to be changing towards shorter cycles through time, an obliquity imprint (around 41 ka periodicity) and a distinct 100 ka eccentricity periodicity that is ranging from 3140 ka to 3230 ka more or less. Compared to an E+T-P curve, we see this single 100 ka cycle by the naked eye and the obliquity, playing a subordinate but not negligible role. Concerning the MCO, we see an indication of a 41 ka (obliquity) imprint from 15589 ka to 15900 ka. We cannot observe shorter periodicities as the sampling resolution wouldn't allow us to see it. The relative contribution of the >63 µm to the bulk $CaCO_3$ AR is in phase with the ETP in the Pliocene and in antiphase with the ETP during the Miocene (as for the bulk $CaCO_3$ AR, Chapter #II) (Figure 4).

We found 100 ka (eccentricity) periodicities in the >63 µm $CaCO_3$ AR and the <32 µm $CaCO_3$ AR (MIS KM5 and MCO), and the <32 µm $CaCO_3$AR seems to be responding to 100 ka antiphased with a high AR when low eccentricity and low AR when high eccentricity (S1, S3). Additionally, we observe a 21 ka (precession) periodicity during the MIS KM5 and 41 ka (obliquity) periodicity during the MCO for the >63 µm $CaCO_3$ AR and the >63 µm $CaCO_3$ AR (S1, S2).

The >63 µm $CaCO_3$ AR and <32 µm $CaCO_3$ AR are in phased with E+T-P in the Pliocene, except during the peak of warmth of the PWP and antiphased during the MCO, suggesting that the coarse fraction (foraminifera) is responding in phase with E+T-P when the conditions are colder and in antiphase with E+T-P when we are at a strong warm peak (PWP middle and all the Miocene interval chosen for this study). Even if the values are different, the variability is consistent between the <63 µm $CaCO_3$ AR (direct approach) and the <32 µm $CaCO_3$ AR (independent) SYRACO approach (Figure 3b).

III.4 Discussion

There is an increase of the relative contribution of foraminifera from Miocene to Quaternary (or decrease of the coccoliths contribution) coherent with what has been founded by Si and Rosenthal (2019). Furthermore, we observe different variability of the relative contribution of foraminifera and coccoliths within the Pliocene and the Miocene so the two main carbonate producers are responding differently for those two periods and the phase relationship between the $CaCO_3$ AR bulk and the foraminifera contribution to it is changing between the Pliocene and the Miocene (Figure 1). For the both time intervals, we do not observe any correlation between the contribution of the coarse fraction to the total pelagic carbonate production and the carbonate production itself (Figure 3), meaning that the changes in the relative contribution of the two main pelagic carbonate producers is not driving the changes in total $CaCO_3$ production (except concerning the Quaternary cold events, where the correlation is a proof of the preferential dissolution of the planktonic foraminifera in presence of dissolution). For the Pliocene and the Miocene, we observe large changes in the correlations between the different size fractions and the bulk $CaCO_3$ AR, and additionally, a large amplitude variability of the coarse fraction contribution to the bulk $CaCO_3$ AR within these two time intervals, highlighting that the relative contribution of the two main pelagic carbonate calcifiers, if remains similar on geological time scale, has changed a lot on shorter orbital time scale. For both the Pliocene and the Miocene, it isn't the coarse fraction $CaCO_3$ production which is driving the $CaCO_3$ AR bulk changes, but the <63 µm $CaCO_3$ production. This means that the two main pelagic carbonate producers responded differently, and that the coccolithophores relative contribution seems to be driving the overall changes. We found a coarse fraction contribution of about 20 to 30 %, realistic and coherent with recent findings by Si and Rosenthal (2019), and Drury et al. (2021). The production within the two groups is changing synchronously and in the same direction but with different amplitudes at both geological and orbital time scale), making their relative contribution to the $CaCO_3$ AR bulk to change.

According to the observations of the WT and $CaCO_3$ AR records vs time (Figures S1-S3), the foraminifera and the coccoliths are not responding to the same orbital parameter and not the same way: the changes of $CaCO_3$ AR of the two groups doesn't seems to covary or being linked by any correlation, meaning that they are changing through the time, but 1) do not seems to be linked and 2) do not seems to be responding to the same forcing, which could also explain the different frequencies observed in the bulk $CaCO_3$ AR record (Chapter #II): one frequency tracking coarse (foraminifera) and one frequency tracking small (coccolithophores) fraction. There is an equilibrium on long time scales between the two groups, so when the $CaCO_3$ AR bulk is increasing, the two groups are increasing, but not necessarily the same amplitude (e.g. between the Miocene and the Pliocene). We emit the idea of a stronger influence of the eccentricity changes on the nannoplankton, for example, as an increase of eccentricity corresponds to an increase of the mean annual solar insolation at all the latitudes (Goosse, 2015) and the nannoplankton are doing photosynthesis, and so, might be highly affected by these changes. Furthermore, some studies are highlighting the high sensitivity of the coccoliths production to eccentricity changes (e.g. Drury et al., 2021; Beaufort et al., 1997, 2022). The orbitally forced variability within the different time intervals has changed a lot and is different between the two groups. As the two mains pelagic calcifiers does not seems to be responding to the same forcing within each time interval, we can expect that if the conditions are drastically changing, it can affect one of the two groups and not the other, affecting the ocean alkalinity and ocean capacity to absorb CO_2 (by biomineralisation processes, Boudreau et al., 2018). When the climate is warmer, we have more carbonate produced by the two groups, with a response of the coccoliths which seems to be stronger during the PWP than the MCO. Furthermore, we observe an increase of the relative contribution of the coarse fraction, so if both the foraminifera and the coccoliths productivity is increasing, the foraminifera productivity seems to be responding with stronger amplitude, making it relative contribution to the total pelagic carbonate production higher. So can we expect an increase in the role of the foraminifera in the surface ocean anthropogenic carbon absorption in the future with warmer climates? Our results are in line with those obtained by Schwab et al. (2013) and Stolz and Baumann (2010) who find a high coccoliths productivity during the MIS 5e, even if during this interval, the coarse fraction increased that much that there is a relative increase of the foraminifera fraction in the sediment.

Our results are also aligned with Holbourn et al. (2014) results, with a lower coarse fraction proportion centred in the MCO interval (corresponding to the lower $d^{18}O$ values. It is possible that above a certain temperature threshold (or CO_2 threshold) the response of the carbonate producers' changes: as the contribution of the coarse fraction is in phase during the Pliocene and antiphase during the Miocene, we suggest that above a certain temperature (or more generally, in some extreme environmental condition) the pelagic carbonate production (especially the planktonic foraminifera) drops. This could be explained as both the planktonic foraminifera and the coccoliths have temperature and more generally environmental optimal conditions (Beaufort et al., 2011; Schmidt et al., 2006), and the tropical species are known to highly sensitive to environmental condition changes (Schmidt et al., 2006).

III.5 Conclusion

The contribution of those two pelagic carbonate producers has not been constant through the time on orbital time scale but remains similar on geological time scale between the Miocene and the Pliocene, and from Neogene to Quaternary outside of the known dissolution intervals of the Quaternary. We observe that the changes in the contribution of the coarse fraction to the total pelagic carbonate production is following orbital cyclicities: precession for the Pliocene, obliquity for the Miocene and eccentricity for both. The coarse fraction $CaCO_3$ AR is responding on precession and obliquity and the small fraction $CaCO_3$ AR is responding to eccentricity, so the two pelagic carbonate calcifiers are responding to different orbital forcing and in a different way. The coccoliths productivity and foraminifera productivity are not absorbing the same amount of carbon, and are sinking following different physics (e.g. ballasting effect). In a general context of climate warming, a drastic change of the carbonate production driven by these two carbonate calcifiers could have an impact on the climate system and ocean capacity to regulate atmospheric CO_2 (Boudreau et al., 2018). It remains to be studied whether this is due to calcification intensity changes (thickness of the shells) or due to a change of species and/or sizes of the particles.

III.6 Data availability

The datatables of this manuscript will be made available upon request to the the main author until their online publication on PANGAEA (https://pangaea.de, last visit: 8th December 2022).

III.7 Acknowledgements

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III.8 Bibliography

Baumann, K.-H., Böckel, B., and Frenz, M.: Coccolith contribution to South Atlantic carbonate sedimentation, in: Coccolithophores, edited by: Thierstein, H. R. and Young, J. R., Springer Berlin Heidelberg, Berlin, Heidelberg, 367–402, https://doi.org/10.1007/978-3-662-06278-4_14, 2004.

Beaufort, L. and Dollfus, D.: Automatic recognition of coccoliths by dynamical neural networks, Marine Micropaleontology, 51, 57–73, https://doi.org/10.1016/j.marmicro.2003.09.003, 2004.

Beaufort, L., Lancelot, Y., Camberlin, P., Cayre, O., Vincent, E., Bassinot, F., and Labeyrie, L.: Insolation cycles as a major control of equatorial Indian Ocean primary production, Science, 278, 1451–1454, 1997.

Beaufort, L., Probert, I., de Garidel-Thoron, T., Bendif, E. M., Ruiz-Pino, D., Metzl, N., Goyet, C., Buchet, N., Coupel, P., Grelaud, M., Rost, B., Rickaby, R. E. M., and de Vargas, C.: Sensitivity of coccolithophores to carbonate chemistry and ocean acidification, Nature, 476, 80–83, https://doi.org/10.1038/nature10295, 2011.

Beaufort, L., Barbarin, N., and Gally, Y.: Optical measurements to determine the thickness of calcite crystals and the mass of thin carbonate particles such as coccoliths, Nature Protocols, 9, 633–642, https://doi.org/10.1038/nprot.2014.028, 2014.

Beaufort, L., Bolton, C. T., Sarr, A.-C., Suchéras-Marx, B., Rosenthal, Y., Donnadieu, Y., Barbarin, N., Bova, S., Cornuault, P., Gally, Y., Gray, E., Mazur, J.-C., and Tetard, M.: Cyclic evolution of phytoplankton forced by changes in tropical seasonality, Nature, 601, 79–84, https://doi.org/10.1038/s41586-021-04195-7, 2022.

Boudreau, B. P., Middelburg, J. J., and Luo, Y.: The role of calcification in carbonate compensation, Nature Geoscience, 11, 894–900, https://doi.org/10.1038/s41561-018-0259-5, 2018.

Brummer, G. J. A. and van Eijden, A. J. M.: “Blue-ocean” paleoproductivity estimates from pelagic carbonate mass accumulation rates, Marine Micropaleontology, 19, 99–117, https://doi.org/10.1016/0377-8398(92)90023-D, 1992.

Chiu, T.-C. and Broecker, W. S.: Toward better paleocarbonate ion reconstructions: New insights regarding the CaCO3 size index, Paleoceanography, 23, PA2216, https://doi.org/10.1029/2008PA001599, 2008.

Clark, P. U. and Huybers, P.: Interglacial and future sea level: Global change, Nature, 462, 856–857, https://doi.org/10.1038/462856a, 2009.

Cullen, J. L. and Curry, W. B.: Variations in planktonic foraminifer faunas and carbonate preservation at Site 927: evidence for changing surface water conditions in the western tropical Atlantic Ocean during the middle Pleistocene, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 207–228, https://doi.org/10.2973/odp.proc.sr.154.111.1997, 1997.

Curry, W. B., Shackleton, N. J., Richter, C., and et al. (Eds.): Proceedings of the Ocean Drilling Program, 154 Initial Reports, Ocean Drilling Program, https://doi.org/10.2973/odp.proc.ir.154.1995, 1995.

Drury, A. J., Liebrand, D., Westerhold, T., Beddow, H. M., Hodell, D. A., Rohlfs, N., Wilkens, R. H., Lyle, M., Bell, D. B., Kroon, D., Pälike, H., and Lourens, L. J.: Climate, cryosphere and carbon cycle controls on Southeast Atlantic orbital-scale carbonate deposition since the Oligocene (30–0 Ma), Clim. Past, 17, 2091–2117, https://doi.org/10.5194/cp-17-2091-2021, 2021.

Fischer, G. and Karakaş, G.: Sinking rates and ballast composition of particles in the Atlantic Ocean: implications for the organic carbon fluxes to the deep ocean, Biogeosciences, 6, 85–102, https://doi.org/10.5194/bg-6-85-2009, 2009.

Foster, G. L., Lear, C. H., and Rae, J. W. B.: The evolution of pCO_2, ice volume and climate during the middle Miocene, Earth and Planetary Science Letters, 341–344, 243–254, https://doi.org/10.1016/j.epsl.2012.06.007, 2012.

Frenz, M., Baumann, K.-H., Boeckel, B., Hoppner, R., and Henrich, R.: Quantification of Foraminifer and Coccolith Carbonate in South Atlantic Surface Sediments by Means of Carbonate Grain-Size Distributions, Journal of Sedimentary Research, 75, 464–475, https://doi.org/10.2110/jsr.2005.036, 2005.

Frenz, M., Henrich, R., and Zychla, B.: Carbonate preservation patterns at the Ceará Rise – Evidence for the Pliocene super conveyor, Marine Geology, 232, 173–180, https://doi.org/10.1016/j.margeo.2006.07.006, 2006.

Gehlen, M., Gangstø, R., Schneider, B., Bopp, L., Aumont, O., and Ethe, C.: The fate of pelagic $CaCO_3$ production in a high CO_2 ocean: a model study, Biogeosciences, 4, 505–519, https://doi.org/10.5194/bg-4-505-2007, 2007.

Goosse, H.: Climate system dynamics and modeling, Cambridge University Press, New York, NY, 358 pp., 2015.

Gröger, M., Henrich, R., and Bickert, T.: Glacial–interglacial variability in lower North Atlantic deep water: inference from silt grain-size analysis and carbonate preservation in the western equatorial Atlantic, Marine Geology, 201, 321–332, https://doi.org/10.1016/S0025-3227(03)00263-9, 2003a.

Gröger, M., Henrich, R., and Bickert, T.: Variability of silt grain size and planktonic foraminiferal preservation in Plio/Pleistocene sediments from the western equatorial Atlantic and Caribbean, Marine Geology, 201, 307–320, https://doi.org/10.1016/S0025-3227(03)00264-0, 2003b.

Harris, S. E., Mix, A. C., and King, T.: Biogenic and terrigenous sedimentation at Ceara Rise, western tropical Atlantic, supports Pliocene–Pleistocene deep-water linkage between hemispheres, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 331–345, https://doi.org/10.2973/odp.proc.sr.154.114.1997, 1997.

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, 19–22, https://doi.org/10.1130/G34890.1, 2014.

Honjo, S. and Erez, J.: Dissolution rates of calcium carbonate in the deep ocean; an in-situ experiment in the North Atlantic Ocean, Earth and Planetary Science Letters, 40, 287–300, https://doi.org/10.1016/0012-821X(78)90099-7, 1978.

Kopp, R. E., Simons, F. J., Mitrovica, J. X., Maloof, A. C., and Oppenheimer, M.: Probabilistic assessment of sea level during the last interglacial stage, Nature, 462, 6, https://doi.org/10.1038/nature08686, 2009.

Landschützer, P., Gruber, N., Bakker, D. C. E., and Schuster, U.: Recent variability of the global ocean carbon sink, Global Biogeochemical Cycles, 28, 927–949, https://doi.org/10.1002/2014GB004853, 2014.

Langer, M. R.: Assessing the Contribution of Foraminiferan Protists to Global Ocean Carbonate Production, Journal of Eukaryotic Microbiology, 55, 163–169, https://doi.org/10.1111/j.1550-7408.2008.00321.x, 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, Astronomy & Astrophysics, 428, 261–285, https://doi.org/10.1051/0004-6361:20041335, 2004.

Liebrand, D., Beddow, H. M., Lourens, L. J., Pälike, H., Raffi, I., Bohaty, S. M., Hilgen, F. J., Saes, M. J. M., Wilson, P. A., van Dijk, A. E., Hodell, D. A., Kroon, D., Huck, C. E., and Batenburg, S. J.: Cyclostratigraphy and eccentricity tuning of the early Oligocene through early Miocene (30.1–17.1 Ma): Cibicides mundulus stable oxygen and carbon isotope records from Walvis Ridge Site 1264, Earth and Planetary Science Letters, 450, 392–405, https://doi.org/10.1016/j.epsl.2016.06.007, 2016.

Past Interglacials Working Group of PAGES: Interglacials of the last 800,000 years, Reviews of Geophysics, 54, 162–219, https://doi.org/10.1002/2015RG000482, 2016.

Pound, M. J., Haywood, A. M., Salzmann, U., and Riding, J. B.: Global vegetation dynamics and latitudinal temperature gradients during the Mid to Late Miocene (15.97–5.33Ma), Earth-Science Reviews, 112, 1–22, https://doi.org/10.1016/j.earscirev.2012.02.005, 2012.

R Core Team: R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria., 2021.

Ramaswamy, V. and Gaye, B.: Regional variations in the fluxes of foraminifera carbonate, coccolithophorid carbonate and biogenic opal in the northern Indian Ocean, Deep Sea Research Part I: Oceanographic Research Papers, 53, 271–293, https://doi.org/10.1016/j.dsr.2005.11.003, 2006.

Ravelo, A. C., Andreasen, D. H., Lyle, M., Olivarez Lyle, A., and Wara, M. W.: Regional climate shifts caused by gradual global cooling in the Pliocene epoch, Nature, 429, 263–267, https://doi.org/10.1038/nature02567, 2004.

Richardson, T. L. and Jackson, G. A.: Small Phytoplankton and Carbon Export from the Surface Ocean, Science, 315, 838–840, https://doi.org/10.1126/science.1133471, 2007.

Roesch, A. and Schmidbauer, H.: WaveletComp: Computational Wavelet Analysis., 2018.

Schiebel, R.: Planktic foraminiferal sedimentation and the marine calcite budget, Global Biogeochemical Cycles, 16, 3-1-3–21, https://doi.org/10.1029/2001GB001459, 2002.

Schmidt, D. N., Lazarus, D., Young, J. R., and Kucera, M.: Biogeography and evolution of body size in marine plankton, Earth-Science Reviews, 78, 239–266, https://doi.org/10.1016/j.earscirev.2006.05.004, 2006.

Schwab, C., Kinkel, H., Weinelt, M., and Repschläger, J.: A coccolithophore based view on paleoenvironmental changes in the open ocean mid-latitude North Atlantic between 130 and 48 ka BP with special emphasis on MIS 5e, Quaternary Science Reviews, 81, 35–47, https://doi.org/10.1016/j.quascirev.2013.09.021, 2013.

Si, W. and Rosenthal, Y.: Reduced continental weathering and marine calcification linked to late Neogene decline in atmospheric CO_2, Nature Geosciences, 12, 833–838, https://doi.org/10.1038/s41561-019-0450-3, 2019.

Stolz, K. and Baumann, K.-H.: Changes in palaeoceanography and palaeoecology during Marine Isotope Stage (MIS) 5 in the eastern North Atlantic (ODP Site 980) deduced from calcareous nannoplankton observations, Palaeogeography, Palaeoclimatology, Palaeoecology, 292, 295–305, https://doi.org/10.1016/j.palaeo.2010.04.002, 2010.

Voelker, A. H. L., Rodrigues, T., Billups, K., Oppo, D., McManus, J., Stein, R., Hefter, J., and Grimalt, J. O.: Variations in mid-latitude North Atlantic surface water properties during the mid-Brunhes (MIS 9–14) and their implications for the thermohaline circulation, Climate of the Past, 6, 531–552, https://doi.org/10.5194/cp-6-531-2010, 2010.

You, Y., Huber, M., Muller, R. D., Poulsen, C. J., and Ribbe, J.: Simulation of the Middle Miocene Climate Optimum, Geophysical Research Letters, 36, 5, https://doi.org/10.1029/2008GL036571, 2009.

Zachos, J. C., Dickens, G. R., and Zeebe, R. E.: An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics, Nature, 451, 279–283, https://doi.org/10.1038/nature06588, 2008.

Ziveri, P., de Bernardi, B., Baumann, K.-H., Stoll, H. M., and Mortyn, P. G.: Sinking of coccolith carbonate and potential contribution to organic carbon ballasting in the deep ocean, Deep Sea Research Part II: Topical Studies in Oceanography, 54, 659–675, https://doi.org/10.1016/j.dsr2.2007.01.006, 2007.

III.9 Appendix/supplements

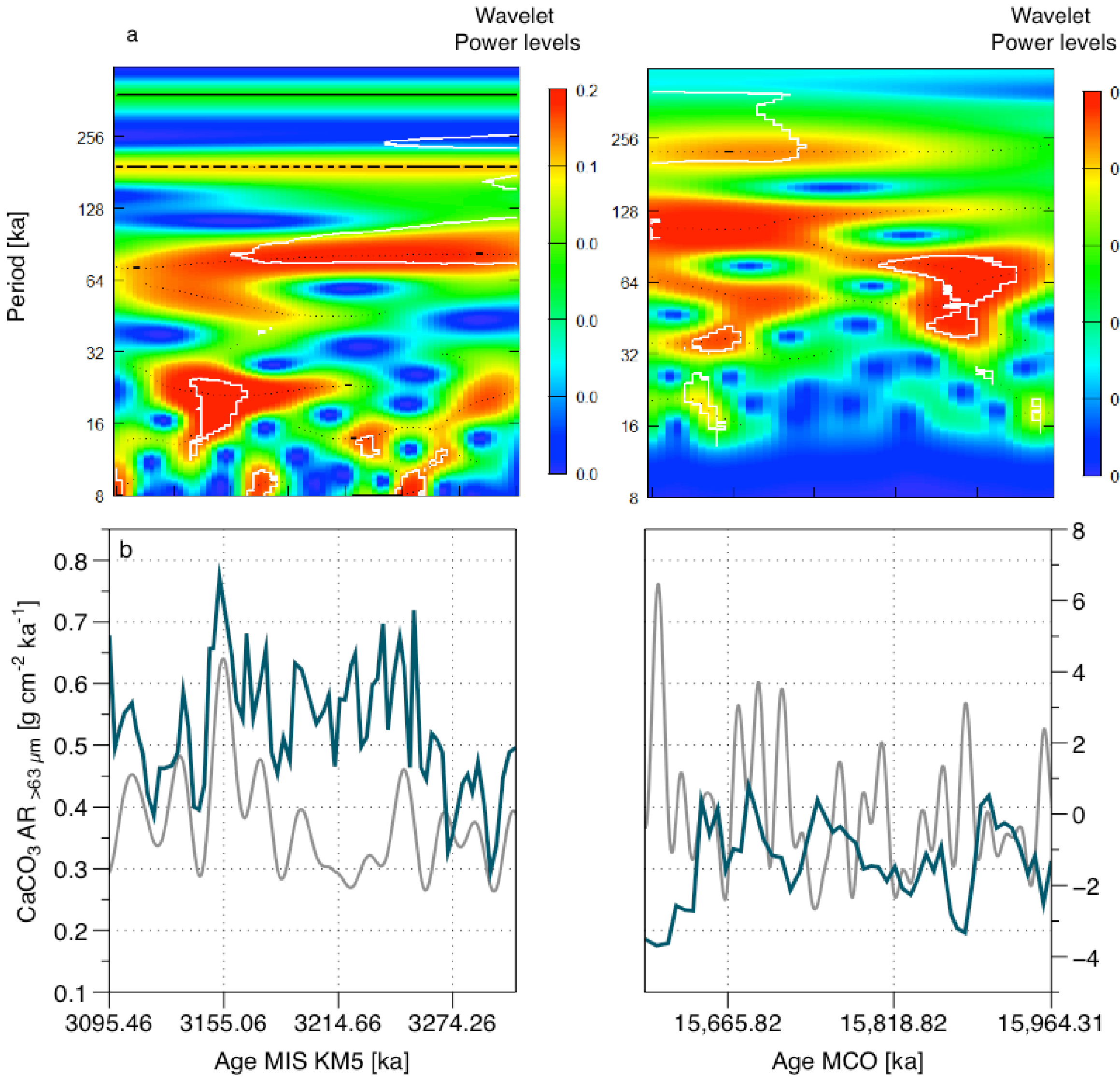

Figure S1. Coarse fraction $CaCO_3$ AR >63 µm wavelet transform and record compared to E+T-P record.

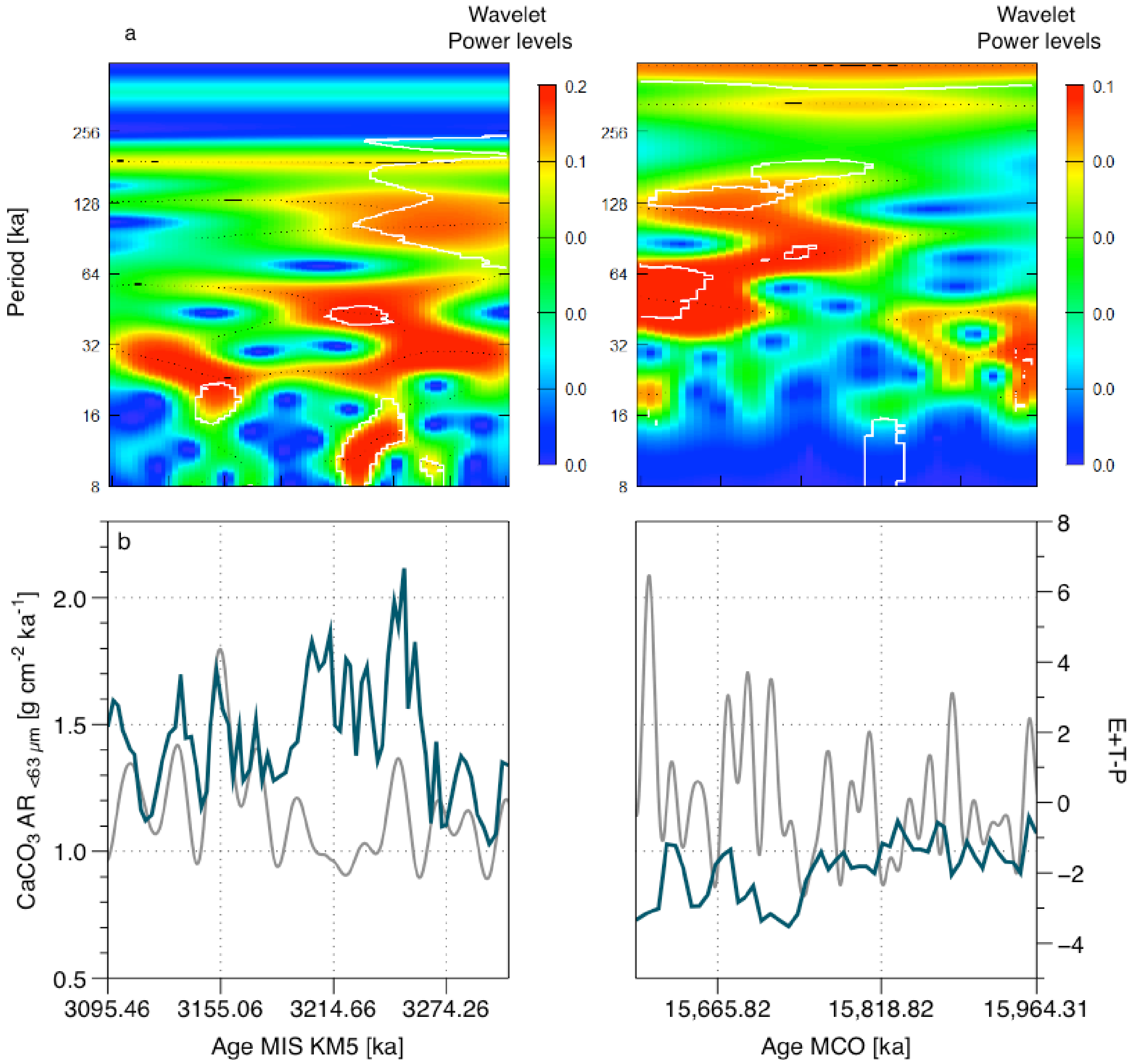

Figure S2. Small fraction CaCO$_3$ AR <63 µm wavelet transform and record compared to E+T-P record.

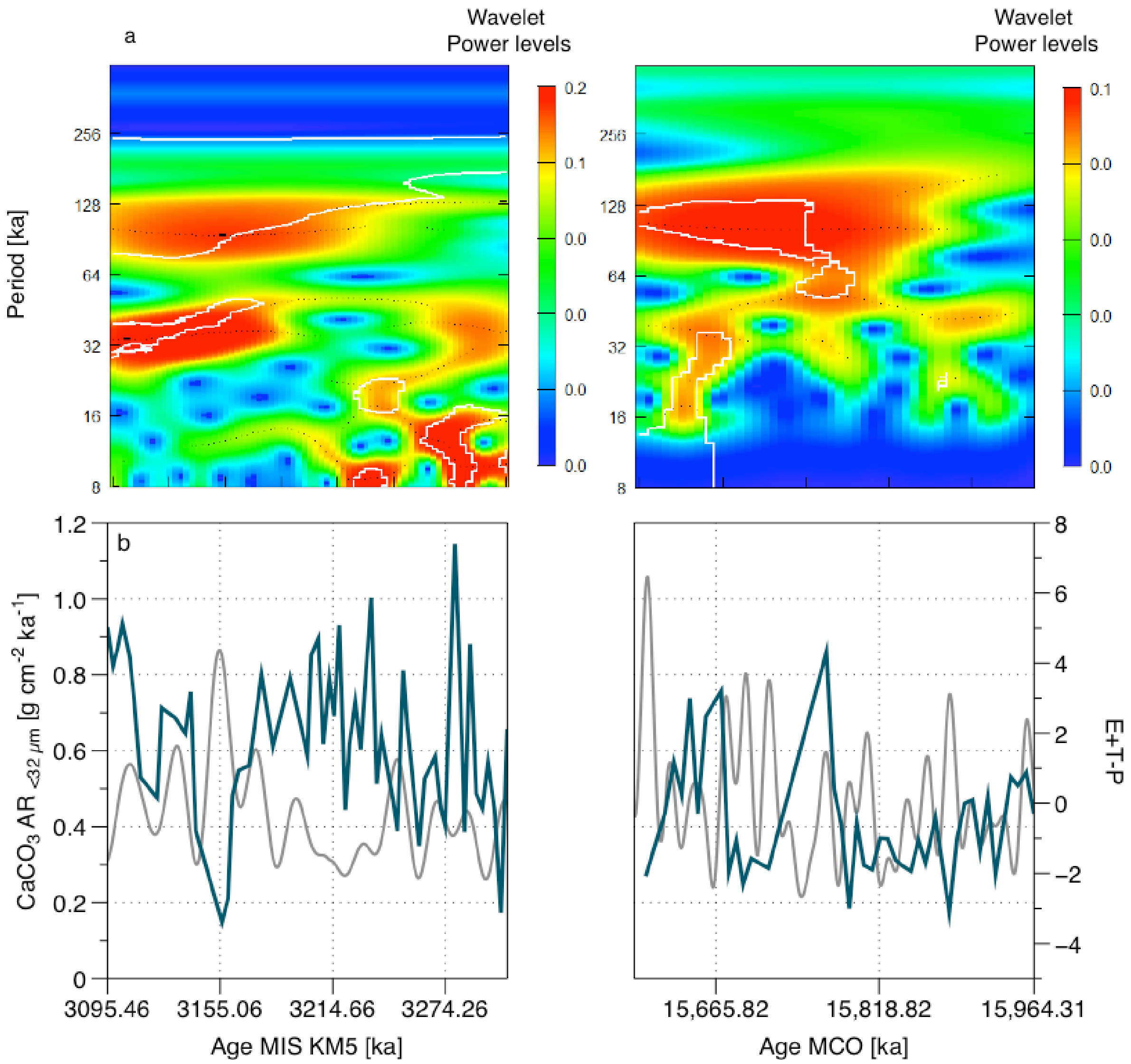

Figure S3. Small fraction $CaCO_3$ AR <32 µm (SYRACO data, without extreme values) wavelet transform and record compared to E+T-P record.

Chapter IV. Population growth of foraminifera and coccolithophores, rather than changes in individual calcification, drove variations of Neogene pelagic carbonate production in tropical Ocean.

(manuscript in preparation)

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Abstract

Changes in pelagic carbonate production can have profound effects on ocean alkalinity and thus on the capacity of the oceans to store dissolved inorganic carbon. Despite the importance of this process for the oceanic carbon cycle, the drivers of changes in carbonate production in the plankton remain largely unconstrained. Here we use automated image recognition techniques to dissect a Neogene orbital-scale record of pelagic carbonate accumulation in the tropical Atlantic (Ceará Rise) into changes of its main components: the flux of planktonic foraminifera and coccolithophore calcite. We show that for both groups at all orbital frequencies as well as between the Miocene and Pliocene, the observed variability in pelagic carbonate flux was driven by changes in population growth. In contrast, the mean size of the calcified skeletons in both groups was negatively correlated with carbonate accumulation, indicating that the observed variation in pelagic carbonate production represents shifts between more productive populations made of smaller individuals and less productive populations made of larger cells. This relationship holds despite different dominant orbital cyclicity in pelagic carbonate production between the Miocene and Pliocene studied intervals, indicating that it likely represents a general characteristic of the tropical pelagic carbonate factory. Therefore, we conclude that to predict the capacity of the ocean to store CO_2 due to the pelagic component of the process of biological compensation, it is only important to predict the population growth of the main planktonic calcite biomineralisers.

IV.1 Introduction

The two main pelagic carbonate producers, the planktonic foraminifera and the coccolithophores are producing more than 2.4 GT carbonate yr^{-1} (Milliman, 1993). This carbonate, by sinking to the sea floor with the death of these pelagic carbonate producers, is stored in the deep ocean, making the ocean the major sink for anthropogenic carbon. It has been recently shown that a change by only ten percent of this carbonate production would have large consequences on the capacity of the ocean to absorb CO_2 (Boudreau et al., 2018).

The pelagic carbonate production is not constant through the time (Lyle et al., 2019; Drury et al., 2021) and the balance between the two main pelagic carbonate producers (planktonic foraminifera and coccoliths), is changing with high amplitude on shorter orbital time scales (Si and Rosenthal, 2019). The response of these two groups 1) is not linked to each other, 2) isn't following the same periodicity/not responding to the same forcing (both on orbital and geological time scale) (Si and Rosenthal, 2019; Chapter #III).

But very little is known about what makes the pelagic carbonate within these two groups change. For the two groups, there are two ways of regulating the calcite production: changes of the population growth, which would be reflected as changes in the flux of skeletal elements, and changes of the average mass of calcite per individual, which would be reflected by changes in mean size and/or mean weight of the skeletal elements. Kiss et al. (2021) studied the drivers of the planktonic foraminifera $CaCO_3$ production changes and found out that this is mainly the number of shell flux which is determining the quantity of $CaCO_3$ produced by this group, rather than their taxonomy or sizes. Other studies like Guidi et al., (2009) are emphasising the importance of the size or the calcification of individual specimens in the regulation of pelagic carbonate flux. Finally, Barker and Elderfield (2002) are proposing the shell weight of foraminifera shells to be an important process to take into account in estimation of future marine carbonate production in the future changing CO_2 world. In the case of the coccoliths, there are several minutes plates of calcite per coccosphere (cell). We will here concentrate on the coccoliths rather than the coccospheres, because this is what we find in the marine sediment (finding coccosphere remains a very rare event). Additionally, for the purpose of this study, the fact that the amount of coccoliths (and so the amount of calcite produced) found belongs to many cells containing few coccoliths or fewer cells containing more coccoliths does not influence the direction of our conclusion about the amount of calcite produced by these organisms. Furthermore, the relationship between the coccosphere size and the number of coccoliths on it (and their sizes) does not seems to be that simple. Some studies have found an increase of the thickness of the coccoliths and more circular shapes with the increase of their sizes added to a relatively constant number of coccoliths per cells for the Cenozoic species (Henderiks, 2008), which is today a discussed statement. Indeed, Yang and Wei, (2003) found a number of coccoliths per coccosphere changing with the division cycles of the cells and with the nutrient availability with a non-negligible intraspecific variability. Sheward et al., (2017) found variable coccosphere sizes and variable number of coccoliths per coccosphere depending on the growth phase of the organisms (species-specific), itself related to the nutrient availability, with a shift towards larger cells and higher number of coccoliths per cells in nutrient depleted conditions. A relationship between how well formed are the coccoliths and coccospheres sizes with their environment has also being highlighted by De Bodt et al. (2010), finding an influence of the pCO_2 (but not temperature) on their well-formation, but no influences on morphology, cell size or calcite production. They are stating that the strongest parameter influencing the coccoliths calcification will be the ocean acidification rather than the warming of the surface ocean. Suchéras-Marx et al., (2022) are concluding on the poorly reproductible size distribution of empirical coccoliths populations using models, underlying that unknown other factors might influence it, and state that the comparison between coccoliths sizes and cell sizes is to be taken carefully and only concern the time of formation of a coccolith. It has been shown that independently from temperature, there is a link between the taxonomy of calcifiers groups in the photic zone, the size of the exported particles and the particles flux (Laws et al., 2000; Guidi et al., 2009, 2015). Some others find a decrease of phytoplankton size and degree of calcification in the open equatorial oceans through the Neogene and do not necessarily co-vary with oceanic structure changes and palaeoproductivity, with a possible link with the decrease of pCO_2 and alkalinity (Suchéras-Marx et al., 2019; Bolton et al., 2016; Hannisdal et al., 2012; Beaufort et al., 2011; Henderiks, 2008; Jones et al., 2013; Iglesias-Rodriguez et al., 2008; von Dassow et al., 2018; Zondervan, 2007). Previous studies did not find a link between the foraminifera shell masses changes and the atmospheric pCO_2 modulations but with the latitude, with the hypothesis that at the equator, the oceanic conditions are more stable through the G-IG cycles than at high latitudes (Zarkogiannis et al., 2019). Concerning variability of the sizes of the foraminifera shells at low latitude, Schmidt et al. (2004) found moderate size fluctuations until 14 Ma and high size increase from the mid Miocene to present, with increase phases corresponding to global cooling events, coherent with what have been found by Todd et al., (2020). The weight of foraminifera shells has been shown to vary following environmental conditions changes (Spero et al., 1997). Barker et al. (2006) suggested that the increase of pelagic carbonate production, with possible link to nannoplankton bloom may be the source of increase of foraminifera shells dissolution, and so a decrease of their weight. We here focus our work on two Neogene warm periods: the MIS KM5 and the MCO, known to be possible analogues for predicted warm values (Ravelo et al., 2004; Pound et al., 2012; You et al., 2009; Foster et al., 2012; Zachos et al., 2008). We decided to work on equatorial latitude to avoid large temperature changes characteristics from the polar regions (Herbert et al., 2016) to be driving the observed signals. We have made the choice to work in the tropical Atlantic Ocean, Ceará Rise.

IV.2 Material and Methods

This study is based on material collected on Ocean drilling program (ODP) Leg 154, Site 927, Ceará Rise, Western Tropical Atlantic Ocean (5°27.77'N, 44°28.84'W) 3315 mbsl, above the regional lysocline (4200 mbsl, Frenz et al., 2006; Curry et al., 1995; Cullen and Curry, 1997) so the observed results are not impacted by dissolution (Brummer and van Eijden, 1992; Liebrand et al., 2016) and the sedimentation rate at this site makes high resolution studies possible. The tropical location reduces the impact of high latitude climate change and important temperature changes on short time scales as well as on long geological time scales. The sampling, described in Chapter #II, has been done in order to make observations on the two proxies on the same samples, so the timings and potential lags between the response of the two proxies are independent from possible sampling or age model bias. We have a total of 72 samples for the MIS KM5 and 50 samples for the MCO. We are here working with the high resolution tuned age model presented in Chapter #II

IV.2.i Coccoliths

The coccoliths samples have been prepared following the protocol of Beaufort et al. (2014) modified as described in Chapter #III. We used SYRACO automated microscope pictures at analysed polarised light to assess the morphometric data of coccoliths (Beaufort et al., 2014; Beaufort and Dollfus, 2004, Aix-Marseille University), and here we made the choice to specifically work with the maxima diameter of the specimens observed. Between 50 and 604 field of views (FOV) has been used (between 1268 and 79684 specimens counted and measured). We obtain as an output the mean size per recognised species or group of species, from which we calculate a median value per sample.

IV.2.ii Planktonic foraminifera

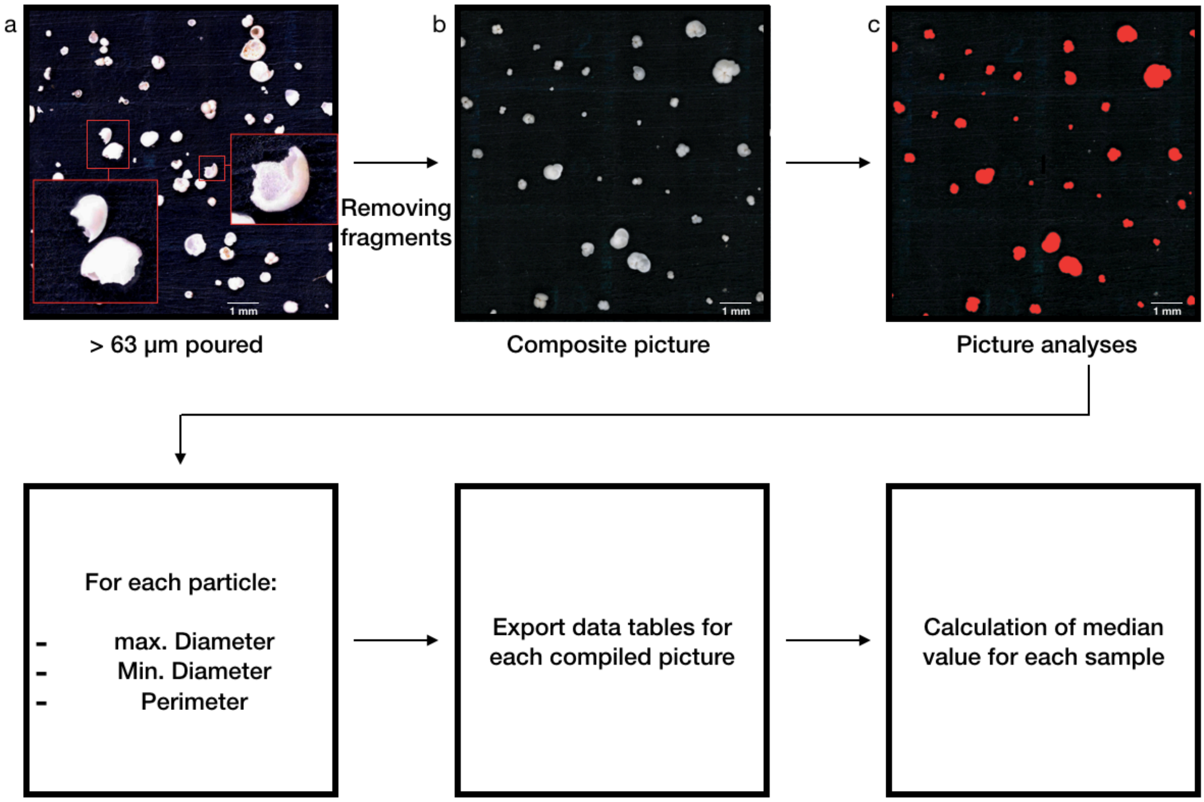


Figure 1. Shematic description of the protocol used for taking pictures and analysing them using the Keyence device. a) Picture taken using the Keyence before to remove the foraminifera fragments. Examples of what is considered as a fragment (and zoom on it) in the red squares. b) Picture taken using the Keyence, after the fragments have been removed. c) Analyses of the particles on the picture taken using the Keyence: the red areas are corresponding to the particles recognised by the Keyence, from which the data are extracted. The three following steps are data processing to assess the final results presented in this study.

The samples are washed and sieved at 63 µm (it has been shown that there is not significant fragments number below 63 µm produced by the the foraminifera dissolution, Chiu and Broecker, 2008). The foraminifera analyses are processed using the Keyence device and software (Bremen University, Figure 1). The coarse fraction is splitted to work with a reasonable amount of material and of particles, around 10 mg (corresponding empirically to the amount of sediment to process the analysis in a reasonable amount of time and have a significant number of specimens). Because none of the foraminifera slides were corresponding to my need, I developed new slides to process the analysis, by painting large binocular reference slides in dark blue for a high contrast with the foraminifera shells (Figure 1). The coarse material is distributed on three to six slides. In order to have optimal pictures, the particles are homogeneously distributed by hand on the slide, in a way that they are neither touching each other, nor touching the edges of the slides. All the -foraminifera- fragments are removed and counted from those slides to work with only the whole foraminifera. Then, calibrated pictures are taken with the automated Keyence binocular software at 100 magnification (each individual picture is 1600 by 1200 pxl and these individual pictures are compiled to have 1 big compiled picture per half a foraminifera slide. From those pictures, we can extract morphometric data for every specimen, from which median values and ratios can be calculated. Between 500 and 4240 foraminifera specimens have been measured per sample.

IV.2.iii Proxies for both planktonic foraminifera and coccolithophores

From these morphometric analyses, we can derive the same calculation and proxies for both the foraminifera and the coccoliths for comparable results, and to evaluate the response of the two proxies using an equivalent approach. For the purpose of this study we have made the choice to work with the maximal diameter parameter, and the final value given for each sample is the median of all the measurements for this sample. Knowing the number of foraminifera and the split of the coarse fraction we worked on, we can assess the number of specimens for 1 g of bulk sediment (BS). With the dry bulk density (DBD) and the sedimentation rate (SR) (paper 1), we calculate the number of Whole Foraminifera (WF) accumulation rate (AR) as: number WF for 1g BS x DBD x SR. The same calculation has been done for the coccoliths, with the number of coccoliths for 1 g sediment (< 32 µm). The carbonate accumulation rate ($CaCO_3$ AR) values are known from Chapters #II and #III.

IV.2.iv Spectral analysis

We observe cyclicities in our newly generated data, and in order to understand what are the dominant cyclicities in our records, we first ran Wavelet transform analysis (WaveletComp 1.1 package on R, Roesch and Schmidbauer, 2018) using R (4.1.2., R Core Team, 2021). To understand what are the relationships between these cyclicities and the actual orbital cyclicities, we ran cross Blackman Tukey spectral analysis, with the actual E+T-P signal (Laskar et al., 2004) (containing all the three orbital signals), using Analyseries software 2.0 (Paillard et al., 1996).

IV.3 results

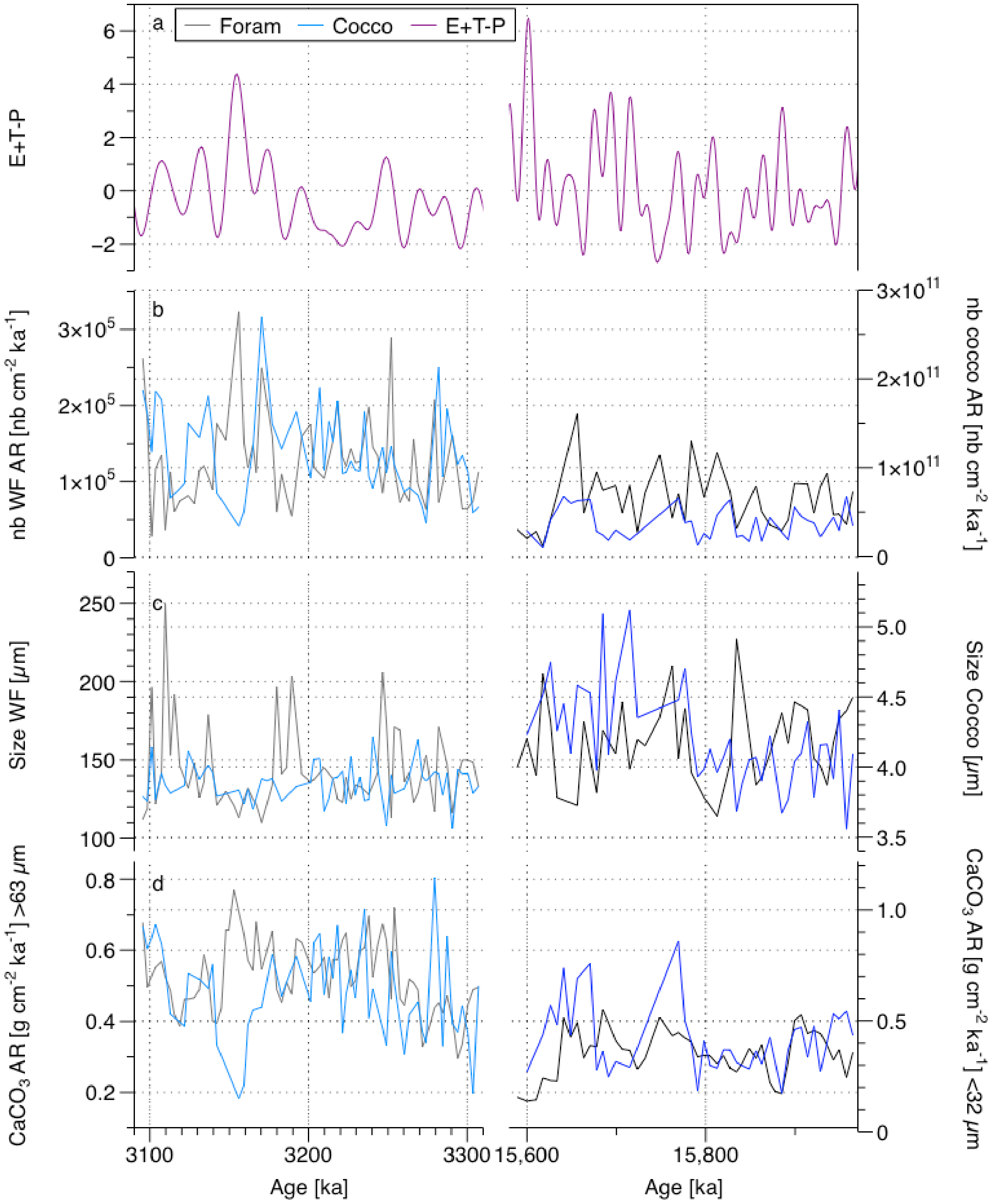


Figure 2. a) E+T-P record (Laskar et al., 2004); b) Number of specimens accumulation rate; c) Median size of the specimens and d) carbonate accumulation rate. All for both the MIS KM5 (light shade) and MCO (dark shades) for both the coccoliths (blue) and the foraminifera (black).

The $CaCO_3$ AR of both size fractions is highly variable at orbital time scale, and increasing from the Miocene to the Pliocene (Figure 2). If we now look at the sizes of the organisms, we do observe a high orbital scale variability too, for both the planktonic foraminifera and the coccoliths. The values of the maximum diameter for the planktonic foraminifera are ranging between 110 µm for the smallest and 196.5 µm for the largest during the Pliocene, and between 114 µm for the smallest and 227 µm for the largest for the Miocene. Concerning the coccoliths, their size is ranging between 3.74 µm for the smallest and 4.21 µm for the largest during the Pliocene, and between 3.56 µm for the smallest and 5.12 µm for the largest for the Miocene. The number of particles counted is also highly variable on orbital time scale, and for both the planktonic foraminifera and the coccoliths and the number of particles for the both groups seems to co-vary. The number of WF AR varies between 2.8×10^4 and 3.2×10^5 for the Pliocene and between 1.5×10^4 and 1.9×10^5 for the Miocene. Concerning the number of coccoliths AR, it varies between 3.4×10^{10} and 2.7×10^{11} for the Pliocene and between 9.8×10^9 and 6.8×10^{10} for the Miocene. On a long geological time scale, there is a decrease of the size and an increase of the number of specimens from the Miocene to the Pliocene. We do observe an overall higher variability of the sizes during the Pliocene than during the Miocene and a higher -variability of the number of specimens during the Pliocene than during the Miocene. All these observations seem to be without lags, neither between the two groups nor between the pelagic calcifiers and the orbital forcing (represented by the E+T-P).

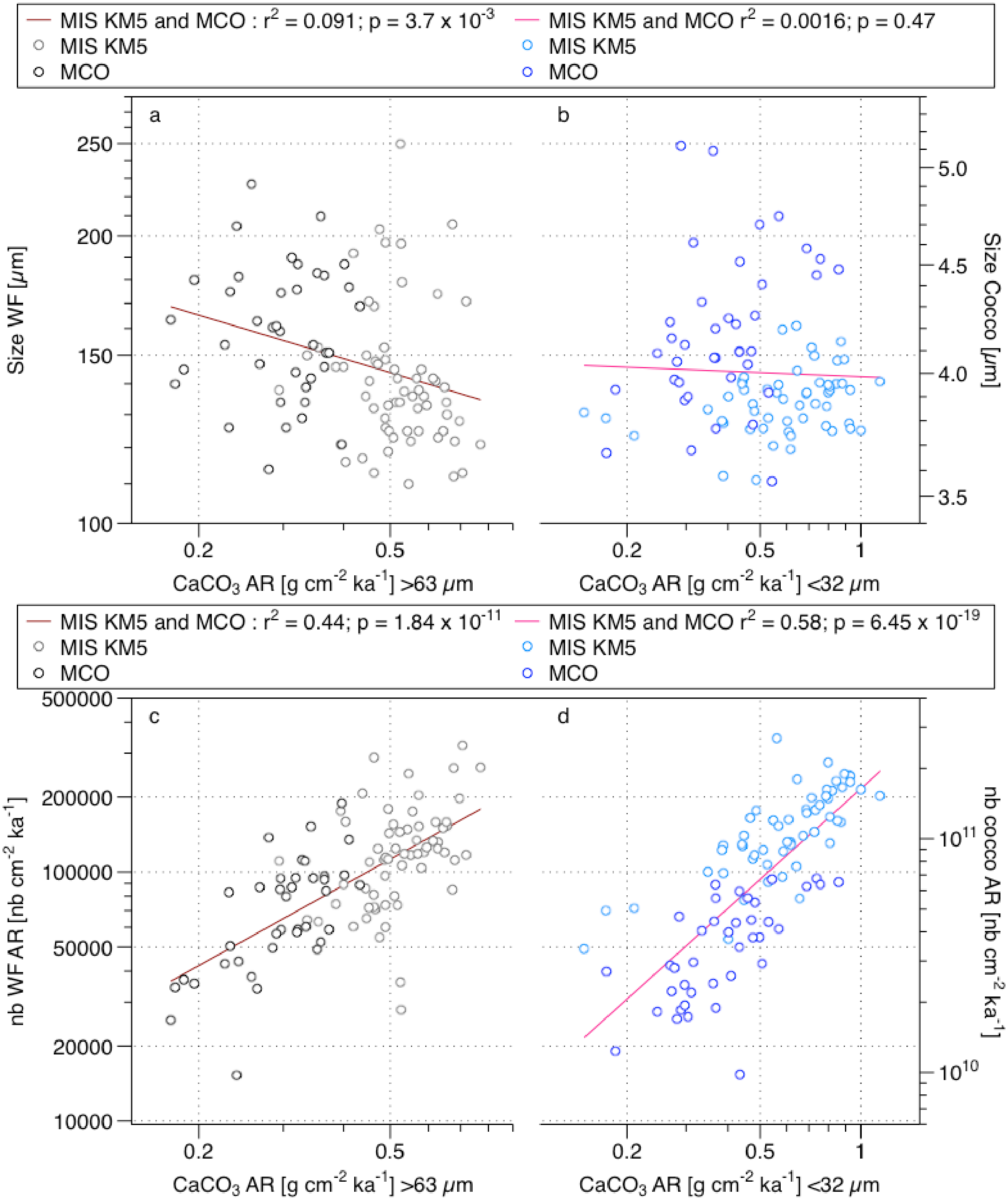


Figure 3. Correlation between a) the size of the WF and the $CaCO_3$ AR >63 µm; b) the size of the coccoliths and the $CaCO_3$AR <32 µm; c) The number of WF AR and the $CaCO_3$ AR >63 µm and d) the number of coccoliths AR and the $CaCO_3$ AR <32 µm. The power regression curves and r^2 are given for all. All for both the MIS KM5 (light shade) and MCO (dark shades) for both the coccoliths (blue) and the foraminifera (black).

There is no correlation between the MD and the $CaCO_3$ AR >63 µm for the two periods of interest (Figure 3b), so the changes of size of the WF is not the principal factor influencing the observed changes in $CaCO_3$ AR >63 µm. The same is observed for the coccoliths sizes and the <32 µm $CaCO_3$ AR

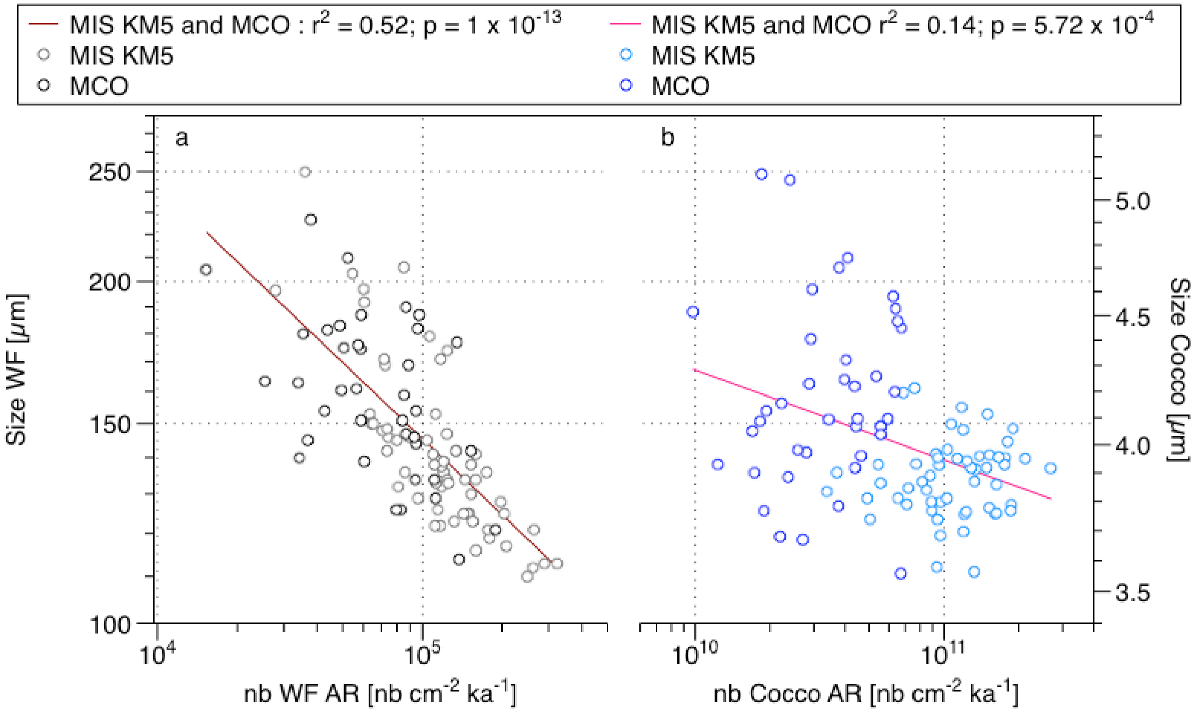


Figure 4. Correlation between a) the size of the WF and the number of WF AR and b) the size of coccoliths and the number of coccoliths AR. The power regression curves and r^2 are given for all. All for both the MIS KM5 (light shade) and MCO (dark shades) for both the coccoliths (blue) and the foraminifera (black).

We observe a (weak) negative (power) correlation so there is a trend towards a decrease of the size with the increase of number (with possibly absolutely no links between those two parameters at all) for the two proxies and for the two intervals (Figure 4). Furthermore, there is a correlation between the number WF AR and the $CaCO_3$ AR >63 µm (Figure 3c) ($r^2 = 0.44$) and between the number of coccoliths AR and the $CaCO_3$ AR <32 µm ($r^2= 0.58$). By opposition, there is no link (or a weak negative trend) between the size of the specimens and the $CaCO_3$ AR for none of the proxies nor the time period, so the $CaCO_3$ AR of the respective fractions is linked to changes due to the change of the number of specimens more than their sizes.

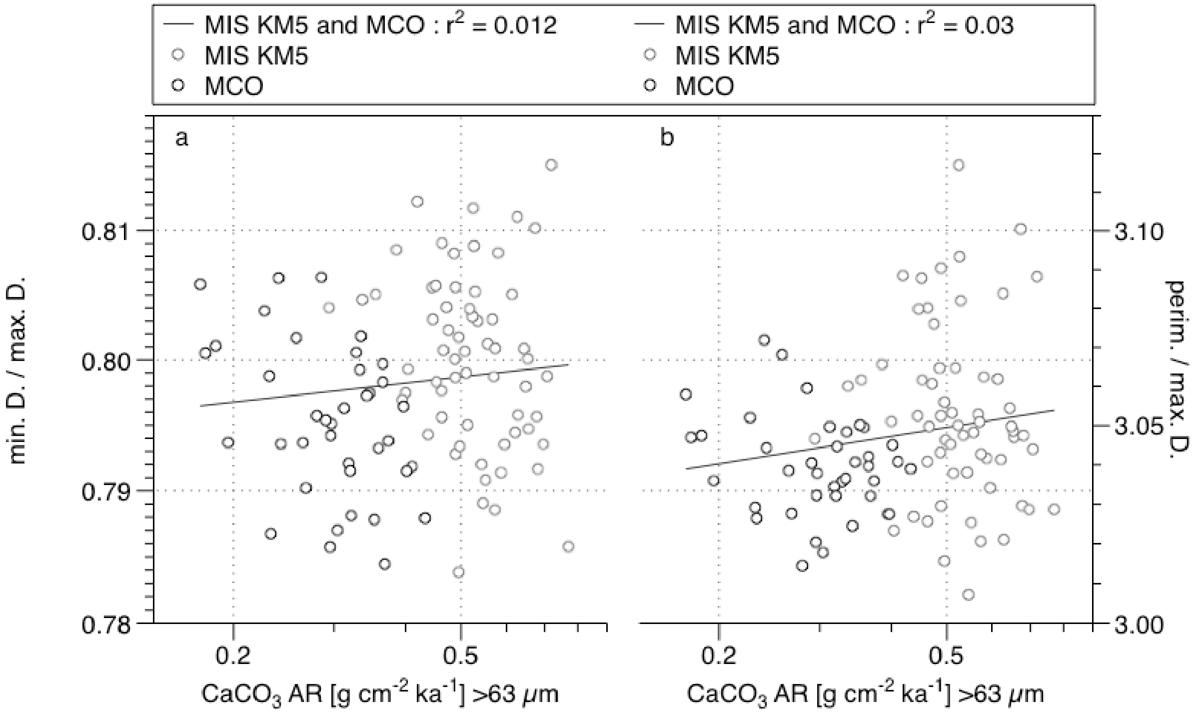
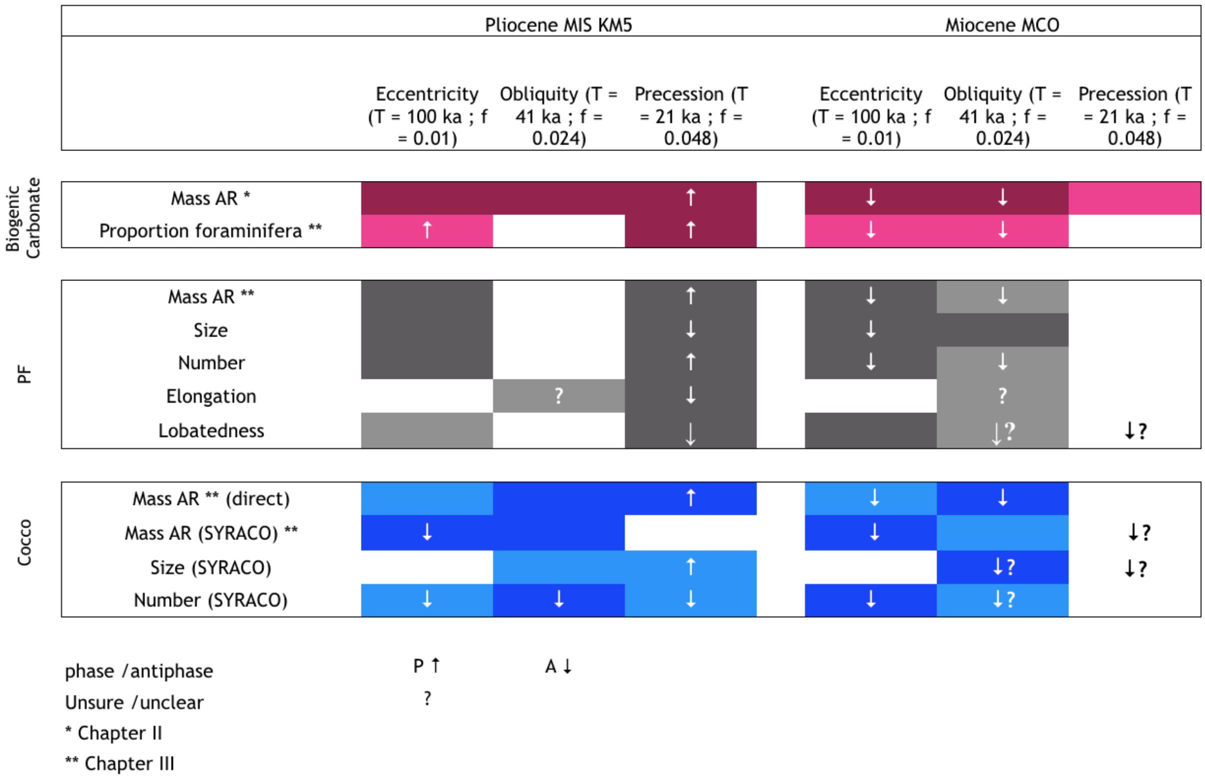


Figure 5. Correlation between a) the min. D. / max. D. and the $CaCO_3$ AR >63 and b) the perim. / max. D. and the $CaCO_3$AR >63. All for both the MIS KM5 (light shade) and MCO (dark shades).

There is no significant relationship between the shape indexes of planktonic foraminifera and the $CaCO_3$ AR >63 µm but on Figure 5 we can see a light relationship between the perim. / max D and the $CaCO_3$ AR >63 µm (the higher $CaCO_3$ AR >63 µm the more lobate) but very weak (low r^2). This makes sense as the higher the index, the more lobate are the shells and highly lobate shells are more calcified. It seems that the high variability of the data (highly noisy signal) makes it difficult to observe a good correlation. It also looks that the higher the min. D. / max. D. the higher the $CaCO_3$ AR >63 µm (the higher $CaCO_3$ AR >63 µm the more round are the planktonic foraminifera shells).

There is no link between the min. D. / max. D. ratio and the size, neither or the Pliocene, nor the Miocene (r^2=0.092): the elongation/roundness is not changing with the size. There is a link between the perim. / max. D. ratio (positive correlation, significant, r^2 = 0.42): “how lobate” so “how calcified they are” normalised to the size is size dependent: the bigger they are the more lobate they are: how heavily calcified the foraminifera is increasing exponentially: there is more calcite because they are bigger but additionally because they are more lobate. This is also tracking that the increase of size isn’t only a change of the size of specimens within one species, but a taxonomic change toward different, bigger species. We observe similar values and trends for both the Pliocene and the Miocene.

As we know that there is a strong orbital imprint in the palaeoclimatic record in the equatorial Atlantic (Pälike et al., 2006) and that the pelagic calcifiers at low latitude are strongly influenced by the orbital cycles (Beaufort et al., 1997), we investigated the periodicity we have in all our records, and their relationship with the actual orbital cycles.



		Pliocene MIS KM5			Miocene MCO		
		Eccentricity (T = 100 ka ; f = 0.01)	Obliquity (T = 41 ka ; f = 0.024)	Precession (T = 21 ka ; f = 0.048)	Eccentricity (T = 100 ka ; f = 0.01)	Obliquity (T = 41 ka ; f = 0.024)	Precession (T = 21 ka ; f = 0.048)
Biogenic Carbonate	Mass AR *			↑	↓	↓	
	Proportion foraminifera **	↑		↑	↓	↓	
PF	Mass AR **			↑	↓	↓	
	Size			↓	↓		
	Number			↑	↓	↓	
	Elongation		?	↓		?	
	Lobatedness			↓		↓?	↓?
Cocco	Mass AR ** (direct)			↑	↓	↓	
	Mass AR (SYRACO) **	↓			↓		↓?
	Size (SYRACO)			↑		↓?	↓?
	Number (SYRACO)	↓	↓	↓	↓	↓?	

phase /antiphase P ↑ A ↓

Unsure /unclear ?

* Chapter II

** Chapter III

Figure 6. Table of the Spectral analyses. (all the figures are either in the previous papers, or in supplements at the end of the draft of this one), SA are run using wavelet transform method on R (Roesch and Schmidbauer, 2018; R Core Team, 2021), coherence spectra are run using cross Blackman-Tukey on Analyseries (Paillard et al., 1996).

We observe that most of the observations made on carbonate production during the Pliocene are responding to both the eccentricity and the precession (with the possibility that the eccentricity in the spectral analyses reflects a multiple of the precession paced signal). Which is surprising, as the main climate signal during this time interval is the obliquity (41 ka) (Lisiecki and Raymo, 2005). This is for both the coccoliths and the PF, even if we observe a trend in all the records concerning the coccoliths to answer at obliquity (41 ka periodicity). During the MCO, we observe that most of our records are eccentricity and obliquity paced, so this time, only partially responding to the climate tracking (Holbourn et al., 2007). If we now have a look to the actual climate E+T-P (tracking eccentricity, obliquity and precession) we observe that the MD of WF is significantly coherent with the precession during the MIS KM5 and significantly coherent with the eccentricity during the MCO both antiphased (the higher the E+T-P, the smaller the WF). If we now look at the number WF AR coherence with the E+T-P, we observe a significant coherence at obliquity and precession periodicities during the MIS KM5, both in phase (the higher the E+T-P, the higher the number of WF flux). During the MCO, the number WF AR is coherent with E+T-P at eccentricity and obliquity periodicities, both antiphased (the higher the E+T-P, the lower the number WF flux). This means that there is a different response of the WF productivity between the Miocene and the Pliocene, and it is very likely that something has changed in the way they answer to the climate forcing between these two time intervals.

IV.4 Discussion

We observe an increase of pelagic carbonate production from the MCO to the MIS KM5, and follow the orbital periodicities within each time interval (without lags). When the total pelagic carbonate production is increasing it is because the pelagic carbonate production within the two groups is increasing, but not the same amplitude (at the origin of the variability of the relative contribution of the two groups to the total pelagic carbonate production through the time). The changes in foraminifera AR are not driven by the changes of sizes but by the changes of their number (they even are smaller), this states contrary results that what has been found by previous work (Guidi et al., 2009). This can be explained by a shift towards at least first order planktic foram patterns where eutrophic areas are dominated by smaller more opportunistic taxa with different life strategy. We do observe the same correlation for the small fraction, with an increase of carbonate accumulation rate of the small fraction well correlated to the increase of the coccoliths number. The presence of a higher number of particles AR during the Pliocene than during the Miocene is at the origin of the higher $CaCO_3$ AR for the two size classes but also of the bulk $CaCO_3$ AR (Chapters #II and #III). This observation is in line with what has been seen in the current carbonate fluxes to the deep ocean (Kiss et al., 2021), with a carbonate production driven by the number of shells rather than their weight or sizes.

The contribution of the coarse fraction to the bulk is increasing with the increase of $CaCO_3$ AR bulk, following the E+T-P and independently of the phase relationship with the E+T-P (in phase during the Pliocene and antiphased during the Miocene, Chapters #II and #III). Our results are coherent with what have been found by Suchéras-Marx et al. (2019) and Bolton et al. (2016), stating a decrease of the coccoliths sizes from the Neogene to present in equatorial oceans. Furthermore, we observe a similar trend for the planktonic foraminifera, which tends to be the opposite direction compared to what has been found by Schmidt et al. (2004). On another hand, we join their conclusion concerning the size increase we observe during the cooling intervals. Furthermore, we did not find either a co-variance between the sizes of these both pelagic carbonate calcifiers and the oceanic structure changes, following the orbital cycles - between and within the two time intervals -, which seems to be forced by another parameter. Our results are also questioning the conclusions by Barker and Elderfield (2002) because if they have linked the increase of pelagic carbonate production to the weight of the foraminifera shells, this does not seem to be the main factor controlling it at all, and it seems to be more their number than their weight to be driving the changes in pelagic carbonate production, on both time scales and both for the Miocene and the Pliocene.

The observation of a $CaCO_3$ AR and number WF AR following the E+T-P for both the Pliocene and Miocene (Figure 6, coherence with E+T-P) is underlying that the number of specimens is driving the total $CaCO_3$ AR by increasing both the planktonic foraminifera and the coccoliths production -not the same order of amplitude- (Chapter #III) and this is following the changes in ocean conditions, directly driven by the orbital periodicities, more than the global climate and ice volume itself. Specifically, for the coccoliths, the changes observed in the flux are so large that it cannot be only an increase of the number of coccoliths per coccosphere, so we propose that the number of coccosphere might have increase too for these intervals, very likely due to favourable environmental conditions (i.e. upwellings, nutrient delivery, light, pCO_2 and temperature). For both the planktonic foraminifera and the coccoliths, the size or the taxonomy doesn't seem to be the major component of the changes in pelagic carbonate production. The size and the number of specimens AR do not seem to co-vary, but we showed a trend to a decrease of the size with the increase of number (without explaining 100 % of the size variability).

This trend is more visible for the coccoliths than for the planktonic foraminifera, so apparently the size and number of coccoliths are more independent than the size and number of planktonic foraminifera (might be because for the foraminifera the variability is higher and the shape is changing more than coccoliths?). If the planktonic foraminifera taxonomy was already expected to be changing between the Pliocene and the Miocene, our shape indexes indicate that it is also changing within the time interval, with fluctuations of how elongated and lobate they are. This shows that not only their number and sizes are changing, but also the species assemblages.

The orbital cyclicities are found in all our records, for both the planktonic foraminifera and the coccoliths and both for the MIS KM5 and the MCO. But if we looked more in detail, the periodicities are different between Miocene and Pliocene and are not always the same for planktonic foraminifera and coccoliths.

IV.5 Conclusion

We aimed to understand the drivers of changes in carbonate production within the two main pelagic carbonate producers (planktonic foraminifera and coccoliths), the timings of it and their orbital scale variability. To do so, we used automated microscopy and image recognition on orbitally resolved samples from two warm periods: the Pliocene warm period and the Miocene climatic optimum, in the tropical Atlantic Ocean (Ceará Rise). For those two time intervals, and for both the planktonic foraminifera and the coccoliths, the specimens were counted and measured, and spectral analysis have been run on all the records we obtained, to 1) identify the main periodicities in it, and 2) identify the relationship between these periodicities and the actual orbital parameters signal.

We here highlighted that the changes of pelagic carbonate production, following the orbital changes more than the global climate state itself (without lags) is explained by an increase of the number of specimens for the two periods of interest. At both orbital time scales and between the Miocene and the Pliocene, carbonate production is driven by population growth rather than changes of size or taxonomy, and we even found a reverse relationship with a shift towards smaller specimens when the $CaCO_3$ production increases. This relationship is valid even with different dominant orbital cyclicity in pelagic carbonate production between the Miocene and Pliocene and for both pelagic carbonate producers, so it is very likely to be a general characteristic of the pelagic carbonate production in the tropical oceans. We observe an increase of $CaCO_3$ AR with the increase of E+T-P, with higher amplitude changes of the foraminifera productivity than the coccoliths, explaining the modulation of their relative contribution to the total carbonate production (also explaining the higher relative contribution of the coccoliths during the low E+T-P -cooler- time intervals. So, with the warming and the orbital forcing, there is an increase of both fractions' productivity, but with different conditions of the different intervals, this increase is stronger for one fraction than the other, with a dominance of the coarse fraction during the most recent time intervals. On long geological time scale, from the warm Miocene (+3 to 8°C compared to actual temperature and a pCO_2 peaking between 460 and 564 ppm) to cooler Pliocene (+2 to 3°C compared to actual temperature and a pCO_2 between 330 and 425 ppm), we observe a decrease of the sizes and an increase of the number of specimens (and increase of the $CaCO_3$ AR). This makes sense, logical, as if we well have warm intervals, and a warming on orbital time scale, we do have a cooling from Miocene to Quaternary on geological time scale. Additionally, the relationship between the number of specimens and their sizes (the higher the number of specimens AR, the smaller) is logical. Indeed, this, added to the light shift toward more round and more lobate specimens we observed for the planktonic foraminifera, is very likely to reflect compositional changes at species level, with differently calcified taxa causing the differences in $CaCO_3$ AR.

With the conditions changing and current global warming, we can expect even higher productivity in the future, particularly for the foraminifera fraction, which could have a drastic impact on the ocean chemistry and capacity of the ocean to absorb (anthropogenic) CO_2 (Boudreau et al., 2018). Increasing the carbonate production and so the CO_2 uptake and export to the deep ocean would have two opposite effects: reduce the ions concentration in the seawater and so increase the carbonate dissolution and via the carbonate counter pump, having a positive feedback on the CO_2 release. In order to evaluate the influence of biological compensation on the future capacity of the ocean to stock CO_2, it is important to estimate the population growth of the two main pelagic carbonate producers.

The question remains about the taxonomic evolutions of both the planktonic foraminifera and the coccolithophores in this context, to see if the observed changes are due to changes of number of specimens with species remaining the same or if the species assemblage is changing as well (or maybe both?) for the two groups on orbital time scales.

IV.6 Data availability

The datatables of this manuscript will be made available upon request to the the main author until their online publication on PANGAEA (https://pangaea.de, last visit: 8th December 2022).

IV.7 Acknowledgements

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IV.8 Bibliography

Barker, S. and Elderfield, H.: Foraminiferal Calcification Response to Glacial-Interglacial Changes in Atmospheric CO_2, Science, 297, 833–836, https://doi.org/10.1126/science.1072815, 2002.

Barker, S., Archer, D., Booth, L., Elderfield, H., Henderiks, J., and Rickaby, R. E. M.: Globally increased pelagic carbonate production during the Mid-Brunhes dissolution interval and the CO_2 paradox of MIS 11, Quaternary Science Reviews, 25, 3278–3293, https://doi.org/10.1016/j.quascirev.2006.07.018, 2006.

Beaufort, L. and Dollfus, D.: Automatic recognition of coccoliths by dynamical neural networks, Marine Micropaleontology, 51, 57–73, https://doi.org/10.1016/j.marmicro.2003.09.003, 2004.

Beaufort, L., Lancelot, Y., Camberlin, P., Cayre, O., Vincent, E., Bassinot, F., and Labeyrie, L.: Insolation cycles as a major control of equatorial Indian Ocean primary production, Science, 278, 1451–1454, 1997.

Beaufort, L., Probert, I., de Garidel-Thoron, T., Bendif, E. M., Ruiz-Pino, D., Metzl, N., Goyet, C., Buchet, N., Coupel, P., Grelaud, M., Rost, B., Rickaby, R. E. M., and de Vargas, C.: Sensitivity of coccolithophores to carbonate chemistry and ocean acidification, Nature, 476, 80–83, https://doi.org/10.1038/nature10295, 2011.

Beaufort, L., Barbarin, N., and Gally, Y.: Optical measurements to determine the thickness of calcite crystals and the mass of thin carbonate particles such as coccoliths, Nature Protocols, 9, 633–642, https://doi.org/10.1038/nprot.2014.028, 2014.

Chapter IV. Population growth of foraminifera and coccolithophores, rather than changes in individual calcification, drove variations of Neogene pelagic carbonate production in tropical Ocean.

Bolton, C. T., Hernández-Sánchez, M. T., Fuertes, M.-Á., González-Lemos, S., Abrevaya, L., Mendez-Vicente, A., Flores, J.-A., Probert, I., Giosan, L., Johnson, J., and Stoll, H. M.: Decrease in coccolithophore calcification and CO_2 since the middle Miocene, Nature Communications, 7, 10284, https://doi.org/10.1038/ncomms10284, 2016.

Boudreau, B. P., Middelburg, J. J., and Luo, Y.: The role of calcification in carbonate compensation, Nature Geoscience, 11, 894–900, https://doi.org/10.1038/s41561-018-0259-5, 2018.

Brummer, G. J. A. and van Eijden, A. J. M.: "Blue-ocean" paleoproductivity estimates from pelagic carbonate mass accumulation rates, Marine Micropaleontology, 19, 99–117, https://doi.org/10.1016/0377-8398(92)90023-D, 1992.

Chiu, T.-C. and Broecker, W. S.: Toward better paleocarbonate ion reconstructions: New insights regarding the $CaCO_3$ size index, Paleoceanography, 23, PA2216, https://doi.org/10.1029/2008PA001599, 2008.

Cullen, J. L. and Curry, W. B.: Variations in planktonic foraminifer faunas and carbonate preservation at Site 927: evidence for changing surface water conditions in the western tropical Atlantic Ocean during the middle Pleistocene, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 207–228, https://doi.org/10.2973/odp.proc.sr.154.111.1997, 1997.

Curry, W. B., Shackleton, N. J., Richter, C., and et al. (Eds.): Proceedings of the Ocean Drilling Program, 154 Initial Reports, Ocean Drilling Program, https://doi.org/10.2973/odp.proc.ir.154.1995, 1995.

Von Dassow, P., Díaz-Rosas, F., Bendif, E. M., Gaitán-Espitia, J.-D., Mella-Flores, D., Rokitta, S., John, U., and Torres, R.: Over-calcified forms of the coccolithophore *Emiliania huxleyi* in high-CO_2 waters are not preadapted to ocean acidification, Biogeosciences, 15, 1515–1534, https://doi.org/10.5194/bg-15-1515-2018, 2018.

De Bodt, C., Van Oostende, N., Harlay, J., Sabbe, K., and Chou, L.: Individual and interacting effects of pCO_2 and temperature on *Emiliania huxleyi*calcification: study of the calcite production, the coccolith morphology and the coccosphere size, Biogeosciences, 7, 1401–1412, https://doi.org/10.5194/bg-7-1401-2010, 2010.

Drury, A. J., Liebrand, D., Westerhold, T., Beddow, H. M., Hodell, D. A., Rohlfs, N., Wilkens, R. H., Lyle, M., Bell, D. B., Kroon, D., Pälike, H., and Lourens, L. J.: Climate, cryosphere and carbon cycle controls on Southeast Atlantic orbital-scale carbonate deposition since the Oligocene (30–0 Ma), Clim. Past, 17, 2091–2117, https://doi.org/10.5194/cp-17-2091-2021, 2021.

Foster, G. L., Lear, C. H., and Rae, J. W. B.: The evolution of pCO_2, ice volume and climate during the middle Miocene, Earth and Planetary Science Letters, 341–344, 243–254, https://doi.org/10.1016/j.epsl.2012.06.007, 2012.

Frenz, M., Henrich, R., and Zychla, B.: Carbonate preservation patterns at the Ceará Rise – Evidence for the Pliocene super conveyor, Marine Geology, 232, 173–180, https://doi.org/10.1016/j.margeo.2006.07.006, 2006.

Guidi, L., Stemmann, L., Jackson, G. A., Ibanez, F., Claustre, H., Legendre, L., Picheral, M., and Gorskya, G.: Effects of phytoplankton community on production, size, and export of large aggregates: A world-ocean analysis, Limnology and Oceanography, 54, 1951–1963, https://doi.org/10.4319/lo.2009.54.6.1951, 2009.

Guidi, L., Legendre, L., Reygondeau, G., Uitz, J., Stemmann, L., and Henson, S. A.: A new look at ocean carbon remineralization for estimating deepwater sequestration, Global Biogeochemical Cycles, 29, 1044–1059, https://doi.org/10.1002/2014GB005063, 2015.

Hannisdal, B., Henderiks, J., and Liow, L. H.: Long- term evolutionary and ecological responses of calcifying phytoplankton to changes in atmospheric CO_2, Global Change Biology, 18, 3504–3516, https://doi.org/10.1111/gcb.12007, 2012.

Henderiks, J.: Coccolithophore size rules — Reconstructing ancient cell geometry and cellular calcite quota from fossil coccoliths, Marine Micropaleontology, 67, 143–154, https://doi.org/10.1016/j.marmicro.2008.01.005, 2008.

Herbert, T. D., Lawrence, K. T., Tzanova, A., Peterson, L. C., Caballero-Gill, R., and Kelly, C. S.: Late Miocene global cooling and the rise of modern ecosystems, Nature Geoscience, 9, 843–847, https://doi.org/10.1038/ngeo2813, 2016.

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 and Planetary Science Letters, 261, 534–550, https://doi.org/10.1016/j.epsl.2007.07.026, 2007.

Iglesias-Rodriguez, M. D., Halloran, P. R., Rickaby, R. E. M., Hall, I. R., Colmenero-Hidalgo, E., Gittins, J. R., Green, D. R. H., Tyrrell, T., Gibbs, S. J., von Dassow, P., Rehm, E., Armbrust, E. V., and Boessenkool, K. P.: Phytoplankton Calcification in a High-CO_2 World, Science, 320, 336–340, https://doi.org/10.1126/science.1154122, 2008.

Jones, B. M., Iglesias-Rodriguez, M. D., Skipp, P. J., Edwards, R. J., Greaves, M. J., Young, J. R., Elderfield, H., and O'Connor, C. D.: Responses of the Emiliania huxleyi Proteome to Ocean Acidification, PLoS ONE, 8, e61868, https://doi.org/10.1371/journal.pone.0061868, 2013.

Kiss, P., Jonkers, L., Hudáčková, N., Reuter, R. T., Donner, B., Fischer, G., and Kucera, M.: Determinants of Planktonic Foraminifera Calcite Flux: Implications for the Prediction of Intra- and Inter- Annual Pelagic Carbonate Budgets, Global Biogeochem Cycles, 35, https://doi.org/10.1029/2020GB006748, 2021.

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, Astronomy & Astrophysics, 428, 261–285, https://doi.org/10.1051/0004-6361:20041335, 2004.

Laws, E. A., Falkowski, P. G., Smith, W. O., Ducklow, H., and McCarthy, J. J.: Temperature effects on export production in the open ocean, Global Biogeochemical Cycles, 14, 1231–1246, https://doi.org/10.1029/1999GB001229, 2000.

Liebrand, D., Beddow, H. M., Lourens, L. J., Pälike, H., Raffi, I., Bohaty, S. M., Hilgen, F. J., Saes, M. J. M., Wilson, P. A., van Dijk, A. E., Hodell, D. A., Kroon, D., Huck, C. E., and Batenburg, S. J.: Cyclostratigraphy and eccentricity tuning of the early Oligocene through early Miocene (30.1–17.1 Ma): Cibicides mundulus stable oxygen and carbon isotope records from Walvis Ridge Site 1264, Earth and Planetary Science Letters, 450, 392–405, https://doi.org/10.1016/j.epsl.2016.06.007, 2016.

Lisiecki, L. E. and Raymo, M. E.: A Pliocene-Pleistocene stack of 57 globally distributed benthic $\delta^{18}O$ records, Paleoceanography, 20, PA1003, https://doi.org/10.1029/2004PA001071, 2005.

Lyle, M., Drury, A. J., Tian, J., Wilkens, R., and Westerhold, T.: Late Miocene to Holocene high-resolution eastern equatorial Pacific carbonate records: stratigraphy linked by dissolution and paleoproductivity, Climate of the Past, 15, 1715–1739, https://doi.org/10.5194/cp-15-1715-2019, 2019.

Milliman, J. D.: Production and accumulation of calcium carbonate in the ocean: budget of a nonsteady state, Global Biogeochemical Cycles, 7, 927–957, 1993.

Paillard, D., Labeyrie, L., and Yiou, P.: Macintosh Program performs time-series analysis, Eos Trans. AGU, 77, 379–379, https://doi.org/10.1029/96EO00259, 1996.

Pälike, H., Frazier, J., and Zachos, J. C.: Extended orbitally forced palaeoclimatic records from the equatorial Atlantic Ceara Rise, Quaternary Science Reviews, 25, 3138–3149, https://doi.org/10.1016/j.quascirev.2006.02.011, 2006.

Pound, M. J., Haywood, A. M., Salzmann, U., and Riding, J. B.: Global vegetation dynamics and latitudinal temperature gradients during the Mid to Late Miocene (15.97–5.33Ma), Earth-Science Reviews, 112, 1–22, https://doi.org/10.1016/j.earscirev.2012.02.005, 2012.

R Core Team: R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria., 2021.

Ravelo, A. C., Andreasen, D. H., Lyle, M., Olivarez Lyle, A., and Wara, M. W.: Regional climate shifts caused by gradual global cooling in the Pliocene epoch, Nature, 429, 263–267, https://doi.org/10.1038/nature02567, 2004.

Roesch, A. and Schmidbauer, H.: WaveletComp: Computational Wavelet Analysis., 2018.

Schmidt, D. N., Thierstein, H. R., and Bollmann, J.: The evolutionary history of size variation of planktic foraminiferal assemblages in the Cenozoic, Palaeogeography, Palaeoclimatology, Palaeoecology, 22, 2004.

Sheward, R. M., Poulton, A. J., Gibbs, S. J., Daniels, C. J., and Bown, P. R.: Physiology regulates the relationship between coccosphere geometry and growth phase in coccolithophores, Biogeosciences, 14, 1493–1509, https://doi.org/10.5194/bg-14-1493-2017, 2017.

Si, W. and Rosenthal, Y.: Reduced continental weathering and marine calcification linked to late Neogene decline in atmospheric CO_2, Nature Geoscience, 12, 833–838, https://doi.org/10.1038/s41561-019-0450-3, 2019.

Spero, H. J., Bijma, J., Lea, D. W., and Bemis, B. E.: Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes, Nature, 390, 497–500, https://doi.org/10.1038/37333, 1997.

Suchéras-Marx, B., Mattioli, E., Allemand, P., Giraud, F., Pittet, B., Plancq, J., and Escarguel, G.: The colonization of the oceans by calcifying pelagic algae, Biogeosciences, 16, 2501–2510, https://doi.org/10.5194/bg-16-2501-2019, 2019.

Suchéras-Marx, B., Viseur, S., Walker, C. E., Beaufort, L., Probert, I., and Bolton, C.: Coccolith size rules – what controls the size of coccoliths during coccolithogenesis?, Marine Micropaleontology, 170, 17, https://doi.org/10.1016/j.marmicro.2021.102080, 2022.

Todd, C. L., Schmidt, D. N., Robinson, M. M., and De Schepper, S.: Planktic Foraminiferal Test Size and Weight Response to the Late Pliocene Environment, Paleoceanography and Paleoclimatology, 35, https://doi.org/10.1029/2019PA003738, 2020.

Yang, T.-N. and Wei, K.-Y.: How many coccoliths are there in a coccosphere of the extant coccolithophorids? A compilation, Journal of Nannoplankton Research, 25, 7–15, 2003.

You, Y., Huber, M., Muller, R. D., Poulsen, C. J., and Ribbe, J.: Simulation of the Middle Miocene Climate Optimum, Geophysical Research Letters, 36, 5, https://doi.org/10.1029/2008GL036571, 2009.

Zachos, J. C., Dickens, G. R., and Zeebe, R. E.: An early Cenozoic perspective on greenhouse warming and carbon-cycle dynamics, Nature, 451, 279–283, https://doi.org/10.1038/nature06588, 2008.

Zarkogiannis, S. D., Kontakiotis, G., Antonarakou, A., Mortyn, P. G., and Drinia, H.: Latitudinal Variation of Planktonic Foraminifera Shell Masses During Termination I, IOP Conf. Series: Earth and Environmental Science, 221, 012052, https://doi.org/10.1088/1755-1315/221/1/012052, 2019.

Zondervan, I.: The effects of light, macronutrients, trace metals and CO_2 on the production of calcium carbonate and organic carbon in coccolithophores—A review, Deep Sea Research Part II: Topical Studies in Oceanography, 54, 521–537, https://doi.org/10.1016/j.dsr2.2006.12.004, 2007.

IV.9. Appendix/supplements

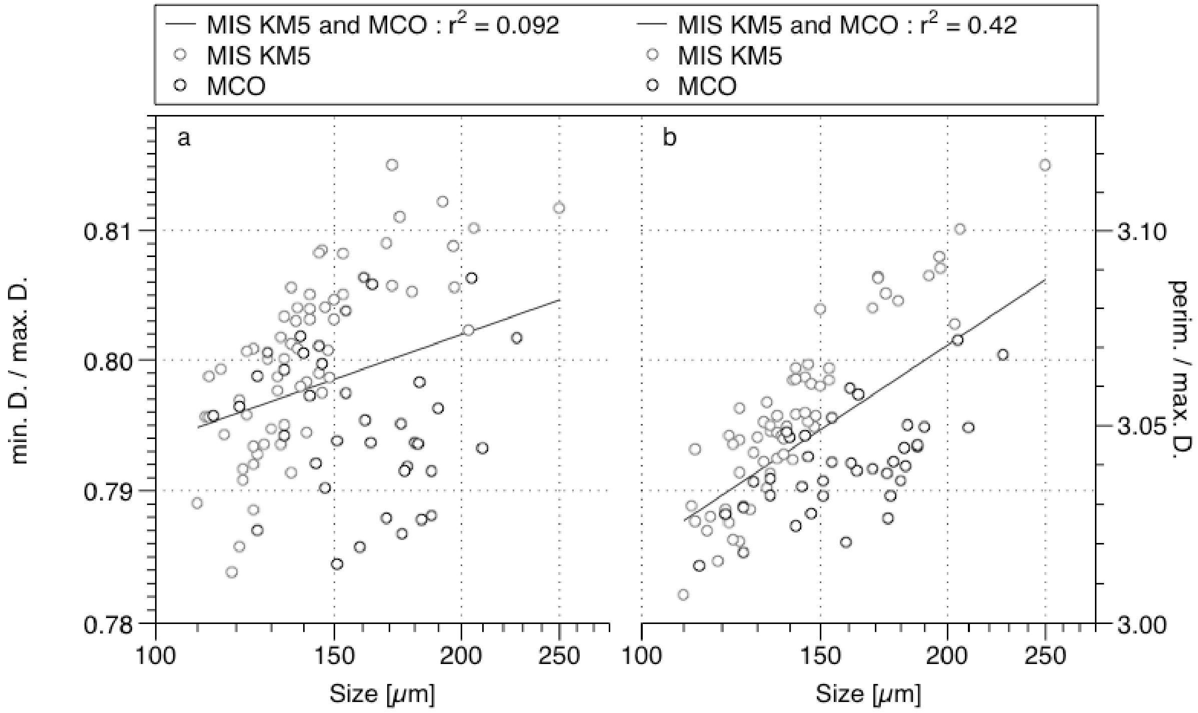

Figure S1. a) Minimum diameter / maximum diameter of the whole foraminifera versus their maximum diameter (size); b) Perimeter / maximum diameter of the whole foraminifera versus their maximum diameter (size).

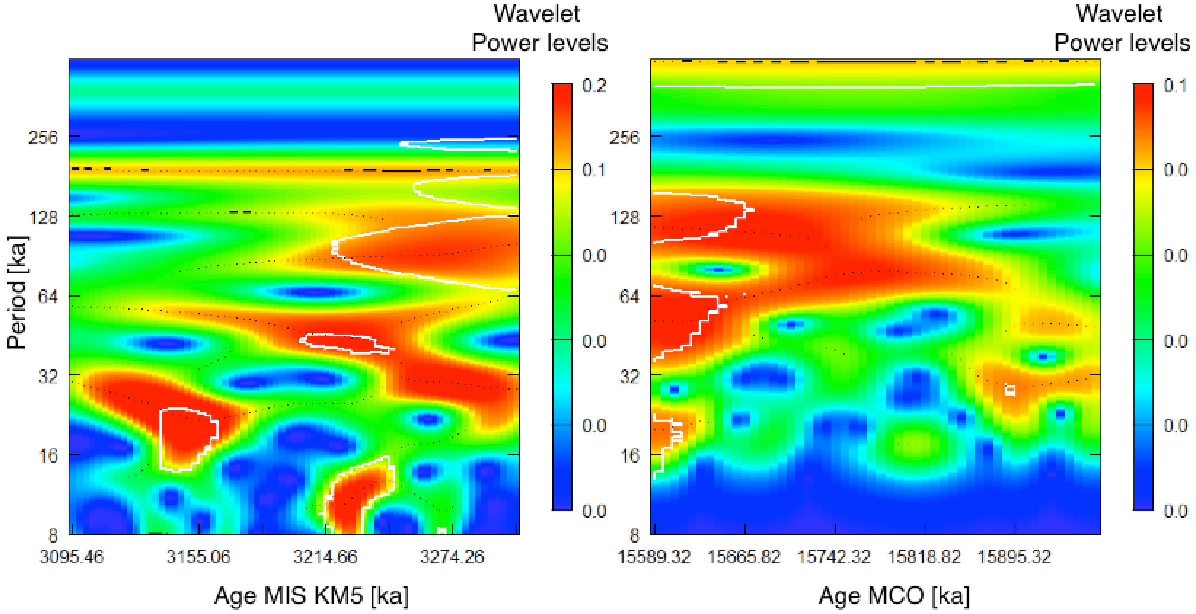

Figure S2. WT analysis of the total $CaCO_3$ AR for the Pliocene and the Miocene

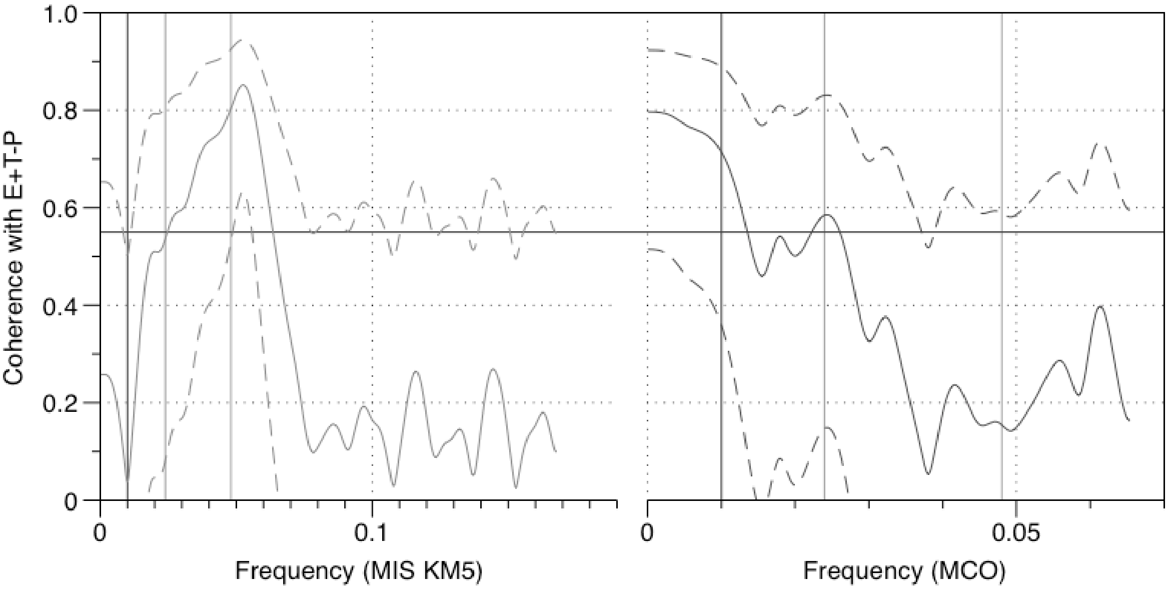

Figure S3. CBT coherence of the total $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

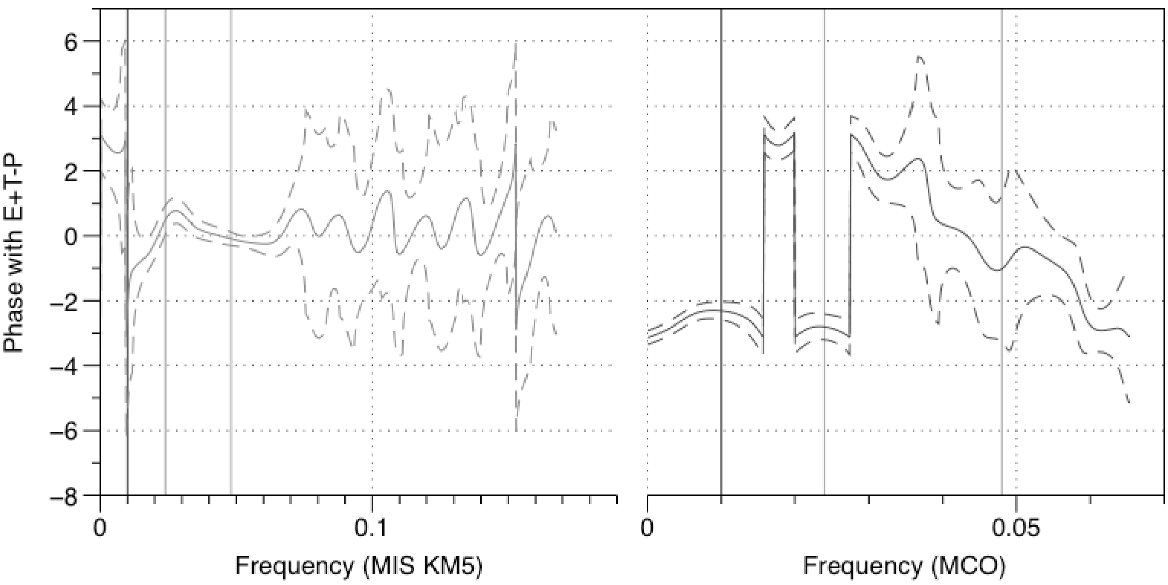

Figure S4. CBT Phase of the total $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

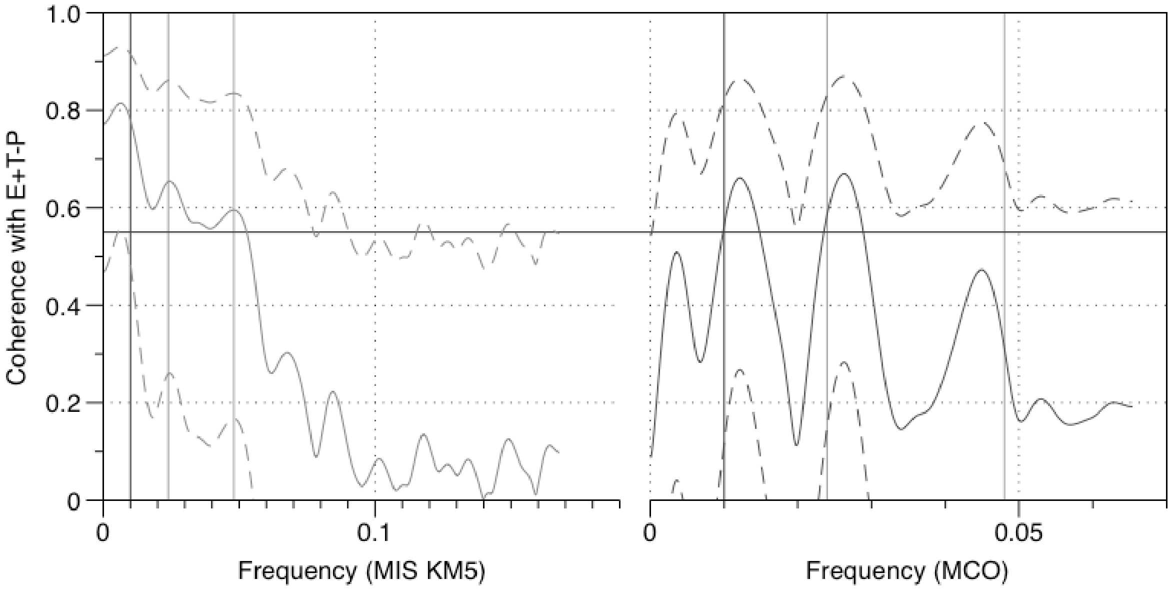

Figure S5. CBT coherence of the contribution of the coarse fraction (>63 µm) to the total $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

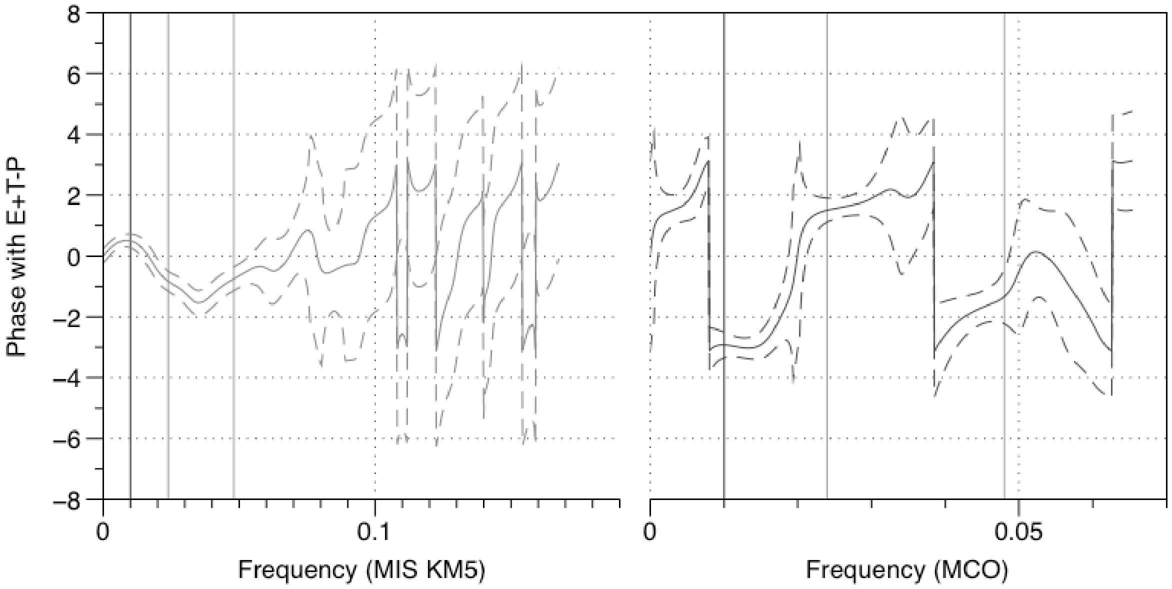

Figure S6. CBT phase of the contribution of the coarse fraction (>63 µm) to the total $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

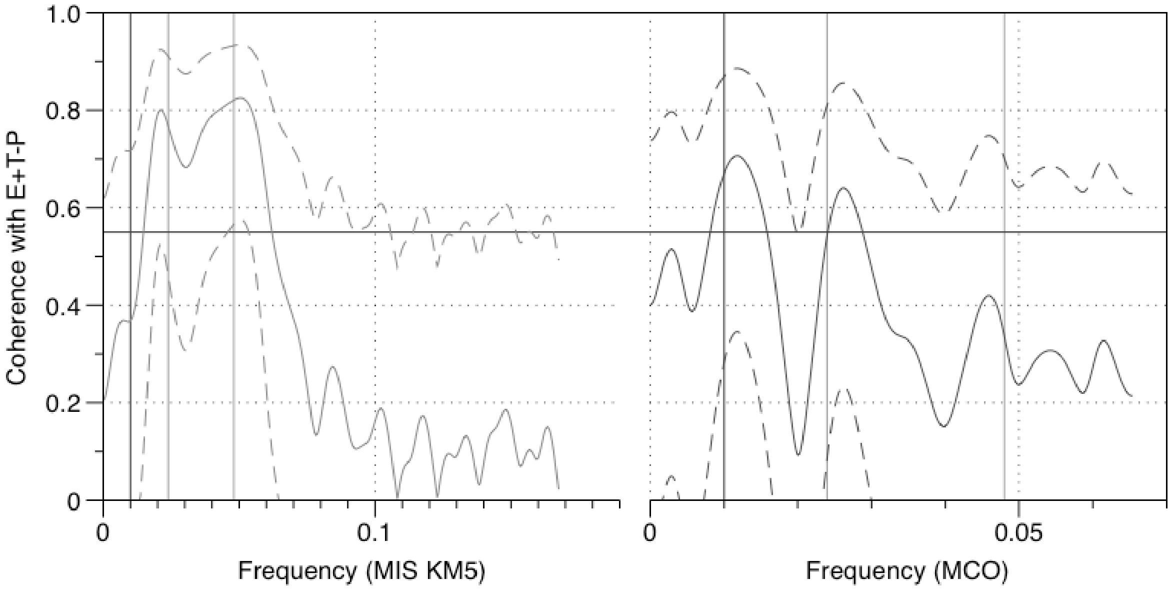

Figure S7. CBT coherence of the coarse fraction (>63 µm) $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

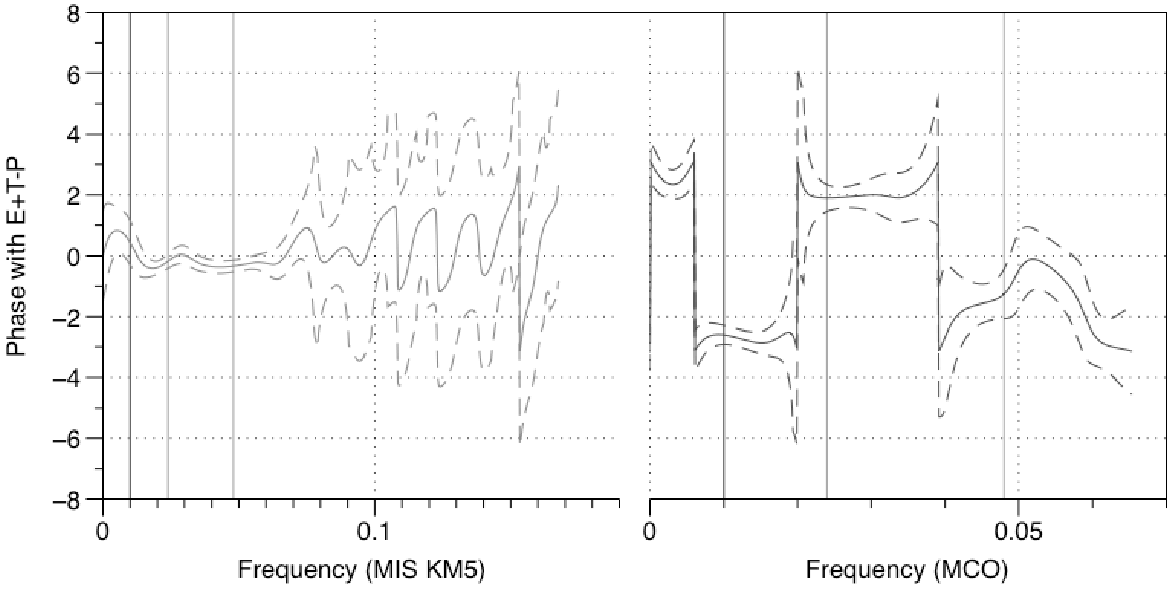

Figure S8. CBT phase of the coarse fraction (>63 µm) $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

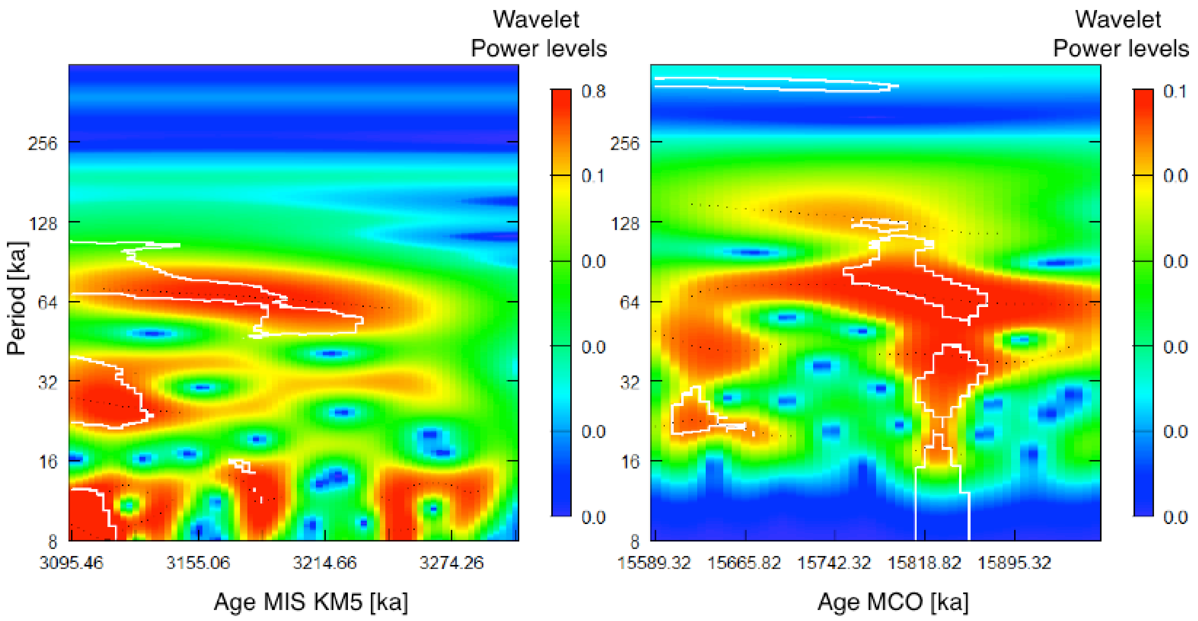

Figure S9. WT analysis of the maximum diameter of the WF for the Pliocene and the Miocene

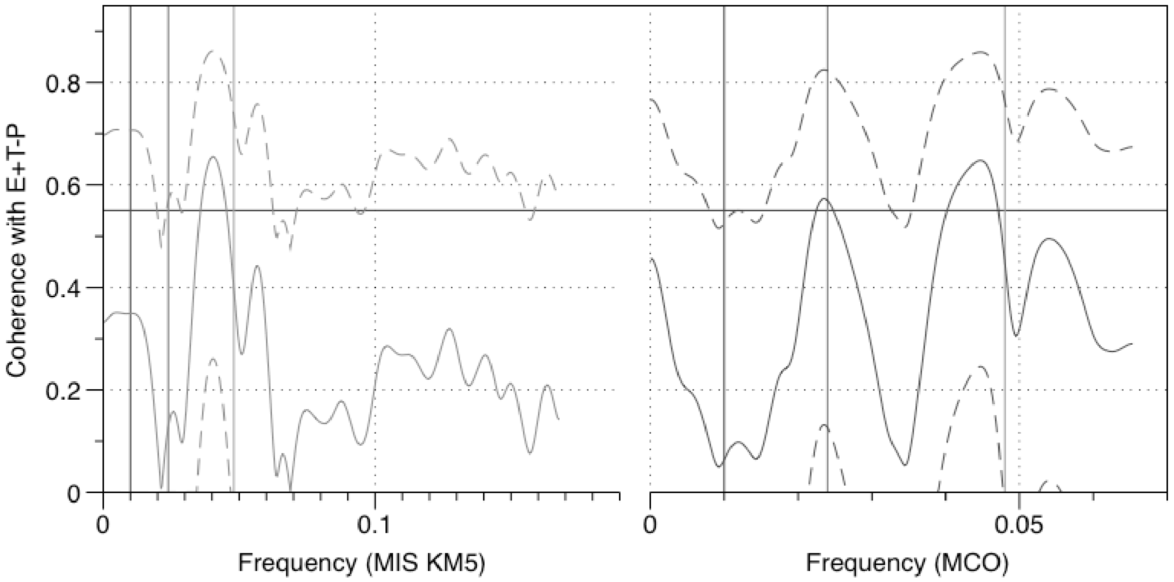

Figure S10. CBT coherence of the maximum diameter of the WF with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

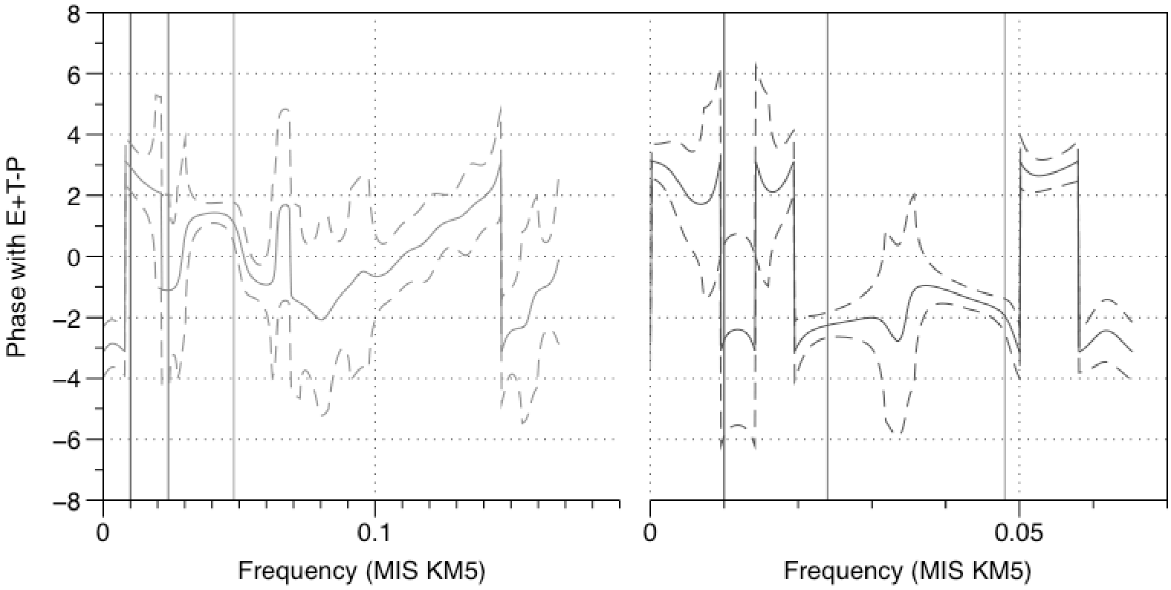

Figure S11. CBT phase of the maximum diameter of the WF with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

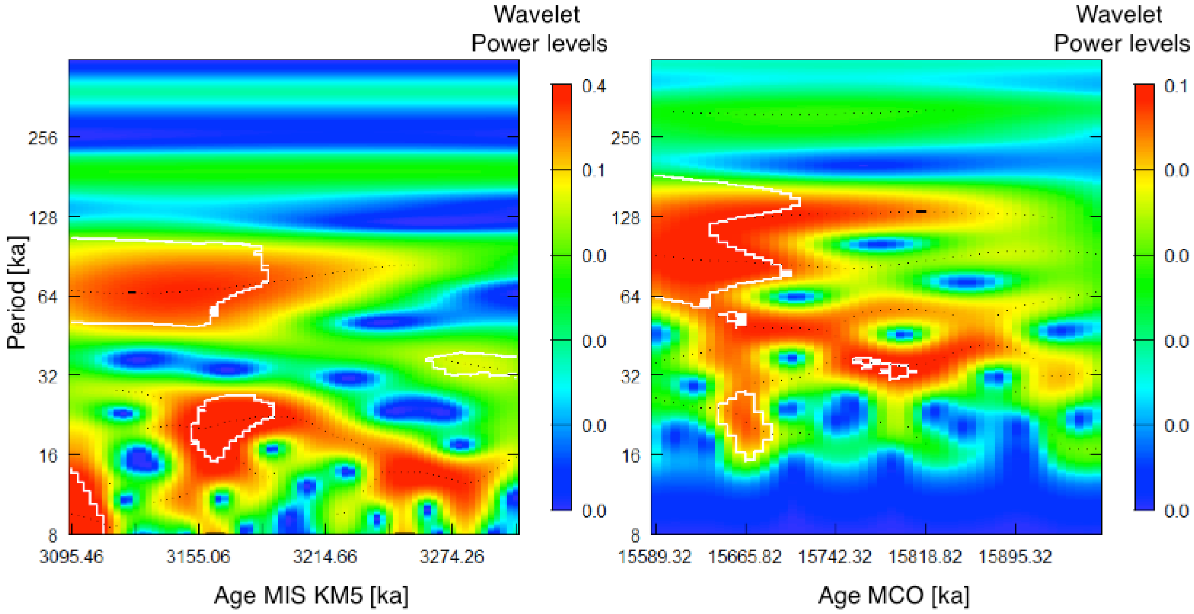

Figure S12. WT analysis of the number of WF AR for the Pliocene and the Miocene

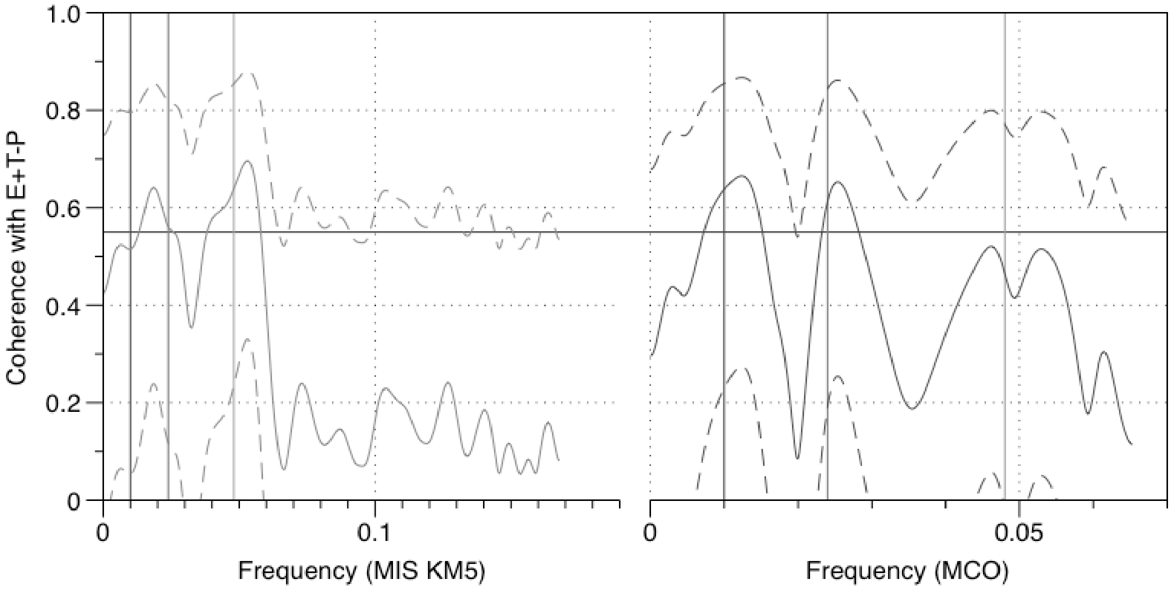

Figure S13. CBT coherence of the number of WF AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

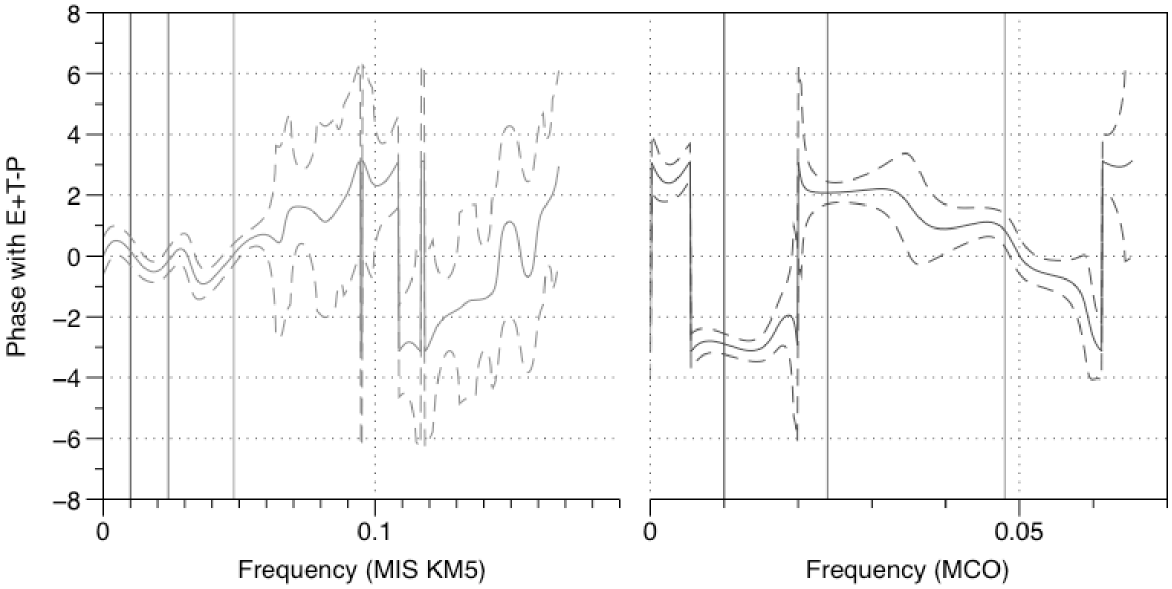

Figure S14. CBT phase of the number of WF AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

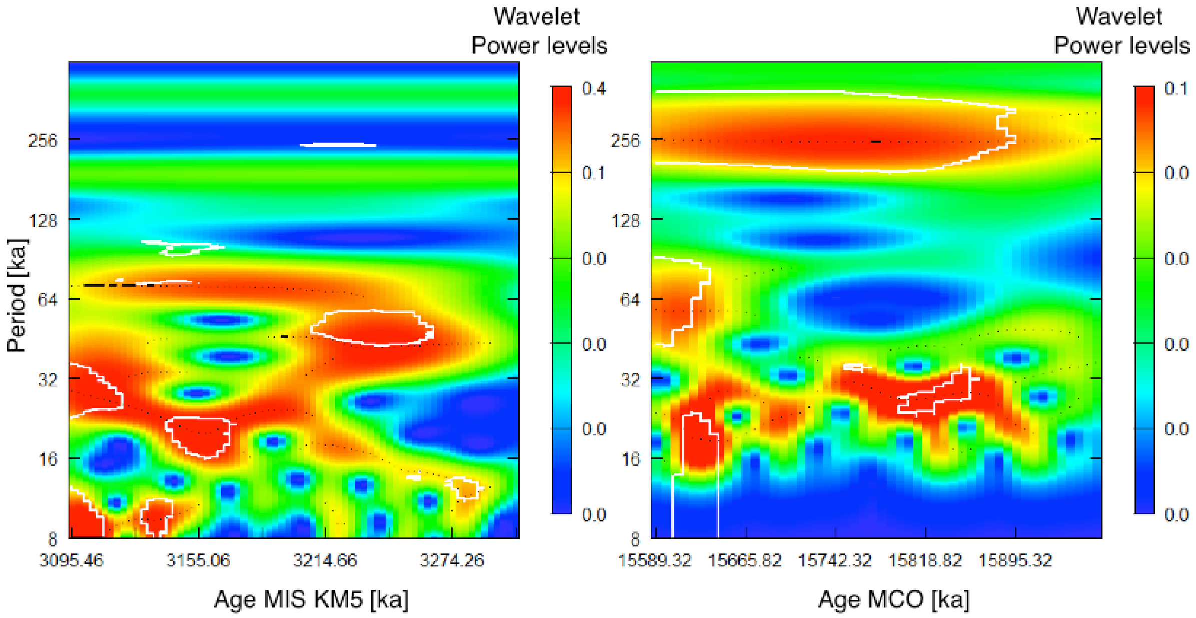

Figure S15. WT analysis of the minimum diameter / maximum diameter of WF for the Pliocene and the Miocene

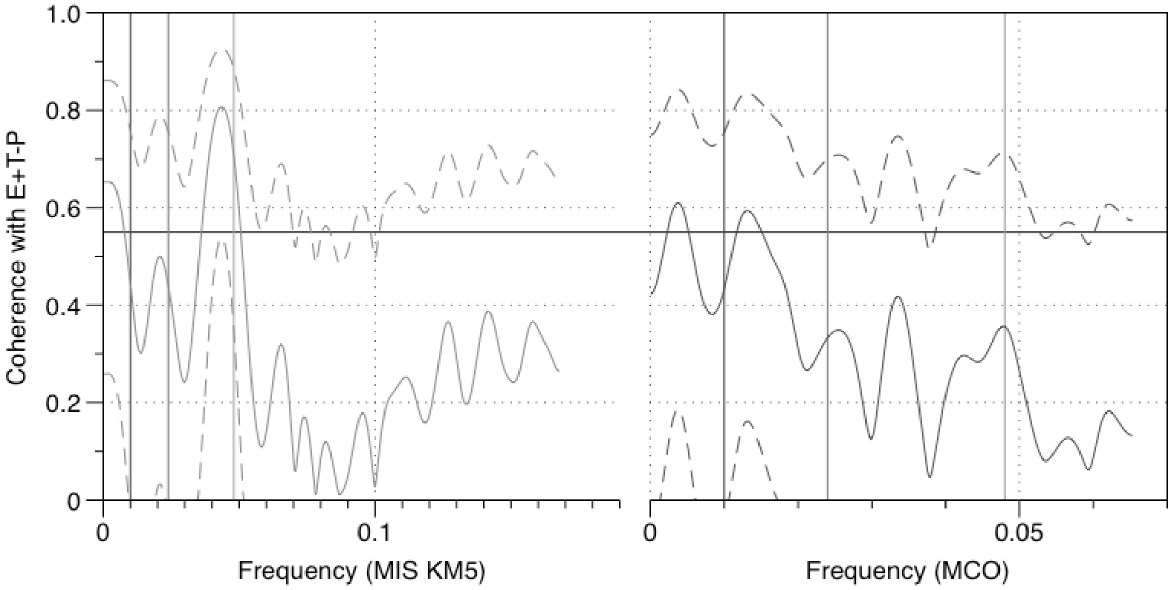

Figure S16. CBT coherence of the minimum diameter / maximum diameter of WF with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

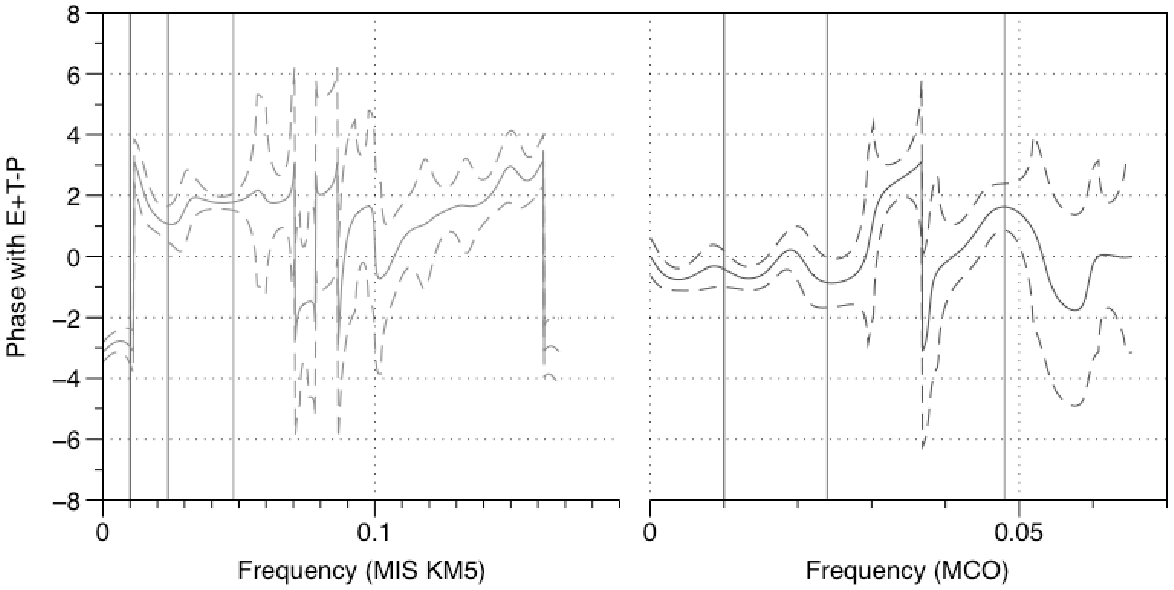

Figure S17. CBT phase of the minimum diameter / maximum diameter of WF with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

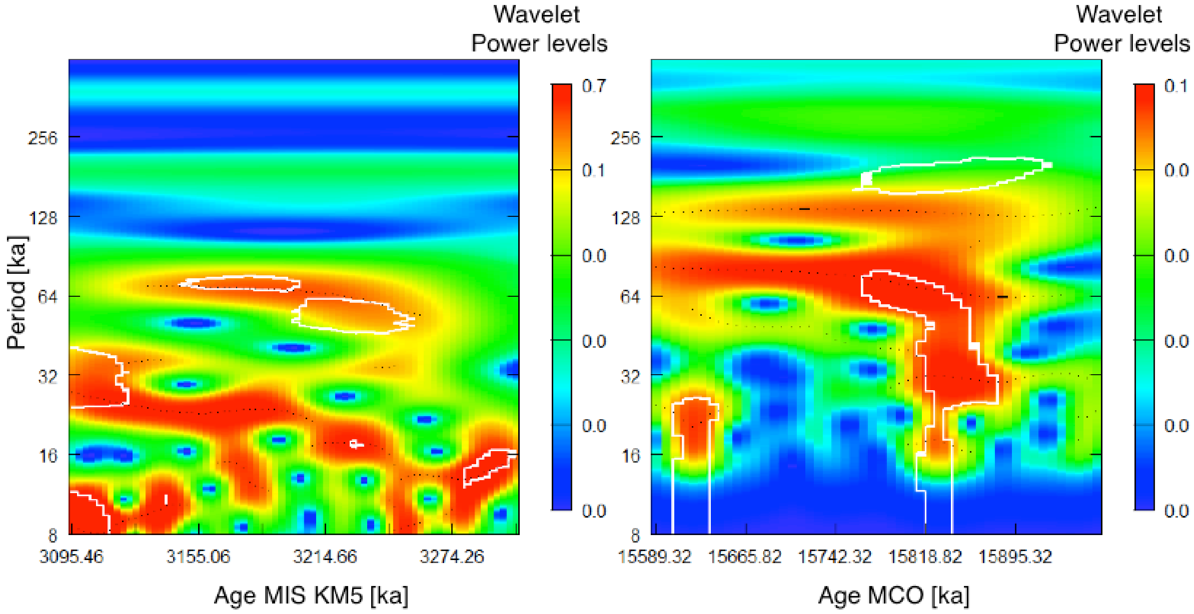

Figure S18. WT analysis of the perimeter / maximum diameter of WF for the Pliocene and the Miocene

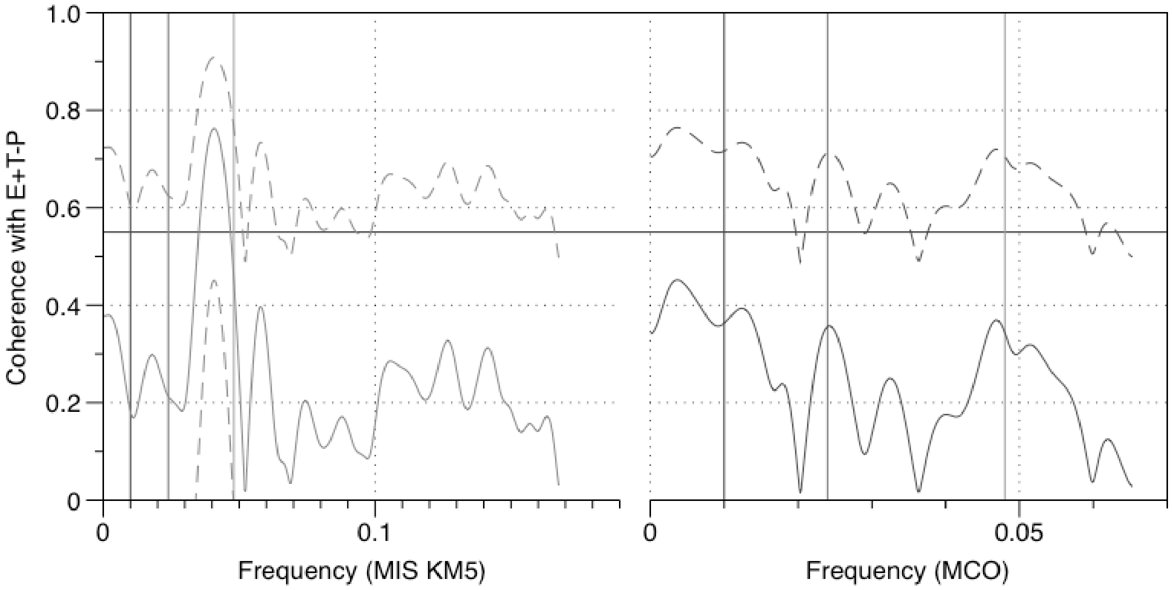

Figure S19. CBT coherence of the perimeter / maximum diameter of WF with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

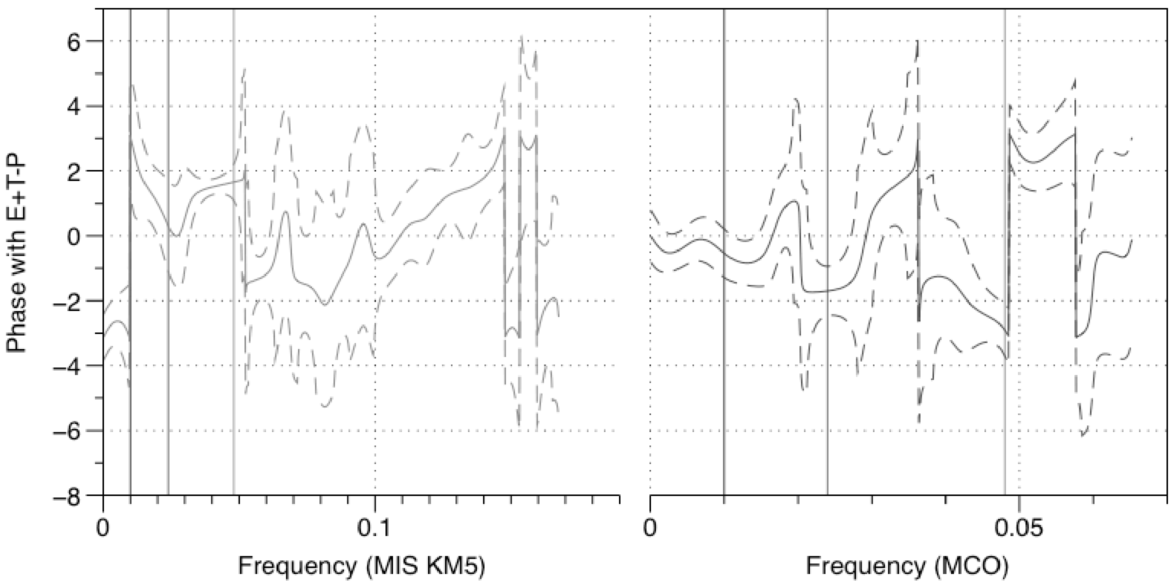

Figure S20. CBT phase of the perimeter / maximum diameter of WF with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

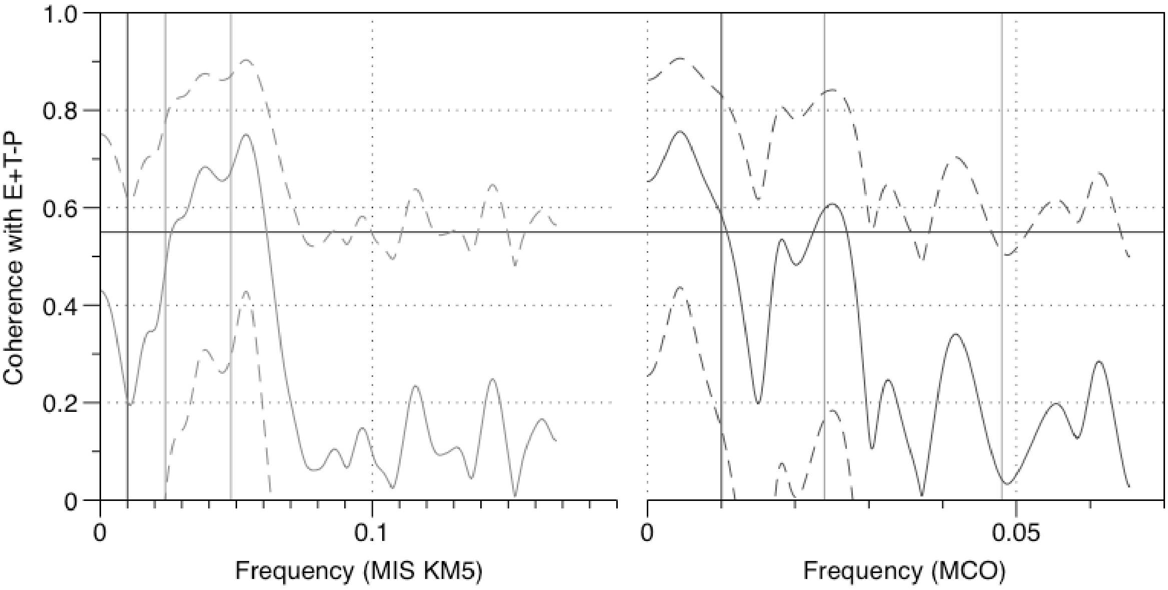

Figure S21. CBT coherence of the small fraction (<63 μm) $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

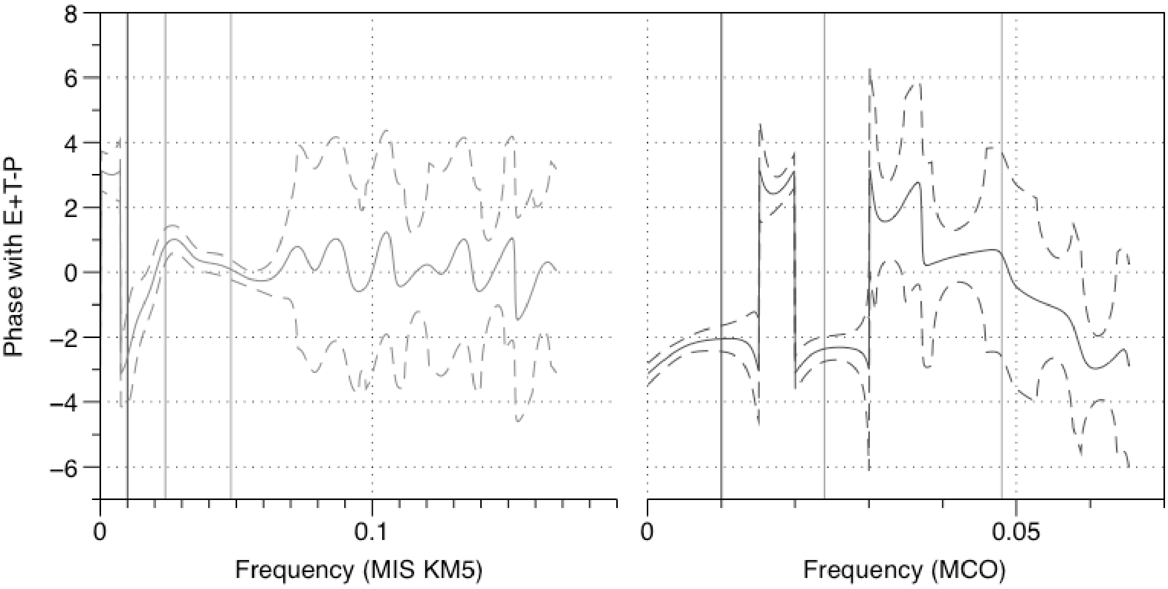

Figure S22. CBT phase of the small fraction (<63 μm) $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

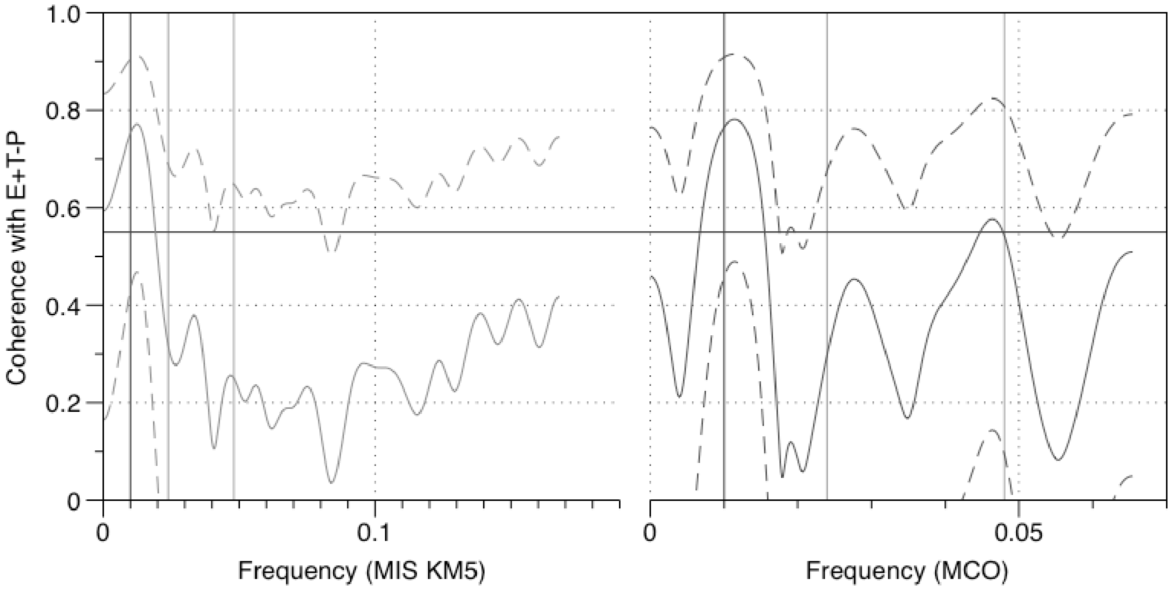

Figure S23. CBT coherence of the small fraction (<32 μm) $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

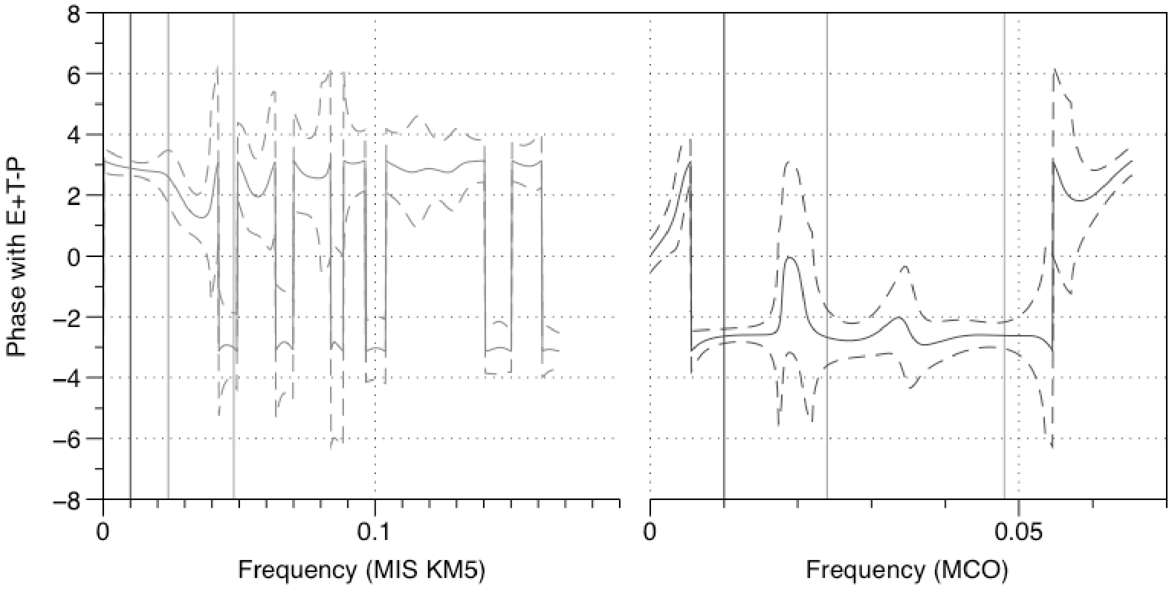

Figure S24. CBT phase of the small fraction (<32 μm) $CaCO_3$ AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

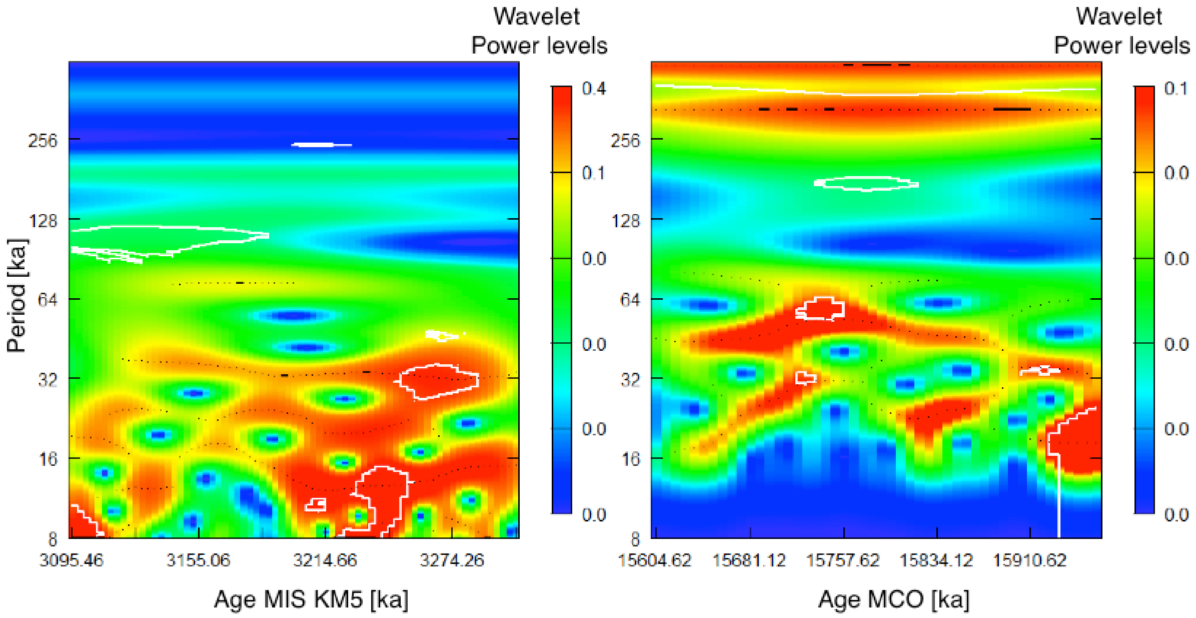

Figure S25. WT analysis of the size of the coccoliths for the Pliocene and the Miocene

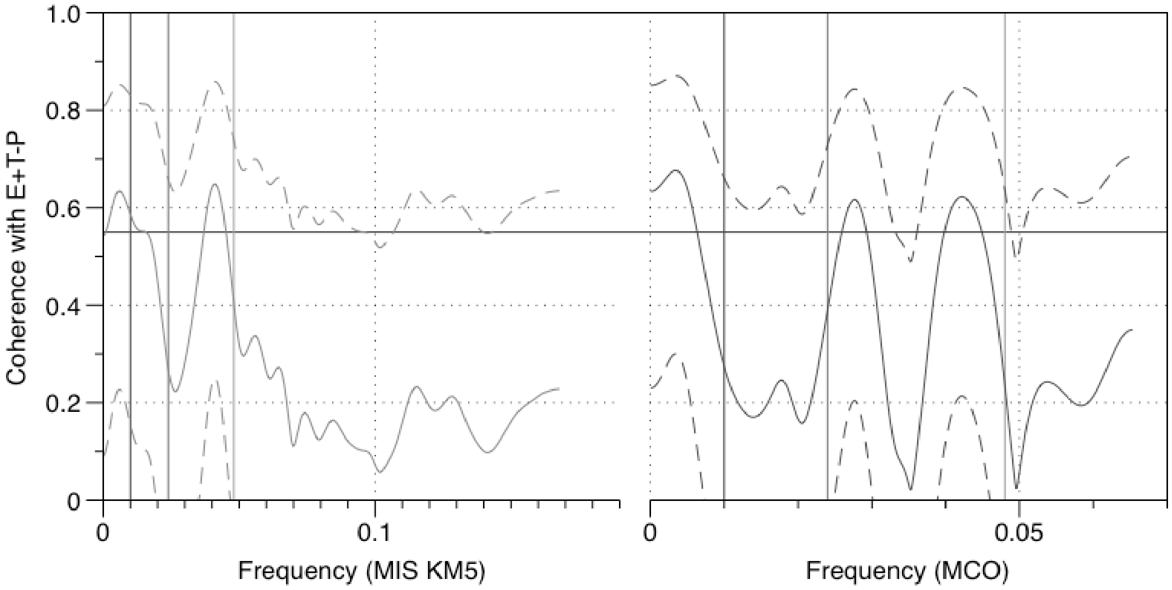

Figure S26. CBT coherence of the size of the coccoliths with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

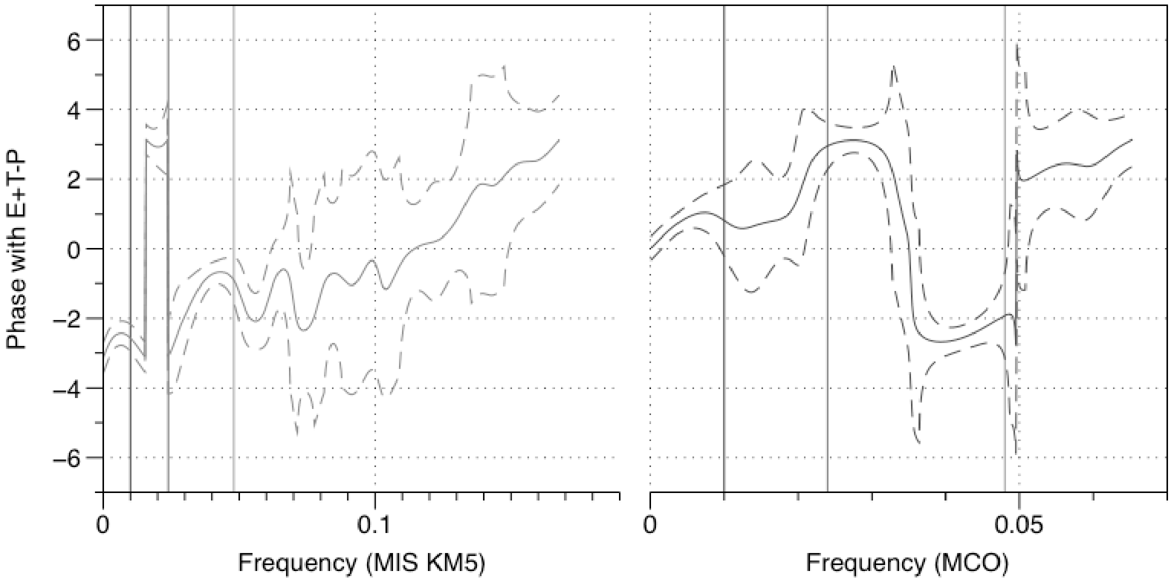

Figure S27. CBT phase of the size of the coccoliths with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

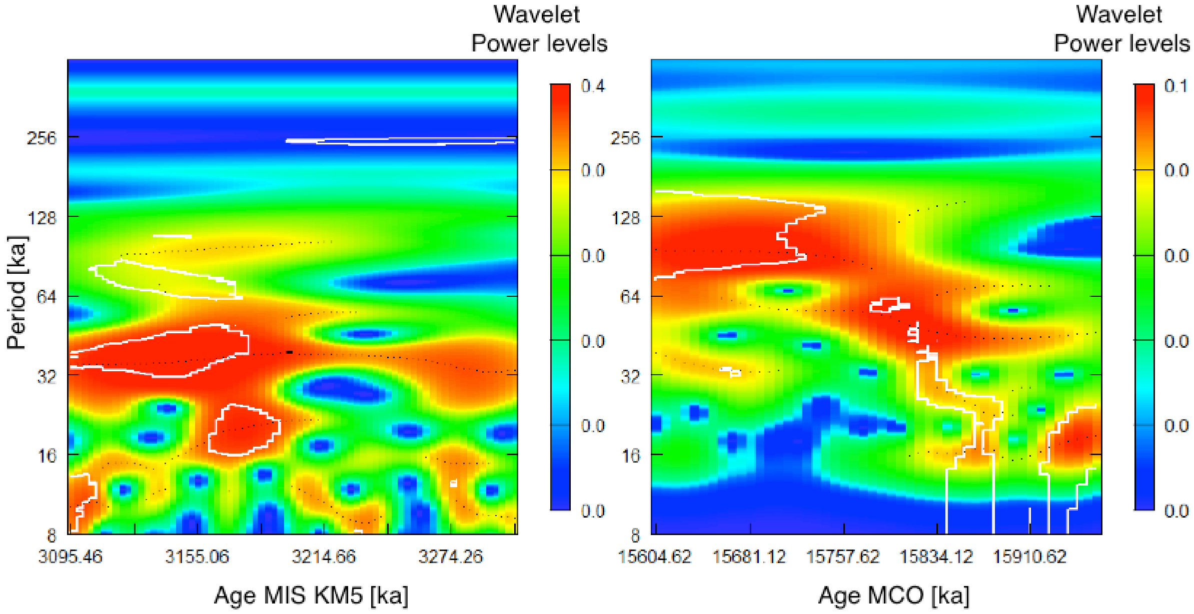

Figure S28. WT analysis of the number of coccoliths AR for the Pliocene and the Miocene

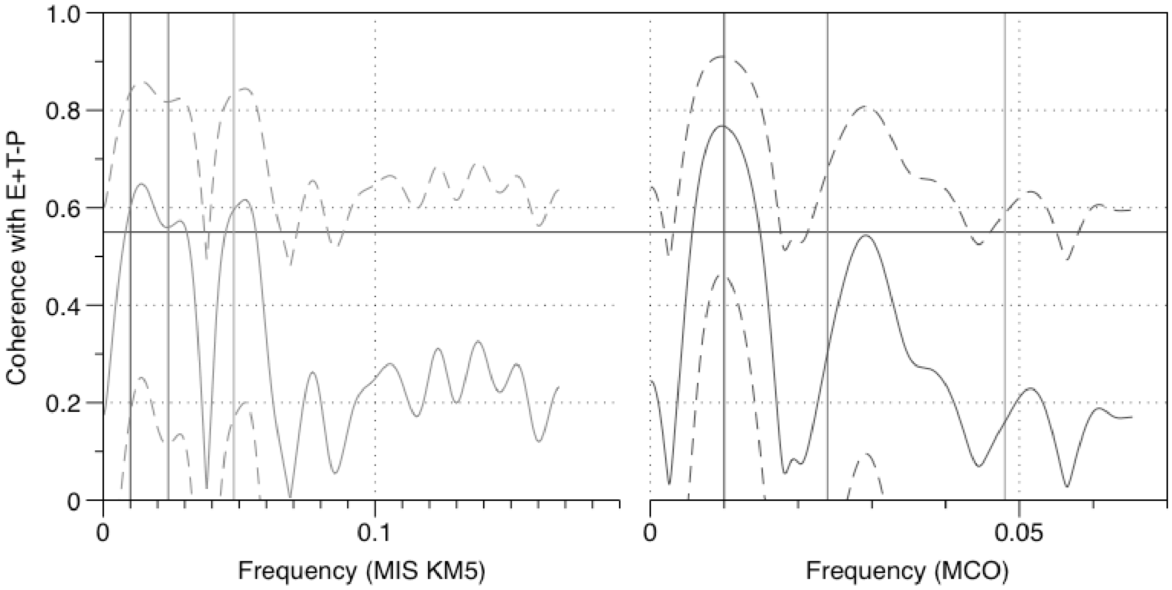

Figure S29. CBT coherence of the number of coccoliths AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene. The horizontal line corresponds to the non-zero coherence at a significance level of 90 %.

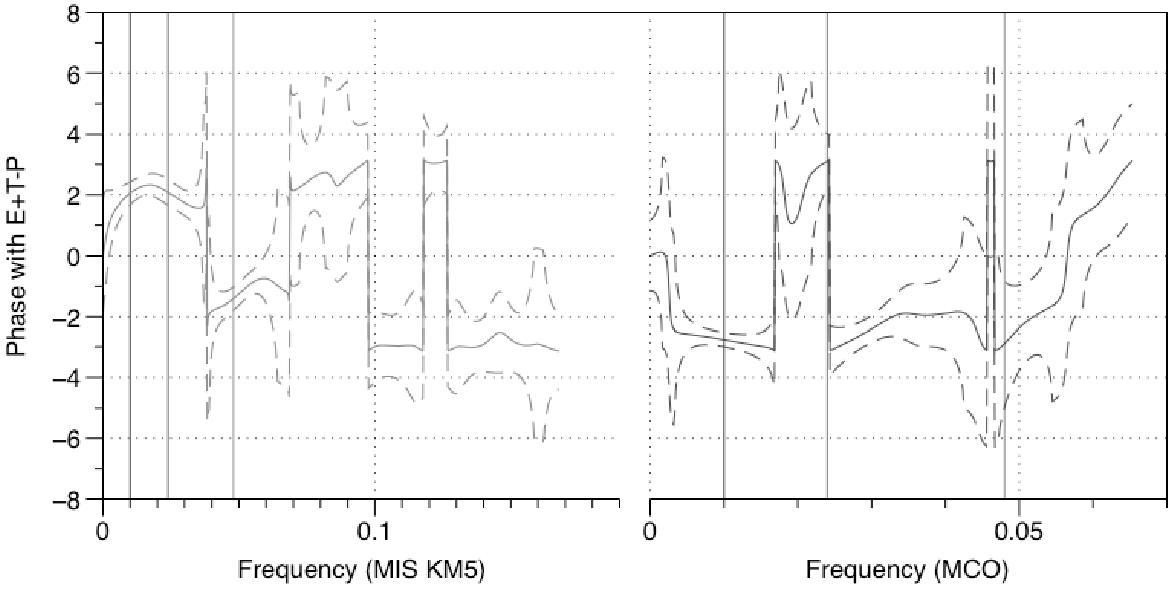

Figure S30. CBT phase of the number of coccoliths AR with ETP for the Pliocene and the Miocene. The vertical lines correspond (from left to right) to the 100 ka (eccentricity), 41 ka (obliquity) and 21 ka (precession) periodicities, for both the Pliocene and the Miocene.

Chapter V. Extended discussion

V.1. Carbonate preservation and single site location

As mentioned by several studies (e.g. Curry et al., 1995; Gröger et al., 2003a, b), the Site 927 carbonate is well preserved, especially during the studied intervals, except during the cold intervals of the Quaternary (II.4.i).

At the Site 927, we observe very low values of carbonate content and AR only during the cold intervals of the Quaternary, as the corrosive AABW started to flow at Ceará Rise location at the initiation of the NHG (Liebrand et al., 2016; Harris et al., 1997).

The fragmentation index is not correlated at all with the $CaCO_3$ AR in the sediment for the Pliocene and Miocene (II.8. Figure S1), which confirms the absence of dissolution in these intervals. Additionally, the Site 927 remains above the lysocline depth since the Early Miocene except during the Quaternary cold intervals, preventing dissolution at that depth (Curry et al., 1995; Paul et al., 2000; Gröger et al., 2003a, b). All these observations confirm that the Site 927 sediments of the four time intervals studied are not affected by dissolution, except episodically during the cold intervals of the Quaternary, so the observed $CaCO_3$ ARs are not driven by dissolution, but by carbonate production. Thanks to the high resolution of this record, the tuned age model (II.3.ii), and the well-preserved carbonate, the core 927 represents a good archive to study the pelagic carbonate production changes at low latitude and orbital modulation of it through the Cenozoic and Quaternary.

By working on single site location, I make sure to avoid possible shift in the temporality of the observation I made. In fact, as I am studying the timings, relationship and direction of the response of both the planktonic foraminifera and the coccoliths, doing my analysis on the same samples preserves me from eventual offset due to age models uncertainty between two sediment cores. Furthermore, I am sure all my organisms were exposed to exactly the same conditions changes, even if they are really local, so the results I obtain are not because some organisms were exposed to slightly different conditions. the disavowal of very localised obsarvation can subsequently be countered by repeating the analyses in different places (see Chapter #VI.2.).

V.2. Bulk carbonate accumulation rate and climate warming

The new high-resolution record obtained for Site 927, equatorial Atlantic Ocean reveals a variability on long geological and an even higher variability on a shorter orbital time scale (Chapter #II). Like Sutherland et al. (2022), we do not find any strong relationship between CO_2 changes and the observed variability in the pelagic carbonate production on geological time scale. Indeed, the four chosen time intervals studied are presenting very different pCO_2 values and the pelagic carbonate production values do not seem to be correlated to it at all. Furthermore, the highest amplitude of changes in the values are within the time intervals, which is not the time scale with the highest pCO_2 changes (which is between the time intervals). We admit that multiple factors might play a role, as on geological time scales, it is not the warmer time intervals that are showing the highest pelagic carbonate production values (we found lower $CaCO_3$ AR values during the MIS KM5 even if this interval was colder than the MCO), also suggested by Bolton et al. (2016), (e.g. alkalinity) might be playing a role on the calcification processes of the pelagic calcifiers. I suggest that the high orbital scale variability of the pelagic carbonate production may reflect regional environmental and climate variability in light, temperature or nutrient delivery rather than global climate and environmental modulations.

Knowing that the two main pelagic calcifiers are the planktonic foraminifera and the coccolithophores and that their relative contribution is important to take in account for understanding the processes behind the changes in pelagic carbonate productivity, as they are two different organisms and may react differently to the orbital and sea surface condition changes due to their different ecological preferences, we separated the $CaCO_3$ AR bulk in different size classes and observed their relative contribution to the total pelagic $CaCO_3$ AR.

V.3. Coccoliths and foraminifera carbonate production, a different response during the Cenozoic warm stages

Focusing on the warming intervals of the Cenozoic (the MIS KM5 and MCO), we have shown a different response of the two mains pelagic calcifiers and also, a different relative contribution to the total pelagic carbonate flux through the time and at different time scales (Chapter #III). This response of the pelagic carbonate calcifiers to the orbital forcing differs as well depending on the time interval. On long, geological time scale, the relative contribution of the two main pelagic carbonate calcifiers (planktonic foraminifera and coccolithophores) to the total pelagic carbonate production remains relatively constant, but on shorter orbital time scale (within the different studied time intervals), we observe a high variability of their relative contribution, which is in line with the results of Si and Rosenthal (2019). The $CaCO_3$ AR in the two size fractions are highly variable on orbital time scale, showing a strong response to the parameters changing at that same pace. The total $CaCO_3$ AR increases are due to an increase of both the coccoliths and the planktonic foraminifera production, but not in the same amplitude, making their relative contribution to the total pelagic carbonate flux change. This relative contribution of the two main pelagic carbonate producers record has a strong orbital imprint, suggesting a different response of the planktonic foraminifera and coccoliths to sea surface condition changes, coherent with the main results of Si and Rosenthal (2019), following the orbital parameters modulations. Indeed, as the $CaCO_3$ AR bulk increases, the contribution of the coarse fraction to the total pelagic carbonate production is increasing, following the actual E+T-P variability (in phase during the Pliocene and antiphase during the Miocene). Our results are in line with those from Si and Rosenthal (2019), with an increase of the coarse fraction relative contribution to the total from the Miocene to the Quaternary, but within the time intervals, the relative contribution of the two main pelagic carbonate producers is not following the same main orbital cyclicity, underlying a different mechanism behind their productivity changes. Additionally, the phase relationship between the coarse fraction contribution to the total pelagic carbonate production and the total $CaCO_3$ AR is changing from antiphased during the Miocene to in-phase during the Pliocene.

For both the Pliocene and the Miocene, it seems that it is the less than 63 μm size fraction which is driving the total $CaCO_3$ AR changes, coherent with what have been found by previously published studies (Si and Rosenthal, 2019; Drury et al., 2021). This changes in relative contribution of the planktonic foraminifera and coccoliths, even if changing with a strong orbital imprint, is not explaining the changes in the total $CaCO_3$ AR, so the proportion of the different pelagic calcifiers is not driving the carbonate flux changes. The contribution of the coarse fraction to the total pelagic carbonate production is in phase with the E+T-P during the Pliocene and in antiphase during the Miocene (as it is as well for the total $CaCO_3$ AR).

One of the possible explanations of the differences I observe in the different records depending on the period is the different sensitivity between Miocene and Pliocene. This difference might be due to different oceanic conditions, as for example, the closure of the Panama Isthmus between the Miocene and the Pliocene (chapter #I.1.ii). This caused a decrease of the water exchanges between the Atlantic and the Pacific Ocean and an enhancement of the AMOC and likely played a role in the NADW initiation (Lunt et al., 2008, 2007; Lear et al., 2003).

The carbon supply controls the coccolithophores growth rates, cell size and the utilisation of carbon for calcification and photosynthesis, and this in different ways depending on the different coccolithophores species, and these became more and more important as the pCO_2 decreases through the Neogene (Hermoso, 2016; Hermoso et al., 2016). As coccolithophores are photosynthetic organisms, they need light to live and their calcification is also dependent on the light supply, with a decreasing calcification with increasing pCO_2 under high light conditions, and no calcification changes with pCO_2 changes under low light conditions (Zondervan, 2007).

The values we find for the coarse fraction contribution to the bulk (about 20 to 30 %) are overall in line with what have been found by previously published studies (Si and Rosenthal, 2019; Drury et al., 2021). Indeed, the planktonic foraminifera contribution to the total carbonate flux has been estimated between 23 and 56 % (Schiebel, 2002).

Due to the fact that the two main pelagic carbonate calcifiers are responding differently to the changes, we can hypothesise that with the current climate change and drastically changing conditions, the two groups could respond differently in the future as well, modifying the ocean capacity to absorb CO_2 (Boudreau et al., 2018). Modelisation of increased atmospheric pCO_2 are already suggesting a decrease of planktonic foraminifera biomass and flux at low latitudes around 10% by 2050 and about 14 % to 18 % by 2100 (but increased flux at high latitudes), reducing the carbonate pump and therefore, contributing to a rising atmospheric pCO_2 (Grigoratou et al., 2022).

V.4. The mechanisms of variability in carbonate flux by coccoliths and foraminifera

We observe a similar response of the planktonic foraminifera and coccoliths to the warming and sea surface condition changes. But as we have a strong orbital imprint in the total $CaCO_3$ AR, especially during the Pliocene and Miocene, and with a different phase relationship, the reasons behind the changes of their productivity must be different between the Pliocene and the Miocene. For both the two mains pelagic carbonate calcifiers (i.e. coccolithophores and planktonic foraminifera), the $CaCO_3$ AR is driven by changes of the number of specimens rather than changes of their sizes or weight, which is in line with the results from Kiss et al. (2021) and goes against the results found by Henehan et al. (2017), stating that the size of the planktonic foraminifera will be a decisive factor in determining the direction of change of the calcification under climate warming and ocean acidification conditions. Furthermore, according to our results, the link with the size, is the reverse of what could be expected, with an increasing size with a decrease of pelagic carbonate production of the corresponding class size. For the foraminifera as well as for the coccoliths, the ocean acidification and decreasing pH does not appear to impact the same way the different species, and each species is showing different optimum conditions (Beaufort et al., 2011; Krumhardt et al., 2017; Doney et al., 2009; Toyofuku et al., 2017; Schmidt et al., 2006).

Concerning the coccoliths sizes, our results are coherent with other studies (e.g. Saruwatari et al., 2016; Bollmann and Herrle, 2007) who found that coccolithophore cell size decreases with increasing temperature, and that coccoliths size, coccolithophores growth rate and coccoliths morphology are affected by temperature and salinity. As previously published results (Suchéras-Marx et al., 2019; Bolton et al., 2016), we also found a decrease of the coccoliths sizes from Neogene to present at tropical latitude. In terms of number of specimens as well, we join the conclusion of previously published studies (e.g. Henriksson, 2000), who found higher abundances during warm SST time intervals. If I compare my results to the results sobtained with time serie, cultures, sediment traps and models, it is consistent, as a decrease od calcification rate of coccoliths and planktonic foraminifera with the increase of pCO_2 and temperature has been found, with more abundant coccoliths (Guitián et al., 2022; Feely et al., 2004; De Bodt et al., 2010; Johnson et al., 2022; Claxton et al., 2022; Krumhardt et al., 2019). Using models, Krumhardt et al. (2019) found a tipping point at pCO2 = 600 ppm, at the one the coccoliths calcification change from increasing to decreasing. De Bodt et al. (2010) found a reduced calcite content per coccolith, with a reduced number of coccoliths per coccosphere (and smaller cell sizes under CO_2 concentration expected via modelisation), and a decrease of the coccoliths production rate in their cultures. The coccoliths response to pH and temperature change is immediate according to the observation made by Johnson et al (2022) on cultures. On a geological time scale, an increase in pCO_2 in the surface ocean is suggested to favour thicker coccoliths with a higher degree of cell-calcification (Bolton et al., 2016). This could be explained during the Miocene and Pliocene by a reduction of the cellular bicarbonate allocation to calcification during the periods of low pCO_2 (Bolton et al., 2016). Our results are coherent with the results of Beaufort et al. (2022) who have shown that the seasonal changes in sea surface conditions are strongly influenced by the eccentricity modulation and strongly influencing the diversity and sizes of the coccoliths, with the existence of a link between the orbital modulation and the pelagic carbonate production on the surface ocean. A low contrast between the seasons at low latitudes is favouring mid-size coccoliths, with a high coccoliths carbonate export and burial while a high contrast is favouring larger coccoliths and lower carbonate export (Beaufort et al., 2022). The local insolation (modulated by the orbital parameters) is influencing the coccolithophores productivity with an enhanced coccolithophores productivity when the insolation is the highest in summer/autumn (Cavaleiro et al., 2018). Some studies as Krumhardt et al. (2017), via modelisation, predicted a decrease of both the growth rate and the calcification in low and mid latitudes with predicted increase of surface ocean pCO_2 (and temperature) by the end of the century, without taking in account the light supply modulations. Concerning the planktonic foraminifera sizes, our results are as well coherent with other studies, some have found an increase of the sizes of planktonic foraminifera shell from Miocene to present, and short-term modulation of the sizes, likely related to sea surface conditions change and global cooling (Schmidt et al., 2006, 2004; Friesenhagen, 2022). The changes of the planktonic foraminifera size are suggested to be related to the strength of the AMOC (Friesenhagen 2022) which could explain the orbital imprint in it. Todd et al. (2020) support the idea that the planktonic foraminifera sizes, if they are related to temperature, are not related to the pCO_2 values but rather to regional environmental changes (e.g. surface ocean currents, light, nutrient delivery). Indeed, the planktonic foraminifera shell sizes are known to be correlated with the environmental parameters (i.e. carbonate system, temperature, nutrient delivery or salinity), and positively correlated with temperature rather than acidification (Song et al., 2022). Furthermore, our results are in line as well with models' output, showing a strong decrease of the maximum body size of marine pelagic communities at low to mid latitude with ocean warming (Lefort et al., 2015). The seawater ion concentration (e.g. $[CO_3^{2-}]$) has been shown to control the planktonic foraminifera test densities (Iwasaki et al., 2019). As the calcification of planktonic foraminifera is made possible by the transformation of bicarbonate ion to carbonate ion inside the cytoplasm, an operation possible under a large range of pCO_2 values, therefore, increasing dissolved CO_2 may not impact marine carbonate production (Toyofuku et al., 2017). Song et al. (2022) suggested that the increasing planktonic foraminifera calcification will increase atmospheric pCO_2, and so the ocean warming will reduce the ocean's capacity to absorb CO_2, contributing to enhancing global warming.

Knowing this, we wanted to understand the periodicity of our records and their coherence and phase relationship with the actual orbital variability (using the actual E+T-P signal, tracking the three orbital parameters modulations, Laskar et al., 2004).

V.5. Orbital imprint in the sea surface carbonate variability

We observe a strong orbital imprint in all of our records, in the total $CaCO_3$ AR as well as in both the planktonic foraminifera AR and coccoliths AR and in the variability of the size and number of specimens within the groups themselves. This was expected, as we know that the pelagic carbonate productivity in the tropical ocean is influenced by the insolation rather than the global climate modulations, directly related to the parameters defining the Earth position on its orbit around the sun (Beaufort et al., 1997).

This pelagic carbonate production response to the orbital changes, and especially to insolation is proposed to be due to the resulting modulations of the sea surface conditions, like the quantity of light or pCO_2 (e.g. Krumhardt et al., 2017; Cavaleiro et al., 2018). Recent studies highlighted that an increase in calcification can be explained by warming conditions, and even more, that it constitutes a positive feedback via a weakening of the CO_2 uptake by the surface ocean, and so, an increase of the atmospheric pCO_2 (Qin et al., 2020).

A complex combination of different factors characterising the sea surface (i.e. oxygen concentration, pCO_2, light, temperature or salinity) are influencing the planktonic foraminifera assemblages (Lessa et al., 2020).

Vervoort et al. (2021) distinguished two groups of orbitally driven feedbacks: the ones influencing the ocean-atmosphere exchanges and the ones adding and removing carbon to the ocean-atmosphere system. Furthermore, they found that in absence of ice, carbonate dissolution, ocean circulation and CO_2 solubility feedback are positive with regards to orbitally driven temperature change. The different parameters defining the climate and environment are responding to different orbital forcing, and so, also exert a different pressure on the modulations of the climate (e.g. the temperature is responding at eccentricity pace, while pCO_2 is responding to precession) (Vervoort et al., 2021). Vervoort et al. (2021) found a similar power spectrum for the carbonate content of the marine sediment and the atmospheric CO_2. They also found a reduced carbonate solubility when a high temperature corresponds to an eccentricity maximum (high ocean alkalinity related to enhanced weathering), but an increased solubility with the precession and obliquity forced increase of carbonate export (consistent with ocean circulation and CO_2 fluxes between the atmosphere and the surface ocean). In the early Cenozoic, this relationship between temperature and carbonate content was reversed, implying different feedbacks on the carbon cycle dynamics (Vervoort et al., 2021). This explains how the orbital parameters can influence the sea surface conditions, and so, the pelagic carbonate productivity changes I observe.

V.6. Bibliography

Beaufort, L., Lancelot, Y., Camberlin, P., Cayre, O., Vincent, E., Bassinot, F., and Labeyrie, L.: Insolation cycles as a major control of equatorial Indian Ocean primary production, Science, 278, 1451–1454, 1997.

Beaufort, L., Probert, I., de Garidel-Thoron, T., Bendif, E. M., Ruiz-Pino, D., Metzl, N., Goyet, C., Buchet, N., Coupel, P., Grelaud, M., Rost, B., Rickaby, R. E. M., and de Vargas, C.: Sensitivity of coccolithophores to carbonate chemistry and ocean acidification, Nature, 476, 80–83, https://doi.org/10.1038/nature10295, 2011.

Beaufort, L., Bolton, C. T., Sarr, A.-C., Suchéras-Marx, B., Rosenthal, Y., Donnadieu, Y., Barbarin, N., Bova, S., Cornuault, P., Gally, Y., Gray, E., Mazur, J.-C., and Tetard, M.: Cyclic evolution of phytoplankton forced by changes in tropical seasonality, Nature, 601, 79–84, https://doi.org/10.1038/s41586-021-04195-7, 2022.

Bollmann, J. and Herrle, J. O.: Morphological variation of Emiliania huxleyi and sea surface salinity, Earth and Planetary Science Letters, 255, 273–288, https://doi.org/10.1016/j.epsl.2006.12.029, 2007.

Bolton, C. T., Hernández-Sánchez, M. T., Fuertes, M.-Á., González-Lemos, S., Abrevaya, L., Mendez-Vicente, A., Flores, J.-A., Probert, I., Giosan, L., Johnson, J., and Stoll, H. M.: Decrease in coccolithophore calcification and CO_2 since the middle Miocene, Nature Communications, 7, 10284, https://doi.org/10.1038/ncomms10284, 2016.

Boudreau, B. P., Middelburg, J. J., and Luo, Y.: The role of calcification in carbonate compensation, Nature Geoscience, 11, 894–900, https://doi.org/10.1038/s41561-018-0259-5, 2018.

Cavaleiro, C., Voelker, A. H. L., Stoll, H., Baumann, K.-H., Kulhanek, D. K., Naafs, B. D. A., Stein, R., Grützner, J., Ventura, C., and Kucera, M.: Insolation forcing of coccolithophore productivity in the North Atlantic during the Middle Pleistocene, Quaternary Science Reviews, 191, 318–336, https://doi.org/10.1016/j.quascirev.2018.05.027, 2018.

Claxton, L. M., McClelland, H. L. O., Hermoso, M., and Rickaby, R. E. M.: Eocene emergence of highly calcifying coccolithophores despite declining atmospheric CO_2, Nat. Geosci., 15, 826–831, https://doi.org/10.1038/s41561-022-01006-0, 2022.

Curry, W. B., Shackleton, N. J., Richter, C., and et al. (Eds.): Proceedings of the Ocean Drilling Program, 154 Initial Reports, Ocean Drilling Program, https://doi.org/10.2973/odp.proc.ir.154.1995, 1995.

De Bodt, C., Van Oostende, N., Harlay, J., Sabbe, K., and Chou, L.: Individual and interacting effects of pCO2 and temperature on Emiliania huxleyi calcification: study of the calcite production, the coccolith morphology and the coccosphere size, Biogeosciences, 7, 1401–1412, https://doi.org/10.5194/bg-7-1401-2010, 2010.

Doney, S. C., Fabry, V. J., Feely, R. A., and Kleypas, J. A.: Ocean Acidification: The Other CO_2 Problem, Annual Review of Marine Science, 1, 169–192, https://doi.org/10.1146/annurev.marine.010908.163834, 2009.

Drury, A. J., Liebrand, D., Westerhold, T., Beddow, H. M., Hodell, D. A., Rohlfs, N., Wilkens, R. H., Lyle, M., Bell, D. B., Kroon, D., Pälike, H., and Lourens, L. J.: Climate, cryosphere and carbon cycle controls on Southeast Atlantic orbital-scale carbonate deposition since the Oligocene (30–0 Ma), Clim. Past, 17, 2091–2117, https://doi.org/10.5194/cp-17-2091-2021, 2021.

Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., and Millero, F. J.: Impact of Anthropogenic CO2 on the CaCO3 System in the Oceans, Science, 305, 362–366, https://doi.org/10.1126/science.1097329, 2004.

Friesenhagen, T.: Test-size evolution of the planktonic foraminifer *Globorotalia menardii* in the eastern tropical Atlantic since the Late Miocene, Biogeosciences, 19, 777–805, https://doi.org/10.5194/bg-19-777-2022, 2022.

Grigoratou, M., Monteiro, F. M., Wilson, J. D., Ridgwell, A., and Schmidt, D. N.: Exploring the impact of climate change on the global distribution of non- spinose planktonic foraminifera using a trait- based ecosystem model, Global Change Biology, 28, 1063–1076, https://doi.org/10.1111/gcb.15964, 2022.

Gröger, M., Henrich, R., and Bickert, T.: Glacial–interglacial variability in lower North Atlantic deep water: inference from silt grain-size analysis and carbonate preservation in the western equatorial Atlantic, Marine Geology, 201, 321–332, https://doi.org/10.1016/S0025-3227(03)00263-9, 2003a.

Gröger, M., Henrich, R., and Bickert, T.: Variability of silt grain size and planktonic foraminiferal preservation in Plio/Pleistocene sediments from the western equatorial Atlantic and Caribbean, Marine Geology, 201, 307–320, https://doi.org/10.1016/S0025-3227(03)00264-0, 2003b.

Guitián, J., Fuertes, M. Á., Flores, J.-A., Hernández-Almeida, I., and Stoll, H.: Variation in calcification of Reticulofenestra coccoliths over the Oligocene–Early Miocene, Biogeosciences, 19, 5007–5019, https://doi.org/10.5194/bg-19-5007-2022, 2022.

Harris, S. E., Mix, A. C., and King, T.: Biogenic and terrigenous sedimentation at Ceara Rise, western tropical Atlantic, supports Pliocene–Pleistocene deep-water linkage between hemispheres, in: Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), Proc. ODP, Sci. Results, 154: College Station, TX (Ocean Drilling Program), vol. 154, 331–345, https://doi.org/10.2973/odp.proc.sr.154.114.1997, 1997.

Henehan, M. J., Evans, D., Shankle, M., Burke, J. E., Foster, G. L., Anagnostou, E., Chalk, T. B., Stewart, J. A., Alt, C. H. S., Durrant, J., and Hull, P. M.: Size-dependent response of foraminiferal calcification to seawater carbonate chemistry, Biogeosciences, 14, 3287–3308, https://doi.org/10.5194/bg-14-3287-2017, 2017.

Henriksson, A. S.: Coccolithophore response to oceanographic changes in the equatorial Atlantic during the last 200,000 years, Palaeogeography, Palaeoclimatology, Palaeoecology, 156, 161–173, https://doi.org/10.1016/S0031-0182(99)00139-X, 2000.

Hermoso, M.: Isotopic record of Pleistocene glacial/interglacial cycles in pelagic carbonates: Revisiting historical data from the Caribbean Sea, Quaternary Science Reviews, 137, 69–78, https://doi.org/10.1016/j.quascirev.2016.02.003, 2016.

Hermoso, M., Chan, I. Z. X., McClelland, H. L. O., Heureux, A. M. C., and Rickaby, R. E. M.: Vanishing coccolith vital effects with alleviated carbon limitation, Biogeosciences, 13, 301–312, https://doi.org/10.5194/bg-13-301-2016, 2016.

Iwasaki, S., Kimoto, K., Sasaki, O., Kano, H., and Uchida, H.: Sensitivity of planktic foraminiferal test bulk density to ocean acidification, Scientific Reports, 9, 9803, https://doi.org/10.1038/s41598-019-46041-x, 2019.

Johnson, R., Langer, G., Rossi, S., Probert, I., Mammone, M., and Ziveri, P.: Nutritional response of a coccolithophore to changing PH and temperature, Limnology & Oceanography, 67, 2309–2324, https://doi.org/10.1002/lno.12204, 2022.

Kiss, P., Jonkers, L., Hudáčková, N., Reuter, R. T., Donner, B., Fischer, G., and Kucera, M.: Determinants of Planktonic Foraminifera Calcite Flux: Implications for the Prediction of Intra- and Inter- Annual Pelagic Carbonate Budgets, Global Biogeochemical Cycles, 35, https://doi.org/10.1029/2020GB006748, 2021.

Krumhardt, K. M., Lovenduski, N. S., Iglesias-Rodriguez, M. D., and Kleypas, J. A.: Coccolithophore growth and calcification in a changing ocean, Progress in Oceanography, 159, 276–295, https://doi.org/10.1016/j.pocean.2017.10.007, 2017.

Krumhardt, K. M., Lovenduski, N. S., Long, M. C., Levy, M., Lindsay, K., Moore, J. K., and Nissen, C.: Coccolithophore Growth and Calcification in an Acidified Ocean: Insights From Community Earth System Model Simulations, J. Adv. Model. Earth Syst., 11, 1418–1437, https://doi.org/10.1029/2018MS001483, 2019.

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, Astronomy & Astrophysics, 428, 261–285, https://doi.org/10.1051/0004-6361:20041335, 2004.

Lear, C. H., Rosenthal, Y., and Wright, J. D.: The closing of a seaway: ocean water masses and global climate change, Earth and Planetary Science Letters, 210, 425–436, https://doi.org/10.1016/S0012-821X(03)00164-X, 2003.

Lefort, S., Aumont, O., Bopp, L., Arsouze, T., Gehlen, M., and Maury, O.: Spatial and body- size dependent response of marine pelagic communities to projected global climate change, Global Change Biology, 21, 154–164, https://doi.org/10.1111/gcb.12679, 2015.

Lessa, D., Morard, R., Jonkers, L., Venancio, I. M., Reuter, R., Baumeister, A., Albuquerque, A. L., and Kucera, M.: Distribution of planktonic foraminifera in the subtropical South Atlantic: depth hierarchy of controlling factors, Biogeosciences, 17, 4313–4342, https://doi.org/10.5194/bg-17-4313-2020, 2020.

Liebrand, D., Beddow, H. M., Lourens, L. J., Pälike, H., Raffi, I., Bohaty, S. M., Hilgen, F. J., Saes, M. J. M., Wilson, P. A., van Dijk, A. E., Hodell, D. A., Kroon, D., Huck, C. E., and Batenburg, S. J.: Cyclostratigraphy and eccentricity tuning of the early Oligocene through early Miocene (30.1–17.1 Ma): *Cibicides mundulus* stable oxygen and carbon isotope records from Walvis Ridge Site 1264, Earth and Planetary Science Letters, 450, 392–405, https://doi.org/10.1016/j.epsl.2016.06.007, 2016.

Lunt, D. J., Valdes, P. J., Haywood, A., and Rutt, I. C.: Closure of the Panama Seaway during the Pliocene: implications for climate and Northern Hemisphere glaciation, Clim Dyn, 30, 1–18, https://doi.org/10.1007/s00382-007-0265-6, 2007.

Lunt, D. J., Foster, G. L., Haywood, A. M., and Stone, E. J.: Late Pliocene Greenland glaciation controlled by a decline in atmospheric CO_2 levels, Nature, 454, 1102–1105, https://doi.org/10.1038/nature07223, 2008.

Paul, H. A., Zachos, J. C., Flower, B. P., and Tripati, A.: Orbitally induced climate and geochemical variability across the Oligocene/Miocene boundary, Paleoceanography, 15, 471–485, https://doi.org/10.1029/1999PA000443, 2000.

Qin, B., Li, T., Xiong, Z., Algeo, T. J., and Jia, Q.: Calcification of planktonic foraminifer *Pulleniatina obliquiloculata* controlled by seawater temperature rather than ocean acidification, Global and Planetary Change, 193, 103256, https://doi.org/10.1016/j.gloplacha.2020.103256, 2020.

Saruwatari, K., Satoh, M., Harada, N., Suzuki, I., and Shiraiwa, Y.: Change in coccolith size and morphology due to response to temperature and salinity in coccolithophore *Emiliania huxleyi* (Haptophyta) isolated from the Bering and Chukchi seas, Biogeosciences, 13, 2743–2755, https://doi.org/10.5194/bg-13-2743-2016, 2016.

Schiebel, R.: Planktic foraminiferal sedimentation and the marine calcite budget, Global Biogeochemical Cycles, 16, 3-1-3–21, https://doi.org/10.1029/2001GB001459, 2002.

Schmidt, D. N., Thierstein, H. R., and Bollmann, J.: The evolutionary history of size variation of planktic foraminiferal assemblages in the Cenozoic,Palaeogeography, Palaeoclimatology, Palaeoecology, 22, 2004.

Schmidt, D. N., Lazarus, D., Young, J. R., and Kucera, M.: Biogeography and evolution of body size in marine plankton, Earth-Science Reviews, 78, 239–266, https://doi.org/10.1016/j.earscirev.2006.05.004, 2006.

Si, W. and Rosenthal, Y.: Reduced continental weathering and marine calcification linked to late Neogene decline in atmospheric CO_2, Nature Geoscience, 12, 833–838, https://doi.org/10.1038/s41561-019-0450-3, 2019.

Song, Q., Qin, B., Tang, Z., Liu, Y., Chen, Z., Guo, J., Xiong, Z., and Li, T.: Calcification of planktonic foraminifer *Neogloboquadrina pachyderma*(sinistral) controlled by seawater temperature rather than ocean acidification in the Antarctic Zone of modern Sothern Ocean, Science China Earth Science, 65, 1824–1836, https://doi.org/10.1007/s11430-021-9924-7, 2022.

Suchéras-Marx, B., Mattioli, E., Allemand, P., Giraud, F., Pittet, B., Plancq, J., and Escarguel, G.: The colonization of the oceans by calcifying pelagic algae, Biogeosciences, 16, 2501–2510, https://doi.org/10.5194/bg-16-2501-2019, 2019.

Sutherland, R., Dos Santos, Z., Agnini, C., Alegret, L., Lam, A. R., Westerhold, T., Drake, M. K., Harper, D. T., Dallanave, E., Newsam, C., Cramwinckel, M. J., Dickens, G. R., Collot, J., Etienne, S. J. G., Bordenave, A., Stratford, W. R., Zhou, X., Li, H., and Asatryan, G.: Neogene Mass Accumulation Rate of Carbonate Sediment Across Northern Zealandia, Tasman Sea, Southwest Pacific, Paleoceanography and Paleoclimatology, 37, https://doi.org/10.1029/2021PA004294, 2022.

Todd, C. L., Schmidt, D. N., Robinson, M. M., and De Schepper, S.: Planktic Foraminiferal Test Size and Weight Response to the Late Pliocene Environment, Paleoceanography and Paleoclimatology, 35, https://doi.org/10.1029/2019PA003738, 2020.

Toyofuku, T., Matsuo, M. Y., de Nooijer, L. J., Nagai, Y., Kawada, S., Fujita, K., Reichart, G.-J., Nomaki, H., Tsuchiya, M., Sakaguchi, H., and Kitazato, H.: Proton pumping accompanies calcification in foraminifera, Nature Communication, 8, 14145, https://doi.org/10.1038/ncomms14145, 2017.

Vervoort, P., Kirtland Turner, S., Rochholz, F., and Ridgwell, A.: Earth System Model Analysis of How Astronomical Forcing Is Imprinted Onto the Marine Geological Record: The Role of the Inorganic (Carbonate) Carbon Cycle and Feedbacks, Paleoceanography and Paleoclimatology, 36, https://doi.org/10.1029/2020PA004090, 2021.

Zondervan, I.: The effects of light, macronutrients, trace metals and CO_2 on the production of calcium carbonate and organic carbon in coccolithophores—A review, Deep Sea Research Part II: Topical Studies in Oceanography, 54, 521–537, https://doi.org/10.1016/j.dsr2.2006.12.004, 2007.

Chapter VI. Conclusion

VI.1. Important results

As a conclusion, I here bring new knowledge on the response of the pelagic calcifiers to the changing climate and environment in a context of climate warming, an important step forward in the understanding of their role in the (inorganic) carbon cycle and indication of the direction of the change that can be expected in the coming years, incrementing the general knowledge on the climate system and dynamics (Figure 1). My new data contributes here to unravel the possible effects of climate change on the different elements of the inorganic (oceanic) carbon cycle. A better understanding of how the system works in natural conditions can help us to estimate the modulations of the temperature and ocean pH, alkalinity, capacity to absorb CO_2 in a context of climate warming. In the unprecedented warming we are now experiencing, with an increase of extreme climatic events and rising sea level, modified oceanic circulation and heat transport and distribution on our planet (Pörtner et al., 2014), this is of much importance. This is crucial in the ongoing climate crisis, to better constraint models and estimate the positive or negative feedback of the surface water pelagic carbonate production to enhance or buffer the temperature increase, but also the pCO_2 increase and capacity of the ocean to absorb and stock CO_2.

After a revision of the age model for the periods of interest in this study, in order to better constraint the age model and so the sedimentation rate, I calculated the $CaCO_3$ AR for four warm intervals, as an approximation of the pelagic carbonate production during these intervals. The $CaCO_3$ AR was not constant through the Cenozoic and Quaternary (Figure 1), with a strong orbital imprint, but at different periodicity depending on the period. I show that the nature of the variability has fundamentally changed since the Miocene. The relative contribution of the two mains pelagic calcifiers (coccoliths and foraminifera) is relatively constant on geological time scale (Ma), but changing with high variability on orbital time scale (ka). When the $CaCO_3$ AR is increasing, it is because of the increase of both the productivity of the planktonic foraminifera and the coccoliths and it is the difference of the amplitude of this change which makes the relative contribution of both the two main pelagic carbonate calcifiers change over time. This relative contribution of the pelagic calcifiers is not driving the changes in $CaCO_3$ AR, but is, as the $CaCO_3$ AR, in phase with E+T-P signal during the Pliocene (dominant cyclicity at precession band) and antiphased with it during the Miocene (dominant cyclicity at eccentricity and obliquity bands). If we now look within each pelagic calcifiers group separately, both the number of specimens and their sizes are highly variable through time, and seem to follow different periodicities. Looking at the sizes of the organisms, the changes are not driving the $CaCO_3$ AR changes, and even more, if any relationship, it is the reverse, with bigger specimens when the $CaCO_3$ AR is low (colder intervals) and smaller specimens when the $CaCO_3$ AR is high (warmer intervals). This is in line with what has been found by Beaufort et al. (2022) but goes the opposite way of what has been suggested by Schmidt et al. (2006) for low latitude foraminifera species. On the other hand, concerning the number of specimens, I do observe a strong correlation with the $CaCO_3$ AR, indicating that the $CaCO_3$ AR change is principally driven by a change of number of specimens, for both the coccoliths and the planktonic foraminifera. With the warming phases within each time intervals (following the orbital forcing, traced by increase of the E+T-P -and not $\delta^{18}O$ with is more tracking high latitudes changes (and ice volume)-), we observe an increase of the number of specimens and a decrease of their sizes. On long geological time scale, from warm Miocene (+3 to 8°C; pCO_2 peaked between 460 and 564 ppm) when the organisms were bigger but smaller number (and lower $CaCO_3$ AR) to the cooler Pliocene (+2 to 3°C; pCO_2 330 to 425 ppm) when the organisms were smaller but higher number (and higher $CaCO_3$ AR), we observe an increase of the number of specimens (and $CaCO_3$ AR). I observe the reversed trends on long geological time scale and on short orbital time scale. This makes sense, as even if we well have warm intervals, and a warming on orbital time scale, we do have a cooling from Miocene to Quaternary on geological time scale, and a reduction of the atmospheric pCO_2, suggested by Bolton et al. (2016) to be a limiting factor for the development of pelagic calcifiers added to the increasing role of the alkalinity. For both the planktonic foraminifera and the coccolithophores, there might be different species/assemblages developing during the warm / high carbonate productivity context and during the cooler / lower productivity events (Schmidt et al., 2006). A shift in the taxonomy (at both orbital and geological time scales) might explain the differences in sizes in both groups as well as the change of the shapes we do observe for the planktonic foraminifera. How heavily calcified the specimens are (e.g. thickness and density of the calcite, how lobate are the organisms, etc..) appears to play a role (e.g. Iwasaki et al., 2019), particularly for the planktonic foraminifera, but this needs to be further studied.

Collectively, these results reveal a previously unnoted significant variability in tropical pelagic carbonate productivity between foraminifera and coccolithophores, implying that in the tropical ocean these calcifiers reacted differently to orbital forcing. Each of our records, the $CaCO_3$ AR bulk, the $CaCO_3$ AR of the coccoliths, $CaCO_3$ AR of foraminifera, their sizes, number of specimens or morphometric records, are showing a variability following the orbital parameters pace, but a different one between the Pliocene (precession and eccentricity) and the Miocene (obliquity and eccentricity). Our results are in line with previously published studies (e.g. Beaufort et al., 1997, 2022) which are suggesting a direct response of the pelagic carbonate production to orbital forcing at low latitude, rather than global climate modulations, and this for the two groups. Additionally, and specifically for the Pliocene, the coccoliths and the foraminifera seem to be responding to a different forcing (obliquity for the coccoliths and precession and eccentricity for the planktonic foraminifera). These responses of the planktonic foraminifera and coccoliths might be related to orbitally driven pCO_2 changes, temperature and insolation changes, directly driven by the orbital parameters' modulations. The orbital parameters influence the temperature, capacity to absorb CO_2 (physically, even without taking in account the biology), and modify the current circulation system, strength of the AMOC circulation, delivery nutrient and quantity of energy received at the surface ocean at low latitude (and with CO_2 increase with temperature increases, this has positive feedback and enhanced the temperature increase). Furthermore, the changing nutrient delivery (for example modulated by the currents system and upwellings), and light availability (especially concerning the coccolith, photosynthetic organisms) is also modulating the pelagic carbonate production, whether or not the conditions are right for the development of organisms. Because of all these, it could explain why at low latitude, the pelagic carbonate producers appear to respond directly to the orbital forcing themselves rather than the global climate modulations.

I conclude that the overall carbonate production by pelagic calcifiers responded to local changes in light, temperature and nutrients delivered by upwelling, which followed long orbital cycles, as well as to long-term shifts in climate and/or ocean chemistry. In the actual context of climate warming, the number of specimens that succeed to develop in the surface ocean with the changing conditions will be crucial for the capacity of the ocean to absorb CO_2 to be preserved. The inferred changes on both time scales were sufficiently large such that when extrapolated on a global scale, they could have played a role in the regulation of the carbon cycle and global climate evolution during the transition from the Miocene warm climates into the Quaternary icehouse.

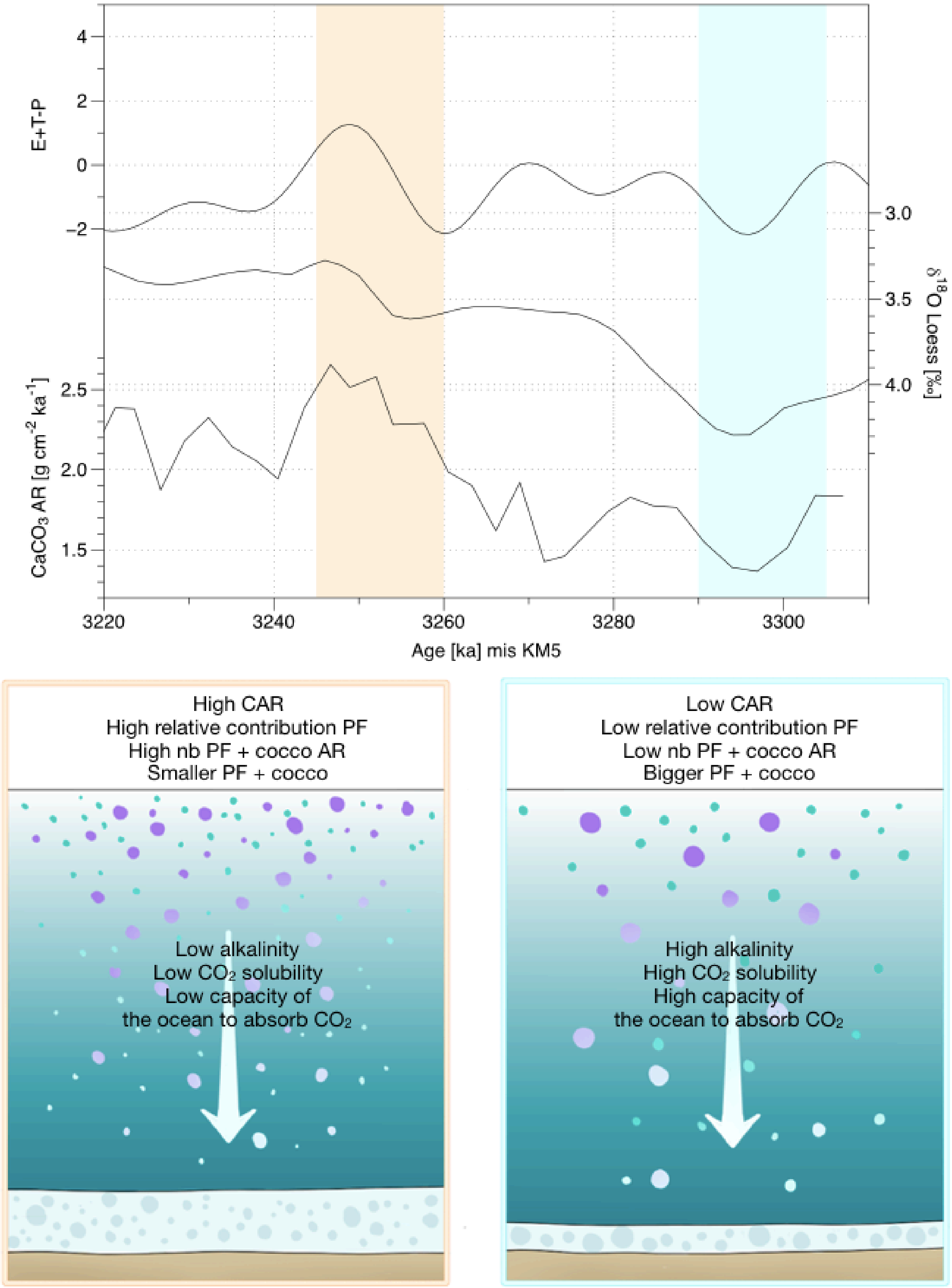

Figure 1. The pelagic carbonate production, general differences between the cold and the warm intervals at orbital time scale, the example of the Pliocene interval. The foraminifera are represented in purple and the coccoliths in blue-green. The Marine carbonate sediment (and oozes) are represented in white. The orange shadow highlights a warm area of the $CaCO_3$ AR record, and the blue shadow a colder area of the $CaCO_3$ AR record.

Taking in account all these results, and knowing that models are predicting climate conditions 1.5 to 5 degrees warmer than present with a pCO_2 up to 1200 ppm and a decrease of the atmosphere to ocean carbon flux from now to 2100 (Intergovernmental Panel On Climate Change, 2021) we predict an increasing pelagic carbonate production for the coming years, with high $CaCO_3$ AR conditions in the future (Figure 2). We state that the relative contribution of the planktonic foraminifera relative to the coccoliths might be hight, with a high number of secimens for both, but smaller specimens. In these conditions, the ocean's alkalinity will be low, with a low CO_2 solubility and so a low capacity of the ocean to absorb CO_2, being positive feedback to the rising atmospheric CO_2 concentration.

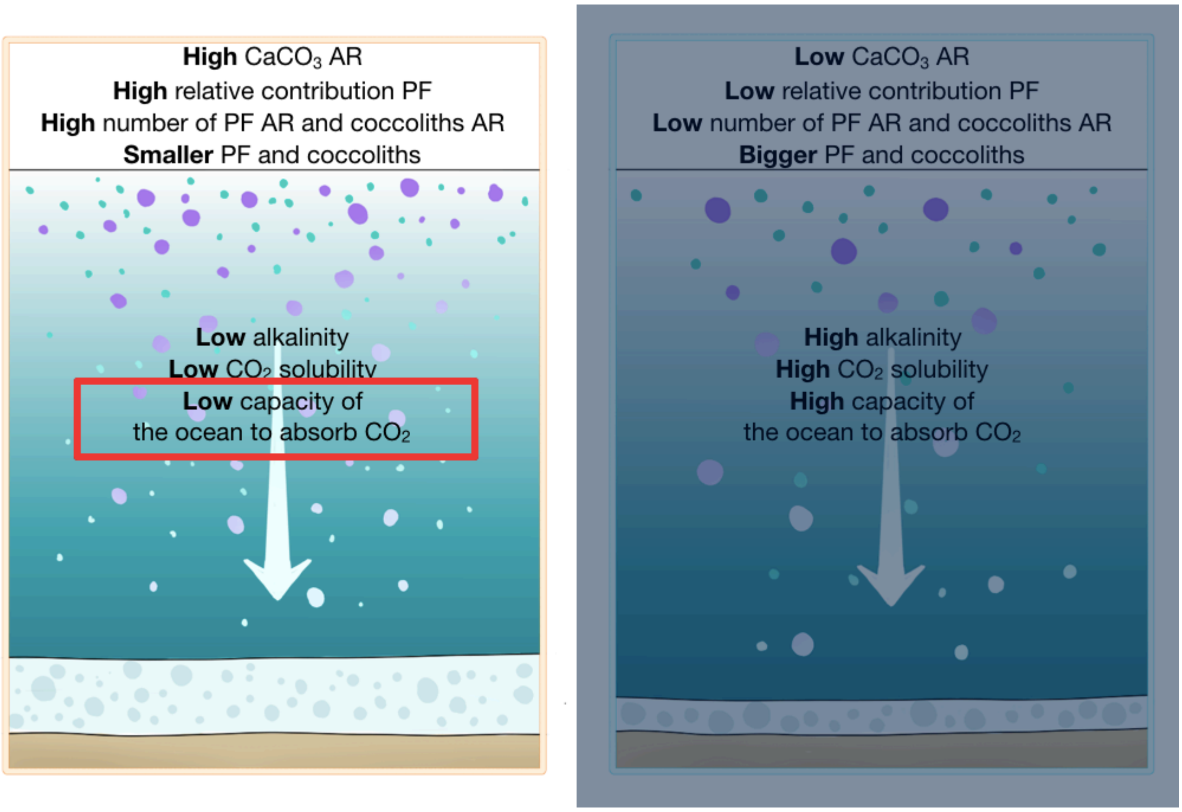

Figure 2. Most probable oceanic conditions predicted for the coming years, taking in account my results and the climate models predictions.

VI.2. Remaining questions: to be continued in future studies

My new results are now raising new questions. I found that the number of specimens is explaining a large part of the $CaCO_3$ AR variability, but not whole, so other parameters explaining the $CaCO_3$ AR changes remains to be studied, for both the coccoliths and the planktonic foraminifera. Indeed, taxonomic changes are expected and known to occur between MCO and MIS KM5 (Schmidt et al., 2006), but what about the orbital scale? And what about the timings of these changes between the coccoliths and planktonic foraminifera? On an orbital time scale, it has been previously shown that the coccoliths taxonomy is changing at low latitude with orbital forcing (Beaufort et al., 1997, 2022). Concerning the planktonic foraminifera, Strack et al. (2022) mentioned a rapid shift in the foraminifera assemblages with temperature increase for the last interglacial, and emitted the idea of a possible shift of the assemblages with the ongoing climate warming, and modulations of the planktonic foraminifera low latitudes diversity have also been shown by Lam and Leckie (2020) at the mid-Pleistocene transition. But it remains to be shown if these changes are similar for the coccoliths and what is the temporality of these changes between the two groups, if it has an influence on the total $CaCO_3$ AR or not and their phase relationship with the actual E+T-P. I already have the coccoliths taxonomy data, so it would be interesting to start future research by this question.

As the observations here are for a tropical area and it is known that the orbital changes imprint is not the same at all the latitudes (e.g. obliquity changes have a stronger influence on high latitudes conditions than low latitudes), it would be interesting to do the same studies in the same ocean (Atlantic) but at different latitudes, from North to South, to see if the observations are latitude-dependant or not. It is already known that the higher latitude the higher the temperature changes and the ice sheets influence (plus the species are potentially different so if it is species dependent, these could change the observations). For example, the high latitudes species have been shown to be less sensitive to temperature changes than low latitudes species, as their range of temperature optima is larger (Schmidt et al., 2006). As the oceanic physics are not the same in all the oceans, it would be of interest to make the same study in tropical area but in other oceans, to test whether or not the changes of number of specimens and their sizes with the climate warming are local or global at tropical latitude. As our resolution for the Miocene interval is just enough for precession changes, it would be interesting to increase the resolution of the sampling in the Miocene, to better see the potential precession signal if present. And finally, can we expect a similar response as what we observed on the even shorter time scale of the current global warming?

VI.3. Bibliography

Beaufort, L., Lancelot, Y., Camberlin, P., Cayre, O., Vincent, E., Bassinot, F., and Labeyrie, L.: Insolation cycles as a major control of equatorial Indian Ocean primary production, Science, 278, 1451–1454, 1997.

Beaufort, L., Bolton, C. T., Sarr, A.-C., Suchéras-Marx, B., Rosenthal, Y., Donnadieu, Y., Barbarin, N., Bova, S., Cornuault, P., Gally, Y., Gray, E., Mazur, J.-C., and Tetard, M.: Cyclic evolution of phytoplankton forced by changes in tropical seasonality, Nature, 601, 79–84, https://doi.org/10.1038/s41586-021-04195-7, 2022.

Boscolo-Galazzo, F., Crichton, K. A., Barker, S., and Pearson, P. N.: Temperature dependency of metabolic rates in the upper ocean: A positive feedback to global climate change?, Global and Planetary Change, 170, 201–212, https://doi.org/10.1016/j.gloplacha.2018.08.017, 2018.

Iwasaki, S., Kimoto, K., Sasaki, O., Kano, H., and Uchida, H.: Sensitivity of planktic foraminiferal test bulk density to ocean acidification, Scientific Reports, 9, 9803, https://doi.org/10.1038/s41598-019-46041-x, 2019.

Lam, A. R. and Leckie, R. M.: Late Neogene and Quaternary diversity and taxonomy of subtropical to temperate planktic foraminifera across the Kuroshio Current Extension, northwest Pacific Ocean, Micropaleontology, 66, 3, 177–268, https://doi.org/10.47894/mpal.66.3.01, 2020.

Pörtner, H. O., Karl, D. M., Boyd, P. W., Cheung, W. W. L., Lluch-Cota, S. E., Nojiri, Y., Schmidt, D. N., and Zavialov, P. O.: Part A: Global and Sectoral Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Field, C.B., V.R. Barros, D.J. Dokken, K.J. Mach, M.D. Mastrandrea, T.E. Bilir, M. Chatterjee, K.L. Ebi, Y.O. Estrada, R.C. Genova, B. Girma, E.S. Kissel, A.N. Levy, S. MacCracken, P.R. Mastrandrea, and L.L. White (eds.)]., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, Climate Change 2014: Impacts, Adaptation, and Vulnerability, 411–484, 2014.

Schmidt, D. N., Lazarus, D., Young, J. R., and Kucera, M.: Biogeography and evolution of body size in marine plankton, Earth-Science Reviews, 78, 239–266, https://doi.org/10.1016/j.earscirev.2006.05.004, 2006.

Strack, A., Jonkers, L., C. Rillo, M., Hillebrand, H., and Kucera, M.: Plankton response to global warming is characterized by non-uniform shifts in assemblage composition since the last ice age, Nature Ecology & Evolution, https://doi.org/10.1038/s41559-022-01888-8, 2022.

Data Availability

The datatables of the first manuscript are available on Pangaea:
Cornuault, Pauline; Westerhold, Thomas; Pälike, Heiko; Bickert, Torsten; Baumann, Karl-Heinz; Kucera, Michal (2022): Carbonate accumulation rate calculation derived from previously published carbonate content data, for the five sites of the Leg 154, Ceara Rise, tropical Atlantic from 0 to 16 Ma.
https://doi.org/10.1594/PANGAEA.945848, Cornuault et al., 2022a,

Cornuault, Pauline; Westerhold, Thomas; Pälike, Heiko; Bickert, Torsten; Baumann, Karl-Heinz; Kucera, Michal (2022): Magnetic susceptibility of ODP Site 154-927, Pliocene Warm Period (3095 to 3307 ka) interval.
https://doi.org/10.1594/PANGAEA.945773, Cornuault et al., 2022b,

Cornuault, Pauline; Westerhold, Thomas; Pälike, Heiko; Bickert, Torsten; Baumann, Karl-Heinz; Kucera, Michal (2022): Oxygen and carbon stable isotopes ratios from benthic foraminifera from Miocene Climatic Optimum (MCO) (15589 to 15964 ka) time interval, ODP Hole 154-927A, Ceara Rise, tropical Atlantic Ocean.
https://doi.org/10.1594/PANGAEA.945812, Cornuault et al., 2022c,

Cornuault, Pauline; Westerhold, Thomas; Pälike, Heiko; Bickert, Torsten; Baumann, Karl-Heinz; Kucera, Michal (2022): Carbonate content analyses and accumulation rate data for the marine isotopic stage (MIS) 5, MIS 9, MIS KM5 and MCO, ODP Site 154-927, Ceara Rise, tropical Atlantic Ocean.
https://doi.org/10.1594/PANGAEA.945789, Cornuault et al., 2022d,

Cornuault, Pauline; Westerhold, Thomas; Pälike, Heiko; Bickert, Torsten; Baumann, Karl-Heinz; Kucera, Michal (2022): Splice composition of ODP Site 154-927, 110.43 mcd to 119.79 mcd interval, Ceara Rise, tropical Atlantic.
https://doi.org/10.1594/PANGAEA.945707, Cornuault et al., 2022e).

The datatables of the second and third manuscript are available upon request to the the main author until their online publication on PANGAEA (https://pangaea.de, last visit: 8th December 2022):

- Coarse and small fraction carbonate content and accumulation rate
- number of specimens and sizes for both the coccoliths and the planktonic foraminifera

Competing interests

The authors declare that they have no conflict of interest.

Appendix

During this PhD, I had the opportunity to participate at conferences and present my work to the international community. Additionally, I made use of my ability to draw to take part in a side project: illustrating three taxonomic identification leaflets for modern planktonic foraminifera, a project from which the first leaflet has been published and the second is about to be submitted. Finally, I had the pleasure to be involved in a huge project led by Luc Beaufort during my Master, from the one the results have been published in Nature.

A1. Conferences participation

Cornuault P. et al. (2022): Pelagic carbonate production during Cenozoic warm periods; The Micropalaeontological society annual conference, November 10th-11th 2022 (Talk).

Meilland J., **Cornuault P.,** Morard R., Brummer G-J., Kucera M. (2022): Identification guide to extant planktonic foraminifera; The Micropalaeontological society annual conference, November 10th-11th 2022 (Poster).

Cornuault P. and Kucera M. (2021): Contribution of foraminifera to pelagic carbonate production during past warm intervals; The Micropalaeontological society Foraminifera Day, August 27th 2021 (Poster).

Cornuault P. et al., (2020): Nature and origin of variations in pelagic carbonate production at Ceara Rise since the Early Miocene; The Micropalaeontological Society 50th Anniversary Conference 2020 (Poster).

A2. Further publications

Meilland, J., **Cornuault, P.**, Morard, R., Brummer, G.-J. A., and Kucera, M., (2022): Identification guide to extant planktonic foraminifera. Part 1: Family Candeinidae and genera Berggrenia, Bolivina, Dentigloborotalia, and Neogallitellia, https://doi.org/10.17895/ICES.PUB.7643, 2022.

Beaufort, L., Bolton, C. T., Sarr, A.-C., Suchéras-Marx, B., Rosenthal, Y., Donnadieu, Y., Barbarin, N., Bova, S., **Cornuault, P.**, Gally, Y., Gray, E., Mazur, J.-C., and Tetard, M., (2022): Cyclic evolution of phytoplankton forced by changes in tropical seasonality, Nature, 601, 79–84, https://doi.org/10.1038/s41586-021-04195-7, 2022.

Meilland, J., **Cornuault, P.**, Morard, R., Brummer, G.-J. A., and Kucera, M., (2022): Identification guide to extant planktonic foraminifera. Part 2: non-spinose macroperforate, Family Globorotaliidae (in prep., to be submitted to ICES).