

Globally enhanced calcification across the coccolithophore *Gephyrocapsa* complex during the mid-Brunhes interval

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ABSTRACT

Evolutionary or adaptative changes in Noelaerhabdaceae coccolithophores occurred in parallel with major changes in carbonate export and burial during scenarios of low orbital eccentricity, with a ~400 kyr recurrence, during the Pleistocene. Coeval with these conditions of enhanced proliferation, here we report that the calcification of specimens was enhanced at a global scale and across multiple species or morphotypes within the *Gephyrocapsa* complex during the Mid-Brunhes (MB) interval. This acme of increased production of organic and inorganic carbon by *Gephyrocapsa*, suggests that such global changes may originate from a common driver. Increased seawater alkalinity, with an appropriately long residence time, is proposed as environmental trigger on the selection of a wide variety of highly calcified and prolific *Gephyrocapsa* taxa. This new perspective highlights the role of orbital forcing in phytoplankton evolution or adaptation, via a global environmental driver in the form of seawater carbon chemistry. Our results fit with earlier proposals appealing for an intensified biological pump and respiration dissolution during this interval. We hypothesize that the *Gephyrocapsa* acme may play a *double-edged* role, by increasing shallow respiration dissolution rates, limiting the removal of alkalinity by burial, which may help to recycle alkalinity and maintain constant levels at the ~400 kyr scale. This idea suggests the potential capacity of the Noelaerhabdaceae coccolithophore acmes to modify the typical behaviour of carbonate compensation in the ocean and that the changes in coccolithophore calcification may be indicative of changes in ocean carbonate chemistry and the operation of the global carbon cycle in the past.

1. Introduction

Coccolithophores, a cosmopolitan group of marine phytoplankton, account for a substantial fraction of global primary production of organic and inorganic carbon (see Brownlee et al., 2021 for a review). The production or fixation of organic carbon occurs through photosynthesis, and the production of inorganic carbon via intracellular precipitation of calcium carbonate structures, named “coccoliths” (Rost et al., 2003). These mechanisms contribute to the so-called organic and inorganic carbon pumps, respectively. While photosynthesis results in a net sink for the dissolved inorganic carbon in the surface ocean (thereinafter referred as DIC), coccolithophore calcification removes alkalinity from seawater in the form of bicarbonate (HCO_3^-) and calcium (Ca^{2+}), which produces a short-term source of CO_2 (Rost and Riebesell, 2004). As such, the relative net intensity of coccolithophore photosynthesis and calcification can change the amount of DIC in surface waters and modulate

the CO_2 exchange between the surface ocean and the atmosphere (Fig. 1). The subsequent sinking of the produced particulate inorganic carbon (PIC) and particulate organic carbon (POC) and rain ratio, or PIC/POC (i.e., the ratio of CaCO_3 to organic carbon that sink down from the ocean's surface (Paasche, 1964), drive the long-term trends of export/ballast of both inorganic and organic carbon towards the deep ocean, its accumulation and burial (Fig. 1). The amount of CaCO_3 that is buried and preserved in sediments, represents a net sink for the alkalinity and DIC consumed during photosynthesis and calcification. On the other hand, the portion of CaCO_3 that is dissolved, returns alkalinity and DIC to the ocean (in a 2:1 ratio) in the form of HCO_3^- and Ca^{2+} (Fig. 1). The degree of dissolution vs. preservation of CaCO_3 is thought to depend on the depth of the horizons of saturation and carbonate compensation. This is controlled by the saturation of CaCO_3 in the water column, in which the concentration of alkalinity and DIC exerts the main control (Broecker and Peng, 1987). The production and export of both CaCO_3

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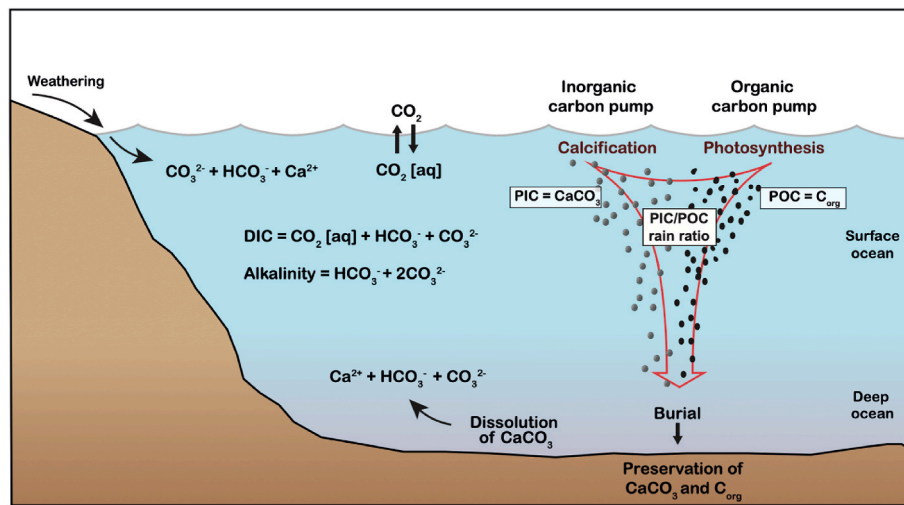


Fig. 1. Simplified scheme of the role of coccolithophores in the carbon cycle.

and organic carbon by coccolithophores play a key role in those processes, influencing the long-term redistribution of carbonate deposition and dissolution in the ocean, with repercussions for the global carbon cycle and climate feedbacks at geological time scales (Archer and Maier-Reimer, 1994; Broecker and Peng, 1987; Sigman and Boyle, 2000; Westbroek et al., 1993).

During the Cenozoic, a wide variety of sedimentological and geochemical proxy records indicate the existence of interconnection between orbitally-forced climatic changes and the expression of the carbon cycle on a long-time scale. The stable isotopes of carbon ($\delta^{13}\text{C}$) in benthic foraminifera stand out among available proxy records showing this orbital variability (De Vleeschouwer et al., 2020; Herbert, 1997; Westerhold et al., 2020; Zachos et al., 2001). This proxy mirrors the isotopic composition of the dissolved inorganic carbon in the seawater ($\delta^{13}\text{C}_{\text{DIC}}$) and its amplitude is considered to respond to the total amount of carbon in the ocean carbon pool (Paillard and Donnadieu, 2014). Although several hypotheses have been proposed to explain the origin of the persistent orbital cyclicity in the benthic $\delta^{13}\text{C}$ records, the mechanism is still unresolved. Nonetheless, a growing body of evidence indicates that changes in global chemical weathering cycles are most likely a key factor able to influence the ocean carbon reservoir and the $\delta^{13}\text{C}_{\text{DIC}}$ at orbital scale (De Vleeschouwer et al., 2020; Ma et al., 2011, 2017; Tian et al., 2011; Wang et al., 2004).

Coccolithophore calcification in the natural environment is thought to respond to changes in ocean carbon chemistry as a first order driver (Bach et al., 2012, 2013, 2015). If climatically-forced rhythms entailed major changes in global seawater carbon chemistry, a change in the intensity of coccolithophore calcification (i.e., the amount of calcite produced per cell) could be expected (Bach et al., 2015). Building on the existing correlation between the rates, or intensity, of coccolithophore calcification and coccolith thickness (Bolton et al., 2016), previous authors have been able to discuss the changes in coccolithophore calcification during certain intervals of the Cenozoic from the morphometric analysis of coccoliths preserved in sediments (Bolton et al., 2016; González-Lanchas et al., 2021b; Guitián et al., 2022; Jin et al., 2018). This approach has never been tested during scenarios of potential changes in the seawater carbon chemistry at orbital scale.

The Noelaerhabdaceae family is one of the most ecologically successful and dominant coccolithophore taxa, after emergence at the Eocene epoch, with the first occurrence of specimens belonging to the genus *Reticulofenestra* located between ~50.2 and 53.70 Ma (Bown and Young, 1998). This coccolithophore family is thought to have played a major role in the long-term operation of the global carbon cycle during the Pleistocene, through impact of its primary production over the net

export of organic and inorganic carbon (Hoogakker et al., 2006; Rickaby et al., 2007; Russon et al., 2010). During that epoch, episodes of globally increased accumulation of inorganic carbon in sediments, led by high proliferation of specimens belonging to this group, occurs together with a reduction in the morphological diversity of its coccoliths (Beaufort et al., 2022). This pattern follows the frequencies of variability of the eccentricity of earth's orbit, with a recurrence of ~400 kyr (Beaufort et al., 2022). These episodes are known as Noelaerhabdaceae acmes and have been interpreted as a response of enhanced proliferation of certain morphotypes within this family, with a better adaptive success, to the reduced seasonality imposed by the conditions of eccentricity minima at the low latitudes (Beaufort et al., 2022).

One of the most outstanding examples of a Noelaerhabdaceae acme episode, occurring at conditions of eccentricity minima, took place during the Mid-Brunhes interval (thereinafter termed as MB), that roughly encompasses the period between the Marine Isotope Stages (MIS) 14 to 7 (~550–280 ka). This interval is characterized by a significant increase in the amplitude of the glacial/interglacial (G/I) cyclicity, starting from MIS12/11 – Termination V (~430 ka), leading to interglacial phases of warmer climates and higher atmospheric concentrations of CO_2 (Jansen et al., 1986; Jouzel et al., 2007). During the MB, the so-called *Gephyrocapsa* complex (i.e., species and/or morphotypes belonging to the genus *Gephyrocapsa* of the Noelaerhabdaceae family (e.g., Bollmann et al., 1998) dominated the net accumulation of pelagic CaCO_3 in oceanic sediments, as a result of increased growth and production rates of this group (Barker et al., 2006; Baumann and Freitag, 2004; Flores et al., 2012; Rickaby et al., 2007). In particular, “*Gephyrocapsa caribbeanica*”, that emerged and proliferated globally within the limits of this interval, has been traditionally considered the main opportunistic species or morphotype representative of this acme episode (Baumann and Freitag, 2004; Flores et al., 2012). Marine records around the globe register, at that time, a period of carbonate dissolution of ~400 kyr duration, the so-called Mid-Brunhes Dissolution Interval (MBDI). This evidence has been suggested to be the result of the enhanced biological pump by increased ballasting of organic carbon (i.e., increased rain ratio) during the acme of *Gephyrocapsa* or “*G. caribbeanica*”, promoting remineralization in the intermediate to deep ocean and intense respiration dissolution (see Barker et al., 2006 and references therein).

Overall, numerous studies have previously proposed that, during the MB, *Gephyrocapsa* significantly contributed to the operation of the global carbon cycle (e.g., Barker et al., 2006; Flores et al., 2012; Rickaby et al., 2007; Saavedra-Pellitero et al., 2017). However, no clues exist yet about the intensity of calcification of the coccolithophores belonging to

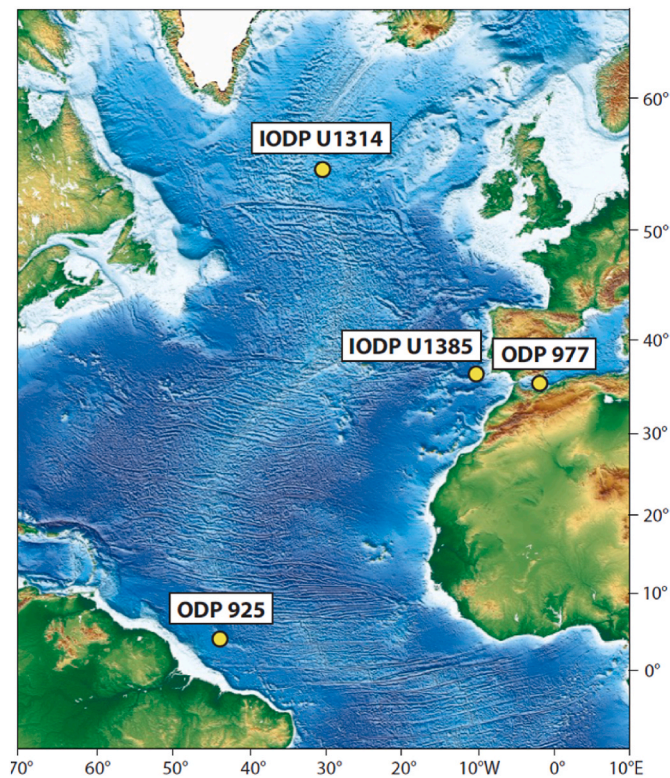


Fig. 2. Location of the sites in this study: IODP U1314, U1385, ODP 977 and 925. Map source: IODP (www.iodp.org).

different species or morphotypes composing the *Gephyrocapsa* complex and, with this, a possible hidden relationship of the evolution or adaptation of this group to the changes in seawater carbon chemistry during this interval. To shed light on this, we applied image analysis techniques (Fuertes et al., 2014) on imaged fossil specimens from subpolar, temperate, and tropical settings of the North Atlantic and the western Mediterranean sea (Fig. 2). The morphometric analyses show that enhanced proliferation of mid-sized *Gephyrocapsa* specimens during the acme episode is latitudinally homogeneous in our record, stretching beyond the equatorial/tropical latitudes towards the subpolar regions. Along with this, intensified calcification is universally expressed by an array of different *Gephyrocapsa* taxa. This response suggests a global scale trigger stimulated the production of both organic and inorganic carbon by the *Gephyrocapsa* complex at individual coccolithophore cellular scale. Ocean alkalinity is proposed to be the main environmental factor exerting selection on morphological features towards the widespread enhanced proliferation of highly calcified *Gephyrocapsa*. Compiling all this evidence, we present a novel hypothesis in which the *Gephyrocapsa* complex may have acted as sink and source of HCO_3^- during the MB. Such a *double-edged* role would have maintained alkalinity in the ocean carbon pool at the period of ~400 kyr duration, exerting an alteration of the typical behavior of the ocean carbonate compensation at this scale.

2. Materials and methods

2.1. Micropaleontological analysis

Samples for analysis of coccolithophore assemblages (coccoliths) were prepared following the settling technique outlined by Flores and Sierro (1997) and studied with the use of a Nikon Eclipse 80i optical microscope with 1000 \times magnification at the University of Salamanca (Spain). A minimum of 400 coccoliths were counted for each sample in a variable number of fields of view.

The *Gephyrocapsa* coccolith counts are presented as absolute values of concentration (N; coccolith g^{-1} sediment) and nannofossil accumulation rates (NAR; nannofossil $\text{cm}^{-2} \text{kyr}^{-1}$) of the total amount of specimens belonging to the complex during the interval (Fig. 4 and Fig. S8). The N and NAR values were produced following the equation by Flores and Sierro (1997). For NAR calculation, the values of wet bulk density from the shipboard Gamma Ray Attenuation of sediments and the sedimentation rates derived from the available age models at each site were considered (Supplementary Text S5).

2.2. Morphometric measurements of *Gephyrocapsa* coccoliths

The same set of slides prepared for the micropaleontological characterization of coccolithophore assemblages were used for image analysis. Between 50 and 60 random fields of view per sample were imaged using a Nikon DS-Fi1 8-bit color digital camera installed on a Nikon Eclipse LV100 POL microscope equipped with circular polarization at the University of Salamanca (Spain). The circular polarization technique is a birefringence-based method that allows for the estimation of individual coccolith size mass and volume based on the direct relationship between the thickness of a calcite particle and the degree of gray color of a pictured pixel (Fuertes et al., 2014). A detailed description of the microscope set-up, thickness calibration and error quantification can be found in the supplementary Text S2 and Table S2.

Images were processed with the use of the software C-Calcula (Fuertes et al., 2014), that provides an automatic quantification of the values of size, mass and volume of individual coccoliths. A minimum of 100 *Gephyrocapsa* coccoliths belonging to each of the size ranges < and >3 μm (respectively termed small and medium *Gephyrocapsa*; see supplementary Text S1 and Table S1) were considered for each sample, after visual evaluation of the output files.

Calculations for Morphological Divergence Index (MDI) were produced from the values of coccolith mass of the small and medium *Gephyrocapsa* groups, following the procedure by Beaufort et al. (2022). The size threshold at 3 μm proposed in that study for the MDI calculation in Noelaerhabdaceae coccoliths, agrees with the major classical taxonomical size criteria for the separation between the small *Gephyrocapsa* and medium *Gephyrocapsa* group followed in this study (Text S1 and Table S1). The average mass of each group was calculated for each sample analyzed in this study, as Log (pg). The MDI is the difference between the two averages.

The angle formed by the inclination of the bridge spanning the central area of the *Gephyrocapsa* coccoliths (>3 μm) has been traditionally used to differentiate between the main species/morphotypes composing the medium sized *Gephyrocapsa* group (see extended descriptions and references in Text S1 and Table S1). This morphometric parameter was manually measured on the pictured coccoliths with the use of the software Nikon NIS-Elements Advanced Research (AR). For this procedure, a number between 50 and 70 medium sized coccoliths were randomly selected from each sample. We established the limits of bridge angle < 40°, between 40 and 60° and > 60° to differentiate the medium *Gephyrocapsa* group into three varieties to separately evaluate its changes in calcification during the MB.

2.3. Calculations for coccolithophore calcification estimation

The existence of an allometric relationship between the changes in coccolith thickness and its size (see Linge Johnsen et al., 2019 and references therein) entails that a size correction is always required to properly determine the changes in thickness which are independent to coccolith size variability. To account for this correction and evaluate the changes in coccolith thickness within the *Gephyrocapsa* complex in our samples, we follow the procedure of previous studies (e.g., O'Dea et al., 2014; Bolton et al., 2016; Jin et al., 2018) and calculate the parameters of Size Normalized (SN) Thickness, k value and PIC/POC, as detailed below.

The Size Normalized (SN) Thickness was calculated following the formula by O'Dea et al. (2014):

$$\text{SN Thickness} = [(\text{ML} - \text{CL}) * S] + \text{CT} \quad (1)$$

Where: ML = mean coccolith length (i.e., size) of all the coccoliths in a sample; CL = size of the individual coccolith; S = slope of the regression between coccolith size and coccolith thickness for all the coccoliths in sample; CT = thickness of the individual coccolith. Values of size correspond to the length of the coccolith major axes.

The k value is an species-specific dimensionless number representative of the fraction of the volume of a cube defined by the surface size of a coccolith (Young and Ziveri, 2000). The empirical determination of this number for a range of extant species/groups can be found in Young and Ziveri (2000). It has traditionally served as a mean to estimate the values of coccolith volume and/or mass from coccolith size measurements (see Young and Ziveri, 2000 for more details). The k value has been discussed to entail an structural change that is related to the changes in coccolith calcification (e.g., Bolton et al., 2016; Jin et al., 2018; Guitián et al., 2022). Following this notion, we back-calculated the k values from the values of coccolith mass and size in this study, using the formula by Young and Ziveri (2000) as in Bolton et al. (2016):

$$k \text{ value} = \text{mass} / [2.7 * \text{size}^3] \quad (2)$$

where 2.7 is the density of calcite ($\text{pg}/\mu\text{m}^3$).

The inorganic/organic carbon ratio (PIC/POC) is, by theoretical definition, the integrated ratio of the rates of calcification to photosynthesis (Rost and Riebesell, 2004). Here we follow the approach in Jin et al. (2018) for the calculation of this ratio from the morphometric parameters of coccolith size and thickness. This calculation is based on the application of the natural dimensional and volumetric relationships for Noelaerhabdaceae coccoliths from Aloisi (2015) and McClelland et al. (2016). A complete and detailed explanation of the protocol is available in Jin et al. (2018).

3. Results and discussion

3.1. Morphology of *Gephyrocapsa* during the MB acme

The records of *Gephyrocapsa* coccolith size and mass from all the studied sites show coherent trends and very similar values during the MB at the different locations (Text S1 and Figures S1-S4). From the beginning of the interval, the *Gephyrocapsa* complex shows low values of average size and mass of the medium *Gephyrocapsa* fraction, which are coincident with relatively increased, or stable, average values of the same morphometric parameters for the small *Gephyrocapsa* fraction (Fig. S1-S4). This relationship is particularly well developed at the central part of the MB, between MIS 13 to 11 and MIS 9 (Fig. S1-S4). From MIS 8 towards the end of the MB, the medium *Gephyrocapsa* fraction experiences a coincident increase in the values of mean coccolith size and mass, compared to stability of the values of the small *Gephyrocapsa* fraction (Fig. S3-S4). The correlation between size and mass changes during the MB (Fig. S5) agrees with early observations (Young and Ziveri, 2000), showing that size changes in *Gephyrocapsa* coccoliths is the main determinant factor of changing individual mass values (see supplementary Text S3).

When the morphometric measurements are integrated into the Morphological Divergence Index (MDI; Beaufort et al., 2022), a similar pattern with a notable degree of agreement along the different latitudes arises (Fig. 3). In line with the interpretation for this index, the lower values of MDI during eccentricity minima in our record (Fig. 3) are considered indicative of a reduction in morphological diversity, that characterizes the enhanced proliferation of Noelaerhabdaceae specimens during the acme episodes of the Pleistocene (Beaufort et al., 2022). The observation of this feature outside the equatorial and tropical latitudes, at the mid latitude Sites 977 and U1385, and the higher mid

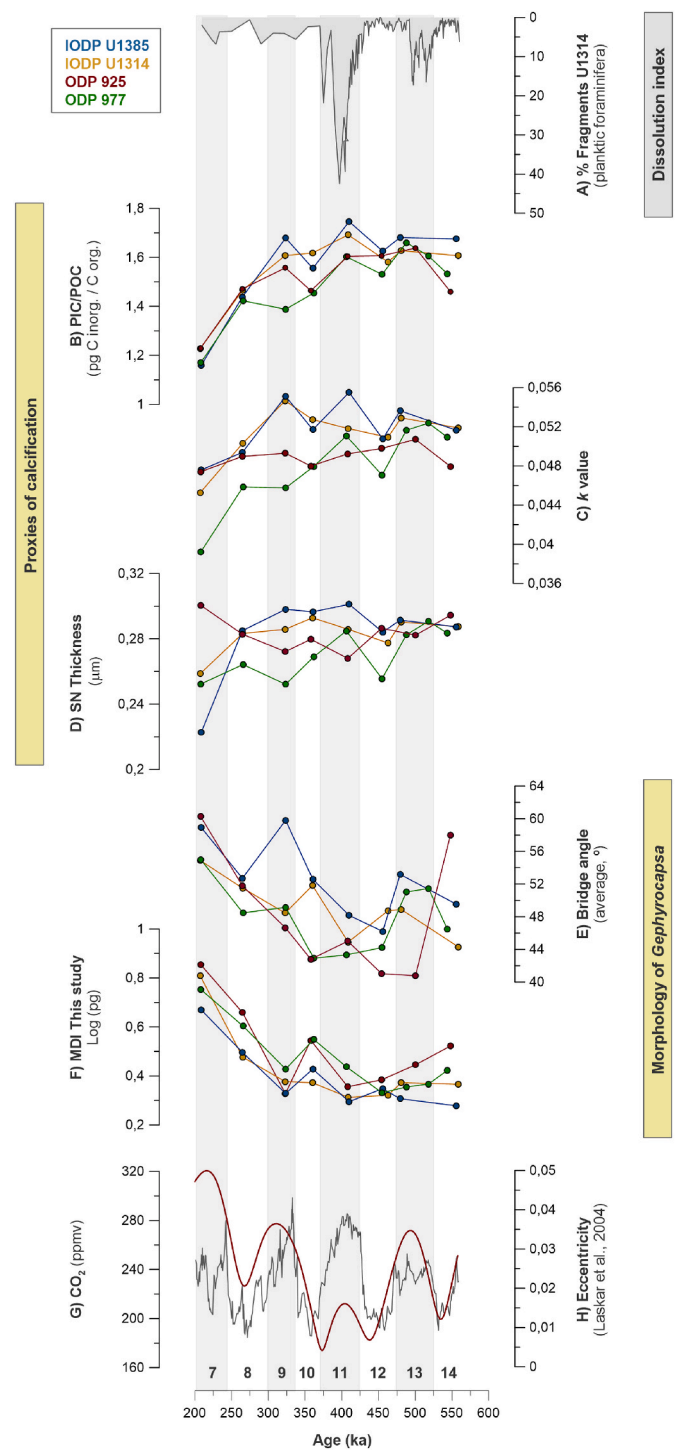


Fig. 3. Relationship between (a) Dissolution estimates by the percentage of fragments of planktic foraminifer in samples from Site IODP U1314; the indexes of coccolithophore calcification, (b) PIC/POC, (c) k value and (d) SN Thickness; the morphological characterization of *Gephyrocapsa* from (e) The mean bridge angle in the medium *Gephyrocapsa* group and (f) Morphological Divergence Index (MDI) for *Gephyrocapsa*; and (g) the pCO_2 changes and (h) the variability of the astronomical parameter of eccentricity (Laskar et al., 2004) during the MB. The procedures for the calculation of indexes and values are found in the section Materials and Methods and supplementary materials. The complete dispersion of the entire set of data measured for the calculation of the mean values in this figure is displayed as whisker and box plots in the Figs. S3 and S4. Gray areas represent the interglacial stages within the MB.

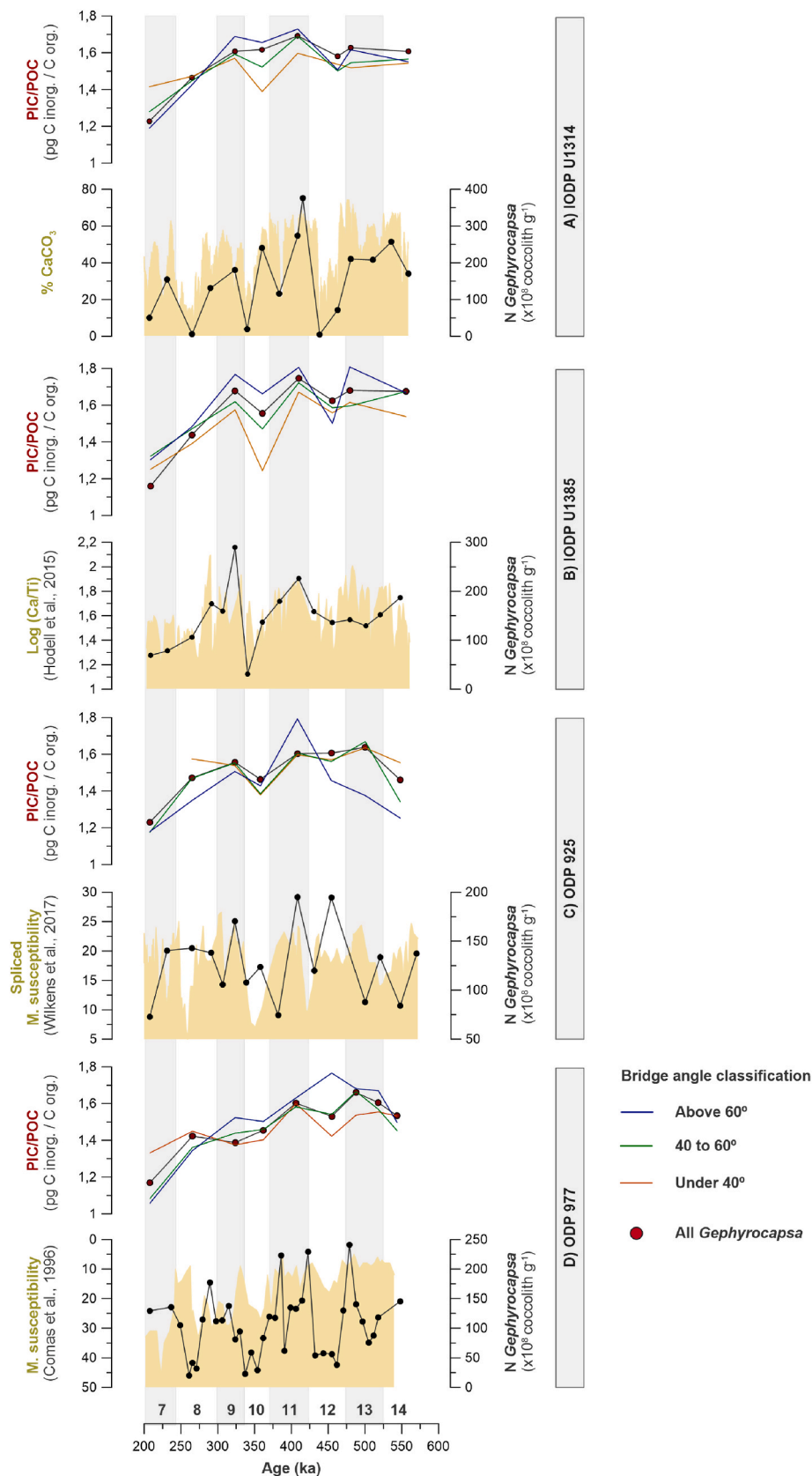


Fig. 4. Relationship between PIC/POC in *Gephyrocapsa*, the absolute concentration of *Gephyrocapsa* coccoliths in sediments (N values, as coccoliths g⁻¹; see Material and Methods) and the available sedimentological profiles from literature that approximate the content of carbonate in sediments between MIS 14 to 7 (see Material and Methods) at the four sites: (a) IODP U1314, (b) U1385, (c) ODP 925 and (d) 977. The color legend for the PIC/POC values at each site corresponds to the classification of the medium *Gephyrocapsa* group using the bridge angle values at each site. Gray bands are indicative of the interglacial stages within the MB.

latitude Site U1314, is a new critical insight in this study (Fig. 3). In summary, it can be stated that *Gephyrocapsa* coccolithophore assemblages are experiencing a response of enhanced proliferation of mid-sized specimens, which is coeval at every latitude of the North Atlantic Ocean and the western Mediterranean region during the MB.

Since the pronounced change in coccolith size and mass described above occurred during the Mid Brunhes Dissolution Interval (MBDI) (Barker et al., 2006), it could be argued that these changes could have been driven, completely or partially, by an intensification of dissolution processes in the water column and/or sediments. Our data provides two lines of evidence that suggest that calcite dissolution played a negligible role on coccolith morphometries. Firstly, the absence of a correspondence between the morphometric trends in *Gephyrocapsa* and the dissolution trend recorded by the planktic foraminiferal fragmentation index of Site U1314 (Fig. 3). Secondly, the coherence between the morphometric trends and MDI at the different studied sites (Fig. 3 and S1–S4), which are located at significantly different regional depths, latitudes, and environments (Fig. 2).

In contrast with the similar evolution of *Gephyrocapsa* size and mass at the different studied locations, the evolution of the mean bridge angle of *Gephyrocapsa* during MB exhibits differences between sites (Fig. 3 and S6). A reduction in values towards the center of the MB is more marked at Sites 925 and 977, in contrast with the more stable evolution of values at the other locations (Fig. 3). This indicates a different morphology of the *Gephyrocapsa* specimens which are proliferating during the acme episode at the different locations and, secondly, a contrasted evolution of the diversity within the *Gephyrocapsa* complex at the different latitudes and environments through time (Fig. 3 and S6; Text S1). Instead of the occurrence and dispersion of a single mid-sized *Gephyrocapsa* morphotype during the MB acme, we consider that this results more likely supports a process of environmental selection over a wide variety of prolific mid-sized taxa, latitudinally distributed during the MB (Fig. 3). Such observation could challenge the existing model, attached to the effect of reduced seasonality in the equator/tropics, as a single forcing mechanism on Noelaerhabdaceae evolution or adaptation during eccentricity minima (Beaufort et al., 2022). In this sense, earlier proposals pointing to the existence of a seawater physicochemical mediator operating on a global scale, as the changes in nutrient delivery or its budget in the ocean (Flores et al., 2012; Rickaby et al., 2007; Zhang et al., 2021), deserve to be considered.

Overall, there is agreement between our data (Fig. 3) and previously available records that *Gephyrocapsa* coccolithophores experienced an enhanced proliferation during the acme episode of the MB (Beaufort et al., 2022; Flores et al., 2012; Rickaby et al., 2007; Zhang et al., 2021). This observation could be interpreted as a result of the intensification in the function of photosynthesis, enhanced growth rate and production of organic carbon by this group. Nonetheless, all available micropaleontological, geochemical and morphometric records fail to assess if the higher growth rates were accompanied by a change in the intensity of calcification (i.e., the production of inorganic carbon per individual cell). Assessing the existence of this possible response within the variety of taxa composing the *Gephyrocapsa* complex is a key point to contribute the understanding about the nature and extent of the processes operating during the MB acme and to decipher the complete dimension of the role of *Gephyrocapsa* during this episode.

3.2. Enhanced calcification of the *Gephyrocapsa* complex

The trends of the three proxies of calcification, the SN Thickness, k value and PIC/POC, for the entire *Gephyrocapsa* complex evidence an increase in values during the MB, namely between MIS 13 to 9, and a pronounced decrease at the end of the interval, through the MIS 8, at all sites (Fig. 3; Supplementary Fig. S7, Text S4 and Table S4). Interestingly, when we separately consider each of the differentiated medium *Gephyrocapsa* varieties after bridge angle classification (Text S1), the trends in the calcification proxies are highly similar for the different

varieties at each site and through latitudes, following the general common trend (Fig. 4). Also, the trends are similar for both the initially differentiated medium and small *Gephyrocapsa* size classes (Figs. S3 and S4). These results unequivocally suggest a common trend of enhanced calcification of the entire *Gephyrocapsa* complex, plausibly representative of physiological change in the cell size normalized calcite content transversal to all the species and/or morphotypes.

Despite the overall similar trends across sites, some differences in the SN Thickness can be recognized (Fig. 3). The SN Thickness profile at the tropical Site 925 displays a different trend of variability compared to that of other locations (Table S3). This fact may suggest that the coccoliths dwelling at this low latitude system could have experienced some degree of dissolution. In fact, in contrast with the rest of locations, the western tropical Atlantic location of Site 925 is more prone to be affected by an overall base degree of dissolution at depths above the lysocline, as a result of the alternating influence of Antarctic Bottom Water and North Atlantic Deep Water during the Pleistocene glacial cycles (Pfuhr and Shackleton, 2004). Nonetheless, this discrepancy at Site 925 is not observed in the profiles of k value and the PIC/POC ratio, that display less variability between sites (i.e., highly similar range of values; Fig. 3) and good correlation between locations (supplementary Text S4 and Table S3). From the results in this study, we suggest that the derived k value and PIC/POC could be more consistent to reflect the changes in coccolithophore calcification and we focus our discussion on these two indexes (Fig. S7).

The coupling between the high concentration of *Gephyrocapsa* coccoliths in sediments and maximum values in sedimentary tracers to approximate the concentration of calcium carbonate in sediments (Fig. 4; see supplementary Text S6), supports the prevailing existing view that the increased production of *Gephyrocapsa* is responsible to increase the global production and accumulation of pelagic carbonate in sediments during the MB. Notably, our results show that, aside from the increased production of carbonate by the higher coccolithophore proliferation and cellular divisions of *Gephyrocapsa* (Barker et al., 2006; Flores et al., 2012; Rickaby et al., 2007), there is an increase in the amount of calcite produced per cell, tracked from the changes in the intensity of calcification of individual coccoliths across multiple *Gephyrocapsa* species or morphotypes (Fig. 4). This feature has never been described, nor quantified before for the MB. Moreover, it has not been observed as an accompanying factor in the ~400 kyr Noelaerhabdaceae acme episodes during the Pleistocene.

Based on our results for the acme of the MB, we consider the existence of a relationship between the production of highly calcified coccoliths during natural bloom episodes, as the MB, and hypothesize about the production of coccoliths in a higher quota per cell. If this were the case, it could be argued that either the production of a greater number of coccoliths per cell and/or the higher intensity of calcification of individual coccoliths may be together the expression of a physiological management aiming to “accommodate” a higher PIC production per cell, in response to certain external/environmental forcing. As a complementary note, our observation about the increase in coccolith calcification accompanied by an overall reduction in the average size, towards the proliferation of mid-sized specimens (Figs. 3 and 4), challenges the idea that a decrease in coccolith size is necessarily coupled with a reduction of the degree of calcification (Suchéras-Marx and Henderiks, 2014).

The taxonomical convention has traditionally considered all individuals with bridge angle around 45° (i.e., between 30 and 65°), average mid-sized values of coccoliths around 3 µm and a qualitative higher robustness, which globally dominates the sedimentary records during the MB, to be ascribed to the concept of “*G. caribbeanica*” (Bollmann et al., 1998; Flores et al., 2012; González-Lanchas et al., 2020, 2021a, 2021b; Saavedra-Pellitero et al., 2017). The universal increase in calcification observed in a wide variety of types within the *Gephyrocapsa* complex together with a variable evolution of diversity and assemblage structure across latitudes (Figs. 3 and 4), suggest that what has been

traditionally clumped as unique "*Gephyrocapsa caribbeanica*" could be the product of the increase in coccolith calcification intensity over a wide variety of morphotypes, latitudinally distributed during the MB. Consequently, we cannot rule out that, instead of just one taxa, multiple different mid-sized *Gephyrocapsa* morphotypes proliferated and calcified more intensely during that episode. In the absence of more precise studies about morphotypic characterization of *Gephyrocapsa* during MB, we suggest the use of *Gephyrocapsa* complex instead of "*G. caribbeanica*", or other species determination, to encompass, at least, all the mid-sized varieties (size $\sim 3\ \mu\text{m}$) or, even, the entire medium *Gephyrocapsa* group (size $\sim 3\text{--}6\ \mu\text{m}$) observed in the fossil record during this interval.

3.3. Ocean alkalinity as the driver of the *Gephyrocapsa* acme?

The synchronous morphometric evidence of the *Gephyrocapsa* acme and increased intensity of calcification across the *Gephyrocapsa* complex in all the studied latitudes (Figs. 3 and 4), suggest the existence of an enhancement in the functions of photosynthesis and calcification of this group during the MB, both mechanisms triggered by a common driver. This appears to represent the existence of a physicochemical seawater mediator, operating on a global scale, stimulating the acme of highly calcified *Gephyrocapsa* during the MB.

The main factors controlling the intensity of coccolithophore calcification in natural environments are still under debate (McClelland et al., 2016; Raven and Crawford, 2012). It has been put forward that changes in temperature, light, nutrients and seawater carbonate chemistry all have an important role (Gafar et al., 2019; Gafar and Schulz, 2018). Changes in temperature, light and nutrients are more regional and highly dependent on the G/I cyclicity (Rehfeld et al., 2018), which means that they may be ruled out as a possible factor controlling the changes in coccolith calcification intensity at the observed longer term scale (Fig. 4). Since the re-equilibrium time of the ocean carbon cycle (i.e., the residence time of carbon in the ocean) is of the magnitude of ~ 100 kyr (Dickens et al., 1995), the changes in seawater carbonate chemistry, together with changes in pH and total alkalinity, are the most suitable candidates for an ocean change at the observed scale (Bach et al., 2015; Müller et al., 2015, 2021). There is emerging consensus that HCO_3^- is the primary inorganic carbon source for calcification, implying that calcification rates increase with increasing amount of HCO_3^- transferred to the coccolithophore intracellular carbon pool (i.e., the intracellular reservoir and source for calcification; Bach et al., 2015; Brownlee and Taylor, 2004). Results from culture observations evidence, furthermore, that both photosynthesis and calcification rates increase with enhanced availability of inorganic carbon substrate (Rickaby et al., 2016) and, in particular, as a response to an increased concentration of HCO_3^- (Bach et al., 2013). The existence of a global process of addition of HCO_3^- , or alkalinity, to the ocean carbon pool during the MB, could easily explain the joint stimulation of both functions and the enhanced proliferation of highly calcified *Gephyrocapsa* specimens registered in our record (Figs. 3 and 4). Therefore, it is worthwhile to explore the possible changes in global seawater alkalinity during the MB, as potential driver.

On the geological perspective, carbon limitation throughout the Pleistocene, due to the long-term Cenozoic CO_2 decline, points to HCO_3^- as likely to have played a key role on long-term changes in coccolithophore calcification. This notion has already been proposed in reference studies about the geological changes in coccolithophore calcification, in order to reconcile the apparent decoupling between $p\text{CO}_2$ and calcification during the Pleistocene, in comparison with its coupling during the late Neogene (Bolton et al., 2016). At orbital timescales, ocean alkalinity is the result of the balance between river input of Ca^{2+} and carbonate ions (i.e., CO_3^{2-} and HCO_3^-) due to terrestrial weathering, and their consumption by marine calcifiers, followed by carbonate burial in the sea floor (Bernier and Bernier, 2004, Fig. 1). The MB interval is characterized by the record of exceptional fluvial discharge and intensified

chemical weathering, starting from 600 ka (i.e., MIS 15), as discussed from sedimentological and geochemical records from different settings (see Chen et al., 2020 and references therein). The intensified weathering from MIS 15 is conspicuous during the Pleistocene and common to multiple records (Yang et al., 2006; Yao et al., 2010), linked to an anomalous climate conditions and duration of this interglacial phase (Chen et al., 2020). We hypothesize that this fact could have critically triggered an anomalous excess of alkalinity in the surface ocean at the beginning of the MB (Fig. 1). The intensification of African and Asian monsoon systems and chemical weathering during the strong interglacials MIS 13, 11 and 9 (Chen et al., 2020; Yao et al., 2010; Yin and Guo, 2008), together with intense denudation and drag during sea level lowstands at glacial MIS 12 and 10 (Chen et al., 2020), could explain a maintained high supply of continental alkalinity during the MB. We consider these facts could have critically contributed to modify the chemical conditions of the surface ocean carbon pool (Fig. 1), thereby facilitating coccolithophorid calcification, and stimulating the proliferation of the different highly calcified *Gephyrocapsa* species or morphotypes observed in our records (Fig. 4).

While the lack of studies directly documenting the influence of changes in alkalinity on coccolith morphometries limit our interpretation, there are several lines of indirect evidence that support this control. As the global distribution of total alkalinity largely matches that of salinity (Millero et al., 1998), this parameter could be considered roughly equivalent to alkalinity. Several studies have documented a strong and positive correlation between coccolith thickness and calcification with salinity in Noelaerhabdaceae, although the cause for this physiological response is unclear (Bollmann and Herrle, 2007; Bollmann et al., 2009; Green et al., 1998; Linge Johnsen et al., 2019). Building on these studies and our results, we propose that alkalinity, rather than salinity, could represent a major control on coccolith calcification and morphometric change. This would be plausibly related to a mechanism of environmental selection over the Noelaerhabdaceae varieties better adapted to different alkalinity levels. Future studies will be needed to validate this hypothesis.

3.4. Hypothesis about the double-edged role of *Gephyrocapsa* during the MB

The increased chemical weathering and anomalous transfer of alkalinity, from the beginning of the MB, would have caused a deepening of the carbonate compensation depth, enhanced preservation of CaCO_3 and a major reduction of $p\text{CO}_2$ at that orbital scale. This is not observed in the $p\text{CO}_2$ (Fig. 3) and global records of reference for the interval (Barker et al., 2006), indicating that, if this addition of alkalinity to the ocean carbon pool had any influence on the acme of *Gephyrocapsa*, the occurrence of coupled changes in the expected mode of compensation of the ocean carbonate system may have occurred.

The enhanced concentrations and accumulation rates of *Gephyrocapsa* coccoliths in our records (Fig. 4 and Fig. S8) are consistent between the different studied locations and with previous studies (Beaufort et al., 2022; Flores et al., 2012; Rickaby et al., 2007; Zhang et al., 2021), supporting the notion that this taxon was an important vector of CaCO_3 to the seafloor during the MB. Building on this, the magnitude of the increase in calcification in our results, over 50 % in the morphometric PIC/POC at all the sites (Fig. 4), fits well with the model output of a $\sim 50\%$ increase in PIC/POC during the MB able to promote an intensification in the biological pump sufficient to maintain the observed constant $p\text{CO}_2$ levels at the 400 kyr scale (Barker et al., 2006). The coupled increase in calcification intensity, or enhanced production of calcite per cell (Figs. 3 and 4), provides an important piece to support an enhancement of the rain ratio and ballast effect promoted by this group during the MB (Barker et al., 2006a; Saavedra-Pellitero et al., 2017). Taking all these evidence together, we propose a hypothesis in which the *Gephyrocapsa* complex may have acted as a sink and source of alkalinity (double-edged role), maintaining any additional alkalinity to

the ocean, from weathering, cycling between the intermediate depths and the surface and promoting the acme in the ocean, as detailed below:

The enhanced chemical weathering from the beginning of the MB would have promoted fertilization, by the enhanced availability of DIC and alkalinity in the surface ocean. This may be possibly complemented by the nutrient addition coupled to the intensified river input, as suggested by previous authors (Rickaby et al., 2007; Zhang et al., 2021). This environmental forcing would have triggered a process of selection and/or adaptation on *Gephyrocapsa*, promoting the observed morphological modification by the proliferation of a variety of mid-sized and highly calcified taxa within the complex (Figs. 3 and 4). Such response translates into enhanced production of organic and inorganic carbon, representing an overall intensification of both functions of photosynthesis and calcification, and acting as an active sink for the increased DIC and alkalinity in the ocean (Fig. 1). The resulting increase in the rain ratio of PIC/POC to the deep ocean (Fig. 1) would have contributed to improve the efficiency of the organic carbon pump during the MB (Barker et al., 2006), now better supported by the role of the more numerous and highly calcified carbonate particles produced by *Gephyrocapsa* (Figs. 3 and 4). The high production, ballast and accumulation of organic carbon, resulting from these processes, may have enhanced the remineralization of organic carbon and the rates of respiration, contributing to promote dissolution of the CaCO_3 above the ocean sea floor (Fig. 1). Such reinforcement in dissolution is in line with the intensity of the MBDI recorded in sedimentary proxies (Barker et al., 2006) and extracted from isotope records (Hoogakker et al., 2006). The higher rates of carbonate dissolution would have returned Ca^{2+} and carbonate ions to the ocean carbon pool, reducing the CaCO_3 burial and maintaining relatively constant levels of seawater alkalinity (Fig. 1). In this sense, the role of the *Gephyrocapsa* complex during the MB could have contributed as a source of recycled alkalinity for the system. This sequence of processes explains a self-sufficient mechanism of recycling and maintenance of alkalinity within the ocean carbon pool, stimulating the *Gephyrocapsa* acme during the MB. We consider, nonetheless, that the activation and duration of the *double-edged* role of *Gephyrocapsa* with seawater alkalinity necessitates an external control, by initial continental weathering stimulation, to be explained. In tune with this, the overall decreased continental chemical weathering after interglacial MIS 9 (Chen et al., 2020; Yao et al., 2010), towards the end of the MB, may have triggered a progressive reduction of the ocean surface DIC and alkalinity. These new environmental conditions may have exerted a different forcing on *Gephyrocapsa*, as observed by the shift towards increased MDI values, and the reduced proliferation of highly calcified specimens, common to all latitudes, from MIS 8 onwards (Figs. 3 and 4). The reduction in the carbonate consumption and ballast effect by the end of acme conditions, would have even amplified the preservation of inorganic carbon in the sea floor, balancing the inputs of alkalinity from continental weathering through carbonate deposition in the deep sea, after a few kyr (Fig. 1). In other words, this represents the recovery of the typical conditions of carbonate compensation towards the end of the interval.

4. Conclusions

Our results evidence a coeval record of the *Gephyrocapsa* acme during conditions of eccentricity minima of the MB at the different latitudes of the Atlantic Ocean and the western Mediterranean. Instead of one morphotype, a different array of *Gephyrocapsa* taxa proliferated at the different environments, evidencing a universal increase in calcification. A response of enhanced production of organic and inorganic carbon by *Gephyrocapsa* coccolithophores during the MB underlies this observation and indicates that both changes were originated by a common driver. Maintained high seawater alkalinity during the interval is proposed as the main environmental trigger for the *Gephyrocapsa* acme, exerting a process of environmental forcing on adaptation/selection of specimens at the different latitudes. The enhanced proliferation of highly calcified

specimens supports the increased rain ratio and strengthened organic carbon pump during the MB, favoring intense dissolution at the ~400 kyr cycle and recycling of alkalinity at this scale. Connecting all these pieces, we propose a novel hypothesis about the *double-edged* role of *Gephyrocapsa* complex during the acme episode of the MB, in which this coccolithophore group would have acted as a sink and source of ocean alkalinity. This role ultimately represents an alteration of the typical behavior of the ocean carbonate compensation during the conditions of low eccentricity.

This perspective critically underscores that the changes in the seawater carbon chemistry should be considered as a important component mediating between orbital forcing and the evolution and/or adaptation of Noelaerhabdaceae coccolithophores. Moreover, it is evidenced that the role of Noelaerhabdaceae coccolithophores can be a piece of the jigsaw in the interaction of the processes modulating the carbon cycle, with a determinant repercussion for the storage of alkalinity in the ocean during the Cenozoic.

Author contribution

The study was conceived by AGL and JAF. The preparation of the samples, analysis of the coccolith assemblages, image analysis, morphometric measurements and calculation of calcification indexes were developed by AGL. Foraminiferal fragmentation counts were performed by AGL and MAG. ASRH and MAG provided resources and assistance during the development of the research. Interpretations, visualization and writing of the manuscript were led by AGL with contribution and feedback of all the coauthors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data generated for this study is archived online at Zenodo Data Archive, as Alba Gonzalez-Lanchas, José-Abel Flores, & Francisco J. Sierro. (2023). Morphological and calcification analysis of *Gephyrocapsa* during the Mid-Brunhes [Data set]. Zenodo. <https://doi.org/10.5281/zenodo.7728197>

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.quascirev.2023.108375>.

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