Biogeosciences, 4, 323–329, 2007
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Biogeosciences

A coccolithophore concept for constraining the Cenozoic carbon cycle

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Received: 7 December 2006 – Published in Biogeosciences Discuss.: 16 January 2007
Revised: 23 May 2007 – Accepted: 6 June 2007 – Published: 19 June 2007

Abstract. An urgent question for future climate, in light of increased burning of fossil fuels, is the temperature sensitivity of the climate system to atmospheric carbon dioxide (pCO_2). To date, no direct proxy for past levels of pCO_2 exists beyond the reach of the polar ice core records. We propose a new methodology for placing a constraint on pCO_2 over the Cenozoic based on the physiological plasticity of extant coccolithophores. Specifically, our premise is that the contrasting calcification tolerance[1] of various extant species of coccolithophore to raised pCO_2 reflects an "evolutionary memory" of past atmospheric composition. The different times of evolution of certain morphospecies allows an upper constraint of past pCO_2 to be placed on Cenozoic timeslices. Further, our hypothesis has implications for the response of marine calcifiers to ocean acidification. Geologically "ancient" species, which have survived large changes in ocean chemistry, are likely more resilient to predicted acidification.

1 Introduction

Anthropogenic pCO_2 is absorbed largely by the oceans, causing acidification of the biologically productive surface waters (The Royal Society, 2005; Kleypas et al., 2006). Corals, foraminifera and pteropods decrease their calcification in response to increased acidification (Gattuso et al., 1999; Kleypas et al., 1999; Bijma et al., 1999; Orr et al., 2005). Despite the intracellular nature of coccolithophore calcification, culture experiments confirm that *Emiliania huxleyi* and its close relative *Gephyrocapsa oceanica* also decrease calcification as pCO_2 increases (Riebesell et al., 2000; Zondervan et al., 2001). Decreased calcification is a negative feedback to acidification on the short term (Zondervan et al., 2001) but poses a serious threat to the sensitive ecologic balance. Ultimately, the rate at which populations acclimatise or adapt to changing ocean chemistry will determine the operation of feedback mechanisms on future climate.

Long-term patterns in coccolithophorid evolution and success seem, however, counterintuitive to this paradigm of low calcification under high pCO_2. Coccolithophore diversity and abundance peaked during the greenhouse Cretaceous world and have since declined (Bown, 2005). In addition, and by contrast to the tests on *E. huxleyi* and *G. oceanica* (Riebesell et al., 2000; Zondervan et al., 2001), recent acidification experiments testing the environmental tolerance of different extant coccolithophore species reveal that the calcification response is species-specific (Langer et al., 2006). Calcification ability[2] in the species *Coccolithus pelagicus* is unaffected by values of pCO_2 up to at least 920 ppmV, and even though calcification ability declines, coccoliths are still produced up to much higher levels (S. Krug, personal communication). By contrast, *Calcidiscus leptoporus* shows an "optimum" calcification ability close to modern day pCO_2 (Langer et al., 2006). Thus, species-specific effects must be considered when evaluating whole ecosystem response to elevated pCO_2. Although representative of few algal strains, these culture results raise a major question: why do different species respond differently to pCO_2?

2 Methodology and hypothesis

With a geological perspective, the ability of different coccolithophore species to calcify in culture under a range of ocean acidity correlates with likely levels of atmospheric

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[1] We define "calcification tolerance" as the tolerance to variable pCO_2 of coccolithophores with respect to calcify normally (with no malformation/incomplete coccolithogenesis).

[2] We define "calcification ability" as the ability to produce coccoliths with no, or only minor, decrease in PIC/POC ratio from those during optimum conditions.

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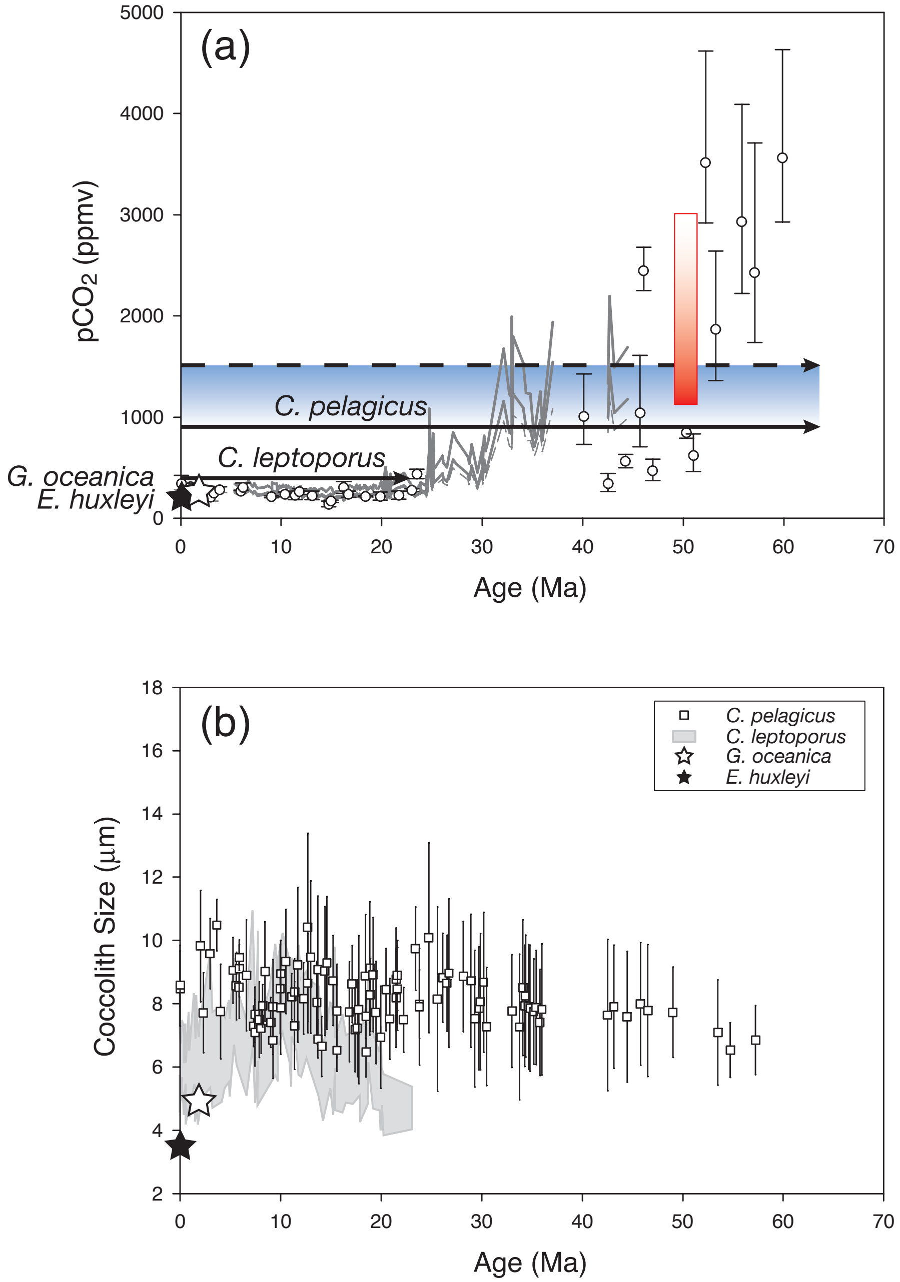

Fig. 1. (a) At face value, the levels of pCO_2 tolerated by different coccolithophore species for calcification in culture experiments (Riebesell et al., 2000; Langer et al., 2006) coincide with levels of pCO_2 from marine proxy reconstructions, based on alkenones (solid and dashed lines; Pagani et al., 2005) and boron isotopes in planktic foraminifera (open circles; Pearson and Palmer, 2000), at the time of emergence of each respective morphospecies; marked by a star for *E. huxleyi* (291–268 ka; closed star) and *G. oceanica* (1.7 Ma; open star), and solid arrows for *C. leptoporus* (23 Ma) and *C. pelagicus* (~63 Ma). The upper pCO_2 tolerance range for *C. pelagicus* is indicated by the blue box with a solid arrow at the maximum pCO_2, thus far tested, at which its calcification remains unaffected (Langer et al., 2006), and dashed arrow showing the potential for this species, with further experiments, to determine the Palaeogene maximum pCO_2. The red box depicts the pCO_2 range in which the sodium carbonate nahcolite precipitates (Lowenstein and Demicco, 2006), fixing minimum early Eocene pCO_2 at 1125 ppmV. **(b)** Mean coccolith size, a proxy for coccolithophore cell size, has remained largely constant for *Coccolithus* during the Cenozoic decline of pCO_2 (open squares ±1 stdev; this study), and for *Calcidiscus* (grey envelope ±1 stdev; Knappertsbusch, 2000) since the Miocene. Both genera are significantly larger than *E. huxleyi* (closed star), which stands out as one of the smallest, but most prolific calcifying coccolithophore alive today and represents the youngest evolutionary addition (291–268 ka) to the fossil record of calcifying haptophytes.

pCO_2 since the emergence of their corresponding morphospecies during the Cenozoic (Fig. 1a). Modern *E. huxleyi* and *G. oceanica* are distinct genetic outliers to most other extant coccolithophore (Fujiwara et al., 1994; Sáez et al., 2003), and group together with other alkenone-producing haptophytes such as the non-coccolith bearing species *Isochrysis galbana*. The morphospecies *E. huxleyi* had a first occurrence ∼291–268 ka and has risen to global dominance since 85 ka, while *G. oceanica* evolved at 1.7 Ma (Thierstein et al., 1977; Raffi et al., 2006). In contrast, the morphospecies *Calcidiscus leptoporus* originated at 23 Ma (Knappertsbusch, 2000) and *Coccolithus pelagicus* in the Palaeocene, ∼63 Ma (Haq and Lohmann, 1976). At face value, the levels of pCO_2 tolerated in cultures of the different coccolithophorid morphospecies coincide with the levels of pCO_2 from proxy reconstructions at the time of their diversification (Pagani et al., 2005; Pearson and Palmer, 2000). This evolutionary view of the culture results holds the potential to place an upper constraint on Cenozoic palaeo-pCO_2, which must have been at least 920 ppmV at the time of evolution of *C. pelagicus*, 63 Ma. With further experiments to push the calcification tolerance of *C. pelagicus* and additional modern representatives of ancient morphospecies, we predict a tight bracketing of palaeo-pCO_2 estimates for the Palaeogene, especially in combination with a fixed minimum early Eocene pCO_2 of 1125 ppmV, as reconstructed by stability fields of sodium carbonates (Fig. 1a; Lowenstein and Demicco, 2006). Our proposed proxy appears to concur with an emerging view of different climate sensitivities before and after the marked draw-down of pCO_2 at the early Oligocene from the greenhouse of the early Cenozoic (Pagani et al., 2005; Lowenstein and Demicco, 2006).

3 Discussion

Our statement that genetically “older” extant species have an “evolutionary memory” of calcification under conditions of higher pCO_2 in these culture experiments, and that this envelope of ability may constrain past pCO_2 estimates, requires detailed consideration. Nonetheless, other evidence suggests that ancient biomineralisation pathways may be recalled by extant species grown in conditions which reflect ocean chemistry of the past. For example, relict modern populations of sublittoral siliceous demosponges (genus *Crambe*), which have Jurassic ancestry, modulate the phenotypic expression of their spicules depending on the experimental concentrations of silicic acid (Maldonado et al., 1999). These organisms only produce lightly silicified spicules in their natural environment, which is likely silicon limited. Under “ancient” chemical conditions of elevated silica concentrations, *C. crambe* proves genetically capable of producing spicule types that are not normally found in natural populations, but have high resemblance to fossil morphotypes (Maldonado et al., 1999). In some organisms or species, the genes that encode biomineralisation may be conservative over time but their genetic expression is sensitive to the environment such that biomineralisation is phenotypically plastic.

Calcification has most likely evolved only once in haptophytes, in the late Triassic. The presence of non-calcifying taxa within the typical “coccolithophore” phylogenetic clades suggests that the biochemical pathways involved in coccolithogenesis have been shut down and possibly reactivated several times in the course of their evolution (deVargas and Probert, 2004). Still, a relatively simple phylogenetic pattern can be derived based on life-cycle observations and related modes of biomineralisation (Young and Bown, 1997). For example, *C. pelagicus* and *C. leptoporus* produce both heterococcoliths (in diploid phase) and holococcoliths (haploid phase), while *E. huxleyi* and *G. oceanica* appear to have lost the ability to produce holococcoliths (they only produce organic scales in haploid phase). The close phylogenetic affinity of *E. huxleyi* and *G. oceanica* to the non-calcifying haptophyte genus *Isochrysis* (Sáez et al., 2004) also suggests that the genetic encoding for calcification is subject to variable evolutionary selection within this organism group, and is susceptible to phenotypic plasticity.

For our proposed evolutionary perspective of constraints on atmospheric pCO_2, the photosynthetic or calcification potential of a species must be optimised for an aspect of ocean carbonate chemistry related to pCO_2 at the time of origin and, become preserved within the genetic make-up since the ocean and atmosphere chemistry changed. Although debate persists regarding the exact interplay between calcification and photosynthesis, calcification requires energy, and in coccolithophores, the only source of this energy can be photosynthesis. Therefore the two processes must be coupled to some degree due to the energy requirement for the transport of Ca^{2+} and CO_3^{2-} into the coccolithophore cells, and control of intracellular pH. In the culture experiments, as in the modern ocean, the carbonate saturation state and pH are inversely proportional to pCO_2, with coherence between lower energetic requirement for calcification at high carbonate saturation and pH, and lower photosynthetic energy available from low pCO_2. In the geological past, carbonate saturation state and pCO_2 were likely decoupled (Tyrrell and Zeebe, 2004). Nevertheless, available long-term reconstructions of ocean pH consistently depict a secular increase in pH during the Cenozoic (Pearson and Palmer, 2000; Tyrrell and Zeebe, 2004). Without further culture experiments of decoupled carbonate system parameters, it is impossible to resolve which aspect of ocean chemistry, and which physiological pathway is fundamental to coccolithogenesis. Because of the intrinsic coupling between photosynthesis and calcification, and between ocean pH and pCO_2, we shall relate the following discussion of which extant coccolithophore species possess an “evolutionary memory” and how such physiological pathways could be preserved, to pCO_2 as the variant parameter.

According to the culture experiments, the different species of coccolithophore fall into two groups: conservative species which have retained the genetic encoding for biomineralisation at past levels of pCO_2, and adaptive species. In the marine realm, it would be expected that populations of planktonic micro-organisms could quickly adapt to their changing environment (e.g. deVargas et al., 2004), such that all extant coccolithophores are adapted to present-day values of pCO_2. As discussed by Langer et al. (2006), the bell-shaped calcification response by *C. leptoporus*, centred around present-day values of pCO_2, is consistent with such adaptation to variable pCO_2 on glacial-interglacial time scales and therefore this species is unsuitable to use as a palaeo-proxy for Miocene pCO_2.

By contrast, the broad, and apparently insensitive response by *C. pelagicus* to variable levels of pCO_2 in culture also suggests adaptation to present-day pCO_2 values, but with conservation of the ability to calcify normally under lower, as well as much higher CO_2 concentrations, and therefore potentially represents an "evolutionary memory" of both the glacial low-pCO_2 and high-pCO_2 Palaeogene worlds. *Coccolithus pelagicus* tolerates conditions (S. Krug, personal communication) beyond the limit of modern surface waters (Orr et al., 2005), which indicates that this species has retained a signature of adaptation to a different past pCO_2. In comparison to other tested coccolithophores, *C. pelagicus* appears conservative in its evolutionary adaptation. This supposition is supported by our coccolith size data[3] for the *Coccolithus* morphospecies lineage. The morphological template and the mean coccolith size, linearly related to cell size (Henderiks and Pagani, in press), have remained largely constant for *Coccolithus* during the Cenozoic decline of pCO_2 (Fig. 1b). In contrast, the Cenozoic ancestors of *Gephyrocapsa* and *Emiliania*, within the *Reticulofenestra* genus, have greatly varied in coccolith size, with largest morphospecies (14–20 μm) occurring during the late Eocene (Backman and Hermelin, 1986). Available morphometric data of *Calcidiscus* morphospecies show a secular decline in mean size since the late Miocene (in the equatorial and southern Indian Ocean; Knappertsbusch, 2000). Based on these data, we argue that such distinct evolutionary size patterns between the coccolithophore lineages imply that the different morphospecies may fall into two groups: morphospecies which are highly adaptive to changing ocean chemistry in terms of their calcification and size, and morphospecies which are highly conservative. Indeed, our fossil morphospecies likely group several cryptic species together (Saéz et al., 2003; deVargas et al., 2004). The coccolith size range of such cryptic species is in fact rather constant, whereas their biogeography and seasonality is highly variable (e.g. Renaud et al., 2002). In this light, the total size range of fossil morphospecies could potentially be a measure for the degree of (cryptic) speciation within each coccolithophore lineage, and thus reflect evolutionary rates and/or genetic plasticity of coccolithogenesis.

Adaptation to a new ecological niche may result in a "cost" in terms of lost ancestral capabilities (e.g. Bell, 1997; Kassen, 2002) such that the adaptive *E. huxleyi* has lost the ability to succeed at high pCO_2. These capabilities may be lost either because they are no longer under selection (neutral) or because of a deleterious effect on fitness in a new niche. Evolution of the lightly calcified *Gephyrocapsa* and *E. huxleyi* with fast growing, small cells provides the advantage of investing energy in cell growth, and an ability to outcompete more heavily calcified coccolithophores in a low pCO_2 world. Indeed the macroevolutionary decrease in coccolith (and thus cell) size during the Neogene (Henderiks et al., 2004) could indicate adaptation of the photosynthetic capacity of small reticulofenestrids and *Calcidiscus* morphospecies to lowered pCO_2. Cells optimise their photosynthesis by increasing surface area to volume, maximizing light acquisition, increasing Rubisco specificity (Tortell, 2000), and carbon concentrating mechanisms (Giordano et al., 2005). Today, *C. pelagicus* represents one of the largest coccolithophores alive, whereas *E. huxleyi* stands out as one of the smallest and appears best adapted to low pCO_2 values, because this species shows no photoinhibition at high light levels or in continuous light (e.g. Nanninga and Tyrrell, 1996; Zondervan et al., 2002), blooms in the uppermost water column, has a carbon concentrating mechanism (Rost et al., 2002) and is likely an adaptive low-pCO_2 specialist. Additionally, *E. huxleyi* and *G. oceanica* cells are produced with an average PIC/POC ratio of 0.6–0.8 compared to 1.6–1.8 for both *C. leptoporus* and *C. pelagicus* (Zondervan et al., 2001, 2002; Langer et al., 2006) which could imply a different partitioning priority for energy between photosynthetic carbon fixation and calcification as a result of the pCO_2 at their time of origin. This would imply that both *C. leptoporus* and *C. pelagicus* precipitate more $CaCO_3$ per mole of C fixed and are efficient calcifiers. By contrast *E. huxleyi* prioritises photosynthetic carbon fixation under low pCO_2 conditions and the cost of calcification to *E. huxleyi* and *G. oceanica* is proportionately larger and expendable as the ocean becomes more acidic.

Conservation of an "evolutionary memory", and phenotypic plasticity may be manifest as generalist or specialist behaviour of the different coccolithophore species with respect to pCO_2 (Richmond et al., 2005). The preservation of *C. pelagicus*' calcification ability may be enhanced because this species prefers a high pCO_2 niche. *C. pelagicus* prevailed in Palaeocene equatorial regions (Haq and Lohmann, 1977), and was only restricted to high pCO_2 subpolar and upwelling niches since the late Pliocene (Sato et al., 2004). By contrast *E. huxleyi* appears photosynthetically optimised for success in the modern ecological niche of low pCO_2. The distribution of the apparently cosmopolitan *E. huxleyi*, and to

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[3] Coccolith morphometric data on 99 deep-sea sediment samples, from various (sub)tropical and temperate sites, ranging in age 2.2 ka–57.3 Ma. Mean coccolith size was determined from 100–200 individual coccolith measurements per sample collected from 4 replicate sprayed slides under polarised light microscopy (Henderiks and Törner, 2006). Further details will be presented and discussed elsewhere.

a lesser extent *C. leptoporus*, correlates well with the consistently low [CO_2(aq)] across the tropical and temperate latitudes (Orr et al., 2005) such that the broad biogeographic distribution actually reflects a narrow ecological niche in terms of [CO_2(aq)].

The broad tolerance to [CO_2(aq)] of *C. pelagicus* is likely a manifestation of the physiological plasticity, maintained at extra energetic cost, of this species and implies conservative evolution as reflected by the relative constancy of cell size and coccolith morphology throughout the last 63 million years (Fig. 1b). The optimisation of *E. huxleyi* to bloom and conquer the majority of the world's oceans has occurred at a cost incurring the loss of competitiveness at high pCO_2. A high degree of selectivity of the photosynthetic machinery for low pCO_2 can be coupled with slow photosynthetic kinetics (Tcherkez et al., 2006) such that in high pCO_2 conditions, the growth rate of *E. huxleyi* shows little reponse.

In terms of underlying genetic mechanisms, currently, little is known about genetic controls on calcification (e.g. Marsh, 2003; Nguyen et al., 2005), or the detailed photosynthetic mechanism of coccolithophores. Coupling of calcification with species-specific Rubisco specificity provides a tangible means to preserve the CO_2/O_2 composition at the time of origin of photosynthetic phyla (Giordano et al., 2005; Tcherkez et al., 2006). The preservation of calcification ability at high pCO_2 in *C. pelagicus* may occur through genetic redundancy (Wagner, 1999), or variance in genetic expression whilst the adaptation of *E. huxleyi* and *C. leptoporus* to the modern low pCO_2 niche could be associated with gene inactivation of pathways associated with high pCO_2 (Hittinger et al., 2004). The high proportion of duplicate genes within plant and algae genomes is indicative of a high rate of retention of duplicate genes (Lynch and Connery, 2000). Gene duplications contribute to the establishment of new gene functions, and may underlie the origin of evolutionary novelty. Duplicate genes can exist stably in a partially redundant state over a protracted evolutionary period (Moore and Purugganan, 2005). A half-life to silencing and loss of a plant gene duplicate is estimated at 23.4 million years such that remnant duplicate genes, which can be reactivated by environmental conditions to encode calcification within coccolithophores under "ancestral" conditions representative of ~60 Ma, appears reasonable.

4 Concluding remarks

Our hypothesis for a novel proxy requires further foundation with experiments on an assortment of ancient morphospecies and strains, and investigation into calcification and photosynthesis under a range of ocean carbonate conditions, nutrient levels and temperatures. Nonetheless, our ideas have implications for the future ocean. With fossil fuel burning and a predicted decrease in pH of ~0.3 over the next 100 years (The Royal Society, 2005), the larger species will likely have an advantage over the now prosperous *E. huxleyi*, as the carbonate system of the ocean reverses towards the acidity of the past. *C. pelagicus* has weathered large and abrupt changes in conditions in the geological past, e.g. the Palaeocene-Eocene thermal maximum (Gibbs et al., 2006), with no apparent impact on physiology, but the adaptive strategies of newcomer *E. huxleyi* may differ significantly, potentially leading to future non-calcifying descendants.

Acknowledgements. We are grateful to S. Krug for sharing his unpublished data with us and informing our hypothesis. We would like to thank M. Lachmann, P. Westbroek, F. Morel and P. Falkowski for their help with discussion and development of the ideas presented here. Interdisciplinary discussions with participants of the IGBP-SCOR workshop on ocean acidification (Lamont-Doherty Earth Observatory, September 2006) further strengthened the potential impacts of our hypothesis. We wish to thank three anonymous referees as well as U. Riebesell for their constructive and challenging comments.

Edited by: J. Bijma

Author contributions

The authors contributed equally to the preparation of this manuscript.

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