

Evidence for a multi-species coccolith volume change over the past two centuries: understanding a potential ocean acidification response

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Abstract. Major questions surround the species-specific nature of coccolithophore calcification in response to rising atmospheric CO₂ levels. Here we present CaCO₃ particle volume distribution data from the coccolith size-fraction of a rapidly accumulating North Atlantic sediment core. Without direct volume measurements on coccoliths produced by individual coccolithophore species, and knowledge of organic, as well as inorganic carbon production, it is not possible to state conclusively the coccolithophore calcification change at this site. However, by analysing the size distribution of CaCO₃ particles in the less than 10 μm sediment fraction, we demonstrate a changing particle volume since the late 20th Century consistent with an increase in the mass of coccoliths produced by the larger coccolithophore species, and potentially a decrease in mass of coccoliths produced by the smaller species, present at this location. This finding has significant implications for the realistic representation of an assemblage-wide coccolithophore CO₂-calcification response in numerical models.

1 Introduction

Phytoplankton mineralization in undersaturated waters is a widespread feature of the oceans, as evidenced by thriving diatom and acantharia populations in waters undersaturated in silica and strontium sulphate respectively. Recent laboratory studies indicate that physiological controls over mineralization, in some phytoplankton, can overcome reductions in

the saturation state of ambient seawater (Iglesias-Rodriguez and Halloran et al., 2008; Langer et al., 2006a; Langer et al., 2006b). Furthermore, *Emiliania huxleyi* has demonstrated an ability to calcify at a saturation state of 0.4 (Langer et al., 2006b). Coccolithophores calcify intracellularly, and as such, the complexity of their calcification response to a modified external seawater carbonate system may result from a variable biological uptake of different forms of dissolved inorganic carbon for calcification, or differences between the manipulation of culture experiments, but may also reflect the physiological tolerance towards changing pH and carbon concentration ability of different coccolithophores (Henderiks and Rickaby, 2007).

An increase in the average coccolith mass, independent of a change in species composition, has been demonstrated to parallel the rise in atmospheric pCO₂ over the past ~220 years, by analysis of the <10 μm sediment fraction from a Sub-polar North Atlantic core (RAPID 21-12-B, 57°27.09' N, 27°54.53' W, situated at 2630 m below sea level) (Iglesias-Rodriguez and Halloran et al., 2008). Here we present a size-distribution analysis of the RAPID 21-12-B <10 μm size fraction, indicating that the increase in coccolith mass occurs across a broad range of coccolithophore species. For core dating see Boessenkool et al. (2007).

2 Methodology

Sediment core RAPID 21-12-B was sampled at continuous 0.5 cm intervals. Approximately 2 to 4 g of the total sediment from each sample was suspended in buffered H₂O and passed through a 10 μm pore-size track-etched polycarbonate filter membrane, using bubble agitation to prevent blocking. Three sub-samples were taken from the <10 μm



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fraction, each suspended in 100 ml of electrolyte (ISOTON II, Beckman Coulter UK Ltd, Buckinghamshire UK), and the particle volume frequency distribution of each fraction, between 0.63 and 10 μm equivalent spherical diameter (ESD), analysed three times using a Beckman Coulter Multisizer III Coulter Counter fitted with a 30 μm aperture. This technique provides a direct measure of particle volume, by recording the volume of electrolyte displaced as the particle passes through the sensing zone of the aperture. These data were collected in 256 bins distributed on a log basis across the 9.37 μm sizing window. After replicate analysis, 500 μl of concentrated HCl was added to each suspension, stirred, left to stand, then stirred again vigorously for 4 min before re-analyzing each sub-sample three times. We have then calculated the difference between pre-acidification and post-acidification volume frequency distributions (typically totaling 80 000 CaCO_3 particles). In order to allow direct comparison of CaCO_3 volume frequency distribution across the time-series, the average of the nine measured replicate CaCO_3 particle counts in each of the 256 bins has been divided by the average of the nine measured replicate total CaCO_3 particle counts in that sample. We consider these data to characterize the $<10 \mu\text{m}$ sedimentary CaCO_3 particle distribution, indirectly representing the coccolith fraction, comprising *Emiliania huxleyi*, small *Gephyrocapsa*, *Gephyrocapsa oceanica*, *Gephyrocapsa muelleriae*, *Gephyrocapsa caribbeanica*, *Oolithotus fragilis*, *Calcidiscus leptoporus*, *Coccolithus pelagicus* var. *pelagicus*, *Helicosphaera carteri* (Iglesias-Rodriguez and Halloran et al., 2008). The high abundance of small coccoliths in the RAPID 21-12-B sediments makes it necessary to normalize the particles counts in each bin by the average number of counts in all bins of that volume. This data is presented as a percentage anomaly from that average value, and allows a clearer comparison of trends occurring in different volume ranges.

3 Results and discussion

Our measurements suggest that the average coccolith mass increases by $\sim 40\%$ over the last 220 years (Fig. 4 in Iglesias-Rodriguez and Halloran et al., 2008), and this shift is associated with a relative increase in the frequency of the large CaCO_3 particles ($>2 \mu\text{m}$ ESD) compared to the small CaCO_3 particles ($<2 \mu\text{m}$ ESD) (Fig. 1, Supplementary materials dataset, Table 1: <http://www.biogeosciences.net/5/1651/2008/bg-5-1651-2008-supplement.zip>). Given that the coccolith species composition is invariant over this interval (Fig. 3 in Iglesias-Rodriguez and Halloran et al., 2008), the trend towards larger CaCO_3 particles can be interpreted as an increase in the volume of coccoliths produced by a range of coccolithophore species. This increase in coccolith volume spans the observed volume range of coccoliths produced by the larger coccolithophore species present in the North Atlantic (Young and Ziveri, 2000). If the increase in average

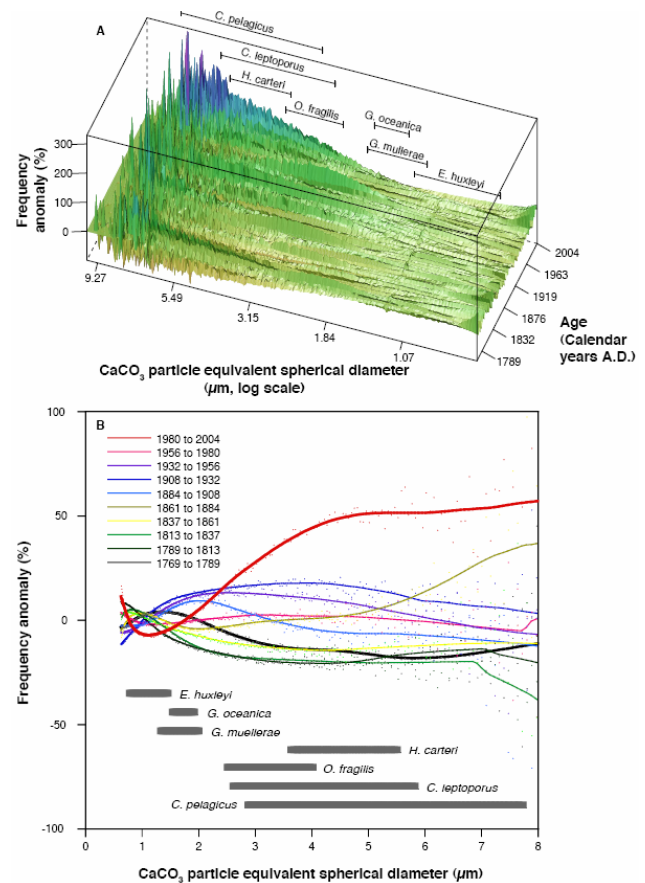


Fig. 1. (A) 3-D surface showing the percentage anomaly in frequency data (with respect to the average value for each volume-bin) for CaCO_3 particles (coccoliths) measured in samples from 1770 to 2004 A.D. Black bars above the main portion of the figure represent the equivalent spherical diameter size-ranges occupied by coccoliths of the major species present in these samples, calculated from Young and Ziveri (2000). (B) Curves representing the size-distribution of particles averaged over ~ 24 year (5.5 cm down core) intervals, presented as a percentage anomaly from the average frequency for each size-bin. Heavy red and black lines represent the most recent, and oldest, data respectively. Data has been fitted with a 15% least squares weighted mean. Data has been truncated at 8 μm because particle counts in bins larger than 8 μm are low, and therefore when ratios are formed data becomes noisy, detracting from the useful signal. Figure 2 presents the full dataset, negating this issue. Grey bars represent the typical range of coccolith-volume equivalent spherical diameters, calculated from Young and Ziveri (2000).

coccolith mass was driven by a change in calcification of a single species, the size-distribution data would show decreasing particle counts in the volume-region initially occupied by that species, coincident with an increasing CaCO_3 particle frequency in the larger volume-region. Comparison of the red and black lines in Fig. 1b (representing the size distribution over the last 12 years, and the pre-industrial to 1960

A.D. averaged signals respectively), shows that the coccolith mass increase occurs across a wide range of the species typically larger than $2\ \mu\text{m}$ ESD.

Our relative increase in the frequency of large particles is necessarily accompanied by a relative decrease in the frequency of small particles. In order to allow examination of the subtle changes occurring within the frequency of the abundant small particles, Fig. 2 presents the volume frequency anomalies in log space. The negative frequency anomaly between 1 to $4\ \mu\text{m}$ ESD, encompassing the upper and lower end member size ranges of the smaller and larger coccolithophores respectively, which develops towards the core-top suggest that coccoliths are moving away from this volume range. This reaffirms that the volume of the coccoliths produced by the larger coccolithophores (*O. fragilis*, *C. leptoporus*, *C. pelagicus* var. *pelagicus*, *H. carteri*) has increased. In addition, the recent relative increase in particle frequency below $1\ \mu\text{m}$ ESD suggests either that, coccoliths produced by the smaller coccolithophores (*E. huxleyi*), are becoming more lightly calcified, or that the decreasing pH of the modern ocean is promoting partial dissolution of these delicate coccoliths. This apparent recent divergence between the volumes of these two size-groups could reflect contrasting physiological controls and evolutionary adaptation.

4 Limitations and considerations

It is clear that indirect observations of the type presented here stimulate as many questions as they answer. However, in parallel with work that can explicitly quantify the coccolith volume changes within individual species, the described technique could provide a way to rapidly and accurately extrapolate calcification measurements across the global ocean, and build up an understanding of the spatial variation as well as the temporal variation in calcification change. It is these results which are urgently needed to allow validation of model output, and will provide confidence in the forward modelling of climate in the context of a calcification- CO_2 feedback. This said, at the present stage, our results are limited to a single core, at best representative of a single ocean basin. Assuming our interpretation of these indirect measurements is correct, and considering there to be a net coccolith mass increase at this site, there are still a number of reasons to exercise caution when exploring such results. The first of these is that due to the added complexities of the marine ecosystem and the slower mixing of the ocean than the atmosphere, when making inferences about the ocean carbonate system at a specific location, one cannot assume the response to reflect exactly that occurring in atmospheric $p\text{CO}_2$. Secondly, as with any sedimentary analysis, the provenience of the sediment, the diagenetic processes which have occurred upon that sediment, and bioturbation must be taken into account, and particular care should be taken when working with drift sediments. However, as a result of the extremely high sedimentation

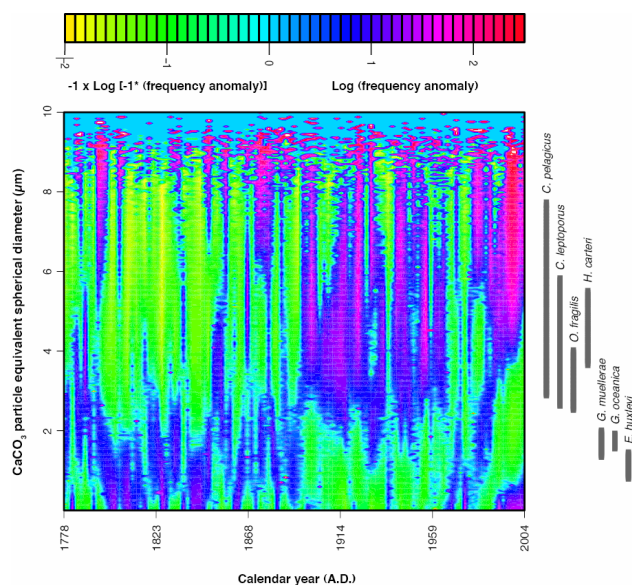


Fig. 2. Contour plot representing the evolution of the particle volume-distribution in log-space, to emphasize the subtle percentage change in the abundant small-volume particles. Colors represent log values of the percentage anomaly in frequency data (with respect to the average value for each size-bin) for CaCO_3 particles (coccoliths) measured in samples spanning 1770 to 2004. Note that negative anomalies are represented by -1 multiplied by the log of the modulus of the percentage frequency anomaly.

tation rates at drift sites, cores of this type may well provide the only opportunity to undertake high resolution sediment analysis in the open ocean over time intervals as short as the Anthropocene, and consequently robust techniques must be developed to work with this material. Despite highlighting these areas of concern, we are satisfied that our results represent a primary signal, because the obtained data shows no significant correlation with the sortable silt based near bottom flow speed record of Boessenkool et al. (2007), itself a record of the sediment sorting. Furthermore, the high rate of sedimentation experienced at this site should have prevented serious bioturbation. We are therefore persuaded that the particle-size trend we present here does not reflect changes in flow-mediating sediment sorting/deposition. Furthermore, we consider the invariance in the coccolith species composition presented in Iglesias-Rodriguez and Halloran et al. (2008) to indicate that no major change in source water has occurred over the interval of investigation.

5 Conclusions

In order to reduce the uncertainty associated with the calcification CO_2 feedback within Earth system models, we need to fully constrain and understand the inter-specific variability of coccolithophore calcification to conditions of ocean acidification. Our sedimentary data appear to indicate that

in the real ocean the larger coccolithophore species increase their calcification in response to anthropogenic CO₂ release. Such a calcification response could be attributed to an alleviation of CO₂ limitation in species that partly rely on the diffusive supply of dissolved carbon dioxide for photosynthesis, as demonstrated by a rise in photosynthetic efficiency with increasing carbon dioxide in cultures of *E. huxleyi* (Rost et al., 2003). Temperature, salinity and nutrient supply have also been shown to influence coccolith size, although where studied, the calcification sensitivity to these factors appears too low to explain the observed trend (Bollmann, 1997; Bollmann and Herrie, 2007; Paasche, 1998; Schmittner et al., 2008; Watabe and Wilbur, 1966). A further and potentially significant influence over coccolith mass is primary production (Beaufort et al., 2007). However, if the observed coccolith volume distribution shift occurred in response to a productivity change, we might expect to see an accompanying shift in species composition, which is not observed (Iglesias-Rodriguez and Halloran et al., 2008). If the change in coccolith size distribution presented here is representative of that elsewhere in the ocean, it may be possible to describe the coccolithophore calcification response to rising levels of atmospheric CO₂ at an assemblage level. Such a description could be incorporated into carbon-cycle models without the need to parameterize individual species, and therefore avoid uncertainty resulting from our poor understanding of the complex inter-species variability.

Although the additional complexity of the ocean system, in comparison with the laboratory environment, prevents us from drawing explicit parallels between the findings we present here and culture findings; it is still of value to discuss our results in the context of coccolithophore culture $\Delta p\text{CO}_2$ experiments. A considerable range of coccolithophore calcification responses have been observed experimentally, following manipulation of the culture medium carbonate system. These range from a decrease in calcification by *E. huxleyi* (Riebesell et al., 2000; Zondervan et al., 2001), through an apparently negligible change by *C. pelagicus* (Langer et al., 2006a) and *E. huxleyi* (Buitenhuis et al., 1999), an increase under elevated [DIC] and an increase followed by a decrease under reduced pH in *E. huxleyi* (Nimer and Merrett, 1993), an increase followed by a decrease in calcification by *Calcidiscus leptoporus* (Langer et al., 2006a), to an increased calcification by *E. huxleyi* (Iglesias-Rodriguez and Halloran et al., 2008), when simulating a high-CO₂ world. Working within the natural system, the coccoliths we have indirectly examined were produced under a relatively narrow range of $p\text{CO}_2$ conditions, increasing from ~280 to 380 ppm. Over this $p\text{CO}_2$ interval Riebesell et al. (2000) and Zondervan et al. (2001) observed a decreased calcification by *E. huxleyi*, Langer et al. (2006) observed an increase in calcification by *C. leptoporus* and arguably *C. pelagicus*, and Iglesias-Rodriguez and Halloran et al. (2008) show a decrease in lith size, but a negligible calcification response. The other studies show either negligible change, or present data unsuitable

for interpretation in this context. Given the contrasting nature of these and our results, we refrain from comparing the findings in detail, but do highlight the overall similarity in pattern, i.e. a general decrease in calcification by the smaller species, and an increase in calcification by the larger species over this interval. The value of our research in this context, is not to confirm one or the other of these culture studies, but to highlight the likelihood of observing different calcification responses within different coccolithophore species, and promoting a move away from the paradigm that all calcifiers will either decrease or increase their calcification as atmospheric CO₂ levels continue to rise.

The next step towards a full understanding of the coccolithophore calcification response over the industrialized era, will be to combine individual species size analysis, taking advantage of new techniques such as that presented by Beaufort (2000), with Coulter Counter analyses capable of measuring coccolith volumes, to constrain how calcification has changed at a species level. Experiments can then be designed and applied to new high-resolution cores, extending the observations we have made to a range of oceanic regimes.

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