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# A multi-species coccolith volume response to an anthropogenically-modified ocean

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## Abstract

Major questions surround the species-specific nature of coccolithophore calcification in response to rising atmospheric CO<sub>2</sub> levels. Here we present CaCO<sub>3</sub> particle volume distribution data from the coccolith size-fraction of a rapidly accumulating North Atlantic sediment core. These data appear to indicate that coccoliths produced by the larger coccolithophore species present at this location increase in mass in parallel with anthropogenic CO<sub>2</sub> release. This finding has significant implications for the realistic representation of an assemblage-wide coccolithophore CO<sub>2</sub>-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 (Henderiks and Rickaby, 2007). 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 and carbon concentration ability of different coccolithophores (Iglesias-Rodriguez and Halloran et al., 2008).

An increase in the average coccolith mass, independent of a change in species composition, has been demonstrated to parallel the rise in atmospheric  $p\text{CO}_2$  over the past ~220 years, by analysis of the <10  $\mu\text{m}$  sediment fraction from a Sub-polar North

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Atlantic core (RAPID 21-12-B, 57°27.09'N, 27°54.53'W, situated at 2630 m) (Iglesias-Rodriguez and Halloran et al., 2008). Here we present a size-distribution analysis of the RAPID 21-12-B <10  $\mu\text{m}$  size fraction, indicating that the increase in coccolith mass occurs across a broad range of coccolithophore species.

## 2 Methodology

Sediment core RAPID 21-12-B was sampled at 0.5 cm intervals. Approximately 2 to 4 g of the total sediment from each sample was suspended in buffered  $\text{H}_2\text{O}$  and passed through a 10  $\mu\text{m}$  pore-size track-etched polycarbonate filter membrane, using bubble agitation to prevent blocking. Three sub-samples were taken from the <10  $\mu\text{m}$  fraction, each suspended in 100 ml of electrolyte (ISOTON II), and the particle volume frequency distribution of each fraction, between 0.63 and 10  $\mu\text{m}$  equivalent spherical diameter (ESD), analysed three times using a Beckman Coulter Multisizer III Coulter Counter fitted with a 30  $\mu\text{m}$  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  $\mu\text{m}$  sizing window. After replicate analysis, 500  $\mu\text{l}$  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  $\text{CaCO}_3$  particles). In order to allow direct comparison of  $\text{CaCO}_3$  volume frequency distribution across the time-series, the average of the nine measured replicate  $\text{CaCO}_3$  particle counts in each of the 256 bins has been divided by the average of the nine measured replicate total  $\text{CaCO}_3$  particle counts in that sample. We consider these data to characterize the <10  $\mu\text{m}$  sedimentary  $\text{CaCO}_3$  particle distribution, representing the coccolith fraction, comprising *Emiliania huxleyi*, small *Gephyrocapsa*, *Gephyrocapsa oceanica*, *Gephyrocapsa muelleriae*, *Gephyrocapsa caribbeanica*, *Oolithotus fragilis*, *Calcidicus lept-*

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porus, *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

The average coccolith mass increases by ~40% over the last 220 years (Fig. 3 in Iglesias-Rodriguez and Halloran et al., 2008), and this shift is associated with a relative increase in the frequency of the large  $\text{CaCO}_3$  particles ( $>2\mu\text{m}$  ESD) compared to the small  $\text{CaCO}_3$  particles ( $<2\mu\text{m}$  ESD) (Fig. 1, Supplementary materials <http://www.biogeosciences-discuss.net/5/2923/2008/bgd-5-2923-2008-supplement.zip> dataset, and Supplementary materials Table 1). Given that the coccolith species composition is invariant over this interval (2005), the trend towards larger  $\text{CaCO}_3$  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 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  $\text{CaCO}_3$  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 AD 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

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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*, *G. oceanica*, *G. muelleriae*), 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 Conclusions

In order to reduce the uncertainty associated with the calcification  $\text{CO}_2$  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  $\text{CO}_2$  release. 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  $\text{CO}_2$  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.

The next step towards a full understanding of the coccolithophore calcification response over the industrialized era, will be to combine individual species size analysis,

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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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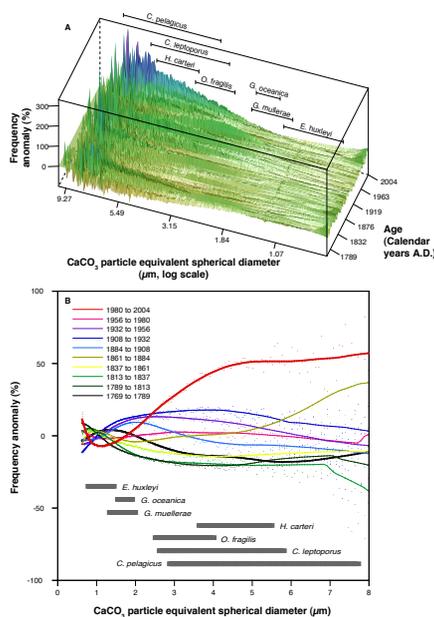
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**Fig. 1.** (a) 3-D surface showing the percentage anomaly in frequency data (with respect to the average value for each volume-bin) for  $\text{CaCO}_3$  particles (coccoliths) measured in samples from 1770 to 2004 AD. Black bars above the main portion 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  $8 \mu\text{m}$  because particle counts in bins larger than  $8 \mu\text{m}$  are low, and therefore when ratios are formed data becomes noisy, detracting from the useful signal. Figure 3 presents the full dataset, negating this issue. Grey bars represent the typical range of coccolith-volume equivalent spherical diameters, 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  $\text{CaCO}_3$  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.

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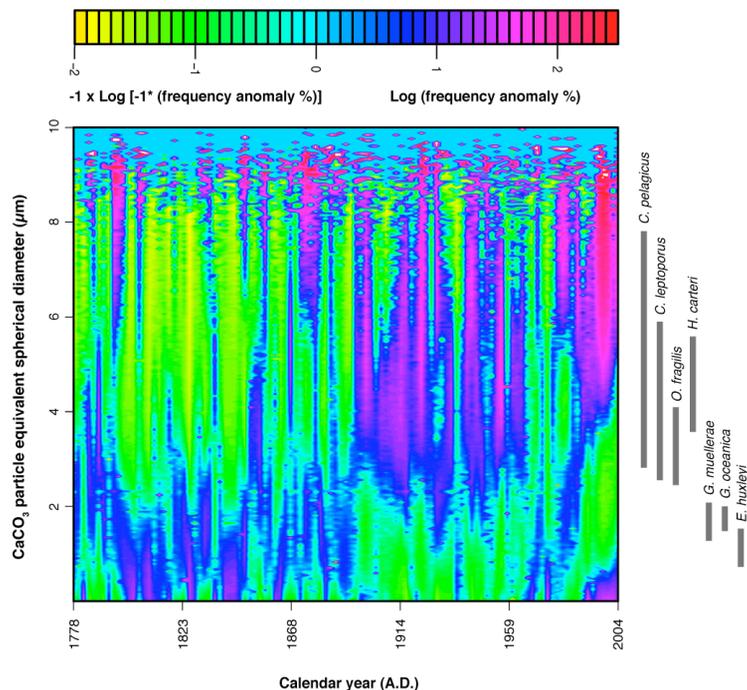
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**Fig. 2.** Contour plot representing the evolution of the particle volume-distribution in log-space, to emphasize the subtle percentage change in the abundant small-volume particles. Colors represent log values of the percentage anomaly in frequency data (with respect to the average value for each size-bin) for  $\text{CaCO}_3$  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

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