Available online at www.sciencedirect.com

ScienceDirect

EPSL

Earth and Planetary Science Letters 253 (2007) 83–95

www.elsevier.com/locate/epsl

# Coccolith chemistry reveals secular variations in the global ocean carbon cycle?

R.E.M. Rickaby [a,*], E. Bard [b], C. Sonzogni [b], F. Rostek [b], L. Beaufort [b], S. Barker [c], G. Rees [d], D.P. Schrag [e]

[a] *Department of Earth Sciences, Oxford University, Parks Road, Oxford OX1 3PR, UK*
[b] *Cerege, Europôle de l'Arbois BP 80, 13545 Aix en Provence Cedex 4, France*
[c] *School of Earth, Ocean and Planetary Sciences, Cardiff University, Main Building, Park Place 10 Cardiff, CF10 3YE, UK*
[d] *Scott Polar Research Institute, University of Cambridge, Lensfield Road, Cambridge CB2 1ER, UK*
[e] *Department of Earth and Planetary Sciences, Harvard University, 20, Oxford Street, Cambridge, MA-02138 USA*

Received 8 March 2006; received in revised form 14 September 2006; accepted 6 October 2006
Available online 15 November 2006
Editor: H. Elderfield

## Abstract

The mismatch between the 100 and 400 k.y. components of Pleistocene climate and the relative power of those terms from the eccentricity of the Earth's orbit remains a challenge to the Milankovitch hypothesis. Coccolithophores have the potential to respond to parameters of orbital forcing other than insolation, and, as a critical component of the ocean carbon cycle, can act to modify the climate response. The first direct comparison of coccolith fraction Sr/Ca, alkenone abundance and automated coccolithophore counts, shows that CF Sr/Ca is largely driven by changing production of bloom species, with unusually high Sr/Ca ratios. The periods of high CF Sr/Ca and high bloom production mark periods of high global coccolithophore production, which correlate inversely with the low amplitude 100 and higher amplitude 400 k.y. eccentricity orbital frequency. ~400 k.y. cycles of coccolithophore bloom production correspond to periods of enhanced carbonate accumulation in some parts of the ocean, deep ocean dissolution in others, positive shifts in global ocean $\delta^{13}C$, and acmes of *Gephyrocapsa caribbeanica* and *Emiliania huxleyi*. The link between production of coccolithophore blooms and eccentricity may be due to orbital control of silica leakage from the Southern Ocean, to the orbitally defined inverse correlation between insolation and growing season length and the asymptotic growth response to these parameters, or to changes in nutrient input from weathering. During the Pleistocene, the eccentricity induced coccolithophore acmes have no apparent influence on atmospheric carbon dioxide ($pCO_2$) due to the shift towards small bloom coccolithophores, or to coupling with increased diatom productivity, or the ballast effect of the calcium carbonate rain, such that Pleistocene climate has no significant variance at the largest amplitude eccentricity forcing of 400 k.y. Coccolithophores and their influence on the carbon cycle may act as a filter between the incident orbital forcing and resultant climate.

*Keywords:* Coccolithophore; Sr/Ca; Eccentricity; 400 k.y.; $pCO_2$; Productivity

## 1. Introduction

Coccolithophores are one of the most important pelagic calcifying organisms in the present ocean to

---

* Corresponding author. Tel.: +44 1865 272034; fax: +44 1865 272072.
*E-mail address:* rosr@earth.ox.ac.uk (R.E.M. Rickaby).

0012-821X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.epsl.2006.10.016

contribute to the organic carbon and carbonate pump of $pCO_2$ from the atmosphere into the deep ocean [1]. As a major primary producer in the ocean, coccolithophores are responsible for fixation and draw down of dissolved inorganic carbon into the deep ocean via the biological pump. Coccolithophores also calcify, and the production and export of calcium carbonate releases $CO_2$. The net influence of coccolithophores on $pCO_2$ therefore depends on the ballast of the plankton, i.e. the density of the particles defining the relative rate of export, and the particulate inorganic: organic carbon ratio (PIC/POC). The export of carbonate from the surface ocean is a more efficient transporter of organic carbon to the deep sea than diatom silica [2–4]. Changes in the production and accumulation of sedimentary carbonate can drive significant changes in $pCO_2$ (e.g. [5–7]), and coccolithophores potentially contribute up to 80% of this global carbonate fraction. In addition, coccolithophores produce dimethyl sulphide (DMS), an important compound in the formation of cloud condensation nuclei [8], and blooms of coccolithophores influence the scattering of light within the oceans [9]. Reconstruction of rates of production of coccolithophores is critical for understanding past climate change both in terms of the carbon cycle and physical climate forcing.

Calcium carbonate ($CaCO_3$) tests provide a wealth of geochemical signatures of the past ocean. Despite their abundance in ocean sediments, palaeoceanographic application of stable isotopes and trace metals in coccolithophores has been limited due to the challenges of identifying micron scale tests and species separation from the clay fraction. Species-specific disequilibrium effects on the stable isotopic composition of the coccoliths [10,11] lead to ambiguity in down-core records of coccolith stable isotopes [12–15]. Recently, our interest has again been piqued in coccolith proxies due to the development of novel ion exchange cleaning and separation procedures for clays [16,17] which allow Sr/Ca measurements to be made on the coccolith fraction of ocean sediments with >70% carbonate. The incorporation of strontium (Sr) into coccolith calcite is proposed as proportional to the growth rate of coccolithophores, when controlled by nitrogen limitation, based on culture experiments of a range of species [18,19] and field studies of sediments [16,20]. This growth rate dependence likely arises from trace metal discrimination during calcium transport to the calcification site in the intracellular calcifying vesicle of the coccolithophore [18]. It is thought that oceanic records of coccolith Sr/Ca may be used to reconstruct a history of coccolithophore productivity which is critical in defining past levels of atmospheric carbon dioxide ($pCO_2$).

Our intention in this study was to investigate changes in coccolith production on a glacial–interglacial timescale and ground-truth the application of coccolithophore Sr/Ca as a proxy for coccolithophore production rates by comparing a glacial–interglacial record of Sr/Ca with automated coccolithophore counts and alkenone accumulation in a core (MD962077) from the SW Indian Ocean. We find that the 100 k.y. changes in coccolithophore Sr/Ca are driven by changes in the production of bloom species and are dwarfed by the amplitude of a longer term and global secular cycle, which is coincident with global cycles in carbonate accumulation, dissolution and organic carbon export. The production of coccolithophore bloom species is maximal at times of low eccentricity. The link to eccentricity may be due to orbital control on silica leakage from the Southern Ocean, to the orbitally defined inverse correlation between insolation and growing season length and the asymptotic growth response to these parameters, or to changes in nutrient input from weathering. Nonetheless, this link between cycles in bloom coccolithophore production and eccentricity forcing may account for the absence of a high amplitude 400 k.y. cycle in the 100 k.y. eccentricity dominated ice core records of $CO_2$ and sea level.

## 2. Methods

1 Ma records of coccolithophore geochemistry were collected from MD962077 (Subtropical Indian Ocean), V28–239 (Equatorial Pacific Ocean), ODP 982 (high latitude North Atlantic); and ~300 k.y. records from MD972140 (western equatorial Pacific) and MD85668 (equatorial Indian Ocean) (Table 1 in the Appendix). Our intention was to obtain data from the multispecies coccolithophore fraction (CF), with minimal contamination from other carbonate components such as foram fragments. Semi-quantitative coccolithophore counts were performed using SYRACO [21], and alkenone abundances measured according to Sonzogni et al., [22] for MD85668, and with an automated method described by Pailler and Bard, [23] for cores MD962077 and MD972140. Precision and accuracy of the protocols were checked in the framework of the international alkenone comparison [24]. The methodology for Sr/Ca analysis was based on that of Stoll and Schrag [16]. All plasticware was acid cleaned before use, and DI water used throughout. 0.5 g of sediment was sieved using 90% proof ethanol through a <20 μm sieve. The collected slurry was poured into 15 ml centrifuge tubes and allowed to settle for 10 min. The supernatant containing the suspended particles was pipetted into a second tube

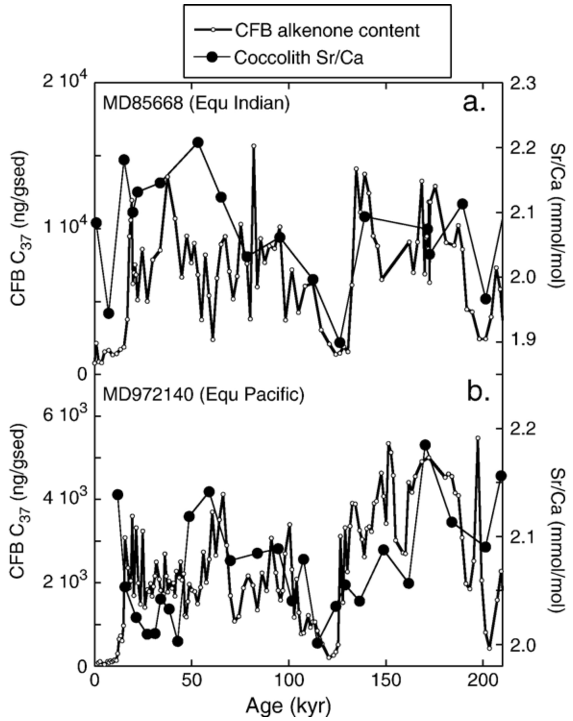

Fig. 1. Comparison of alkenone content (open circles), calculated on a carbonate free basis, and coccolithophore Sr/Ca (filled circles) for the last 210 k.y. from (a) MD85668 and (b) MD972140. This implies that CF Sr/Ca is a robust measure of coccolithophore production rate. Due to the linear sedimentation rates in this area, the alkenone content is a good indicator of alkenone flux to the sediments.

and allowed to settle for a further 24 h. The supernatant, considered to contain the major clay fraction, was pipetted away and filtered for recycling. The remaining $<10$ μm fraction was dried and a subsample taken and rinsed 3 times with to ensure elimination of any relict ethanol. A small fraction was weighed into boats for analysis by stable isotope mass-spectrometry. The remaining fraction of sediment for trace metal analysis was shaken for 3 h with a reducing reagent MNX (50 g

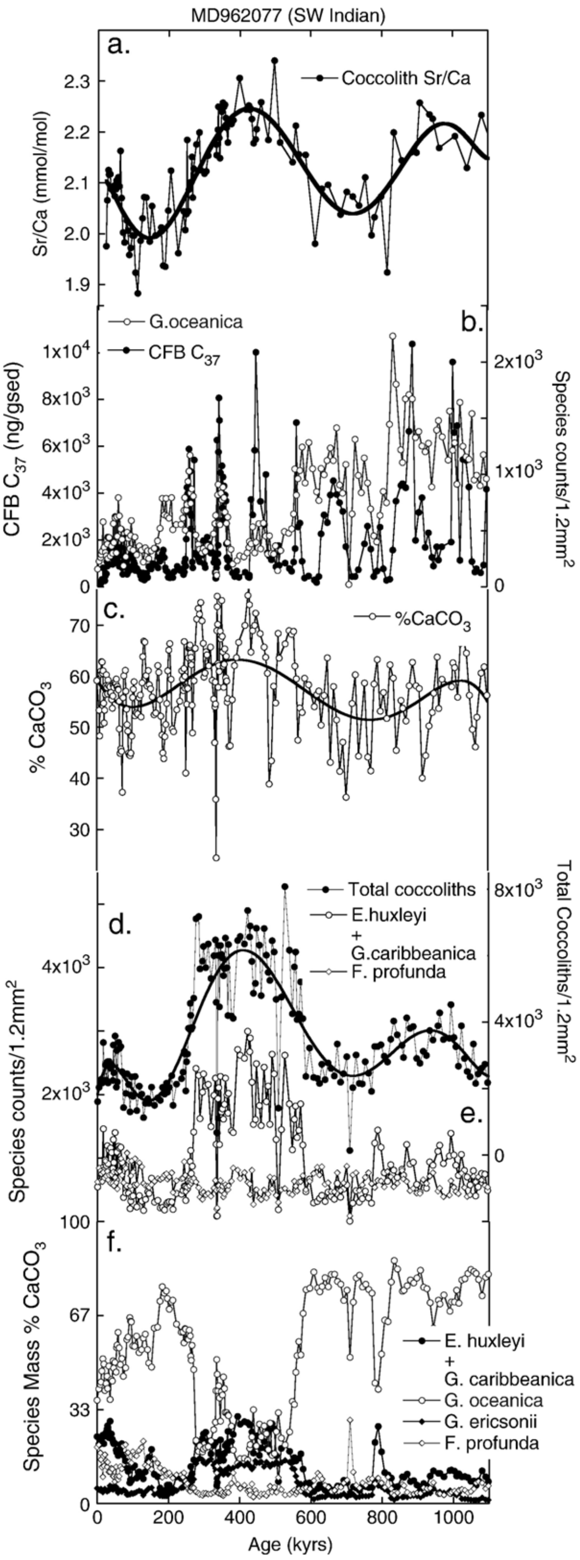

Fig. 2. Comparison of (a) CF Sr/Ca (large black circles), (b) alkenone content (black circles) and G. oceanica counts, (c) carbonate % (open circles), (d) total coccolith counts (black circles), (e) species composition derived from computerised counts of *G. caribbeanica* and *E. huxleyi (*open circles), and *F. profunda* (open diamonds), and (f) the mass % of carbonate contributed by each species calculated using masses from [45], for core MD962077 from the S. W. Indian Ocean. The units for the counts using SYRACO are based on a representation of counts of a number of fields of view of 1.2 mm$^2$ of a slide and should be viewed as qualitative. The alkenone content has been calculated on a carbonate free basis (CFB) to avoid bias by the record of %CaCO$_3$. The smoothed curves were plotted as a ninth order polynomial to highlight the secular changes.

$NH_2OH$-HCl, 400 ml concentration $NH_4OH$, 600 ml $H_20$) to break down manganese and iron oxides, and for a further 3 h with IONX (67.6 ml concentration $NH_4OH$ up to 1.0 l) to exchange any Sr and Ca ions present in the clays. The final step was a brief 30 s rinse to etch away any adsorbed metals. After dissolution in QD 2%$HNO_3$, samples were analysed by ICPAES [25] or Q-ICPMS [26] with precision better than 0.5%.

The chronology of the cores have been previously presented (MD85668 [27]; MD972140 [28]; ODP 982 [29]; V28–239 [30], and is based on correlation of $\delta^{18}$O for MD962077. Our sites are situated above the modern day lysocline and the good agreement between coccolith $\delta^{18}$O, foraminifera $\delta^{18}$O and alkenone derived SST from core MD962077 attests to the pristine geochemical signature preserved in the coccolithophores. However, fine fraction Sr/Ca is not influenced strongly by differing degrees of calcite undersaturation [31].

## 3. Results

### *3.1. CF Sr/Ca as proxy for coccolithophore production rate*

CF Sr/Ca shows a positive correlation with the abundance of alkenones for the last 210 k.y. (Fig. 1): high alkenone abundance and Sr/Ca during glacial periods, and the converse during interglacials. *E. huxleyi* and *Gephyrocapsa oceanica* are the only extant coccolithophorid species known to synthesise alkenones and so CF Sr/Ca appears to measure the production rates of either or both of these two species. On longer timescales, up to 1 Ma, the glacial–interglacial signal of CF Sr/Ca is dwarfed by a longer term, secular change (Fig. 2a). In MD962077, the change in Sr/Ca envelopes or modulates the high amplitude glacial–interglacial cycle in alkenone content (Fig. 2b) in the sediment, and parallels cycles in the total flux of coccolithophores (Fig. 2d) to the sediment and the secular trends in carbonate content of the sediment (Fig. 2c).

From our semi-quantitative automated coccolithophore counts, there is a glacial–interglacial variation in the production of *G. oceanica*, which correlates well with the down-core alkenone abundance, and reaffirms that *Gephyrocapsa* spp, rather than *E. huxleyi*, are largely responsible for the alkenone content of late Quaternary sediments (Fig. 2b, [32]). The glacial–interglacial variations of the alkenone abundance are tightly correlated to other paleoproductivity proxies measured in the same core (e.g. TOC, U content; Bard et al. in prep.). A similar glacial–interglacial variability in primary production was also proposed by Rosenthal et al. [33], based on a

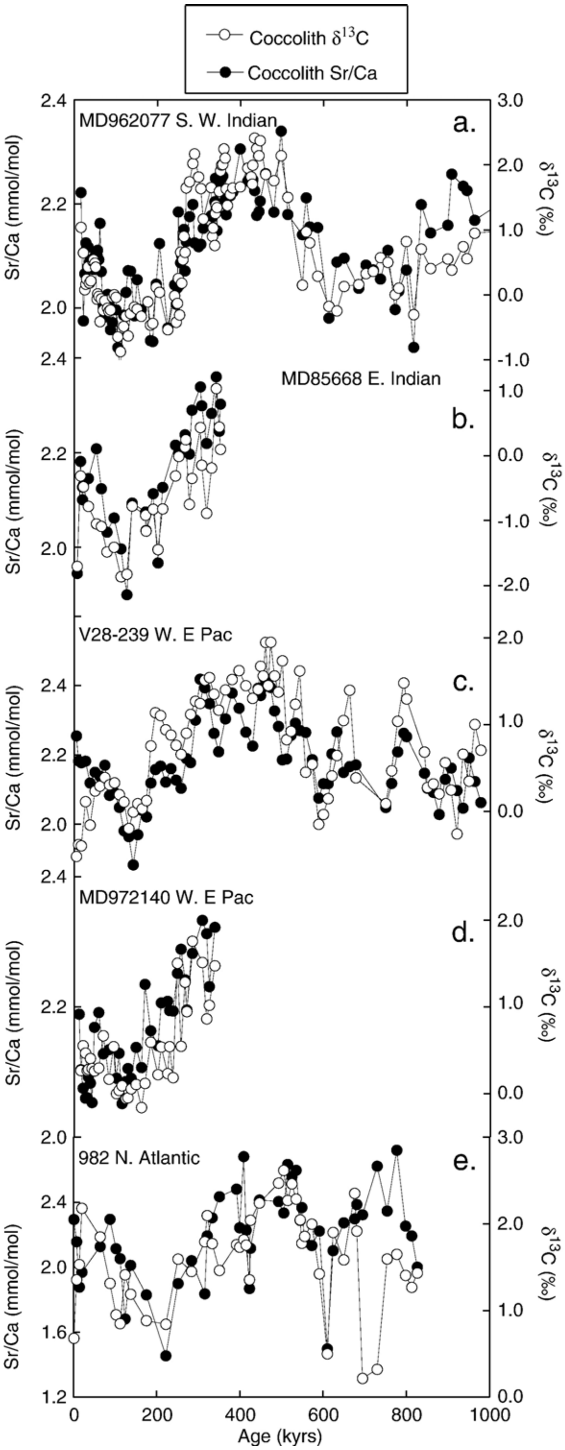

Fig. 3. $\delta^{13}$C (open circles) and Sr/Ca (closed circles) measured in the CF from global ocean cores: (a) MD962077 S. W. Indian Ocean, (b) MD 85668 Equatorial Indian Ocean, (c) V28–239, (d) MD972140 west Equatorial Pacific, (e) ODP 982 N. Atlantic.

shorter core from the same region. The large range of alkenone abundances may also partly be linked to enhanced preservation under less oxic sedimentary conditions associated with the higher primary production (e.g. [34]). Due to its relatively large mass, compared to the other coccolithophore species counted in the core, the enhanced production of *G. oceanica* may contribute to the higher glacial %$CaCO_3$ at this site. Whilst a full understanding of these glacial–interglacial cycles is beyond the scope of our study, which is focused on the much longer term changes, the production of *G. oceanica* appears instrumental in driving the sedimentary changes associated with inference of primary productivity.

By contrast, the CF Sr/Ca, and total coccolith counts do not reflect such large glacial–interglacial variations as the alkenones, and the production of *G. oceanica* has little impact on the CF Sr/Ca. Instead, our secular cycles in CF Sr/Ca parallel the rise to global dominance of rapidly growing coccolithophores (Fig. 2e, [35,36]). Small *Gephyrocapsa*, indicative of high rates of mixed layer productivity, display acmes between 1.25 Ma to 930 ka [37] ~500–260 ka [24] and their more recent relative *E. huxleyi* has been rising to dominance in the last 85 ka [38]. In most cases, these species are replaced by *Florisphaera profunda* in the interim, a lower thermocline dweller which prefers a stable upper water column [39], but *F. profunda* remains fairly constant throughout MD962077. Our CF Sr/Ca is high when *G. caribbeanica* or *E. huxleyi* dominate, and inferred primary production is high, whilst low Sr/Ca is associated with lower primary production. This long term trend in CF Sr/Ca is replicated in cores from a range of sites in the ocean indicating that it is a global signal (Fig. 3), but is likely too large to be explained by a global change in oceanic Sr/Ca [40].

The peak in CF Sr/Ca centred around 400 ka correlates with a zenith in the production of the species *G. caribbeanica*, reported for a number of sites around the world [35,38,41,42], and the recent rise in Sr/Ca

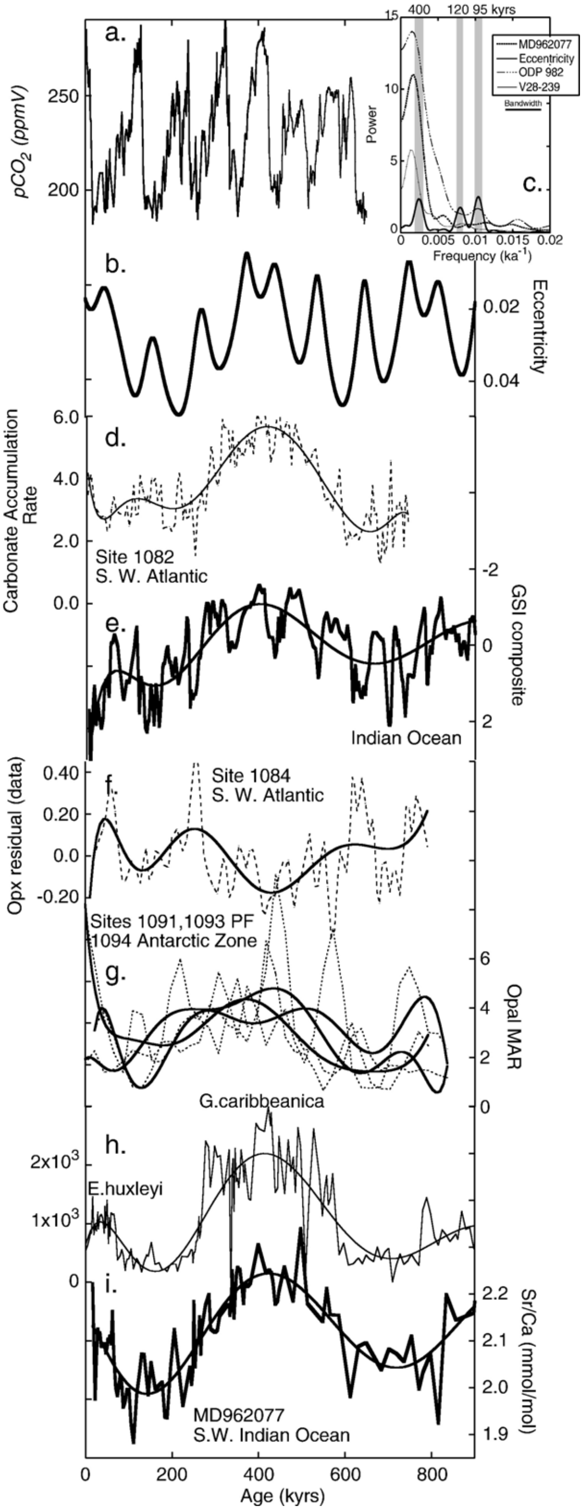

Fig. 4. Comparison of constraints on the carbon cycle, phytoplankton change and orbital variations over the last 900 k.y. (a) The ~650 k.y. record of $pCO_2$ from the EPICA ice core [59], (b) the eccentricity orbital parameter (note axis is reversed), (c) frequency spectrum of coccolithophore Sr/Ca from ODP 982, V28–239 and MD962077 compared to eccentricity, (d) an example of the global change in carbonate accumulation rate from Site 1082 S. W. Atlantic (data from [42]), (e) an example of the global cycle of carbonate dissolution using the GSI composite measure of dissolution intensity from [57], (f) an indicator of low latitude opal accumulation from Site 1084 (S. W. Atlantic, from [62]), (g) opal mass accumulation rates from Atlantic sites 1091, 1093 (polar front), and 1094 (Antarctic Zone) in the Southern Ocean (data from [86], (h) coccolithophore species counts performed using SYRACO. Associated with the increase in *G. caribbeanica*, there is also a threefold increase in the number of coccoliths/g. (i) a curve of Sr/Ca in the coccolith fraction from MD962077.

recorded in most of our records parallels a rise to dominance of *E. huxleyi*, a species capable of higher growth rates than those of other coccolithophore species [43]. It has been proposed that the modern bloom species, *E. huxleyi*, has a distinctly enriched Sr content because their liths comprise calcite crystals almost entirely with a radially oriented *c*-axis that incorporate relatively high amounts of the larger Sr cation [44], and that this characteristic crystal orientation may be exclusive to bloom species including *G. caribbeanica* and *G. ericsonii*. From a mass balance (Fig. 2f) using the extremes of the species-specific Sr/Ca [19] and the average masses [45], it is possible to attain the ~0.4 mmol/mol average amplitude of the CF Sr/Ca signal by the changing relative contributions of carbonate from bloom species to the sediments. Nonetheless, the extreme high Sr/Ca of the bloom species *E. huxleyi* used in this approach is attained at the highest growth rate so it is impossible to rule out increased coccolithophore production as well as changes in species associated with elevated CF Sr/Ca during these acme zones. Indeed, the zenith in production of *E. huxleyi*, and the small gephyrocapsids parallels a cycle in total coccoliths (Fig. 2d) and, from our mass calculations, a trebling of coccolithophore carbonate accumulation. The highest values of the peak in global CF Sr/Ca also coincides with the crest of a peak in long term %carbonate, centred around 400 k.y. (Fig. 2c) and recorded globally in carbonate accumulation ([42], e.g. Fig. 4d). The prevalence of these bloom species drives increased carbonate export and accumulation.

Our results imply that changing species composition is critical to interpretation of CF Sr/Ca. Nonetheless, the distinctive crystallography of bloom species, enriched in Sr, affords application of CF Sr/Ca as a measure of bloom species production which, on this 1 Ma timescale, is indicative of enhanced coccolithophore production and accumulation in the sediments.

## 4. Discussion

### 4.1. Secular changes in the global ocean carbon cycle

Over the last 1 Ma, the global ocean carbon cycle experiences a range of oscillations in concert with our inferred changes in global ocean coccolithophore production rates. Our secular trends in CF Sr/Ca are paralleled by similar long term, high amplitude oscillations in CF $\delta^{13}$C (Fig. 3). Although the amplitude of these $\delta^{13}$C trends is likely amplified by the changing abundances of bloom species [46], such trends in CF $\delta^{13}$C have also been noted from the Tasman Sea [47], and secular changes in $\delta^{13}$C also pervade planktonic and benthic foraminifera records from the Indian [48,49], Pacific Ocean [50,51], Caribbean Sea [52] and the South China Sea [36,53]. Near ~400 k.y. cycles in organic carbon burial are also inferred in the eastern Indian Ocean from the abundance of *Uvigerina proboscidea*, a benthic foraminifera which dominates areas with a continuous supply of organic matter [54]. The periods of increased bloom coccolithophore production may be accompanied by enhanced overall oceanic primary productivity and export of organic carbon. Alternatively, the shift towards more carbonate production and export from the surface ocean promotes the export of organic carbon to the deep sea either by a ballasting effect, or because of the bloom production [2–4]. We attribute this $\delta^{13}$C signature to a secular cycle in the whole ocean carbon reservoir. The peak in the production and burial ratio of organic carbon: inorganic calcite must reflect a change in this ratio by 1:1 [55] and could be caused by increased global primary productivity. Alternatively, a shift within or towards species, such as the blooming coccolithophores with a lower $CaCO_3/C_{org}$ ratio and extra ballast could drive the maximum of the positive $\delta^{13}$C signature centred around 400 k.y.

In addition, there is a wealth of evidence to suggest a secular cycle in global ocean carbonate accumulation both on the shelf [56] and in deep ocean basins. If steady state applies, and there is no change in weathering fluxes to the ocean, then such increases in carbonate accumulation in some areas of the ocean must be balanced by decreased accumulation elsewhere. Our enhanced coccolithophore production and accumulation may be balanced by the secular cycle in global ocean carbonate dissolution, which peaks as the globally recognised mid-Brunhes dissolution event (Fig. 4e; [57]; see Barker et al. [42] for a full discussion). Secular cycles in global coccolithophore production appear to force a domino-effect of ocean wide changes in organic matter burial via carbonate ballasting of the organic carbon export, which drives enhanced carbonate accumulation in some parts of the ocean and a globally recognised dissolution event.

A tantalising proposition is that this secular cycle in coccolithophore productivity may buffer the 100 k.y. eccentricity dominated record of atmospheric $pCO_2$ against the imposed and higher amplitude 400 k.y. eccentricity forcing (Fig. 4a, b; [42]). One of the remaining enigmas surrounding the Milankovitch theory of climate is that during the late Pleistocene, the eccentricity variations at periods near 100 k.y. are smaller than those at 413 k.y., yet there is no corresponding spectral peak near 400 k.y. in records of $\delta^{18}$O [58] or $pCO_2$ [59]. Periods of enhanced coccolithophore production should lead to increased efflux of oceanic $CO_2$ from the calcification process to the atmosphere. However, if the increased coccolithophore production is accompanied by increased carbon export, either via the ballast effect of an increased flux of carbonate, or an increase in global ocean productivity, then the enhanced efflux in $CO_2$ may be counterbalanced such that atmospheric $CO_2$ becomes insensitive to such large scale changes in coccolithophore production. But what drives such cycles in coccolithophore production?

### *4.2. Secular cyclicity of coccolithophore production*

The secular trend of our CF Sr/Ca parallels acmes of a single, coccolithophore species, capable of rapid growth rates, which emerges to dominate the sediments. Evolutionary adaptation is the likely process for the dominance of *Gephyrocapsa* during the mid-Brunhes, and the dominance of *E. huxleyi* in the modern ocean (Fig. 4h, [35,40]). We infer a long term cycle in the ocean environment with periodic optimal conditions for rapid coccolithophore growth. However, there is no single control on coccolithophore production, rather a range of hypotheses [60].

The secular nature of the cycles in coccolithophore production is a clue to possible chemical or physical forcing mechanisms. Changes in the ocean budget of short residence time nutrients, such as nitrate or phosphate, are unlikely to yield such long term trends. Aspects of ocean chemistry which could lead to secular oscillations include budget variations in carbon or calcium with residence times of 100 k.y. and 1 Ma respectively. Alternatively, the long response time of continental weathering and riverine input (80% of available Si input to ocean) may influence the whole ocean budget of silica [61] and the competitive success of coccolithophores [62]. A physical component of the climate system characterised by a long response time, are the polar ice sheets, which could influence coccolith production via sea level [63].

### *4.3. Eccentricity forcing?*

The omnipresent signature of near 400 k.y. cycles in Cenozoic records of the ocean carbon cycle point to our preferred hypothesis to account for secular Pleistocene coccolithophore production cycles, that is, as a response to the 400 k.y. frequency of orbital eccentricity. Near 400 k.y. cycles in the carbonate, and organic carbon content of sediments, and foraminiferal $\delta^{13}C$ pervade the geological record [64] to the Middle Cretaceous, and are perceived to be indicative of large variations in the productivity of planktonic ecosystems [65] The response of the oceanic carbon cycle to orbital frequencies, is a strong feature of the climate system [66]. Application of spectral analysis to our records of CF Sr/Ca [67] (Fig. 4c) resolves a small spectral peak at ~100 k.y., and a large peak at ~500 k.y. which we cannot resolve from that of the 400 k.y. eccentricity forcing within the bandwidth of our frequency resolution. We believe that coccolithophore production is intricately linked to orbital eccentricity forcing, as has previously been hypothesised [68]. Indeed, the ratio of the 400 k.y. to 100 k.y. amplitude of the eccentricity forcing cycle of ~2.5–3.0:1 is closely matched by the response of CF Sr/Ca. The long residence time of carbon in the ocean could act as an efficient buffer of shorter period forcing frequencies such as precession and may enable the longer term 400 k.y. and 100 k.y. frequencies to dominate the record ([69], Palike pers. comm.). Alternatively, an amplification in the response of phytoplankton to the long term amplitude modulating 100 and 400 k.y. eccentricity frequencies may result if the response is truncated at the low temperature end of the orbital forcing cycle [70].

Even though eccentricity forcing should be too weak to generate climate cycles or response of any significance, there seems to be a pervasive relationship between the ocean carbon cycle and eccentricity throughout the Cenozoic record. The linkage between eccentricity and productivity is manifested in the Pleistocene as cycles in the prevalence of bloom coccolithophorids across the latitudes and carbonate export. We cannot provide a conclusive mechanism, but we shall explore below three ideas to account for such an orbital linkage.

#### *4.3.1. Eccentricity control of coccolithophore blooms?*

We have developed a new idea to relate the production of blooming coccolithophores with eccentricity. Rather than considering orbital controls on insolation alone, we appeal to a recent proposal that the length of day, as well as light intensity, is critical in determining the growth rate of a blooming coccolithophore population [71]. We hypothesise that eccentricity influences phytoplankton growth rates through an interannual interplay between light intensity and length of growing season. Culture studies of phytoplankton demonstrate that phytoplankton growth rates respond to day length, and that day length is as important as light intensity [72]. *E. huxleyi*, and its close analogue *G. caribbeanica*, are cosmopolitan and primarily bloom forming species, and their distribution is relatively independent of water temperature and nutrients. Instead, there is a strong correlation between the most intense *E. huxleyi* blooms, daylight at the lower latitudes and the summer solstice at the high latitudes. So, how does eccentricity influence a combination of light intensity and the number of daylight hours or long summer days?

The number of daylight hours on a particular day over the last 800 k.y. displays a strong variance with obliquity [67]. However, the influence of eccentricity and the phase of precession of the orbit on Earth's mean radial velocity gives rise to substantial interannual and seasonal contrasts of daylight hours, exemplified by the dates of the solstices and autumnal equinoxes relative to a fixed vernal equinox [73], (Fig. 5). Earth moves faster near perihelion and slower near aphelion according to Kepler's second law of planetary motion. When perihelion reaches an equinox or solstice at the beginning of a season then that season and the prior season are equally short. In the same year the opposite two seasons are equally long, and vice versa in the opposite hemisphere. To consider the eccentricity and precession controls on growing season length, we hypothesise that coccolithophores bloom on days with >12 h of daylight (but alternative thresholds are equally valid), and we plot interannual daylight hours at 60°N for a precession cycle centred at 212 ka, which has a high amplitude due to large eccentricity (Fig. 5). A generality emerges that, due to the eccentricity of the Earth's orbit around the sun, and Kepler's second law, the longest growing season must occur when the earth is furthest from the sun (aphelion) with the least intense daily insolation, and the shortest growing season at perihelion with the most intense daily insolation. This inverse contrast in season length and insolation becomes more extreme as eccentricity increases [74].

*E. huxleyi*, and by analogy *G. caribbeanica*, are exceptional light-loving species. *E. huxleyi* shows no photoinhibition at high light intensity, and persists unusually in conditions of continuous light. The growth rate response curve of *E. huxleyi* to changes in photon flux density or insolation is asymptotic and levels off at a saturating light intensity (Fig. 5b; e.g. [75–77]) because *E. huxleyi* is able to protect the photosynthetic apparatus from excess energy [78]. Similarly, growth rate response to the light:dark cycle is likely asymptotic as maximal growth rates are observed for *E. huxleyi* at daylengths >16 h [79]. As a result of the orbitally defined inverse relationship between growing season length and insolation, the inverse combination of the two asymptotic growth rate response leads to maximal bloom formation at intermediate conditions of the most intense insolation for the longest growing season orbitally possible (Fig. 5b). We should emphasise

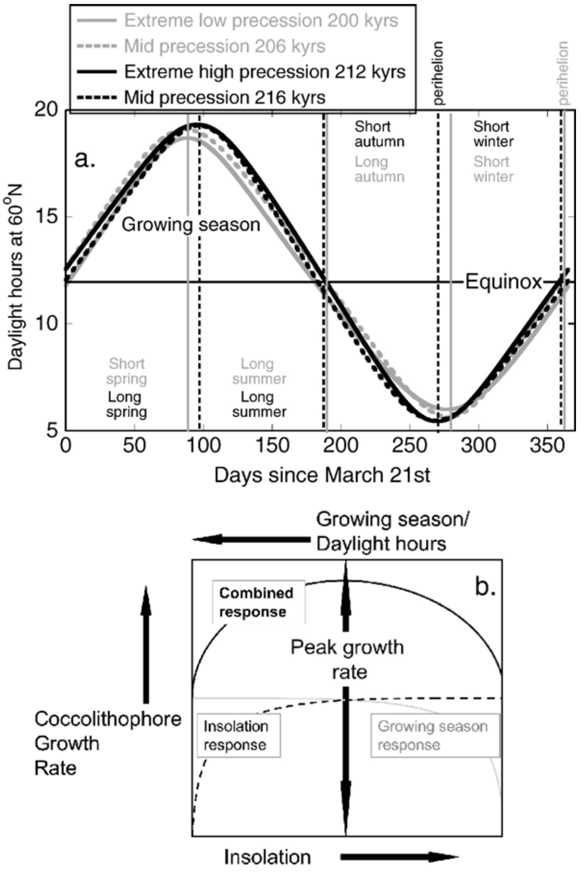

Fig. 5. (a) The effect of eccentricity and precession on number of daylight hours at 60°N demonstrated by the interannual evolution of daylight hours at an extreme low in precession 200 k.a. (continuous, grey); mid-precession cycle 206 k.a. (dashed, grey); extreme high in precession 212 k.a. (continuous, black); and mid precession cycle 216 k.a. (dashed, black). The amplitude of this precession cycle is due to the modulation by high eccentricity at this time. Perihelion is marked for 212 k.a. at the winter solstice (dashed black vertical line), and at the vernal equinox for 206 k.a. (continuous grey vertical line). The other vertical lines indicate the lengths of the different quartiles of the year and are labelled nominally: spring (vernal equinox to summer solstice), summer (summer solstice to autumnal equinox), autumn (autumnal equinox to winter solstice), and winter (winter solstice to vernal equinox) for 212 k.a. (dashed black vertical line) and 206 k.a. (continuous grey vertical line). The difference in season length processes: at 200 k.a., spring and summer are short and autumn and winter are long; at 206 k.a., winter and spring are short and summer and autumn are long (annotated in grey); at 212 k.a., spring and summer are long and winter and autumn are short (annotated in black); and at 216 k.a., spring and winter are long and summer and autumn are short. It emerges that due to the eccentricity of the Earth's orbit, the longest growing season must fall at aphelion and the shortest growing season at perihelion. (b) A schematic representation of the hypothesised combined response of coccolithophore growth rate (continuous black line) as a result of the asymptotic increasing growth rate with increasing insolation (dashed black line) and growth season (continuous grey line; as determined by number of days with >12 h daylight). Due to eccentricity of the orbit, insolation and growing season length are anticorrelated which results in a hypothesised maximum combined coccolithophore growth rate at intermediate conditions, best achieved by a low eccentricity orbit.

that this mechanism could be amplified should the phytoplankton response to day/season length or insolation have an optimum rather than an asymptote. We propose, therefore that the maximal coccolithophore blooms occur during periods of lowest eccentricity, as demonstrated by our records of coccolith Sr/Ca, alkenone flux and coccolithophore counts, where variations of Earth's mean radial velocity are minimal and the growing season is consistently half a year, independent of precession, and light intensity is maximised for that growing season.

This mechanism would predict a higher amplitude response at the high latitudes, as is in deed recorded in the higher amplitude CF Sr/Ca in our most northerly core. However, the caveat is that eccentricity at the equatorial latitudes only changes annual insolation and not the length of growing season, such that the blooming coccolithophores apparently prefer to bloom under consistent conditions of year-round insolation rather than the variable conditions of a highly eccentric orbit. It may be possible to account for this in terms of the specialist ecological niche of the blooming species with optimum high light conditions. Ecological modelling indicates that as the environmental cycle period increases and the conditions become more stable, the community will shift towards dominance by specialists and much enhanced biomass [80] such that opportunistic blooming coccolithophores can thrive under the more stable conditions of the low eccentricity ocean.

### *4.3.2. Winter nutrient supply or silica leakage?*

Another mechanism to account for the coccolithophore preference for symmetrical seasons is to consider the length of winter in the same hemisphere, or summer in the opposite hemisphere. Winter-mixing replenishes nutrients to surface waters for the spring bloom. At aphelion, with the longest growing season, the winter in the same hemisphere will occur at perihelion and is the shortest winter with most intense insolation, implying increased stratification of the winter water column. This could limit winter resupply of nutrients to surface waters, for the long summer ahead.

Alternatively, eccentricity could influence coccolithophore production via the "Si leakage hypothesis" [81–83] and the symmetry of seasons in the southern hemisphere driving efficient utilisation of silica. In low eccentricity conditions of the modern Southern Ocean, diatoms efficiently strip Si from the surface waters [84], and the world ocean thermocline is supplied with Si poor Subantarctic mode Water (SAMW), such that north of 30°S diatom production is low, and coccolithophores flourish. With high eccentricity, at aphelion (perihelion) in the northern hemisphere summer, the southern hemisphere experiences a long cold (short moderate) winter and a short warm (long cool) summer, conditions which may limit efficient utilisation of high southern latitude silica, hence flushing the global thermocline with Si-rich waters and limiting coccolithophore production. In support of such a mechanism, secular changes in low latitude coccolithophore production appear to be out of phase with low latitude diatom production, and in phase with high latitude diatom production over the last million years. Whilst we cannot extrapolate globally, there is a long term cycle of similar wavelength and anticorrelation with CF Sr/Ca in records of opal flux from Namibian upwelling ([62], Fig. 4f), and near monospecific diatom layers at 30°S in the Atlantic between 544 and 534 ka [85], which point to flourishing diatoms in the low latitudes when coccolithophores are impoverished. Southern Ocean opal accumulation rates cycle in phase with the oscillations in coccolithophore productivity ([86], Fig. 4g). Qualitative evidence supports a secular silica leakage hypothesis of an ocean which oscillates between 1) thriving low latitude coccolithophores and polar diatoms (recent and ~400 k.a.), a highly productive global ocean, versus 2) an ocean with blooming diatoms only at low latitudes and limited high latitude diatom production (600 and 200 k.a.). Because the control for the balance between diatom and coccolithophore productivity lies only in the high latitude Southern Ocean, the eccentricity control on the symmetry of seasons at these latitudes would yield a response in the blooming coccolithophores of similar magnitude at a range of latitudes. Further, this theory sits neatly with the modelling results of [42] because an intrinsic feature of increased coccolithophore production at low latitudes is increased high latitude production of diatoms which enhances carbon export, counterbalances the efflux of $CO_2$ from the increased calcification, and results in atmospheric $pCO_2$ being insensitive to such large changes in coccolithophore production, and the buffering of the anticipated 400 k.y. cycle in Vostok $pCO_2$. We propose that the coccolithophore preference for low eccentricity, symmetrical seasons, filters the orbital influence of 400 k.y. forcing from the climate response.

### *4.3.3. Weathering and the terrestrial biosphere?*

Although unlikely within the current bounds of observations of the carbon cycle, weathering proxies (Peucker-Ehrenbrink and Ravizza, 2000) and models (Hoogakker et al., 2006), the cycle of coccolithophore production over the last 1 Ma could be driven by a ~400 ka cycle in weathering supply. Marine isotope stages 6 and 16, the glacials which envelope the coccolithophore acme, appear to have extreme glacial conditions with maximal extent of the grounded ice shelf of the West Antarctic Ice Shelf [87] and build up of massive Eurasian ice sheets, inferred from IRD in the Arctic Ocean [88]. By contrast, marine isotope stages 15-11, which correlate with our maxima in coccolithophore production, are a prolonged period of near interglacial conditions on the continent at Lake Baikal [89]. This extended and stable climatic optimum on the continents has been associated with high terrestrial productivity, intense weathering and pedogenesis [90]. Since land plants greatly accelerate the weathering rates of silicate rocks by injecting $CO_2$ and organic acids via root respiration and exudation, this prolonged period of high terrestrial productivity could result in increased fluxes of both nutrients and alkalinity to the oceans and promote the 400 ka cycle in coccolithophore productivity. The terrestrial biosphere has been shown to resonate at orbital frequencies [91] and even displays a non-linear amplified response to eccentricity [92]. Whilst the non-linear relationship between terrestrial productivity and eccentricity is not understood, by analogy with the mechanism proposed for the coccolithophores, the symmetry of seasons at low eccentricity may be optimal for vegetation growth due to the balance between water supply during the winter and insolation for growth during the summer. The advantage of this proposed mechanism is that the eccentricity driven vegetation response would be largest at the high latitudes, but would yield a coccolithophore response which was ocean wide, as seen in our CF Sr/Ca records. Furthermore, eccentricity induced changes in the terrestrial carbon reservoir could help account for the global ocean trends in $\delta^{13}C$, and influence the possible longer term cycles in extent of the high latitude ice sheets [88,89] via albedo feed back [93]. Even though this mechanism appears to account for most of the observations, in order to account for all, the production and accumulation of blooming coccolithophores must still outweigh any increase in supply of alkalinity from weathering in order to explain the long term trend of the mid-Brunhes dissolution. The challenge for future research is to fully constrain the linkage between the terrestrial biosphere and Pleistocene weathering fluxes over the last 1 Ma.

## 5. Conclusions

CF Sr/Ca in the Pleistocene provides a robust measure of coccolithophore bloom production owing to the unusually high Sr/Ca values in bloom species. Over the last 1 Ma, CF Sr/Ca and bloom production correlates with periods of low eccentricity: the largest amplitude signal has a frequency of near 400 k.y. and records maximal CF Sr/Ca during periods of enhanced coccolith production, and carbonate accumulation associated with the global zenith of the bloom forming species *G. caribbeanica* (~550–250 k.a.) and the more recent rise to dominance of *E. huxleyi* (~150–0 k.a.). We argue that these secular cycles in bloom coccolithophore production, have no influence on atmospheric $CO_2$, either due to the ballast nature of the calcite rain, or by concurrent increased diatom production, or by the production of plentiful small coccolithophores with a low PIC/POC ratio changing the $CaCO_3$: $C_{org}$ in a 1:1 ratio all of which draw down the excess $CO_2$ produced by increased calcite precipitation into the deep ocean. The compelling mechanism to account for the secular coccolithophore production cycles links it with the ~400 k.y. eccentricity forcing. Such a mechanism may operate through eccentricity control on the silica leakage from the Southern Ocean, or changing input from weathering to the ocean both of which results in an oscillation to a productive ocean with blooming low latitude coccolithophores and high latitude diatoms and vice versa. Alternatively, an inverse relationship exists between growing season length and insolation, which becomes more extreme with increasing eccentricity. Coccolithophores may bloom optimally when the maximal season length is paired with the maximal insolation orbitally possible, which can only occur when eccentricity is minimal. This proposed link between orbital eccentricity and bloom coccolithophore production, with little influence on atmospheric $CO_2$ due to enhanced ballast or diatom export may explain the absence of a 400 k.y. cycle in atmospheric $CO_2$, and potentially in the Pleistocene climate system.

## Acknowledgements

We are grateful to Ethan Goddard and John Arden for assistance with the analyses, and especial thanks and happy memories to Nick Shackleton, and IODP for providing samples. Thanks also go to Wolf Berger and Giuseppe Cortese for supplying original datasets, to Heather Stoll and Timothy Herbert for insightful reviews, and the authors have benefited from discussion with Claus-Dieter Hillenbrand, Heiko Palike, Marie-France Loutre, and John Rickaby. We thank the EU for financial support of the STOPFEN network, and support from NERC grant: NER/B/S/2002/00393.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2006.10.016.

## References

[1] P. Westbroek, C.W. Brown, J. Vanbleijswijk, C. Brownlee, G.J. Brummer, M. Conte, J. Egge, E. Fernandez, R. Jordan, M. Knappertsbusch, J. Stefels, M. Veldhuis, P. Vanderwal, J. Young, A model system approach to biological climate forcing: the example of *Emiliania huxleyi*, Glob. Planet. Change 8 (1993) 27–46.

[2] R.A. Armstrong, C. Lee, J.I. Hedges, S. Honjo, S.G. Wakeham, A new, mechanistic model for organic carbon fluxes in the ocean based on the quantitative association of POC with ballast minerals, Deep-Sea Res., Part 2, Top. Stud. Oceanogr. 49 (2002) 219–236.

[3] R. Francois, S. Honjo, R. Krishfield, S. Manganini, Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean, Glob. Biogeochem. Cycles 16 (2002) (Art. No. 1087).

[4] C. Klaas, D. Archer, Association of sinking organic matter with various types of mineral ballast in the deep sea: implications for the rain ratio, Glob. Biogeochem. Cycles 16 (2002) (Art. No. 1116).

[5] D. Archer, E. Maier-Reimer, Effect of deep-sea sedimentary calcite preservation on atmospheric $CO_2$ concentration, Nature 367 (1994) 260–263.

[6] D.M. Sigman, D.C. McCorkle, W.R. Martin, The calcite lysocline as a constraint on glacial/interglacial low-latitude production changes, Glob. Biogeochem. Cycles 12 (1998) 409–427.

[7] D.M. Sigman, E. Boyle, Glacial/interglacial variations in atmospheric carbon dioxide, Nature 407 (2000) 859–869.

[8] G. Malin, M. Steinke, Dimethyl sulfide production: what is the contribution of the coccolithophores? in: H.R. Thierstein, J.R. Young (Eds.), Coccolithophores — From Molecular Processes to Global Impact, Springer, New York, 2004, pp. 127–164.

[9] T. Tyrrell, P.M. Holligan, C.D. Mobley, Optical impacts of oceanic coccolithophore blooms, J. Geophys. Res.-oceans 104 (C2) (1999) 3223–3241.

[10] W.C. Dudley, P. Blackwelder, L. Brand, J.C. Duplessy, Stable isotopic composition of coccoliths, Mar. Micropaleontol. 10 (1986) 1–8.

[11] C.K. Paull, W.M. Balch, Oxygen isotopic disequilibrium in coccolith carbonate from phytoplankton blooms, Deep-Sea Res., Part 1, Oceanogr. Res. Pap. 41 (1994) 223–228.

[12] D.E. Goodney, S.V. Margolis, W.C. Dudley, P. Kroopnick, D.F. Williams, Oxygen and carbon isotopes of recent calcareous nannofossils as paleoceanographic indicators, Mar. Micropaleontol. 5 (1980) 31–42.

[13] T.F. Anderson, J.C. Steinmetz, Isotopic and biostratigraphical records of calcareous nannofossils in a Pleistocene core, Nature 294 (1981) 741–744.

[14] C.K. Paull, H.R. Thierstein, Comparison of fine fraction with monospecific foraminiferal stable isotopic stratigraphies from pelagic carbonates across the last Glacial termination, Mar. Micropaleontol. 16 (1990) 207–217.

[15] W.C. Dudley, C.S. Nelson, Quaternary surface-water stable isotope signal from calcareous nannofossils at DSDP Site-593, Southern Tasman Sea, Mar. Micropaleontol. 13 (1989) 353–373.

[16] H. Stoll, D.P. Schrag, Coccolith Sr/Ca as a new indicator of coccolithophorid calcification and growth rate, Geochem. Geophys. Geosyst. 1 (5) (2000), doi:10.1029/1999GC000015.

[17] H.M. Stoll, P. Ziveri, Separation of monospecific and restricted coccolith assemblages from sediments using differential settling velocity, Mar. Micropaleontol. 46 (2002) 209–221.

[18] R.E.M. Rickaby, D.P. Schrag, U. Riebesell, I. Zondervan, Growth-rate dependence of Sr incorporation during calcification of *Emiliania huxleyi*, Glob. Biogeochem. Cycles 16 (2002) (2001GB001408).

[19] H.M. Stoll, P. Ziveri, M. Geisen, I. Probert, J.R. Young, Potential and limitations of Sr/Ca ratios in coccolith carbonate: new perspectives from cultures and monospecific samples from sediments, Philos. Trans. R. Soc. Lond. 360(A) (2002) 719–747.

[20] K. Billups, R.E.M. Rickaby, D.P. Schrag, Cenozoic pelagic Sr/Ca records: exploring a link to paleoproductivity, Paleoceanography 19 (2004) (art. no. PA3005).

[21] L. Beaufort, D. Dollfus, Automatic recognition of coccoliths by dynamical neural networks, Mar. Micropaleontol. 51 (2004) 57–73.

[22] C. Sonzogni, E. Bard, F. Rostek, R. Lafont, A. Rosell-Melé, G. Eglinton, Core-top calibration of the alkenone index versus sea surface temperature in the Indian Ocean, Deep-Sea Res. II 44 (1997) 1445–1460.

[23] D. Pailler, E. Bard, High frequency palaeoceanographic changes during the past 140 000 yr recorded by the organic matter in sediments of the Iberian Margin, Palaeogeogr. Palaeoclimatol. Palaeoecol. 181 (2002) 431–452.

[24] A. Rosell-Melé, et al., Precision of the current methods to measure the alkenone proxy UK37′ and absolute abundance in sediments: results of an interlaboratory comparison study, Geochem. Geophys. Geosyst. (G-cubed) 2 (2001) 1–28 (2000GC000141).

[25] D.P. Schrag, Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates, Paleoceanography 14 (1999) 97–102.

[26] D.J. Harding, J. Arden, R.E.M. Rickaby, in press, Precise Analysis of Trace Element/Calcium Ratios in Carbonates Samples Using Quadrupole Inductively Coupled Plasma Mass Spectrometry, Geochem. Geophys. Geosyst. 7 (2006) Q06003, doi:10.1029/2005GC001093.

[27] E. Bard, F. Rostek, C. Sonzogni, Interhemispheric synchrony of the last deglaciation inferred from alkenone palaeothermometry, Nature 385 (1997) 707–710.

[28] T. deGaridel-Thoron, Y. Rosenthal, F. Bassinot, L. Beaufort, Stable sea surface temperatures in the western Pacific warm pool over the past 1.75 million years, Nature 433 (2005) 294–298.

[29] M.E. Raymo, D.W. Oppo, B.P. Flower, D.A. Hodell, J.F. McManus, K.A. Venz, K.F. Kleiven, K. McIntyre, Stability of North Atlantic water masses in face of pronounced climate variability during the Pleistocene, Paleoceanography 19 (2004) (art. no. PA2008).

[30] N. Shackleton, N. Opdyke, Oxygen isotope and paleomagnetic stratigraphy of Pacific core V28–239 Late Pliocene to Latest Pliocene, in: R. Cline, J. Hays (Eds.), Investigations of Late Quaternary Paleoceanography and Paleoclimatology, Geol. Soc. Am. Mem., vol. 145, 1976, pp. 449–464.

[31] G.H. Andreasen, M.L. Delaney, Bulk calcite size fraction distribution and Sr/Ca composition for deep-sea sediments at selected age horizons, Mar. Geol. 169 (2000) 185–205.

[32] P.J. Müller, M. Cepek, G. Ruhland, R.R. Schneider, Alkenone and coccolithophorid species changes in Late Quaternary sediments from the Walvis Ridge: implications for the alkenone

paleotemperature method, Palaeogeogr. Palaeoclimatol. Palaeoecol. 135 (1997) 71–96.

[33] Y. Rosenthal, E.A. Boyle, L. Labeyrie, D. Oppo, Glacial enrichments of authigenic Cd and U in Subantarctic sediments: a climatic control on the elements' organic budget? Paleoceanography 10 (1995) 395–413.

[34] A. Schulte, E. Bard, Past changes in biologically mediated dissolution of calcite above the lysocline recorded in Indian Ocean sediments, Quat. Sci. Rev. 22 (2003) 1757–1770.

[35] J. Bollmann, K.H. Baumann, H.R. Thierstein, Global dominance of Gephyrocapsa coccoliths in the late Pleistocene: selective dissolution, evolution, or global environmental change? Paleoceanography 13 (1998) 517–529.

[36] P.X. Wang, J. Tian, X.R. Cheng, C.L. Liu, J. Xu, Carbon reservoir changes preceded major ice-sheet expansion at the mid-Brunhes event, Geology 31 (2003) 239–242.

[37] S. Gartner, Paleoceanography of the mid-Pleistocene, Mar. Micropaleontol. 13 (1988) 23–46.

[38] H.R. Thierstein, K. Geitzenauer, B. Molfion, N.J. Shackleton, Global synchronicity of late Quaternary datum levels: validation by oxygen isotopes, Geology 5 (1977) 400–404.

[39] B. Molfino, A. McIntyre, Precessional forcing of nutricline dynamics in the Equatorial Atlantic, Science 249 (1990) 766–769.

[40] H.M. Stoll, D.P. Schrag, S.C. Clemens, Are seawater Sr/Ca variations preserved in Quaternary foraminifera? Geochim. Cosmochim. Acta 63 (1999) 3535–3547.

[41] K.-H. Baumann, T. Freitag, Pleistocene fluctuations in the northern Benguela Current system as revealed by coccolith assemblages, Mar. Micropaleontol. 52 (2004) 195–215.

[42] S. Barker, R.E.M. Rickaby, D. Archer, H. Elderfield, L. Booth, J. Henderiks, Globally increased pelagic carbonate production during the Mid-Brunhes Dissolution Interval and the $CO_2$ paradox of MIS 11. Quat. Sci. Rev. (submitted for publication), doi:10.1016/j.quascirev.2006.07.018.

[43] L.E. Brand, Physiological ecology of marine coccolithophores, in: A. Winter, W. Siesser (Eds.), Coccolithophores, Cambridge University Press, Cambridge, 1994, pp. 39–49.

[44] R.E.M. Rickaby, H.M. Stoll, J. Henderiks, S. Shaw, H. Elderfield, Blooming Coccolithophores, Goldschmidt Abstract, 2006.

[45] J.R. Young, P. Ziveri, Calculation of coccolith volume and its use in calibration of carbonate flux estimates, Deep-Sea Res., Part 2, Top. Stud. Oceanogr. 47 (2000) 1679–1700.

[46] P. Ziveri, H. Stoll, I. Probert, C. Klass, M. Geisen, G. Ganssen, J. Young, Stable isotope 'vital effects in coccolith calcite, Earth Planet. Sci. Lett. 210 (2003) 137–149.

[47] W.C. Dudley, C.S. Nelson, The influence of nonequilibrium isotope fractionation on the Quaternary calcareous nannofossil stable-isotope signal in the Southwest Pacific-Ocean, DSDP Site-594, Mar. Micropaleontol. 24 (1994) 3–27.

[48] J. Chen, J.W. Farrell, D.W. Murray, W.L. Prell, Timescale and paleoceanographic implications of a 3.6 M.y. oxygen isotope record from the northeast Indian Ocean (Ocean Drilling Program Site 758), Paleoceanography 10 (1995) 21–47.

[49] J.W. Farrell, T.R. Janecek, Late Neogene paleoceanography and paleoclimatology of the northeast Indian Ocean (Site 758), in: J. Weissel, J. Peirce, E. Taylor, J. Alt, et al., (Eds.), Proc. ODP, Sci. Results, vol. 121, Ocean Drilling Program, College Station, TX, 1991, pp. 297–355.

[50] H. Schmidt, W.H. Berger, T. Bickert, G. Wefer, 1993. Quatenary carbon isotope record of pelagic foraminifers: Site 806, Ontong Java Plateau, in Proceedings of the Ocean Drilling Program, Scientific Results, vol. 130, edited by W.H. Berger, L.W. Kroenke, L.A. Mayer, pp. 397–410, Ocean Drilling Program, Texas A and M University, College Station, TX.

[51] A.C. Mix, N.G. Pisias, W. Rugh, J. Wilson, A. Morey, T.K. Hagelberg, Benthic foraminifer stable isotope record from Site 849 (0–5 Ma): local and global climate changes, Proc. Ocean Drill. Program Sci. Results 138 (1995) 371–412.

[52] D.W. Oppo, M.E. Raymo, G.P. Lohmann, A.C. Mix, J.D. Wright, W.L. Prell, A Delta-C-13 record of upper North-Atlantic deep-water during the past 2.6-million years, Paleoceanography 10 (1995) 373–394.

[53] P. Wang, J. Tian, X. Cheng, C. Liu, J. Xiu, Major Pleistocene stages in a carbon perspective: the South China Sea record and its global comparison, Paleoceanography 19 (2004), doi:10.1029/2003PA000991 (Art no: PA4005).

[54] A.K. Gupta, H. Dhingra, J.-L. Melice, D.M. Anderson, Earth's eccentricity cycles and Indian summer monsoon variability over the past 2 million years: evidence from deep-sea benthic foraminifera, Geophys. Res. Lett. 28 (2001) 4131–4134.

[55] B.A.A. Hoogakker, E.J. Rohling, M.R. Palmer, T. Tyrrell, R.G. Rothwell, Underlying causes for long-term global ocean d13C fluctuations over the last 1.20 Myr, Earth Planet. Sci. Lett. 248 (2006) 1–15.

[56] A.W. Droxler, G.A. Haddad, D.A. Mucciarone, J.L. Cullen, Pliocene–Pleistocene aragonite cyclic variations in holes 714A and 716B (The Maldives) compared with hole 633A (The Bahamas): records of climate-induced CaCO3 preservation at intermediate depths, Proc. Ocean Drill. Program Sci. Results 115 (1990) 539–567.

[57] F.C. Bassinot, L. Beaufort, E. Vincent, L.D. Labeyrie, F. Rostek, P.J. Muller, X. Quidelleur, Y. Lancelot, Coarse fraction fluctuations in pelagic carbonate sediments from the tropical Indian-Ocean — a 1500-K.y. Record of carbonate dissolution, Paleoceanography 9 (1994) 579–600.

[58] J. Imbrie, A. Berger, E.A. Boyle, et al., On the structure and origin of major glaciation cycles. 2. the 100,000-year cycle, Paleoceanography 8 (1993) 699–735.

[59] U. Siegenthaler, T.F. Stocker, E. Monnin, D. Luthi, J. Schwander, B. Stauffer, D. Raynaud, J.M. Barnola, H. Fischer, V. Masson-Delmotte, J. Jouzel, Stable carbon cycle–climate relationship during the late Pleistocene, Science 310 (2005) 1313–1317.

[60] J.R. Young, http://www.nhm.ac.uk/hosted_sites/ina/CODENET/ 2002.

[61] P. Treguer, D.M. Nelson, A.J. Vanbennekom, D.J. Demaster, A. Leynaert, B. Queguiner, The silica balance in the world ocean — a reestimate, Science 268 (1995) 375–379.

[62] W.H. Berger, C.B. Lange, M.E. Perez, The early Matuyama Diatom Maximum off SW Africa: a conceptual model, Mar. Geol. 180 (2002) 105–116.

[63] P.G. Falkowski, O. Schofield, M.E. Katz, B. Van De Schootbrugge, A.K. Knoll, Why is the land green and the ocean red? in: H.R. Thierstein, J.R. Young (Eds.), Coccolithophores — From Molecular Processes to Global Impact, Springer, New York, 2004, pp. 429–453.

[64] F. Woodruff, S.M. Savin, Mid-Miocene isotope stratigraphy in the deep- sea: high-resolution correlations, paleoclimatic cycles, and sediment preservation, Paleoceanography 6 (1991) 755–806.

[65] T.D. Herbert, A long marine history of carbon cycle modulation by orbital–climatic changes, Proc. Natl. Acad. Sci. U. S. A. 94 (1997) 8362.

[66] J.C. Zachos, N.J. Shackleton, J.S. Revenaugh, H. Palike, B.P. Flower, Climate response to orbital forcing across the Oligocene–Miocene boundary, Science 292 (2001) 274–278.

[67] D. Paillard, L. Labeyrie, P. Yiou, Macintosh Program Performs Time-Series Analysis, www.agu.org/eos_elec© 1996 American Geophysical Union. EOS 77, 379.

[68] L. Beaufort, Y. Lancelot, P. Camberlin, O. Cayre, E. Vincent, F. Bassinot, L. Labeyrie, Insolation cycles as a major control on equatorial Indian Ocean primary production, Science 278 (1997) 1451–1454.

[69] N.J. Shackleton, The 100,000-year ice-age cycle identified and found to lag temperature, carbon dioxide, and orbital eccentricity, Science 289 (2000) 1897–1902.

[70] D.A. Short, J.G. Mengel, T.J. Crowley, W.T. Hyde, G.R. North, Filtering of Milankovitch cycles by Earths geography, Quat. Res. 35 (1991) 157–173.

[71] W.M. Balch, Re-evaluation of the physiological ecology of coccolithophores, in: H.R. Thierstein, J.R. Young (Eds.), Coccolithophores — From Molecular Processes to Global Impact, Springer, New York, 2004, pp. 165–190.

[72] L.E. Brand, R.E. Guillard, The effects of continuous light and light intensity on the reproduction rates of twenty-two species of marine phytoplankton, J. Exp. Mar. Biol. Ecol. 50 (1981) 119–132.

[73] P. Huybers, C. Wunsch, Rectification and precession signals in the climate system, Geophys. Res. Lett. 30 (19) (2003) (Art. No. 2011).

[74] P. Huybers, Early Pleistocene glacial cycles and the integrated summer insolation forcing, Science 313 (2006) 508–511.

[75] M.V. Nielsen, Photosynthetic characteristics of the coccolithophorid Emiliania huxleyi (Prymnesiophy-ceae) exposed to elevated concentrations of dissolved inorganic carbon, J. Phycol. 31 (1995) 715–719.

[76] I. Zondervan, B. Rost, U. Riebesell, Effect of $CO_2$ concentration on the PIC/POC ratio in the coccolithophore *Emiliania huxleyi* grown under light-limiting conditions and different daylengths, J. Exp. Mar. Biol. Ecol. 272 (2002) 55–70.

[77] B. Rost, U. Riebesell, Coccolithophores and the biological pump: responses to environmental changes, in: H.R. Thierstein, J.R. Young (Eds.), Coccolithophores — From Molecular Processes to Global Impact, Springer, New York, 2004, pp. 76–99.

[78] G.N. Harris, D.J. Scanlan, R.J. Geider, Acclimation of *Emiliania huxleyi* (Prymnesiophyceae) to photon flux density, J. Phycol. 41 (2005) 851–862.

[79] E. Paasche, Marine plankton algae grown with light-dark cycles. I. *Coccolithus huxleyi*, Physiol. Plant 20 (1967) 946–956.

[80] C.E. Richmond, D.L. Breitburg, K.A. Rose, The role of environmental generalist species in ecosystem function, Ecol. Model. 188 (2005) 279–295.

[81] M.A. Brzezinski, C.J. Pride, V.M. Franck, D.M. Sigman, J.L. Sarmiento, K. Matsumoto, N. Gruber, G.H. Rau, K.H. Coale, A switch from Si(OH)(4) to $NO_3$-depletion in the glacial Southern Ocean, Geophys. Res. Lett. 29 (2002) (Art. No. 1564).

[82] K. Matsumoto, J.L. Sarmiento, M.A. Brzezinski, Silicic acid leakage from the Southern Ocean: a possible explanation for glacial atmospheric $pCO(_2)$, Glob. Biogeochem. Cycles 16 (2002) (Art. No. 1031).

[83] J.L. Sarmiento, N. Gruber, M.A. Brzezinski, J.P. Dunne, High-latitude controls of thermocline nutrients and low latitude biological productivity, Nature 427 (2004) 56–60.

[84] O. Ragueneau, P. Treguer, A. Leynaert, R.F. Anderson, M.A. Brzezinski, D.J. DeMaste, R.C. Dugdale, J. Dymond, G. Fischer, R. Francois, C. Heinze, E. Maier-Reimer, V. Martin-Jezequel, D.M. Nelson, B. Queguiner, A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy, Glob. Planet. Change 26 (2000) 317–365.

[85] F.X. Gingele, F. Schmieder, Anomalous South Atlantic lithologies confirm global scale of unusual mid-Pleistocene climate excursion, Earth Planet. Sci. Lett. 186 (2001) 93–101.

[86] G. Cortese, R. Gersonde, C.D. Hillenbrand, G. Kuhn, Opal sedimentation shifts in the World Ocean over the last 15 Myr, Earth Planet. Sci. Lett. 224 (2004) 509–527.

[87] C.D. Hillenbrand, D.K. Futterer, H. Grobe, T. Frederichs, No evidence for a Pleistocene collapse of the West Antarctic Ice Sheet from continental margin sediments recovered in the Amundsen Sea, Geo Mar. Lett. 22 (2002) 51–59.

[88] R.F. Spielhagen, et al., Arctic Ocean evidence for late Quaternary initiation of northern Eurasian ice sheets, Geology 25 (1997) 783–786.

[89] A.A. Prokopenko, D.F. Williams, M.I. Kuzmin, E.B. Karabanov, G.K. Khursevich, J.A. Peck, Muted climate variations in continental Siberia during the mid-Pleistocene epoch, Nature 418 (Jul 4 2002) 65–68.

[90] G. Kukla, V. Cilek, Plio-pleistocene megacycles: record of climate and tectonics, Palaeogeogr. Palaeoclimatol. Palaeoecol. 120 (1996) 171–194.

[91] M. Lyle, L. Heusser, T. Herbert, A. Mix, J. Barron, Interglacial theme and variations: 500 k.y. of orbital forcing and associated responses from the terrestrial and marine biosphere, U.S. Pacific Northwest, Geology 29 (2001) 1115–1118.

[92] K.J. Willis, A. Kleczkowski, S.J. Crowhurst, 124,000-year periodicity in terrestrial vegetation change during the late Pliocene epoch, Nature 397 (1999) 685–688.

[93] R.G. Gallimore, J.E. Kutzbach, Role of orbitally induced changes in tundra area in the onset of glaciation, Nature 381 (1996) 503–505.