

Paläontologische Zeitschrift
2005, Vol. **79/1**, p. 93–112, 31–03–2005

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58

The significance of extant coccolithophores as indicators of ocean water masses, surface water temperature, and paleoproductivity: a review

KARL-HEINZ BAUMANN, Bremen; HARALD ANDRULEIT, Hannover; BABETTE BÖCKEL, Bremen;
MARKUS GEISEN, Bremerhaven & HANNO KINKEL, Kiel

with 13 figures

BAUMANN, K.-H.; ANDRULEIT, H.; BÖCKEL, B.; GEISEN, M. & KINKEL, H. 2005. The significance of extant coccolithophores as indicators of ocean water masses, surface water temperature, and paleoproductivity: a review. – *Paläontologische Zeitschrift* **79** (1): 93–112, 13 figs., Stuttgart, 31. 3. 2005.

Abstract: Coccolithophores are one of the main groups of marine phytoplankton playing key roles in the marine ecosystem as primary producers and in marine biogeochemistry. These organisms have gained considerable attention as they play a unique role in the global carbon cycle because of their combined effects on both the organic carbon and the carbonate pump. Although steady advances in research on coccoliths as biogeochemical agents and palaeontological proxies were obtained knowledge of the biology of these organisms has only progressed considerably in recent years. It has been confirmed that holococcolithophores are not autonomous but stages in the life cycle of heterococcolithophores. A general introduction to the taxonomy and biology of extant coccolithophores is followed by a brief overview of the environmental parameters affecting these phytoplanktonic organisms and their biogeography. Another chapter summarizes the investigations on coccolithophores in the Arabian Sea which have been conducted during the past years to produce a synthesis of the production of living coccolithophores in the photic zone, their transformation to settling assemblages, their accumulation on the seafloor, and their final burial in the sediments. In the following, applications of coccolithophores to palaeoenvironmental analyses are provided as case studies. In particular, the usage of both ecologically restricted species, such as *Florisphaera profunda*, for palaeoproductivity studies and of a new coccolithophore-based palaeothermometry for surface-water reconstructions are presented. In addition, haptophyte-specific biomarkers (long-chain alkenones) are reviewed and their applicability for palaeoceanographical reconstructions is demonstrated.

Keywords: coccolithophores • phytoplankton • Recent • Quaternary • biology • ecology • paleoproxy • alkenones • carbonate producer

Kurzfassung: Coccolithophoriden, einzelliges marines Phytoplankton, stellen eine der Hauptprimärproduzenten in den Ozeanen dar. Diesen haptophyten Algen kommt als Karbonatproduzenten und photoautotrophe Organismen eine bedeutende Rolle im Kohlenstoffkreislauf zu, den sie sowohl über die Karbonat- als auch über die biologische Pumpe beeinflussen. Trotz der intensiven Fortschritte in der Bearbeitung als Träger biogeochemischer Informationen und ihrer steigenden Bedeutung als Paläoumweltindikatoren ist der Kenntnisstand über die Biologie von Coccolithophoriden erst in jüngster Zeit wesentlich erweitert worden. Es hat sich gezeigt, dass Holococcolithophoriden keine autonomen Organismen, sondern Phasen im Lebenszyklus von Heterococcolithophoriden sind. Nach einer Einführung in die Taxonomie und Biologie von Coccolithophoriden werden die Umweltparameter, die diese Phytoplanktongruppe beeinflussen, vorgestellt und ihr Vorkommen sowohl geographisch als auch ökologisch beschrieben. Das folgende Kapitel stellt beispielhaft die Bildung des geologischen Signals von Coccolithophoriden dar. Hierzu wurden Planktongemeinschaften aus dem Oberflächenwasser mit Sinkgemeinschaften aus Partikelfallen sowie den unterlagernden Oberflächensedimentgemeinschaften verglichen und bewertet. In den folgenden Fallstudien wird auf die Bedeutung von Coccolithophoriden als Paläoumweltindikatoren eingegangen. Insbesondere werden die Anwendung einzelner, ökologisch relevanter Arten, wie die in der tieferen photischen Zone lebende *Florisphaera profunda*, für Paläoproductivitätsrekonstruktionen sowie eine neue, auf Coccolithophoridenarten basierende Rekonstruktion von Oberflächenwassertemperaturen dargestellt. In vielen paläozeanographischen Arbeiten werden Haptophyten-spezifische Biomarker (langkettige Alkenone) intensiv für Temperaturrekonstruktionen genutzt. Im Vergleich zu anderen planktischen Karbonatproduzenten zeigt sich, dass Coccolithophoriden heute und im Pleistozän einen wesentlichen Anteil am Eintrag von (anorganischen) Kohlenstoff in das geologische Archiv ausmachen.

Schlüsselwörter: Coccolithophoriden • Phytoplankton • rezent • Quartär • Biologie • Ökologie • Paläoproxy • Alkenone • Karbonatproduzenten

Addresses of the authors: KARL-HEINZ BAUMANN and BABETTE BÖCKEL, FB Geowissenschaften, Univ. Bremen, Postfach 330440, D-28334 Bremen. – HARALD ANDRULEIT, Federal Institute for Geosciences and Natural Resources, Postfach 510153, D-30631 Hannover. – MARKUS GEISEN, Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen 12, D-27570 Bremerhaven. – HANNO KINKEL, Institute for Geosciences, Univ. Kiel, Olshausenstr.40, D-24118 Kiel.

1 Introduction

2
3 The living coccolithophores are marine, unicellular phytoplankton, belonging to the phylum Haptophyta and the division Prymnesiophyceae (JORDAN & CHAMBERLAIN 1997). Their morphology is characterised by an exoskeleton composed of numerous minute calcite platelets – the coccoliths – that are readily preserved in the sedimentary record.

10 Coccolithophores are one of the main groups of marine phytoplankton playing key roles in the marine ecosystem as primary producers and in marine biogeochemistry, owing to their great abundance, fast turnover rates, and their capability to carry out photosynthesis and calcification (WINTER & SIESSER 1994; BOWN 1998). They are, from a quantitative point of view, among the most important pelagic calcifying organisms in the modern ocean (BAUMANN et al. 2004; HAY 2004). The evolution of calcareous nannoplankton resulted in a major shift in the locus of global calcification from the continental shelves towards deep oceans, which fundamentally changed ocean chemistry and global sedimentation patterns. Recently, coccolithophores have gained increased attention as they play a unique role in the global carbon cycle and are peculiar because of their combined effects on both, the biological carbon and the carbonate pump. Because of their biochemical effects (dimethylsulfide – which act as a source molecule for cloud nucleation) they are likely to produce additional feedback to climate change (WESTBROEK et al. 1993).

32 In addition, coccoliths are phenomenally abundant in sea-floor sediments, and preserve the composition of the overlying photic-zone communities due to protected and accelerated sedimentation in faecal pellets or in marine snow. Therefore, they are valuable indicators of palaeoceanographical change. Coccolithophores have one of the most abundant fossil records of any phylum and this fossil record is continuous from their first occurrence in the Late Triassic to the present day (e.g. BOWN et al. 2004). These diverse properties have prompted intensive research on extant coccolithophores over the past decades. Within the present paper we provide a review of the state of the art of knowledge on extant coccolithophores and on their utility for palaeoenvironmental and palaeoceanographical reconstructions. An overview is presented on their biology, ecology and biogeography, of the transformation of living communities to fossil assemblages, and examples are given on their application in geological studies. In particular, the usage of species for palaeoproductivity studies and a new coccolithophore-based palaeothermometry for surface-water reconstructions are presented. In addition, haptophyte-specific biomarkers (long-chain alkenones) are reviewed and their applicability for palaeoceanographical reconstructions is demonstrated.

Biology of coccolithophores

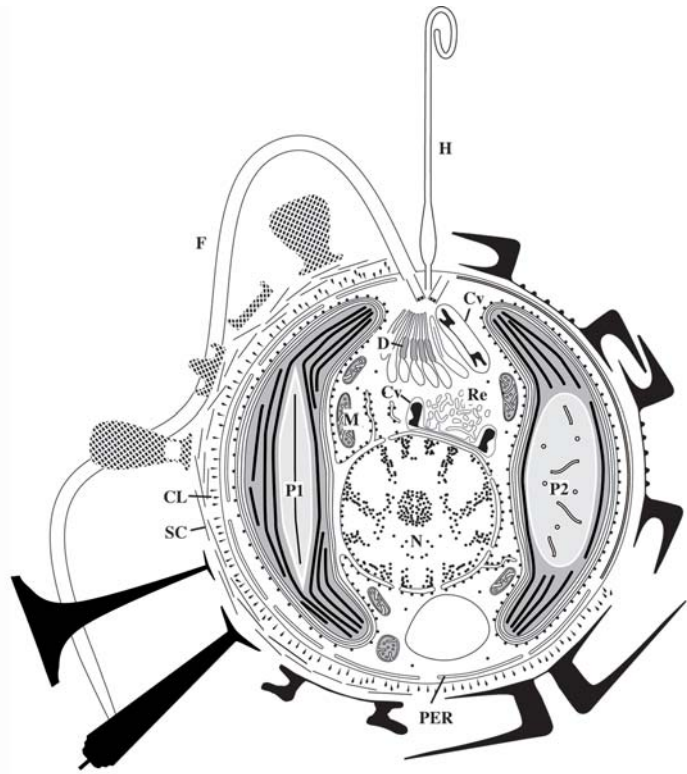
Their long evolutionary record, high evolutionary turnover and enormous abundance in sediments have made them ideal biostratigraphical marker fossils and hence they have been widely used for dating of sediments and classical palaeological work. It was however only in the beginning of the 20th century that researchers (e.g. KAMPTNER 1927; LOHMANN 1902; MURRAY & BLACKMAN 1898) started observing and exploring the biology of the organisms. Although steady advances in research on coccoliths as biogeochemical agents and palaeontological proxies were obtained, these have not been paralleled by information in the biology of the species. Knowledge of the biology of coccolithophores has, however, progressed considerably in recent years due to increased numbers of culture studies and meticulous observations in plankton samples and are most recently reviewed and summarized by BILLARD & INOUE (2004).

Coccolithophores include all haptophyte algae possessing calcified scales (coccoliths) at some stage in their life cycle. Following the taxonomic revision of the division Haptophyta recently proposed by EDVARDSEN et al. (2000), coccolithophores belong to the class Prymnesiophyceae, which also features non-calcifying organisms. Coccolithophores generally occur as single cells and their typical features have been previously compiled in earlier reviews (PIENAAR 1994; INOUE 1997; BILLARD & INOUE 2004; summarized in Fig. 1).

The taxonomy of coccolithophores is based on the morphology of the coccoliths that cover their cell. Two major groups exist, the holo- and heterococcoliths (Fig. 2), of which the heterococcolithophore stage is more common. Whereas holococcoliths are formed out of numerous, minute euhedral calcite crystallites the heterococcoliths are formed of a radial array of variably shaped crystal units (see e.g. YOUNG et al. 1992, 1997). Formation of the heterococcoliths takes place intracellularly (PIENAAR 1994; WESTBROEK et al. 1989). In contrast, biomineralization of holococcoliths appears to occur outside the cell (ROWSON et al. 1986, YOUNG et al. 1999). Within these basic categories, various terms are used by workers on living coccolithophores and based on morphological characteristics of certain taxa: cricoliths, helicoliths, etc. for heterococcoliths; calyptroliths, crystalloliths, etc. for holococcoliths (for terminology see YOUNG et al. 1997; Fig. 2). The abundance of such terms reflects the high diversity of coccolith morphology. In addition, two families of extant coccolithophores produce so-called nannoliths (Ceratolithaceae, Braarudosphaeraceae) which are anomalous calcareous structures lacking the typical features of hetero- or holococcoliths. Today the extant coccolithophore biodiversity based on the dominant diploid stage is estimated to be in the order of 200 species (YOUNG et al. 2003).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58

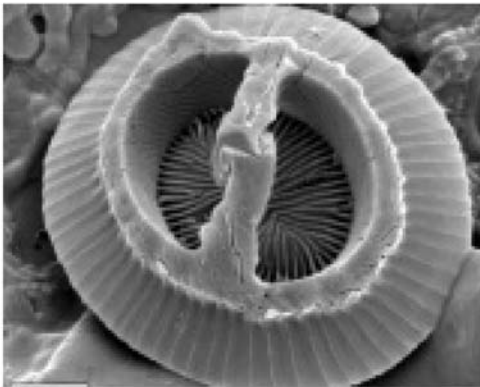
Fig. 1. Schematic representation of the cell structures of coccolithophores. Morphological features and different types of coccoliths seen in various species are combined in this figure. Two types of coccolith-forming vesicles found in *Pleurochrysis* (top) and *Emiliana* (bottom) are illustrated. Pyrenoid (P1) is typical in the coccolithophores and pyrenoid (P2) is seen in *Emiliana* and *Gephyrocapsa*. Heterococcoliths are plotted black and holococcoliths are blotted by a lattice pattern. –CL: columnar deposit, Cv: coccolith forming vesicle, D: peculiar dilation of Golgi body, F: flagellum, H: haptonema, M: mitochondrial profiles, N: nucleus, P1: pyrenoid traversed by thylakoids, P2: pyrenoid traversed by tubular structures, PER: peripheral endoplasmic reticulum, Re: reticular body, SC: unmineralized organic scales (modified from BILLARD & INNOUYE 2004).



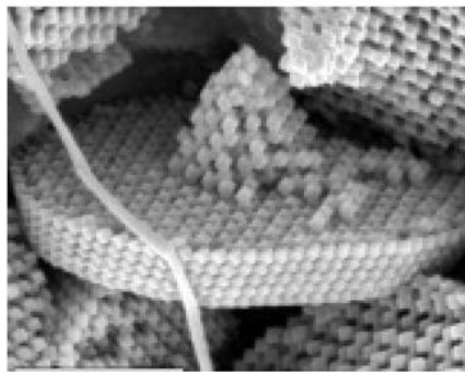
Combination coccosphere
(*Calcidiscus leptoporus* with holococcoliths previously assigned to *Syracolithus quadriperforatus*)



Coccosphere
(*Gephyrocapsa oceanica*)



Heterococcolith
(*Gephyrocapsa oceanica*)



Holococcolith
(*Syracolithus catilliferus*)

Fig. 2. Examples for the general terminology used in coccolithophorid algae.

Coccolithophore life cycles

The dominant reproductive mode of coccolithophores is asexually by mitotic division and, generally following mitotic division, the coccoliths are redistributed on the daughter cell. In many haptophytes however a complex life cycle has also been demonstrated, which involves two or more morphologically distinct phases. The typical coccolithophore life cycle consists of a diploid stage, which is covered with heterococcoliths and a motile, haploid stage usually covered by holococcoliths (Fig. 3). Thus, it has been confirmed that holococcolithophores and probably other anomalous coccolithophores as well are not autonomous, as previously been thought, but stages in the life cycle of heterococcolithophores. For a more comprehensive review on life cycles in haptophytes, the reader is referred to BILLARD (1994), BILLARD & INUYOYE (2004) and HOUDAN et al. (2003).

Although this alternating life cycle has been demonstrated in culture (PARKE & ADAMS 1960; GEISEN et al. 2002; HOUDAN et al. 2003) and by combination cells from field samples (CORTÉS 2000; CROS et al. 2000; GEISEN et al. 2002) little is known for about the causative factors that trigger phase changes. There are, however, hints that holococcolithophores thrive in more oligotrophic waters such as the eastern Mediterranean. Summarizing available data it can be speculated that the

ability to rapidly undergo phase transitions is an important tool for the genetic recombination and hence evolution for marine planktonic biota which are being challenged by constantly changing environments.

Culture studies

Coccolithophores can be maintained in clonal culture and where such cultures are available physiological experiments can be conducted (BRAND 1994). Until recently most such experiments were conducted on *Emiliana huxleyi* (BRAND 1981, 1982), but recently data have become available from different species, e. g. *Calcidiscus leptoporus* (QUINN et al. 2003), *Syracosphaera pulchra*, *Helicosphaera carteri* and *Umbilicosphaera* spp. (GEISEN et al. 2004). These tests have provided evidence that coccolith morphology is stable if tested under different ecological parameters and hence under strong genetic control and not ecophenotypic in nature (GEISEN et al. 2004). Conducting experiments using different environmental parameters and testing the stability of the morphology and size (biometrics) of the coccoliths allows for a better understanding of the constraints of a species concept which is – in the case of the fossil record – entirely based on the morphology of the coccoliths. In addition biological experiments can be

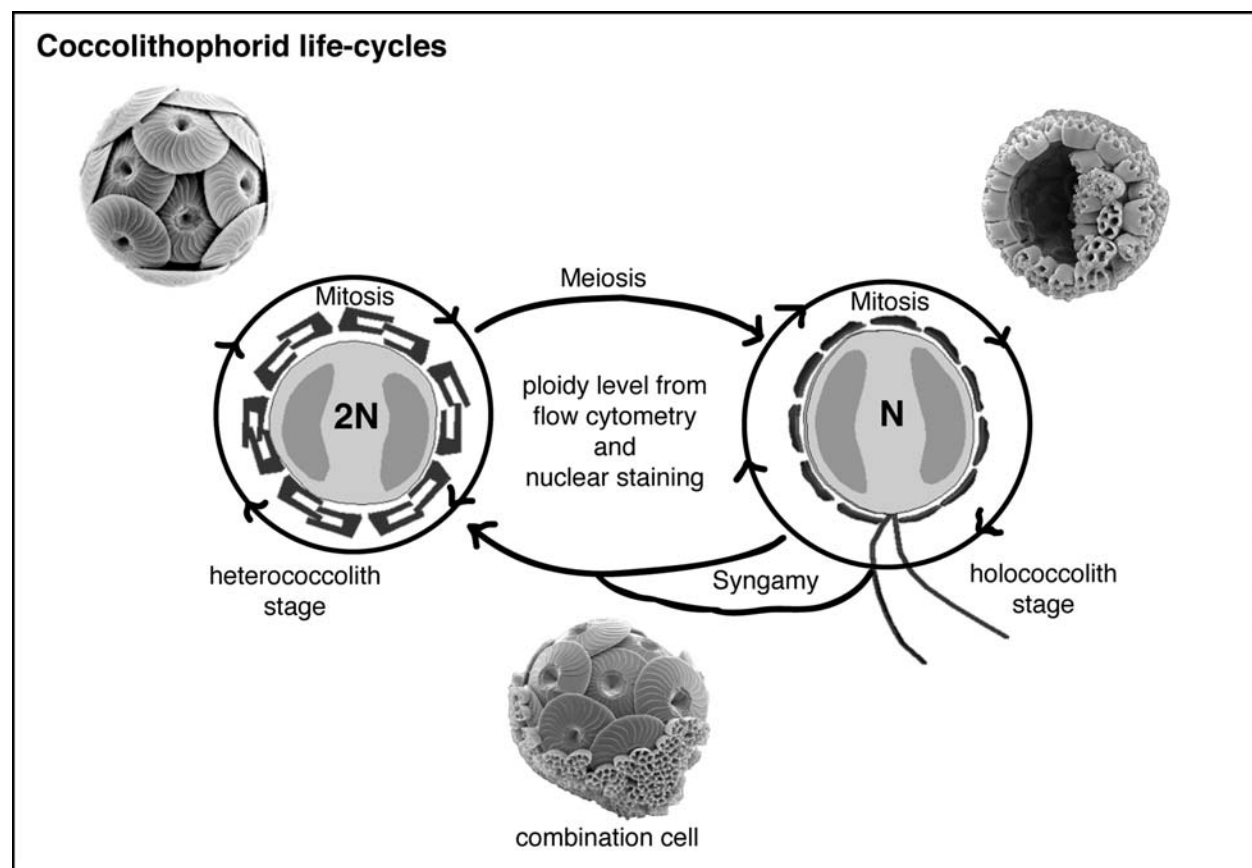


Fig. 3. Schematic illustration of coccolithophorid life cycles (from GEISEN et al. 2002).

used to model changes to global biogeochemical cycles, e. g. the carbon cycle (RIEBESSELL et al. 2000), but also to deliver basic parameters for ecosystem models (e. g. RIEGMAN et al. 1998).

Cultures have furthermore been available to test, if the morphological variability relates to true genetic change. Results from this research have broadly supported the higher level taxonomy of coccolithophores (generic, familial and ordinal groupings) (EDVARDSEN et al. 2000; FUJIWARA et al. 2001; MEDLIN et al. 1997; SAEZ et al. 2004), but have challenged species concepts with the discovery of pseudo-cryptic speciation in coccolithophores – which may provide insight into the process of speciation (SAEZ et al. 2003; GEISEN et al. 2004).

Coccolithophore ecology and biogeography

Factors affecting living coccolithophores

Coccolithophores rely on photosynthesis as their prime nutritional mode restricting them to the photic zone of

the oceans. Within the uppermost water column, there are a number of environmental parameters that are known to affect plankton communities in general, on both spatial and temporal scales.

Water temperature has often been thought of as one of the most important factors. This may be due to the fact that during many investigations only temperature and salinity measurements were taken. MCINTYRE & BÉ (1967) showed that most common species had relatively narrow temperature ranges, although subsequent workers extended these ranges. Thus, temperature seems to play a role in controlling the largest scale distribution of species, largely defining broad latitudinally arranged biogeographical zones. However, on smaller scales temperature ranges are less informative and important, as no water-body has annual temperature fluctuations covering an extremely large range. For subtropical populations temperature change is perhaps unimportant, whereas for subpolar communities, temperature plays a more prominent role due to the formation and breakdown of the seasonal thermocline (ANDRULEIT et al. 2003).

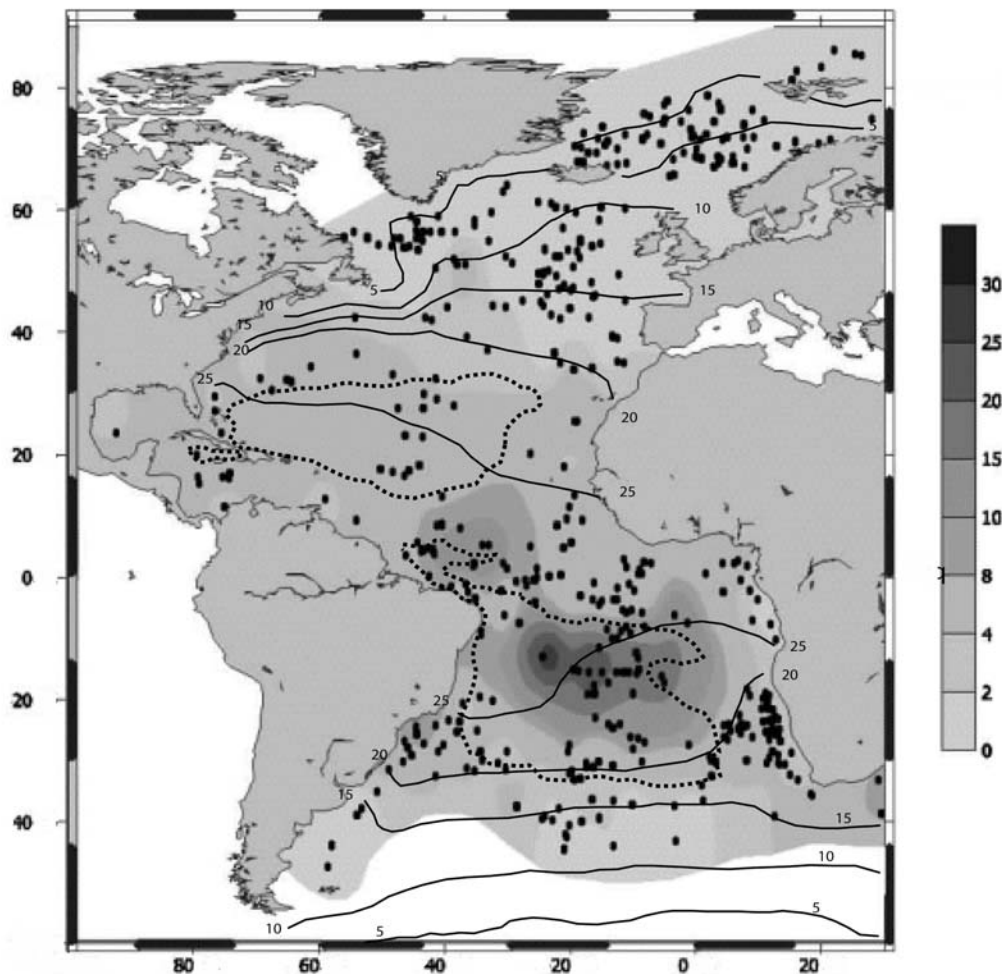


Fig. 4. Relative abundances of *Umbilicosphaera sibogae* (excluding the deep-dwelling species *Florisphaera profunda*) in Atlantic Ocean surface sediments (modified from ZIVERI et al. 2004). Solid line = annual mean sea-surface temperature. Dotted line = centre of oligotrophic gyre.

1 Most coccolithophores live in the open ocean and
 2 so are adapted to salinities of 32–37 ppt. However sev-
 3 eral species have a wider salinity tolerance (BRAND
 4 1994) and are known from low salinity environments,
 5 such as fjords. Coccolithophorid species diversity is
 6 highest in stratified, warm oligotrophic environments,
 7 where salinity values are relatively high. The rather
 8 euryhaline characteristic of the coccolithophores is indi-
 9 cated by the occurrence of 52 species in the Gulf of Elat
 10 (Aqaba), where the mean salinity is 41 ppt (WINTER et
 11 al. 1979). In contrast, in areas characterised by lower sa-
 12 linities, such as the coastal areas, coccolithophorid di-
 13 versity is relatively low, and the species may be special-
 14 ised (i.e. benthic or partly calcified). Sediments of the
 15 North Sea only contain a sparse, low diverse nanoflora
 16 mainly restricted to *Emiliana huxleyi* (HOUGHTON
 17 1988, 1991). At present, only one coccolithophorid spe-
 18 cies, *Hymenonas roseola*, is known to inhabit freshwa-
 19 ter environments.

20 All phytoplankton require certain nutrients for their
 21 growth and biochemical reactions. The most important
 22 nutrients are considered to be nitrate and phosphate. In
 23 particular, in coccolithophores, nitrate is essential for
 24 growth and calcification; however, at unnatural high nu-
 25 trient concentrations calcification is inhibited. Phos-
 26 phate seems to act as a controlling agent for calcifica-
 27 tion. It has been shown that phosphate concentrations
 28 were lower in waters where coccolithophores, mainly *E.*
 29 *huxleyi*, bloomed (TOWNSED et al. 1994; VAN DER WAL
 30 et al. 1995). Thus, at least *E. huxleyi* seems to have high
 31 phosphate uptake kinetics and so can compete in low
 32 phosphate environments. In eutrophic (nutrient-rich) en-
 33 vironments coccolithophores are often outcompeted by
 34 diatoms forming relatively minor components of the to-
 35 tal communities. Nonetheless, certain coccolithophorid
 36 species (notably many placolith-bearing species) are
 37 adapted to such conditions. Since productivity is much
 38 greater in eutrophic conditions, a very large proportion
 39 of total coccolith production occurs under such condi-
 40 tions. Nonetheless, many coccolithophores are K-select-
 41 ed, i.e. adapted to oligotrophic conditions. Coccolitho-
 42 phores as a group achieve their highest relative
 43 abundances within phytoplankton communities in such
 44 oligotrophic environments. The effect of tropic levels on
 45 coccolithophorid ecology is discussed in WINTER &
 46 SIESSER (1994), and detailed case studies are given by,
 47 e.g. KINKEL et al. (2000).

48 As coccolithophores are photosynthetic organisms,
 49 they require light for carbon fixation. Most species
 50 therefore live in the upper photic waters (<50–80 m), but
 51 may become photo-inhibited close to the surface. *Emil-*
 52 *iana huxleyi* is unusual in this respect in that it appears
 53 to be uninhibited by high light levels (TYRELL & MERI-
 54 CO 2004). This may account for its success at outcom-
 55 peting other species when it forms gigantic blooms. In
 56 contrast, some species, such as *Florissphaera profunda*,
 57 inhabit the lower photic zone (= LPZ), which is charac-
 58 terised by low light levels (<1% to 4% of the surface ir-

radiance!). The LPZ is usually a permanent feature of
 the subtropical gyres, but may develop in well-stratified
 waters in equatorial and temperate regions during sum-
 mer months. Thus, it is not surprising that the LPZ flora
 is rare or absent in turbulent waters, i.e. in coastal or up-
 welling areas.

Coccolithophore biogeography

Individual species typically occur in all the world's
 oceans but with more or less limited latitudinal distribu-
 tion. Three to four broad coccolithophorid floral zones
 are previously recognised (MCINTYRE & BÉ 1967;
 GEITZENAUER 1977; WINTER & SIESSER 1994): Subarc-
 tic, Temperate, Subtropical, Tropical and Subantarctic.
 These floral zones are consistently recognisable espe-
 cially in oceanic plankton samples, and have been asso-
 ciated with major water masses. However, this is a
 simplistic distribution that does not take into account
 coastal currents, gyres, eddies, upwelling and rather ob-
 scures species-specific biogeography. In addition, it
 does not show any difference between North and South
 Atlantic distribution. In the classical present coccolitho-
 phorid biogeography the species assemblages are rather
 similar to their counterparts in the opposing hemisphere.

This has recently been revised for a few particular
 species in the Atlantic Ocean (ZIVERI et al. 2004). In es-
 pecially, *Calcidiscus leptoporus* and *Umbilicosphaera*
sibogae surprisingly show much higher abundances in
 the South Atlantic than in the North Atlantic, whereas
 the absence of *Coccolithus pelagicus* in the sub-Antarctic
 is already well-known. The biogeographical distribu-
 tion of *C. pelagicus* primarily reflects the well-docu-
 mented smaller sub-Arctic species (BAUMANN 1995)
 with clear abundance maxima in the northern Atlantic,
 corresponding rather closely to areas with mean temper-
 atures below 10°C. However, the *Umbilicosphaera* pat-
 tern is more ambiguous, since the North and South At-
 lantic show broadly similar habitats in terms of
 temperature, salinity, productivity and macronutrients.
 Other species also show preferences for habitats not
 seen before. In particular, *Syracosphaera pulchra* shows
 a warm water low productivity preference whilst *Hel-*
icosphaera carteri shows a warm water higher produc-
 tivity distribution. This is a clearer distribution than
 might have been expected since f.e. *S. pulchra* has not
 been regarded as one of the typical oligotrophic special-
 ists.

From the amount of information available on the
 oceanic scale distribution of nanoplankton, three
 groups of species could be separated with distinct mor-
 phologies and biogeographies (YOUNG 1994). There-
 fore, particular environments are dominated by charac-
 teristic assemblages, which can be distinguished by their
 coccolith types and coccosphere morphology (Fig. 5).
 Placolith-bearing species have been recorded to be char-
 acteristic for meso- to eutrophic environments such as
 upwelling areas (equatorial divergence and coastal up-

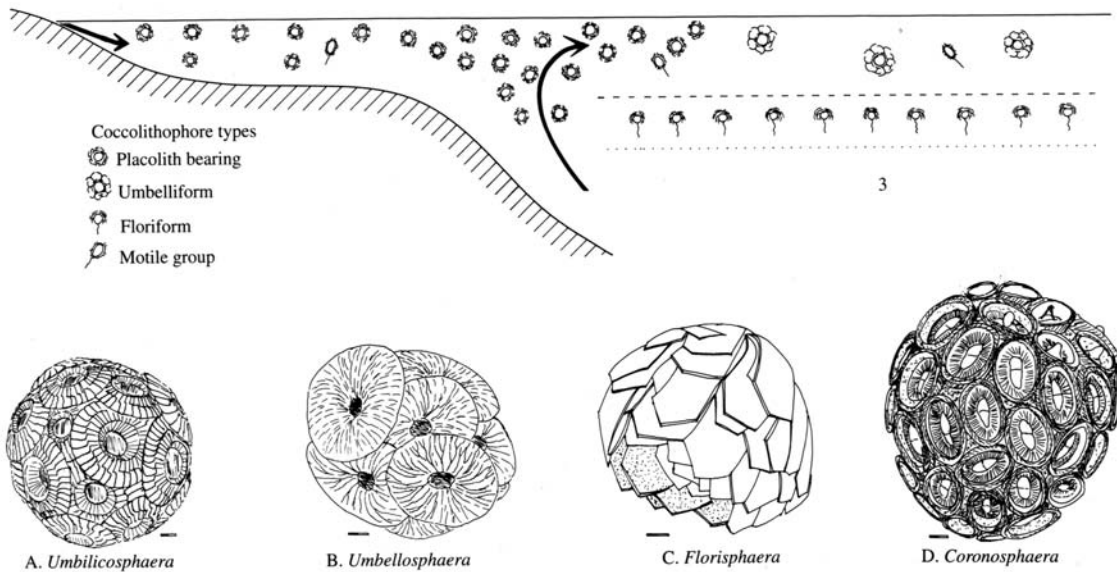


Fig. 5. Characteristic assemblages distinguished by their coccolith types and coccosphere morphology (modified from YOUNG 1994).

welling) and shelf seas, where they often reach bloom proportions. They mainly include *Emiliana huxleyi*, *Gephyrocapsa* spp., *Umbilicosphaera* spp. and a few other species. Their coccoliths are composed of a proximal and distal shield joined by a central column. Umbelliform assemblages, composed of *Umbellosphaera* spp. and *Discosphaera tubifera*, bear coccoliths with large processes, which flare distally to produce a double-layered coccosphere. They dominate oligotrophic mid-ocean environments. The floriform species form coccospheres with a dense asymmetrical mass of coccoliths surrounding a much smaller cell. They mainly characterise the deep photic zone assemblage in a stable water column of low- to mid-latitudes deep photic zone assemblage in a stable water column of low- to mid-latitudes.

Transformation of living communities to fossil assemblages: a case study from the northern Arabian Sea

Assessment of the quality and accuracy of the information preserved in the sedimentary record is a basic prerequisite for the development of comprehensive palaeo-reconstructions. This chapter summarizes the investigations on coccolithophores in the Arabian Sea which have been conducted during the past years to produce a synthesis of the production of living coccolithophores in the photic zone, their transformation to settling assemblages, their accumulation on the seafloor, and their final burial in the sediments (Fig. 6).

The hydrography of the Arabian Sea is controlled by the SW-monsoon in summer (June to September) and the NE-monsoon (December to February) in winter. In

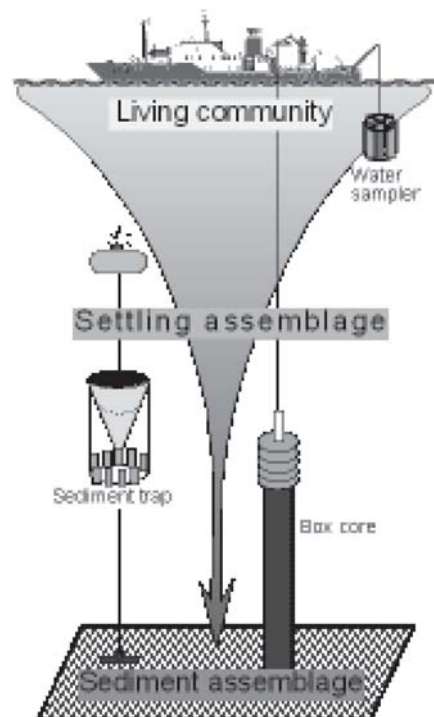


Fig. 6. Illustration of the different realms of the used datasets. Water samples help to investigate extant coccolithophores but only give a snapshot of the persistently changing communities. Sediment traps collect already altered settling assemblages over a longer period up to years. The preserved fossil record is thus strongly altered and impoverished.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58

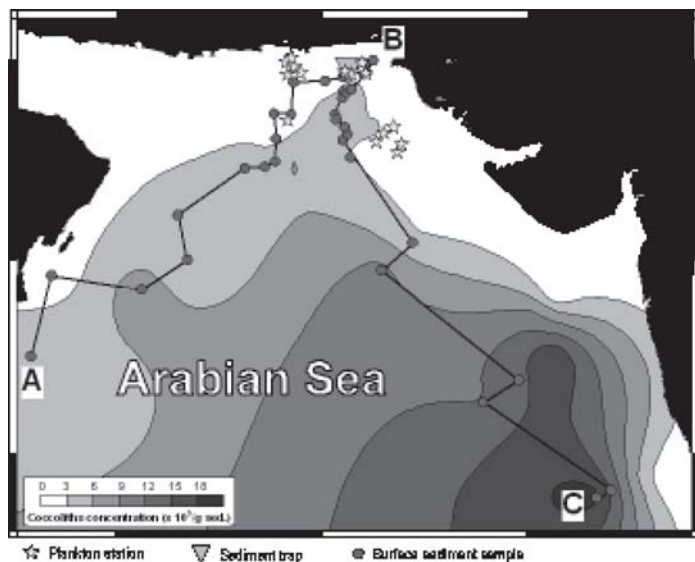


Fig. 7. Map of the Arabian Sea with isolines of absolute coccolith concentrations in surface sediments. Locations of 16 plankton stations, the trap mooring, and surface sediment samples are shown.

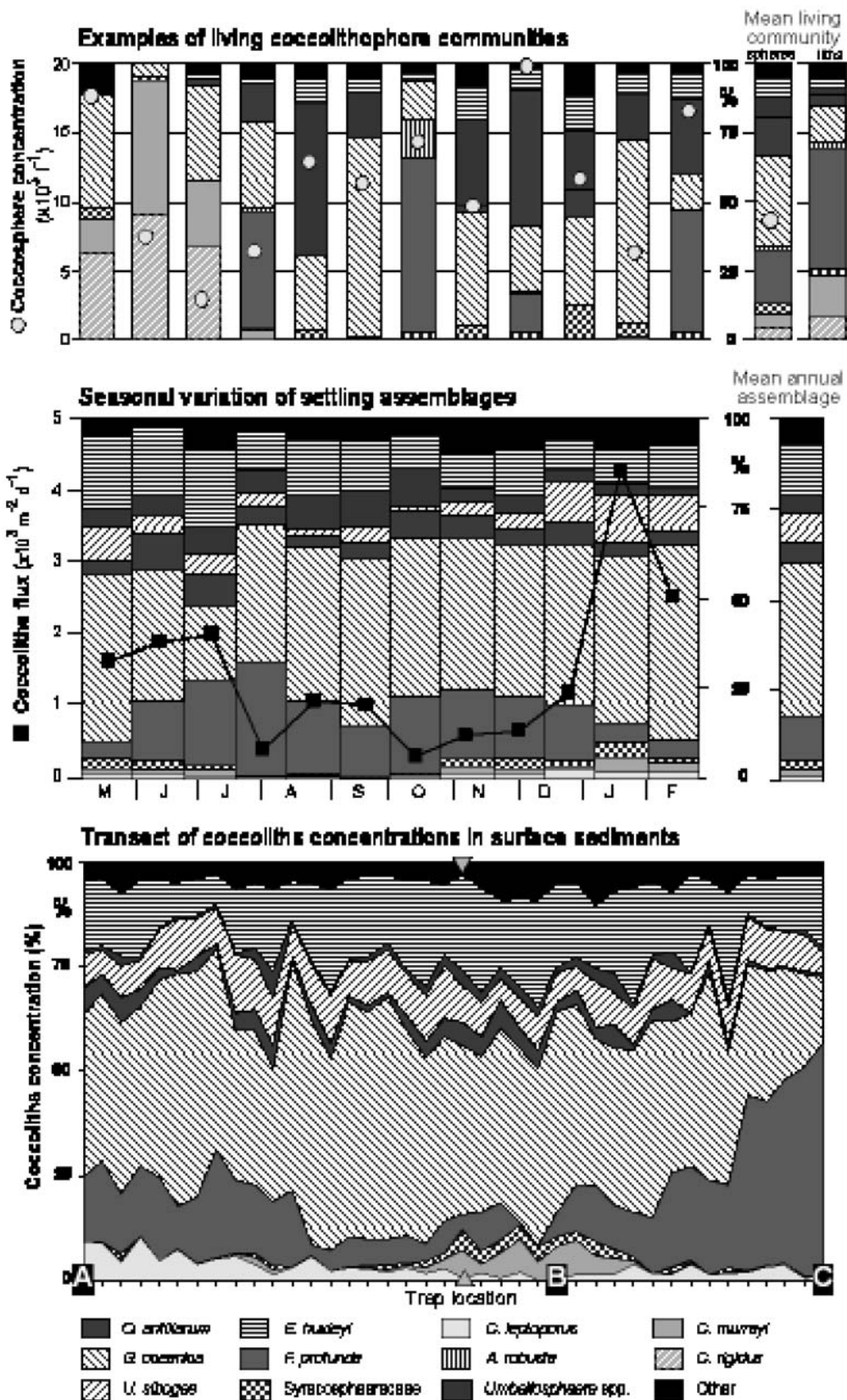
addition to monsoonal upwelling during the SW-monsoon along the western boundary of the Arabian Sea due to Ekman transport, wind-induced deep mixing is responsible for high productivity and increased particle fluxes during both monsoon seasons (BANSE & MCCLAIN 1986). A large number of samples from different realms were used for the present study (Figs. 6, 7) and identical or corresponding approaches were followed to provide a basis for the comparison and discussion of the different datasets.

A plankton study on samples retrieved during September 1993 at the end of the SW-monsoon in the northeastern Arabian Sea (Fig. 8) yielded a rather heterogeneous pattern with regard to species composition in surface waters, apparently as a result of short-term local variability in ecological conditions (ANDRULEIT et al. 2003). Therefore, a “mean plankton community” was calculated from 71 plankton samples of 16 stations by taking the average abundance of each species (for further details see ANDRULEIT et al. in press). Obviously, this mean community exhibits a species composition, which hardly ever occurs in natural living communities (Fig. 8). For example the co-occurrence of *Florisphaera profunda*, *Umbellosphaera* spp., and *Calciosolenia murrayi* should never be found since the three taxa inhabit rather different ecological niches. This mean community was taken as a basis for a qualitative comparison of the export out of the plankton realm with the settling assemblages retrieved from sediment traps at 590 m depth (ANDRULEIT et al. in press; Fig. 8).

When comparing the plankton with the sediment traps, striking differences but also high similarities become obvious. Only a few species with significant relative abundances in the plankton, such as *Algirosphaera robusta* and *Calcipappus rigidus*, were not important contributors to the settling assemblages. This may be interpreted as a hint to the processes, which alter the living

communities during their transformation to settling assemblages. Only the coccolithophores, which were incorporated without total destruction into fast sinking faecal pellets or marine snow aggregates are likely to be preserved (HONJO 1976, 1980). Biological breakage and dissolution due to grazing is probably a major alteration factor for the coccolithophore communities (HARRIS 1994). Delicate forms are preferentially destroyed, whereas heavily calcified or blooming species probably have a higher preservation potential (ANDRULEIT, 1997). However, without further grazing of the zooplankton or incorporation into aggregates (marine snow), many coccolithophores would possibly not be transformed into settling and sediment assemblages, but could disintegrate and eventually be dissolved in the upper water column (YOUNG 1994; MILLIMAN et al. 1999).

Nevertheless, much of the plankton communities are preserved in the traps, despite the fact that all settling assemblages were naturally subject to severe alteration processes. Taking the different ecological tolerances and niches of the entrapped taxa into account it becomes obvious that several communities contributed to the settling assemblage. Thereby, altered and mixed seasonal species assemblages are produced which still reflect information of the former living communities but their record has to be unravelled carefully. The annual trap record of the northeastern Arabian Sea is, therefore, well suited to give a representative annual pattern of the coccolithophorid succession in that region. Absolute as well as relative abundances exhibit changes in the assemblage, which can be correlated to the monsoon seasons (ANDRULEIT et al. 2000). High fluxes were recorded at the beginning of the SW (summer) and the NE (winter) monsoons, with highest fluxes during the latter (December to February). However, the great variety of species compositions seen in the plankton samples is not preserved in the annual cycle (Fig. 8). Instead a rather



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58

Fig. 8. Comparison of living coccolithophore communities with settling assemblages and coccolith assemblages from surface sediments. Despite the great variety of living communities only a smoothed record characterizes the trap assemblages. The mean living community of September is shown for comparison with the trap assemblage of October (regarding a time lag of approximately 14 days to the trap depth of 590 m). The annual mean of the trap assemblages is shown for comparison with the spatial distribution of coccoliths in surface sediment samples across the northern Arabian Sea (ANDRULEIT et al. in press).

smoothed signal consisting of similar species compositions with only gradual intra-annual changes characterize the settling assemblages.

The sediment trap was located in the northeastern region and should therefore display an annual averaged assemblage, which is similar to the underlying surface sediment assemblage (ANDRULEIT & ROGALLA 2002). Indeed, when comparing the mean trap record with the sedimentary record a remarkable high match can be seen (Fig. 8). There is a high agreement in the species composition (disregarding rare species grouped as "other"), and even the proportions are almost the same. This means that the information record of the traps is transformed into the sediment almost without biases in the relative species abundances. The intra-annual species succession in the trap reflects the changing environmental conditions while the annual mean closely resembles the sedimentary record where only a mixed signal of the two monsoon seasons is preserved.

As shown in previous studies (BAUMANN et al. 1999, 2000) and above it is possible to trace the record of coccolithophores from living communities to sediment assemblages on the basis of relative species abundances. A full quantitative approach, however, is much more difficult. Additionally, resuspension and lateral advection, which affect the surface sediment assemblages as well as the settling assemblages found in the traps, overprint and increase the downward fluxes. This phenomenon seems to be quite common and affects most sediment traps in the catchment area of continental shelves and slopes (ANDRULEIT 1997; BEAUFORT & HEUSSNER 1999; ANDRULEIT et al. 2000; SPRENGEL et al. 2000). Strongly calcified resistant forms (e.g. *C. leptopus*) have a high preservation potential and, thus, become more prominent during the alteration process, whereas other species such as *E. huxleyi* are abundant due to seasonal high productivity. Therefore, either a robust structure or high cell densities in surface waters are basic prerequisites to become preserved in the fossil record.

Palaeoenvironmental significance of coccolithophores

Coccolithophores have been relatively little used for Pleistocene palaeoclimatic and palaeoceanographic reconstruction by comparison with other plankton groups. This is primarily due to their high rate of evolutionary divergence, compounded by a succession of assemblages dominated by a few, relatively cosmopolitan species that are tolerant to a wide range of conditions. However, recent advances that have come from intensive study of fine-scale variations in particular species have made some single species/species groups a particularly useful tool for palaeoenvironmental reconstructions (e.g. GEISEN et al. 2004). Case studies briefly presented in the following include the response of the total coccolithophore assemblages as well as single species such as *Ge-*

phyrocapsa oceanica to palaeoproductivity changes in the equatorial Atlantic during the last 140,000 years together with palaeoproductivity estimates based on the deep-dwelling *Florisphaera profunda*. A recently developed *Gephyrocapsa*-based SST transfer function is presented. In addition, their significance as carbonate producers is reviewed followed by an introduction into biomarker studies on coccolithophores.

Coccolithophores in the equatorial Atlantic Ocean: response to palaeoproductivity changes during the last 140,000 years

Biogeographic distribution patterns of coccoliths in surface sediments are commonly used to infer temperature conditions and circulation patterns (e.g. MCINTYRE 1967; ROTH & COULBOURN 1982; HOUGHTON 1988; BAUMANN et al. 1999, 2000), as well as productivity gradients (MOLFINO & MCINTYRE 1990; BEAUFORT et al. 1997). In surface sediments underlying the oligotrophic water masses of the equatorial Atlantic, deep-dwelling species such as *Florisphaera profunda* and *Gladiolithus flabellatus* (the so-called Lower Photocline Zone = LPZ flora) are most abundant and variations within their occurrences were explained in terms of changes in nutricline depth (MOLFINO & MCINTYRE 1990). Accordingly, high abundances of the LPZ flora are associated with a deep nutricline and deep thermocline, whereas low abundances are characteristic for a shallow nutricline and thermocline. In addition, relative abundances of *F. profunda* have been used as an excellent indicator for reconstructing past changes in the thermocline dynamics especially of the equatorial Atlantic (MOLFINO & MCINTYRE 1990; MCINTYRE & MOLFINO 1996; BASSINOT et al. 1997), but also for the northwestern Pacific (AHAGON et al. 1993) and the Indian Ocean (OKADA & MATSUOKA 1996; BEAUFORT et al. 1997). In particular, BEAUFORT et al. (1997) indicated that the %-abundance of *F. profunda* in surface sediments seems to be a function of the primary productivity and, thus, providing a robust transfer function for paleoproductivity estimates; this has successfully been applied to Late Quaternary sediments from the Atlantic, Indian, and Pacific Oceans (BEAUFORT et al. 1997; HENRIKSON 2000).

A good example of the use of fossil distribution patterns of coccolithophores in reconstructing surface waters is that of KINKEL et al. (2000). They used species composition, coccolith numbers /g sediment, and coccolith accumulation rates for interpretation of changes in the surface water productivity. During the past 140,000 years the surface water circulation of the equatorial Atlantic changed drastically, mainly due to changing wind stress and advection of cool and nutrient rich waters from the south-eastern Atlantic, which caused an intensification and lateral expansion of the equatorial upwelling area. This is monitored in the coccolithophore assemblages of two sediment cores from the southern and western equatorial Atlantic (Fig. 9).

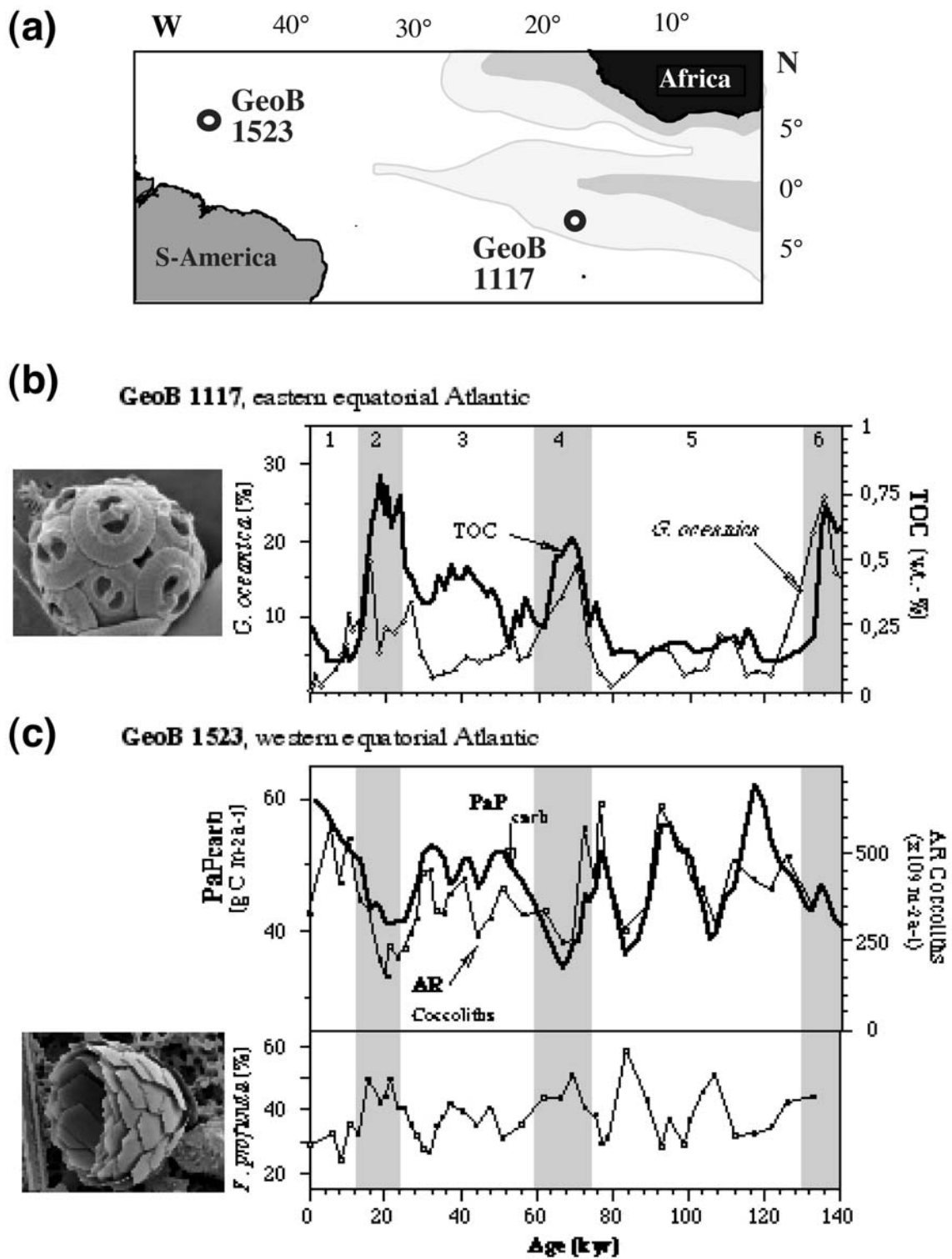


Fig. 9. – (a) Location of sediment cores GeoB 1117 and GeoB 1523. The grey shadings indicate higher phytoplankton pigment concentrations ($> 0.4 \text{ mg/m}^3$) recorded by the Coastal Zone Color Scanner (CZCS) from 1979–1986. Comparison of (b) the total organic carbon contents (TOC) and the relative abundance of *G. oceanica* in sediment core GeoB 1117, and (c) between the paleoproductivity estimations (PaPcarb), the coccolith accumulation rate, as well as the relative abundance of the deep-dwelling species *F. profunda* in sediment core GeoB 1523 (modified from KINKEL et al. 2000).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58

1 A striking increase in coccolith numbers and coccolith accumulation rates has been observed in sediment
2 core GeoB 1117 from the southern equatorial Atlantic
3 during the last glacial (KINKEL et al. 2000). This in-
4 crease was attributed to a lateral extension of the equa-
5 torial upwelling area and increased advection of cool
6 and nutrient rich water masses from the southeastern At-
7 lantic via the eastern boundary currents. This is also sup-
8 ported by the floral composition of the coccolithophore
9 assemblages. In particular, the relative abundances of
10 *Gephyrocapsa oceanica* corroborate the organic carbon
11 contents, with maxima in isotope stages 2, 4 and 6 (Fig.
12 9b). Higher abundances of *G. oceanica* were previously
13 described from upwelling areas of the Indian Ocean, the
14 Benguella Upwelling, and the Gulf of California (e.g.
15 KLEIJNE et al. 1989; GIRAUDEAU 1992; ZIVERI & THUN-
16 NELL 2000).

17
18 In the western equatorial Atlantic (GeoB 1523) an
19 opposite trend was observed during glacial periods,
20 which probably was caused by a deepening of the ther-
21 mocline and its seasonal coverage is limited to the west-
22 ernmost parts. Highest coccolith numbers and accumu-
23 lation rates are observed during the Holocene and in
24 isotope stage 5. During the last glacial interval (isotope
25 stages 2–4) the numbers are slightly lower with minima
26 occurring in stage 2 and 4 (Fig. 9c). Further indication
27 for decreased surface water productivity is given by
28 high abundances of *Florisphaera profunda*, as proposed
29 in several studies (MOLFINO & MCINTYRE 1990; OKA-
30 DA & MATSUOKA 1996; BEAUFORT et al. 1997). In
31 GeoB 1523, *F. profunda* is the most abundant species,
32 making up between 24 and 58% of the assemblage. The
33 records of the coccolith accumulation rate together with
34 the palaeoproductivity estimates (Fig. 9c) and the rela-
35 tive abundance of *F. profunda* show contrasting cyclic
36 variations throughout the entire core, with peaks in *F.*
37 *profunda* abundance rather consistently corresponding
38 to minima of coccolith accumulation rate. This contrast
39 is probably a result of varying nutrient supply to the up-
40 per euphotic zone where the majority of coccolitho-
41 phores reside. The nutrient availability is controlled by
42 the depth of the nutricline, which can be monitored by
43 the abundance of *F. profunda*. Together with *G. flabel-*
44 *latus* this is the only common species that is restricted to
45 the lower euphotic zone (~60 to ~180 m water depth) of
46 the tropical and subtropical oceans (OKADA & HONJO
47 1973), where light becomes limited. If the nutricline is
48 shallow, coccolithophore production in the upper eup-
49 hotic zone is enhanced, and the abundance of *F. pro-*
50 *funda* is minimal. An increase in the relative abundance
51 of this species thus can be attributed to a weakened up-
52 welling intensity with a deep thermocline and nutricline.

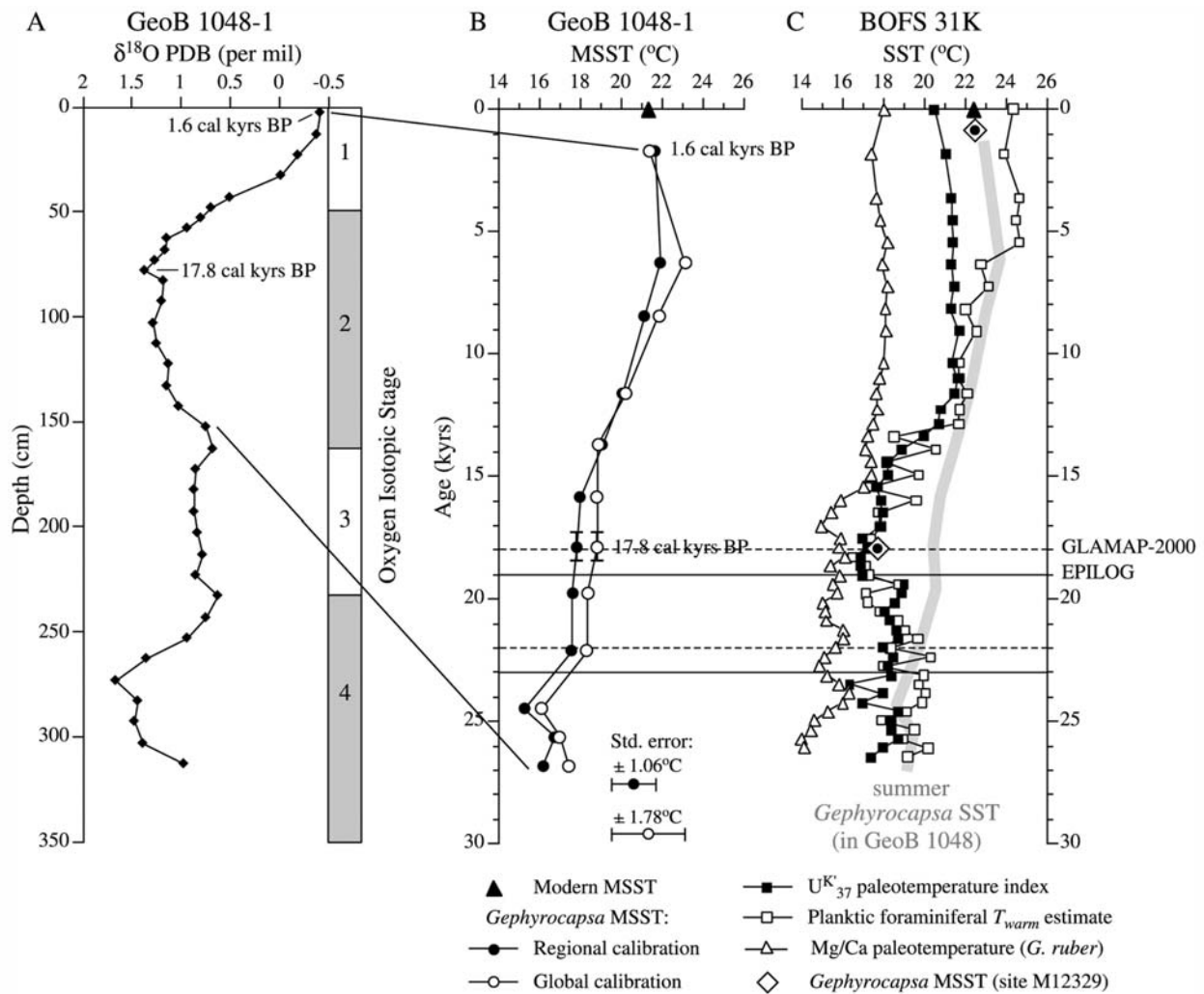
54 Coccolithophore-derived palaeotemperature 55 estimates

56 Various methods have already been established to re-
57 construct late Quaternary sea surface temperatures
58

(SSTs) from oceanic sediments: statistical estimates based on microfossil assemblage compositions, trace elements and oxygen isotopes in foraminiferal carbonate, as well as alkenone unsaturation ratios (summary by MIX et al. 2001; and see below). Qualitative SST changes have been derived previously from the relative abundances of certain *Gephyrocapsa* species (WEAVER & PUJOL 1988; TAKAHASHI & OKADA 2000). Observed down-core patterns were consistent with the expected glacial-interglacial temperature variability, reflecting decreased temperatures during glacial periods.

Recently, BOLLMANN et al. (2002) introduced a global sea surface temperature calibration based on the relative abundance of different morphotypes within the coccolithophore genus *Gephyrocapsa*. The authors showed that this temperature transfer function has potential for the reconstruction of paleotemperatures in the temperature range from 14.0°C to 29.4°C. The standard error of 1.78°C is comparable to that of foraminifera transfer functions. The use of this temperature transfer function as an additional palaeo-thermometer for the late Pleistocene and Holocene was most recently been applied and validated in sediments off NW Africa (HENDERICKS & BOLLMANN 2004; Fig. 10). A good correspondence was found between the *Gephyrocapsa*-based and alkenone-derived palaeotemperatures. Both data sets indicate a glacial drop in SST of about 3°C compared to Holocene values. Similar results come from the Mg/Ca palaeotemperature record, although consistently cooler temperatures were inferred from this proxy. Largest discrepancies, both in terms of down-core amplitude changes and same-age temperature estimates, were found with available planktic foraminiferal data (Fig. 10). This was mainly attributed to differences in the season of production, ecologic preferences and habitats, and/or preservation.

In addition to the down-core record, sediment samples corresponding to the Last Glacial Maximum (LGM) were analysed in order to derive palaeo-SST maps off Northwest Africa. The authors found lowest glacial temperatures (14–15.5°C) offshore Morocco and south of the volcanic Canary Islands, likely due to intensified upwelling related to stronger trade winds. Smallest glacial-interglacial temperature fluctuations were found off Cape Blanc (2.5–4°C), and larger fluctuations (up to 6°C) occurred in the remaining region. Thus, *Gephyrocapsa*-derived temperature estimates provide support that the main activity of coastal upwelling must have migrated to the north during the LGM, away from today's perennial upwelling centre offshore Cape Blanc (21°N). Previous authors have postulated a change in direction and/or seasonality of the NE trade winds in this area.



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58

Fig. 10. – **A:** Fine fraction carbonate oxygen isotope stratigraphy of sediment core GeoB1048 off Cape Blanc. – **B:** Downcore palaeotemperature records in core GeoB 1048. Mean SST estimates based on regional and global *Gephyrocapsa* transfer functions. – **C:** SST estimates based on alkenones and planktic foraminifera, as well as the Mg/Ca ratio in foraminiferal calcite (shallow-dwelling species *G. ruber*) in BOFS core 31K (modified from HENDERICKS & BOLLMANN 2004).

The importance of coccolithophores as carbonate producers

Coccolithophores influence biogeochemical cycles and the global climate system by contributing significantly to the oceanic pumps of organic carbon (via photosynthesis) and carbonate (via calcification) and hence affect the surface ocean CO₂ balance (BRAND 1994; WESTBROEK et al. 1993; WINTER & SIESSER 1994). However, there is relatively little data on the contribution of different planktic calcifying organisms (e.g. coccolithophores, foraminifera, pteropods) to the global calcium carbonate production, but it is estimated that about 20–60% of the pelagic marine carbonate production is provided by coccoliths (e.g. MILLIMAN 1993; ZIVERI et al. 1999).

For estimation of coccolithophore carbonate a new methodology allows the conversion of coccolith flux rates into mass fluxes (BEAUFORT & HEUSSNER 1999;

YOUNG & ZIVERI 2000). Thereby, the carbonate mass estimate includes a given shape factor of coccolith types, the density of calcite, and the average length of a species.

Calculation of the global ocean carbonate budget includes carbonate production, accumulation, and dissolution, but published estimations of the carbonate budget vary widely. The quantity of biogenic carbonate produced annually in the surface ocean broadly is in the order of 1.0–1.3 gigatons (WESTBROEK et al. 1993), from which about 85% dissolves in the water column or at the sediment-water interface. Other authors assume that about 60% of the carbonate accumulates in sediments, whereas the remaining 40% are dissolved (MILLIMAN 1993). Information on the ocean-floor distribution of carbonate, which is the main component of deep-sea sediments above the lysocline, is already available (ARCHER 1996). Reliable estimates as to the relative proportions of the various pelagic carbonate producers,

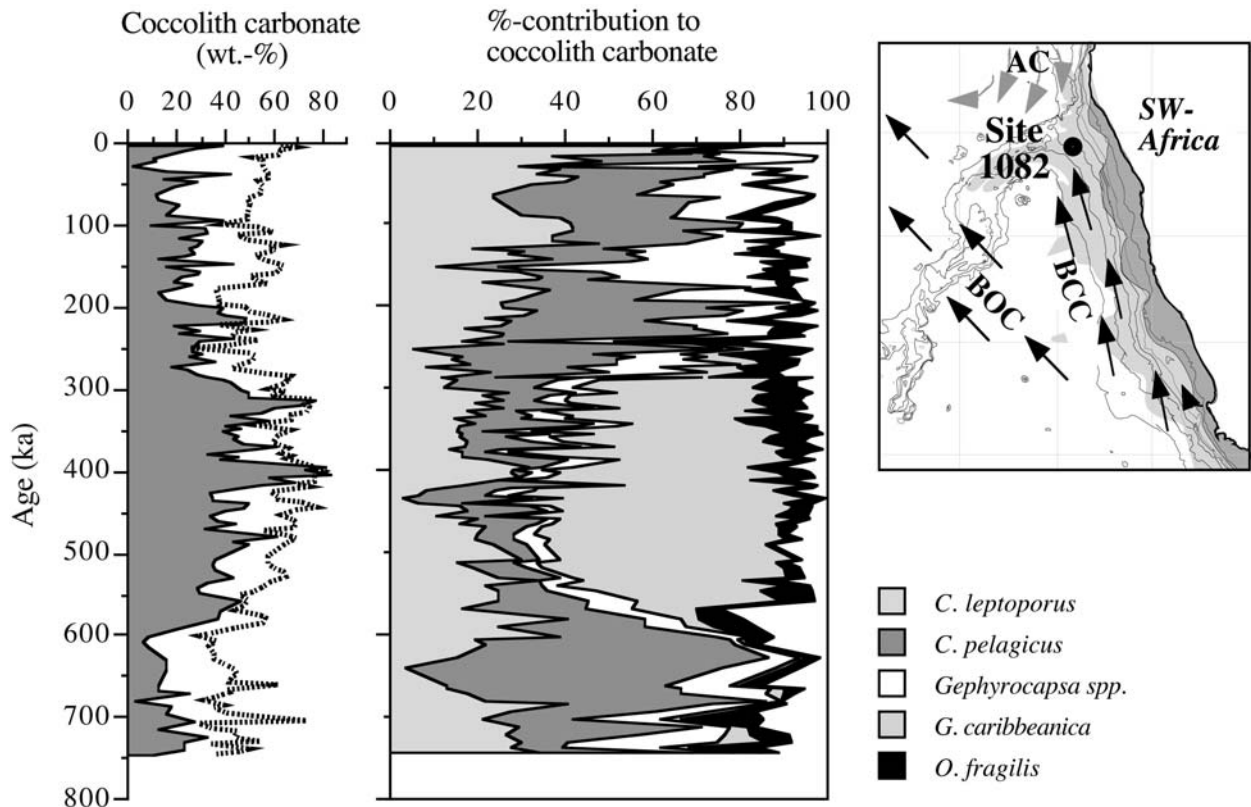


Fig. 11. Absolute coccolith carbonate content (wt-%; dotted line – total carbonate content) and %-contribution of the dominant coccolith carbonate producing species (modified from BAUMANN & FREITAG 2004). Besides a few rather massive species such as *C. leptoporus* and *C. pelagicus*, the numerically important gephyrocapsids, i.e. *G. caribbeanica*, likely produce a relatively high proportion of the coccolith carbonate.

however, are still sparse (e.g. GIRAUDEAU et al. 2000; SCHIEBEL et al. 2002; BAUMANN et al. 2004a, b). Recent studies on South Atlantic surface sediments clearly reveal a variable pattern of carbonate sedimentation and accumulation for planktic foraminifera and coccolithophores, respectively (BAUMANN et al. 2004a). Whilst coccolith carbonate dominates the oligotrophic gyres of the South Atlantic, carbonate produced by planktic foraminifera is more important in more fertile, mesotrophic to eutrophic areas, such as the equatorial divergence zone. Mass estimates of coccolith carbonate burial in surface sediments of the South Atlantic document coccoliths to be major carbonate contributors in most mid-Atlantic Ridge sediments, exceeding up to 70 wt-%. In contrast to these oligotrophic areas, they are of minor importance in sediments accumulating on the continental margins, here accounting for only a fifth of the carbonate fraction.

Moreover, based on estimates of mean coccolith masses, species-specific coccolith carbonate was calculated for the South Atlantic Ocean (BAUMANN et al. 2004b). Even though absolute numbers of most species, particularly of *Oolithotus fragilis*, *Rhabdosphaera clavigera*, *Coccolithus pelagicus*, and *Helicosphaera carteri*, are many times lower than total numbers of *Emiliana huxleyi*, these subordinate massively calcifying

species contribute most to coccolith carbonate. Despite the large cell numbers generated by *E. huxleyi* and *F. profunda*, as single species they are of minor importance to coccolithophore carbonate production. Although absolute accumulation of coccolith carbonate in upwelling regions is estimated to be about three times higher than in the oligotrophic gyres, the latter areas are about 5 to 10 times larger. This means that total accumulation of coccolith-carbonate in oligotrophic areas exceeds by far that of the upwelling regimes, and is therefore important with respect to the geological archive.

Coccoliths also build up the dominant part of the total carbonate in the Pleistocene as shown for Site 1082 off SW-Africa (BAUMANN & FREITAG 2004) where they constitute a significant fraction of the carbonate content during most of the last 680ka (Fig. 11). Only few species significantly contribute to the coccolith carbonate. The relatively massive species *C. leptoporus* and *C. pelagicus* as well as the numerically dominant gephyrocapsids are the most important contributors. The calculated coccolith carbonate content is obviously linked to the bulk carbonate record and, therefore, is indicative for the development of the productivity regime of this area.

The dominance of coccolith carbonate of up to >80 wt-% (>95% of the total carbonate) during the mid-Brunhes time (580 to 280 ka) indicate that a change in

the productivity of the northern Benguela upwelling system have occurred. This time interval is characterised by a significant increase in carbonate (total as well as in coccolith derived CaCO_3) that is associated with the appearance of *Gephyrocapsa caribbeanica* (Fig. 11). Before and after this event the carbonate is clearly more diluted by other components such as biogenic opal, organic carbon, and terrigenous matter. For Site 1082, these bulk proxies indicate a decline in absolute rates of productivity for the past 580 ka (BAUMANN & FREITAG 2004). However, from the present data it is obvious that fluctuations and total amount of productivity remained on a very low level only during the *G. caribbeanica* interval whereas it slightly increased after about 280 ka. *G. caribbeanica* seems to be a good equivalent to the modern cosmopolitan species *E. huxleyi*, an assumption mainly based on its dominance and global distribution. Therefore it can be concluded, that the distribution of this species seems to be relatively independent both of water temperature and nutrient level, although its extremely high numbers also point to at least seasonally nutrient-enriched subpolar to subtropical waters, and to the fact that they most probably are bloom-forming coccolithophores. Nevertheless, its significance for carbonate burial during the mid-Brunhes time interval is conspicuous.

Sea surface temperature reconstructions by alkenones

In addition to work on floristic analysis, geochemical palaeo-proxies based on coccolithophorid-derived material have become increasingly important, notably alkenone palaeothermometry. The history of coccolithophore biomarker research is not as straight forward as one might think, but started with the detection of a series of novel long chain ketones in sediments from the Walvis Ridge, commonly referred to as long chain alkenones (LCA) (BOON et al. 1978). Two years later their structure was confirmed and the biosynthesis of these molecules was detected in cultures of the extant coccolithophore species *Emiliania huxleyi* (VOLKMAN et al. 1980). Further studies of Prymnesiophyceae showed,

that LCAs are common among several species of the order Isochrysidales, and that the unsaturation pattern observed among them is related to growth temperature (MARLOWE et al. 1984; Fig. 12).

In a subsequent study (BRASSELL et al. 1986) demonstrated that the unsaturation index of LCAs, the so called U_{37}^K index co-varied with stable oxygen isotope values ($\delta^{18}\text{O}$) of planktic foraminifera in a Quaternary sediment core, indicating, that this might be a new proxy for reconstructing past sea surface temperatures (SST). The original unsaturation index included the di-, tri-, and tetraunsaturated C37-Methylketones:

$$U_{37}^k = \frac{(C_{37:2} - C_{37:4})}{(C_{37:2} + C_{37:3} + C_{37:4})}$$

Since tetra-unsaturated methylketones are relatively rare in most oceanic sediments, only occur in high latitudes and areas of reduced salinities, this unsaturation index was simplified to the so called

$$U_{37}^{K'} = \frac{(C_{37:2})}{(C_{37:2} + C_{37:3})}$$

The calibration of $U_{37}^{K'}$ against temperature on particulate organic matter from the Pacific and Atlantic Ocean as well as in laboratory cultures of *E. huxleyi* provided the first paleo-SST transfer function based on these new biomarkers (Fig. 12). Since then, this method has been widely applied in Late Quaternary paleoceanographic research.

This approach was further validated by a core-top calibration using a large globally distributed dataset (MÜLLER et al. 1998; Fig. 12). Within this study the highest correlation between $U_{37}^{K'}$ and annual mean sea-surface temperature was found and the linear regression yielded an equation, that was almost identical to the one found by (PRAHL & WAKEHAM 1987). The fact, that $U_{37}^{K'}$ is used as a proxy for annual mean temperature, might be a little surprising, given the strong seasonality in coccolithophore production (BIJMA et al. 2001). Therefore shifts in seasonality have to be taken into account, especially in comparison with other SST-proxies (NÜRNBERG et al. 2000). Coccolithophore production is highest during colder seasons in tropical and subtropical environments, and during warmer seasons in high latitudes (BIJMA et al. 2001). However, this is not reflected

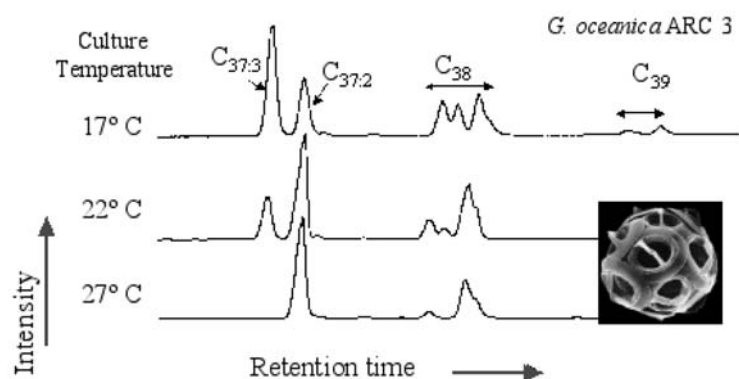
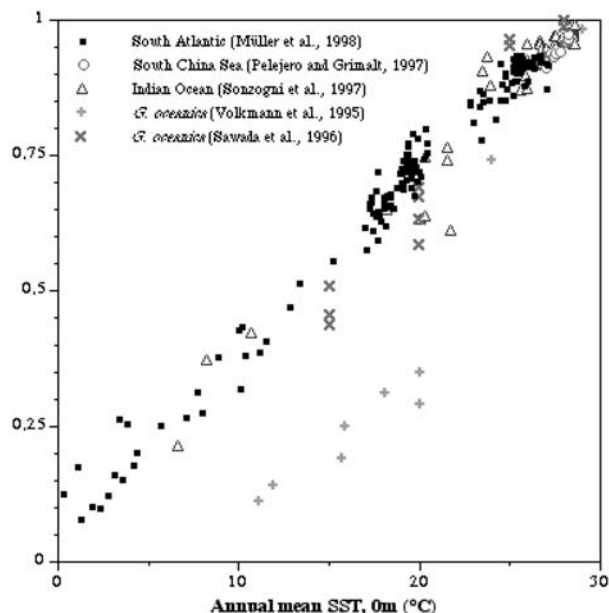


Fig. 12. Partial gas chromatograms of the long-chain, unsaturated alkenone compositions measured in cultures of *G. oceanica* (strain ARC 3) grown isothermally in batch cultures at three different temperatures (KINKEL unpubl. data).

1 in the global core-top calibration of $U_{37}^{K'}$ and SST. Moreover, the comparison between $U_{37}^{K'}$ and production weighted SST, which takes into account primary productivity seasons (MÜLLER et al. 1998), does not provide a better fit than annual SST.

2 The calibration of core-top sediments is assumed to be valid between 60°N and 60°S, since data from higher latitudes do not fit the linear trend. Several studies have tried to improve the method in higher latitudes (SIKES & VOLKMAN 1993; ROSELL-MELÉ et al. 1995), but it appears, that factors other than temperature might influence the $U_{37}^{K'}$ index in cold waters. The application of the method to Late Quaternary sediments in the northern North Atlantic clearly demonstrated, that other mechanisms than temperature must be acting on the unsaturation degree of LCAs, and it was speculated that salinity might be one influencing component (ROSELL-MELÉ et al. 2002). Besides the cold end of the calibration, there is no linear response of $U_{37}^{K'}$ to SST at temperatures above 27°C (PELEJERO & GRIMALT 1997; SONZOGNI et al. 1997), which has been taken into account for studies in tropical regions (PELEJERO et al. 1999). In addition, several regional calibrations were set up which provided different $U_{37}^{K'}$ -SST equations, especially along the California margin and in the Mediterranean (HERBERT et al. 1998; TERNOIS et al. 1997).

3 Besides the apparent robust calibrations of core-tops (Fig. 13), serious doubts arose from various culture studies and investigations of particulate organic matter in the water column, that yielded $U_{37}^{K'}$ -temperature relationships, that were not in line with the original equation



4 Fig. 13. Relationships between $U_{37}^{K'}$ and annual mean SST (0 m) for surface sediments from the global ocean (own compilation). The obtained global core-top calibration ($U_{37}^{K'} = 0.033 T + 0.044$) of MÜLLER et al. (1998) is absolutely identical to the *E. huxleyi* equation of PRAHL & WAKEHAM (1987).

of PRAHL & WAKEHAM (1987) and the global core-top data of MÜLLER et al. (1998). Laboratory culture experiments with *Gephyrocapsa oceanica* pointed towards species specific $U_{37}^{K'}$ -temperature relationships as the cause for deviations from the original calibration (VOLKMAN et al. 1995). However, similar results were found in cultures of both *E. huxleyi* and *G. oceanica*, with no consistent pattern arising, that could be attributed to one of them (CONTE et al. 1995; SAWADA et al. 1996; CONTE et al. 1998). In particular, the comparison of $U_{37}^{K'}$ values and the species composition of Late Quaternary nannofossil assemblages show no influence of species composition on the climatic signal that is incorporated in the biomarkers (MÜLLER et al. 1997; VIL-LANUEVA et al. 2002).

5 Although there is some evidence for a diagenetic alteration of the $U_{37}^{K'}$ signal depending on the degradation rate of organic matter during early sedimentary burial (e.g. HOEFS et al. 1998), this process might only be taken into account in environments where redox parameters fluctuate strongly over time, which is not likely in open marine sediments. Recently it has been shown, that LCAs might be suspect to re-sedimentation and lateral advection (BENTHIE & MÜLLER 2000) which could distort the temperature reconstruction locally, and even more lead to temporal offsets between planktic foraminifera (or other microfossils) and biomarkers of several thousand years within the same sample (OHKOUCHI et al. 2002).

6 LCAs have a fossil record that date back to the early Cretaceous. However, it is not known, which group of coccolithophores can be assigned to LCA biosynthesis in the Cretaceous. For younger time intervals alkenones in the open marine environment are most likely produced by members of the order *Isochrydales*, with the genera *Reticulofenestra*, *Gephyrocapsa* and *Emiliania* being the dominating coccolithophores in most nannoplankton assemblages since the Eocene. The rise of the genus *Reticulofenestra* in the Eocene coincides with a general change in the unsaturation pattern of LCAs, similar to those observed in the modern ocean. Thus it is likely, that the $U_{37}^{K'}$ paleotemperature approach can be applied for the last 50 Ma. To date the longest time series of $U_{37}^{K'}$ temperatures extends back into the Pliocene (MARLOW et al. 2000), but failed in older sediments, most likely due to strong diagenesis in open marine settings (PAGANI et al. 1999).

7 Future perspectives

8 In recent years, the information on coccolithophore biology has increased considerably. Culture tests have provided evidence that coccolith morphology is rather stable if tested under different ecological parameters and hence under strong genetic control (for details see GEISEN et al. 2004). Nevertheless, many ecological questions to newly evolved species remain unsolved. In addition, ecophenotypic variability cannot be excluded

in nature. Consequently, the details of palaeoenvironmental and -oceanographical reconstructions have not really been extended.

An increasing need therefore is the determination of present-day biogeographical distribution patterns as well as their comparison to external controls in terms of biogeography, trophic level and seasonal succession. Thus, more data on the variability of coccolithophores in both species numbers and composition are useful for the identification of environmental tracers and to add to the palaeoecological meaning of some of the coccolithophorid species. In addition, more information from sediment trap studies are needed to better understand the transformation of a living coccolithophorid community in the plankton into a coccolith assemblage of the underlying deep-sea sediments.

Analysis of coccoliths in sediment cores give useful information about the location of different water masses in the past and consequently about the palaeoecology and palaeoceanography in this area. However, there still is a lack in understanding the controls on the coccolithophores as part of the total phytoplankton primary production in order to use the record of coccolith production as a primary productivity proxy.

For paleoceanographical reconstructions in general, the calcium carbonate shells produced by foraminifera have been widely used, whereas knowledge of the potential of coccolith calcite as a recorder of geochemical proxies is poor. Yet, within the last years a number of studies have taken up promising approaches that try to explore geochemical composition and isotope studies in coccoliths (ZIVERI et al. 2003; STOLL & ZIVERI 2004). The huge potential of coccoliths in stable oxygen and carbon isotopes was already demonstrated twenty years ago, when it was shown, that fractionation affects in coccoliths are much larger than those in planktonic foraminifera (DUDLEY et al. 1986). However, the difficulty to separate coccoliths from bulk sediments and process monospecific samples, have hampered the geochemical proxy evaluation and application of coccoliths. With a modified settling method STOLL & ZIVERI (2002) partly overcame this problem and provided a feasible method to measure geochemical and stable isotope composition of near monospecific coccolith assemblages. Already this approach was applied to Late Quaternary and Paleogene sediments, with promising results from Sr/Ca ratios in coccoliths, which should provide a growth rate proxy for coccolithophores (STOLL et al. 2002).

In addition to the methods mentioned above, compound specific carbon isotopes of coccolithophorid-derived alkenones can be used to reconstruct the p CO₂ conditions of surface waters in which they grew. Although this method has been applied to Miocene sediment sequences (PAGANI et al. 1999), serious problems result from the fact, that carbon isotope fractionation are not only a function of p CO₂, but are influenced by other parameters like cell geometry and growth rate, which

are difficult to assess from the fossil record (e. g. BENTH-IEN et al. 2002). Therefore, we need to combine geochemical assessments of coccolithophorid growth rates, stable carbon isotopes in coccolith calcite and morphometry to narrow the large uncertainties that still prohibit exact p CO₂ reconstructions.

Acknowledgements

We are grateful to many unnamed individuals who have helped with sample preparation, discussions, comments, and data. The paper has benefited from constructive comments by JEREMY YOUNG (NHM, London) and PATRIZIA ZIVERI (VUA, Amsterdam).

References

- AHAGON, N.; TANAKA, Y. & UJIE, H. 1993. *Florisphaera profunda*, a possible nannoplankton indicator of late Quaternary changes in sea-water turbidity at the northwestern margin of the Pacific. – *Marine Micropaleontology* **22**: 255–273.
- ANDRULEIT, H. 1997. Coccolithophore fluxes in the Norwegian-Greenland Sea: seasonality and assemblage alterations. – *Marine Micropaleontology* **31**: 45–64.
- ANDRULEIT, H.; ROGALLA, U.; STÄGER, S.; BRUNS, A. in press. From living communities to fossil assemblages: origin and fate of coccolithophores in the northern Arabian Sea. – *Micropaleontology*.
- ANDRULEIT, H. & ROGALLA, U. 2002. Coccolithophores in surface sediments of the Arabian Sea in relation to environmental gradients in surface waters. – *Marine Geology* **186**: 505–526.
- ANDRULEIT, H.; STÄGER, S.; ROGALLA, U. & CEPEK, P. 2003. Living coccolithophores in the northern Arabian Sea: ecological tolerances and environmental control. – *Marine Micropaleontology* **49**: 157–181.
- ANDRULEIT, H.A.; VON RAD, U.; BRUNS, A. & ITTEKKOT, V. 2000. Coccolithophore fluxes from sediment traps in the northeastern Arabian Sea off Pakistan. – *Marine Micropaleontology* **38**: 285–308.
- ARCHER, D.E. 1996. An atlas of the distribution of calcium carbonate in sediments of the deep sea. – *Global Biogeochem Cycles* **10** (1): 159–174.
- BANSE, K. & MCCLAIN, C.R. 1986. Winter blooms of phytoplankton in the Arabian Sea as observed by the coastal zone color scanner. – *Marine Ecology, Progress Series* **34**: 201–211.
- BASSINOT, F.C.; BEUFORT, L.; VINCENT, E. & LABEYRIE, L. 1997. Changes in the dynamics of western equatorial Atlantic surface currents and biogenic productivity at the “Mid-Pleistocene Revolution” (930 ka). – In: SHACKLETON, N.J.; CURRY, W.B.; RICHTER, C. & BRALOWER, T. J., eds., *Proceedings of the Ocean Drilling Program, Scientific Results*: 269–284, College Station, TX (Ocean Drilling Program).
- BAUMANN, K.-H. 1995. Morphometry of Quaternary *Coccolithus pelagicus* coccoliths from northern North Atlantic and its paleoceanographical consequences. – In: FLORES, J.A. & SIERRA, F.J., eds., *5th International Nannoplankton Association Conference in Salamanca Proceedings*: 11–21.
- BAUMANN, K.-H. & FREITAG, T. 2004. Pleistocene fluctuations in the northern Benguela Current system as revealed by coccolith assemblages. – *Marine Micropaleontology*.
- BAUMANN, K.-H.; ANDRULEIT, H. & SAMTLEBEN, C. 2000. Coccolithophores in the Nordic Seas: Comparison of living communities with surface sediment assemblages. – *Deep-Sea Research II* **47**: 1743–1772.
- BAUMANN, K.-H.; BÖCKEL, B. & FRENZ, M. 2004b. Coccolith contribution to South Atlantic carbonate sedimentation. – In: THIERSTEIN, H.R. & YOUNG, J.R., eds., *Coccolithophores – From molecular processes to global impact*: 367–402, Berlin (Springer).

- 1 BAUMANN, K.-H.; CEPEK, M. & KINKEL, H. 1999. Coccolithophores as
2 indicators of ocean water masses, surface-water temperature, and
3 paleoproductivity – Examples from the South Atlantic. – In:
4 FISCHER, G. & WEFER, G., eds., Use of proxies in paleoceanog-
5 raphy: Examples from the South Atlantic: 117–144, Berlin
6 (Springer).
- 7 BAUMANN, K.-H.; BÖCKEL, B.; DONNER, B.; GERHARDT, S.; HENRICH,
8 R.; VINK, A.; VOLBERS, A.; WILLEMS, H. & ZONNEVELD, K.A.F.
9 2004a. Contribution of calcareous plankton groups to the carbon-
10 ate budget of South Atlantic surface sediments. – In: WEFER, G.;
11 MULITZA, S. & RATMEYER, V., eds., The South Atlantic in the
12 Late Quaternary: reconstructions of material budget and current
13 systems: 81–99, Berlin (Springer).
- 14 BEAUFORT, L.; LANCELOT, Y.; CAMBERLIN, P.; CAYRE, O.; VINCENT,
15 E.; BASSINOT, F. & LABEYRIE, L. 1997. Insolation cycles as a ma-
16 jor control of Equatorial Indian Ocean Primary Production. –
17 Science **278**: 1451–1454.
- 18 BEAUFORT, L. & HEUSSNER, S. 1999. Coccolithophorids on the conti-
19 nental slope of the Bay of Biscay – production, transport and con-
20 tribution to mass fluxes. – Deep-Sea Research II **46**: 2147–2174.
- 21 BENTHIE, A. & MÜLLER, P.J. 2000. Anomalously low alkenone tem-
22 peratures caused by lateral particle and sediment transport in the
23 Malvinas Current region, western Argentine Basin. – Deep-Sea
24 Research I **47**: 2369–2393.
- 25 BENTHIE, A.; ANDERSEN, N.; SCHULTE, S.; MÜLLER, P.J.; SCHNEI-
26 DER, R.R. & WEFER, G. 2002. Carbon isotopic composition of the
27 C37:2 alkenone in core top sediments of the south atlantic ocean.
28 Effects of CO₂ and nutrient concentrations. – Global Biogeo-
29 chemical Cycles **16** (1): 1012, doi: 10.1029/2001GB001433.
- 30 BIJMA, J.; ALTABET, M.; CONTE, M.; KINKEL, H.; VERSTEEGH, G.J.M.;
31 VOLKMAN, J.K.; WAKEHAM, S.G. & WEAVER, P.P.E. 2001. Pri-
32 mary signal: Ecological and environmental factors. – Report from
33 Working Group 2, Geochemistry, Geophysics, Geosystems **2**:
34 2000GC000051.
- 35 BILLARD, C. 1994. Life cycles. – In: GREEN, J.C. & LEADBEATER, B.S.C.,
36 eds., The Haptophyte Algae: 167–186, Oxford (Clarendon Press).
- 37 BILLARD, C. & INNOUYE, I. 2004. What is new in coccolithophore bio-
38 logy? – In: THIERSTEIN, H.R. & YOUNG, J.R., eds., Coccolitho-
39 phores – From molecular processes to global impact: 1–29,
40 Berlin (Springer).
- 41 BOLLMANN, J.; HENDERIKS, J. & BRABEC, B. 2002. Global calibration
42 of *Gephyrocapsa* coccolith abundance in Holocene sediments for
43 paleotemperature assessment. – Paleoceanography **17**: 10.1029/
44 2001PA001433.
- 45 BOON, J.J.; VAN DER MEER, F.W.; SCHUYL, P.J.W.; DE LEEUW, J.W.;
46 SCHENK, P.A. & BURLINGAME, A.L. 1978. Organic geochemical
47 analysis of core samples from Site 362, Walvis Ridge, DSDP Leg
48 40. – In: BOLLI, H.M. & RYAN, W.B.F., eds., Initial Reports
49 DSDP Leg 40: 627–637, Washington D.C. (U.S. Government
50 Printing Office).
- 51 BOWN, P.R. 1998. Calcareous nannofossil biostratigraphy. – 315 pp.,
52 London (Chapman & Hall).
- 53 BOWN, P.; LEES, J.A. & YOUNG, J.R. 2004. Calcareous nannoplankton
54 evolution and diversity through time. – In: THIERSTEIN, H.R. &
55 YOUNG, J.R., eds., Coccolithophores – From molecular processes
56 to global impact: 481–508, Berlin (Springer).
- 57 BRAND, L.E. 1981. Genetic variability in reproduction rates in marine
58 phytoplankton populations. – Evolution **38**: 1117–1127.
- 59 BRAND, L.E. 1982. Genetic variability and spatial patterns of genetic
60 differentiation in the reproductive rates of the marine coccolitho-
61 phores *Emiliania huxleyi* and *Gephyrocapsa oceanica*. – Limnol-
62 ogy and Oceanography **27**: 236–245.
- 63 BRAND, L.E. 1994. Physiological ecology of marine coccolithophores.
64 – In: WINTER, A. & SIESSER, W.G., eds., Coccolithophores: 39–
65 49, Cambridge (Cambridge University Press).
- 66 BRASSELL, S.C.; EGLINTON, G.; PFLAUMANN U. & SARNTHEIN, M.
67 1986. Molecular stratigraphy: a new tool for climatic assessment.
68 – Nature **320**: 129–133.
- 69 CONTE, M.H.; THOMPSON, A.; EGLINTON, G. & GREEN, J.C. 1995. Lipid
70 biomarker diversity in the coccolithophorid *Emiliania huxleyi*
71 (Prymnesiophyceae) and the related species *Gephyrocapsa oce-
72 anica*. – Journal of Phycology **31**: 272–282.
- 73 CONTE, M.H.; THOMPSON, A.; LESLEY, D. & HARRIS, R.P. 1998. Ge-
74 netic and physiological influences on the alkenone/alkenoate ver-
75 sus growth temperature relationship in *Emiliania huxleyi* and
76 *Gephyrocapsa oceanica*. – Geochimica et Cosmochimica Acta
77 **62** (1): 51–68.
- 78 CORTÉS, M.Y. (2000). Further evidence for the heterococcolith-holococ-
79 colith combination *Calcidiscus leptoporus*-*Crystallolithus rig-
80 idus*. – Marine Micropaleontology **39**: 35–37.
- 81 CROS, L.; KLEJNE, A.; ZELTNER, A.; BILLARD, C. & YOUNG, J. R.
82 2000. New examples of holococcolith-heterococcolith combina-
83 tion coccospheres and their implications for coccolithophorid bi-
84 ology. – Marine Micropaleontology **39**: 1–34.
- 85 DUDLEY, W.C.; BLACKWELDER, P.; BRAND, L. & DUPLESSY, J.C. 1986.
86 Stable isotopic composition of coccoliths. – Marine Micropale-
87 ontology **10**: 1–8.
- 88 EDVARDSEN, B.; EIKREM, W.; GREEN, J.C.; ANDERSEN, R.A.; YEO
89 MOON-VAN DER STAAY, S. & MEDLIN, L.K. 2000. Phylogenetic
90 reconstructions of the Haptophyta inferred from 18S ribosomal
91 DNA sequences and available morphological data. – Phycologia
92 **39**: 19–35.
- 93 FUJIWARA, S.; TSUZUKI, M.; KAWACHI, M.; MINAKA, N. & INOUE, I.
94 2001. Molecular phylogeny of the haptophyta based on the *rbcl*
95 gene and sequence variation in the spacer region of the RUBIS-
96 CO operon. – Journal of Phycology **37**: 121–129.
- 97 GEISEN, M.; BILLARD, C.; BROERSE, A.T.C.; CROS, L.; PROBERT, I. &
98 YOUNG, J.R. 2002. Life-cycle associations involving pairs of
99 holococcolithophorid species: intraspecific variation or cryptic
100 speciation? – European Journal of Phycology **37**: 531–550.
- 101 GEISEN, M.; YOUNG, J.R.; PROBERT, I.; SÁEZ, A.G.; BAUMANN, K.-H.;
102 BOLLMANN, J.; CROS, L.; DE VARGAS, C.; MEDLIN, L.K. &
103 SPRENGEL, C. 2004. Species level variation in coccolithophores.
104 – In: THIERSTEIN, H.R. & YOUNG, J.R., eds., Coccolithophores –
105 From molecular processes to global impact: 327–366, Berlin
106 (Springer).
- 107 GEITZENAUER, K.R.; ROCHE, M.B. & MCINTYRE, A. 1977. Coccolith
108 biogeography from North Atlantic and Pacific surface sediments.
109 – In: RAMSAY, A.T.S., ed., Oceanic Micropaleontology: 973–
110 1008, London (Academic Press).
- 111 GIRAudeau, J. 1992. Distribution of Recent nannofossil beneath the
112 Benguela system: southwest African continental margin. – Marine
113 Geology **108**: 219–237.
- 114 GIRAudeau, J.; BAILEY, G.W. & PUJOL, C. 2000. A high-resolution
115 time-series analyses of particle fluxes in the northern Benguela
116 coastal upwelling system: carbonate record of changes in produc-
117 tion and particle transfer processes. – Deep-Sea Research II **47**:
118 1999–2028.
- 119 HARRIS, R.P. 1994. Zooplankton grazing on the coccolithophore *Emil-
120 ianiana huxleyi* and its role in inorganic carbon flux. – Marine Biol-
121 ogy **119**: 431–439.
- 122 HAY, W.W. 2004. Carbonate fluxes and calcareous nannoplankton. – In:
123 THIERSTEIN, H.R. & YOUNG, J.R., eds., Coccolithophores – From
124 molecular processes to global impact: 509–528, Berlin (Springer).
- 125 HENDERICKS, J. & BOLLMANN, J. 2004. The *Gephyrocapsa* sea surface
126 palaeothermometer put to the test: comparison with alkenone and
127 foraminifera proxies off NW Africa. – Marine Micropaleontology
128 **50**: 161–184.
- 129 HENRIKSON, A.S. 2000. Coccolithophore response to oceanographic
130 changes in the equatorial Atlantic during the last 200,000 years.
131 – Palaeogeography, Palaeoclimatology, Palaeoecology **156**:
132 161–173.
- 133 HERBERT, T.D.; SCHUFFERT, J.D.; THOMAS, D.; LANGE, C.; WEINHE-
134 IMER, A.; PELEO-ALAMPAY, A. & HERGUERA, J.-C. 1998. Depth
135 and seasonality of alkenone production along the California mar-
136 gin inferred from a core top transect. – Paleoceanography **13** (3):
137 263–271.
- 138 HOEFS, M.J.L.; VERSTEEGH, G.J.M.; RIJSTRA, W.I.C.; DE LEEUW,
139 J.W. & SINNINGHE DAAMSTE, J.S. 1998. Postdepositional oxic

- degradation of alkenones: Implications for the measurements of paleo sea surface temperatures. – *Paleoceanography* **13** (1): 42–49.
- HOUDAN, A.; BILLARD, C.; MARIE, D.; NOT, F.; SÁEZ, A.G.; YOUNG, J.R. & PROBERT, I. 2003. Flow cytometric analysis of relative ploidy levels in holococcolithophore-heterococcolithophore (Haptophyta) life cycles. – *Systematics and Biodiversity* **1** (4): 453–465.
- HONJO, S. 1976. Coccoliths: production, transportation and sedimentation. – *Marine Micropaleontology* **1**: 65–79.
- HONJO, S. 1980. Material fluxes and modes of sedimentation in the mesopelagic and bathypelagic zones. – *Journal of Marine Research* **38** (1): 53–97.
- HOUGHTON, S.D. 1988. Thermocline control on coccolith diversity and abundance in recent sediments from the Celtic Sea and English Channel. – *Marine Geology* **83**: 313–319.
- HOUGHTON, S.D. 1991. Coccolith sedimentation and transport in the North Sea. – *Marine Geology* **99**: 267–274.
- INOUE, I. 1997. Systematics of haptophyte algae in Asia-Pacific waters. – *Algae (The Korean Journal of Phycology)* **12**: 247–261.
- JORDAN, R.W. & CHAMBERLAIN, A.H.L. 1997. Biodiversity among haptophyte algae. – *Biodiversity and Conservation* **6**: 131–152.
- KAMPTNER, E. 1927. Beitrag zur Kenntnis adriatischer Coccolithophoriden. – *Archiv für Protistenkunde* **58**: 173–184.
- KINKEL, H.; BAUMANN, K.-H. & CEPEK, M. 2000. Coccolithophores in the equatorial Atlantic Ocean: Response to seasonal and Late Quaternary surface water variability. – *Marine Micropaleontology* **39**: 87–112.
- KLEJNE, A.; KROON, D. & ZEVENBOOM, W. 1989. Phytoplankton and foraminiferal frequencies in Northern Indian Ocean and Red Sea surface waters. – *Netherlands Journal of Sea Research* **24**: 531–539.
- LOHMANN, H. 1902. Die Coccolithophoridae, eine Monographie der Coccolithen bildenden Flagellaten, zugleich ein Beitrag zur Kenntnis des Mittelmeerauftriebs. – *Archiv für Protistenkunde* **1**: 89–165.
- MARLOW, J.R.; LANGE, C.B.; WEFER, G. & ROSELL-MELÉ, A. 2000. Upwelling intensification as part of the Pliocene-Pleistocene climate transition. – *Science* **290**: 2288–2291.
- MARLOWE, I.T.; GREEN, J.C.; BRASSELL, S.C.; EGLINTON, G. & COURSE, P.A. 1984. Long chain (n-C₃₇-C₃₉) alkenones in the Prymnesiophyceae. Distribution of alkenones and other lipids and their taxonomic significance. – *British Phycological Journal* **19** (3): 203–216.
- MCINTYRE, A. 1967. Coccoliths as paleoclimatic indicators of Pleistocene glaciation. – *Science* **158**: 1314–1317.
- MCINTYRE, A. & BÉ, A. 1967. Modern Coccolithophoridae in the Atlantic Ocean. I. Placoliths and crytholiths. – *Deep-Sea Research* **14**: 561–597.
- MCINTYRE, A. & MOLFINO, B. 1996. Forcing of Atlantic equatorial and subpolar millennial cycles by precession. – *Science* **274**: 1867–1870.
- MEDLIN, L.K.; KOOISTRA, W.H.C.F.; POTTER, D.; SAUNDERS, J.B. & ANDERSEN, R.A. 1997. Phylogenetic relationships of the “golden algae” (haptophytes, heterokont chromophytes) and their plastids. – *Plant Systematics and Evolution, Supplement* **11**: 187–219.
- MILLIMAN, J.D. 1993. Production and accumulation of calcium carbonate in the ocean: budget of a non steady state. – *Global Biogeochemical Cycles* **7** (4): 927–957.
- MILLIMAN, J.D.; TROY, P.J.; BALCH, W.M.; ADAMS, A.K.; LI, Y.-H. & MACKENZIE, F.T. 1999. Biologically mediated dissolution of calcium carbonate above the chemical lysocline? – *Deep-Sea Research I* **46**: 1653–1669.
- MIX, A.; BARD, E. & SCHNEIDER, R.R. 2001. Environmental processes of the Ice Age: Land, Oceans, Glaciers (EPILOG). – *Quaternary Science Reviews* **20**: 627–657.
- MOLFINO, B. & MCINTYRE, A. 1990. Precessional forcing of nutricline dynamics in the equatorial Atlantic. – *Science* **249**: 766–769.
- MÜLLER, P.J.; CEPEK, M.; SCHNEIDER, R. & RUHLAND, G. 1997. Alkenone and coccolithophorid changes in Late Quaternary sediments from the Walvis Ridge: Implications for the alkenone paleotemperature method. – *Palaeogeography, Palaeoclimatology, Palaeoecology* **135**: 71–96.
- MÜLLER, P.J.; KIRST, G.; RUHLAND, G.; VON STORCH, I. & ROSELL-MELÉ, A. 1998. Calibration of the alkenone paleotemperature index U₃₇^k based on core-tops from the eastern South Atlantic the global ocean (60°N-60°S). – *Geochimica et Cosmochimica Acta* **62** (10): 1757–1772.
- MURRAY, G. & BLACKMAN, V.H. 1898. On the nature of the coccospheeres and rhabdospheres. – *Philosophical Transactions of the Royal Society (B)* **190**: 427–441.
- NÜRNBERG, D.; MÜLLER, P. & SCHNEIDER, R.R. 2000. Paleo sea-surface temperature calculations in the equatorial East Atlantic from Mg/Ca ratios in planktic foraminifera; a comparison to sea-surface temperature estimates from U₃₇^k, oxygen isotopes, and foraminiferal transfer function. – *Paleoceanography* **15** (1): 124–134.
- OKADA, H. & HONJO, S. 1973. The distribution of oceanic coccolithophorids in the Pacific. – *Deep-Sea Research* **20**: 355–374.
- OKADA, H. & MATSUOKA, M. 1996. Lower-photoc nannoflora as an indicator of the late Quaternary monsoonal paleo-record in the tropical Indian Ocean. – In: MOGOULEVSKY, A. & WHATLEY, A.M., eds., *Microfossils and Oceanic Environments*: 231–245, Aberystwyth (Aberystwyth Press).
- OHKOCHI, N.; EGLINTON, T.I.; KEIGWIN, L.D. & HAYES, J.M. 2002. Spatial and temporal offsets between proxy records in a sediment drift. – *Science* **298**: 1224–1227.
- PAGANI, M.; ARTHUR, M.A. & FREEMAN, K.H. 1999. Miocene evolution of atmospheric carbon dioxide. – *Paleoceanography* **14** (3): 273–292.
- PARKE, M. & ADAMS, I. 1960. The motile (*Crystallolithus hyalinus* Gaarder & Markali) and non-motile phases in the life history of *Coccolithus pelagicus* (Wallich) Schiller. – *Journal of the Marine Biological Association* **39**: 263–274.
- PELEJERO, C. & GRIMALT, J.O. 1997. The correlation between the U₃₇^k index and sea surface temperatures in the warm boundary; the South China Sea. – *Geochimica et Cosmochimica Acta* **61** (22): 4789–4797.
- PELEJERO, C.; GRIMALT, J.O.; HEILIG, S.; KIENAST, M. & WANG, L. 1999. High-resolution U₃₇^k temperature reconstructions in the South China Sea over the past 220 kyr. – *Paleoceanography* **14** (2): 224–231.
- PIENAAR, R.N. 1994. Ultrastructure and calcification of coccolithophores. – In: WINTER, A. & SIESSER, W.G., eds., *Coccolithophore*: 13–37, Cambridge (Cambridge University Press).
- PRAHL, F.G. & WAKEHAM, S.G. 1987. Calibration of unsaturation patterns in long-chain ketone compositions for paleotemperature assessment. – *Nature* **330**: 367–369.
- QUINN, P.; THIERSTEIN, H.R.; BRAND, L.E. & WINTER, A. 2003. Experimental evidence for the species character of *Calcidiscus leptoporus* morphotypes. – *Journal of Paleontology* **77** (5): 825–830.
- RIEBESELL, U.; ZONDERVAN, I.; ROST, B.; TORTELL, P.D.; ZEEBE, R.E. & MOREL, F.M.M. 2000. Reduced calcification of marine plankton in response to increased atmospheric CO₂. – *Nature* **407**: 364–367.
- RIEGMAN, R.; STOLTE, W. & NOORDELOOS, A.A.M. 1998. A model system approach to biological climate forcing: the example of *Emiliania huxleyi*. – *Netherlands Institute for Sea Research, NIOZ-Rapport* **8**: 1–32.
- ROSELL-MELÉ, A.; EGLINTON, G.; PFLAUMANN, U. & SARNTHEIN, M. 1995. Atlantic core-top calibration of the U₃₇^k index as a sea-surface palaeotemperature indicator. – *Geochimica et Cosmochimica Acta* **59**: 3099–3107.
- ROSELL-MELÉ, A.; JANSEN, E. & WEINELT, M. 2002. Appraisal of a molecular approach to infer variations in surface ocean freshwater inputs into the North Atlantic during the last glacial. From process studies to reconstruction of the palaeoenvironment. – *Advances in Palaeoceanography* **34**: 143–152, Amsterdam (Elsevier).

- ROTH, P.H. & COULBOURN, W.T. 1982. Floral and solution patterns of coccoliths in surface sediments of the North Pacific. – *Marine Micropaleontology* **7**: 1–52.
- ROWSON, J.D.; LEADBEATER, B.S.C. & GREEN, J.C. 1986. Calcium carbonate deposition in the motile (*Crystallolithus*) phase of *Coccolithus pelagicus* (Prymnesiophyceae). – *British Phycological Journal* **21**: 359–370.
- SÁEZ, A.G.; PROBERT, I.; GEISEN, M.; QUINN, P.; YOUNG, J.R. & MEDLIN, L.K. 2003. Pseudo-cryptic speciation in coccolithophores. – *Proceedings of the National Academy of Sciences* **100**: 7163–7168.
- SAWADA, K.; HANDA, N.; SHIRAIWA, Y.; DANBARA, A. & MONTANI, S. 1996. Long-chain alkenones and alkyl alkenoates in the coastal and pelagic sediments of the Northwest North Pacific, with special reference to the reconstruction of *Emiliania huxleyi* and *Gephyrocapsa oceanica* ratios. – *Organic Geochemistry* **24** (8-9): 751–764.
- SCHIEBEL, R. 2002. Planktic foraminiferal sedimentation and the marine calcite budget. – *Global Biogeochemical Cycles* **16** (4): 13/1–21.
- SIKES, E.L. & VOLKMAN, J.K. 1993. Calibration of alkenone unsaturation ratios (U_{37}^k) for paleotemperature estimation in cold polar waters. – *Geochimica et Cosmochimica Acta* **57** (8): 1883–1889.
- SONZOGNI, C.; BARD, E.; ROSTEK, F.; DOLLFUS, D.; ROSELL, M.A. & EGLINTON, G. 1997. Temperature and salinity effects on alkenone ratios measured in surface sediments from the Indian Ocean. – *Quaternary Research* **47** (3): 344–355.
- SPRENGEL, C.; BAUMANN, K.-H. & NEUER, S. 2000. Seasonal and interannual variation of coccolithophore fluxes and species composition in sediment traps north of Gran Canaria (29°N 15°W). – *Marine Micropaleontology* **39**: 157–178.
- STOLL, H.M.; ROSENTHAL, Y. & FALKOWSKI, P. 2002. Climate proxies from Sr/Ca of coccolith calcite: calibrations from continuous culture of *Emiliania huxleyi*. – *Geochimica et Cosmochimica Acta* **66**: 927–936.
- STOLL, H.M. & ZIVERI, P. 2002. Separation of monospecific and restricted coccolith assemblages from sediments using differential settling velocity. – *Marine Micropaleontology* **46**: 209–221.
- STOLL, H.M. & ZIVERI, P. 2004. Coccolithophorid-based geochemical paleoproxies. – In: THIERSTEIN, H.R. & YOUNG, J.R., eds., *Coccolithophores – From Molecular Processes to Global Impact*: 529–563, Berlin (Springer).
- TAKAHASHI, K. & OKADA, H. 2000. The paleoceanography for the last 30,000 years in the southeastern Indian Ocean by means of calcareous nannofossils. – *Marine Micropaleontology* **40**: 83–103.
- TERNOIS, Y.; SICRE, M.-A.; BOIREAU, A.; CONTE, M.H. & EGLINTON, G. 1997. Evaluation of long-chain alkenones as paleo-temperature indicators in the Mediterranean Sea. – *Deep-Sea Research I*: 271–286.
- TOWNSED, D.W.; KELLER, M.D.; HOLLIGAN, P.M.; ACKLESON, S.G. & BALCH, W.M. 1994. Blooms of the coccolithophore *Emiliania huxleyi* with respect to hydrography in the Gulf of Maine. – *Continental Shelf Research* **14**: 979–1000.
- TYRELL, T. & MERICO, A. 2004. *Emiliania huxleyi*: bloom observations and the conditions that induce them. – In: THIERSTEIN, H.R. & YOUNG, J.R., eds., *Coccolithophores – From Molecular Processes to Global Impact*: 75–98, Berlin (Springer).
- VAN DER WAL, P.; KEMPERS, R.S. & VELDHIJ, M.J.W. 1995. Production and downward flux of organic matter and calcite in the North Sea bloom of the coccolithophore *Emiliania huxleyi*. – *Marine Ecology, Progress Series* **126**: 247–265.
- VILLANUEVA, J.; FLORES, J.A. & GRIMALT, J.O. 2002. A detailed comparison of the U_{37}^k and coccolith records over the past 290k years; implications to the alkenone paleotemperature method. – *Organic Geochemistry* **33** (8): 897–905.
- VOLKMAN, J.K.; BARRETT, S.M.; BLACKBURN, S.I. & SIKES, E.L. 1995. Alkenones in *Gephyrocapsa oceanica*; implications for studies of paleoclimate. – *Geochimica et Cosmochimica Acta* **59** (3): 513–520.
- VOLKMAN, J.K.; EGLINTON, G.; CORNER, E.D.S. & FORSBERG, T.E.V. 1980. Long-chain alkenes and alkenones in the marine coccolithophorid *Emiliania huxleyi*. – *Phytochemistry* **19**: 2619–2622.
- WEAVER, P.P.E. & PUJOL, C. 1988. History of the last deglaciation in the Alboran Sea (western Mediterranean) and adjacent north Atlantic as revealed by coccolith floras. – *Palaeogeography, Palaeoclimatology, Palaeoecology* **64**: 35–46.
- WESTBROEK, P.; BROWN, C.W.; VAN BLEISWIJK, J.; BROWNLEE, C.; BRUMMER, G.J.; CONTE, M.; EGGE, J.; FERNANDEZ, E.; JORDAN, R.; KNAPPERTSBUSCH, M.; STEFELS, J.; VELDHIJ, M.; VAN DER WAAL, P. & YOUNG, J.R. 1993. A model system approach to biological climate forcing. The example of *Emiliania huxleyi*. – *Global Planetary Change* **8**: 27–46.
- WESTBROEK, P.; YOUNG, J.R. & LINSCHOOTEN, K. 1989. Coccolith production (Biominalization) in the marine alga *Emiliania huxleyi*. – *Journal of Protozoology* **36**: 368–373.
- WINTER, A. & SIESSER, W.G. 1994. *Coccolithophores*. – 242 pp., Cambridge (Cambridge University Press).
- WINTER, A.; REISS, Z. & LUTZ, B. 1979. Distribution of living coccolithophorid assemblages in the Gulf of Elat (Aqaba). – *Marine Micropaleontology* **4**: 197–223.
- YONG, J. 1994. Variation in *Emiliania huxleyi* coccolith morphology in samples from the Norwegian EHUX experiment, 1992. – *Sarsia* **79**: 417–425.
- YOUNG, J.R. & ZIVERI, P. 2000. Calculation of coccolith volume and its use in calibration of carbonate flux estimates. – *Deep-Sea Research II* **47**: 1679–1700.
- YOUNG, J.R.; DAVIS, S.A.; BOWN, P.R. & MANN, S. 1999. Coccolith ultrastructure and biomineralisation. – *Journal of Structural Biology* **126**: 195–215.
- YOUNG, J.R.; DIDYMUS, J.M.; BOWN, P.R.; PRINS, B. & MANN, S. 1992. Crystal assembly and phylogenetic evolution in heterococcoliths. – *Nature* **356**: 516–518.
- YOUNG, J.R.; GEISEN, M.; CROS, L.; KLEIJNE, A.; SPRENGEL, C.; PROBERT, I. & OSTERGAARD, J.B. 2003. A guide to extant coccolithophore taxonomy. – *Journal of Nannoplankton Research, Special Issue 1*: 1–125.
- YOUNG, J.R.; BERGEN, J.A.; BOWN, P.R.; BURNETT, J.A.; FIORENTINO, A.; JORDAN, R.W.; KLEIJNE, A.; VAN NIEL, B.E.; ROMEIN, A.J.T. & VON SALIS, K. 1997. Guidelines for coccolith and Calcareous nannofossil terminology. – *Palaeontology* **40** (4): 875–912.
- ZIVERI, P. & THUNELL, R.C. 2000. Coccolithophore export production in Guaymas Basin, Gulf of California: response to climate forcing. – *Deep-Sea Research II* **47**: 2073–2100.
- ZIVERI, P.; YOUNG, J.R. & VAN HINTE, J.E. 1999. Coccolithophore export production and accumulation rates. – *GeoResearch Forum* **5**: 41–56.
- ZIVERI, P.; BAUMANN, K.-H.; BÖCKEL, B.; BOLLMANN, J. & YOUNG, J.R. 2004. Present-day coccolithophore biogeography in the Atlantic Ocean. – In: THIERSTEIN, H.R. & YOUNG, J.R., eds., *Coccolithophores – From Molecular Processes to Global Impact*: 403–428, Berlin (Springer).
- ZIVERI, P.; STOLL, H.; PROBERT, I.; KLAAS, C.; GEISEN, M.; GANSEN, G. & YOUNG, J. 2003. Stable isotope ‘vital effects’ in coccolith calcite. – *Earth Planetary Science Letters* **210** (1-2): 137–149.