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Primary signal: Ecological and environmental factors—Report from Working Group 2

J. Bijma
Geosciences, University of Bremen, P.O. Box 330440, D-28334 Bremen, Germany

Presently at Alfred Wegener Institute for Polar and Marine Research, P.O. Box 120161, D-27515 Bremerhaven, Germany (jbijma@awi-bremerhaven.de)

M. Altabet
CMAST, University of Massachusetts at Dartmouth, 706 Rodney French Boulevard, New Bedford, Massachusetts 02744-1221 (maltabet@umassd.edu)

M. Conte
Woods Hole Oceanographic Institution, Clark Laboratory, MS-25, 360 Woods Hole Road, Woods Hole, Massachusetts 02543-1543 (mconte@whoi.edu)

H. Kinkel and G. J. M. Versteegh
Department of Marine Biogeochemistry and Toxicology, Netherlands Institute of Sea Research, P.O. Box 59, 1790 AB Den Burg, Texel, Netherlands (kinkel@nioz.nl; gerardv@nioz.nl)

J. K. Volkman
CSIRO Marine Research, GPO Box 1538, Hobart, Tasmania 7001, Australia (John.Volkman@marine.csiro.au)

S. G. Wakeham
Skidaway Institute of Oceanography, 10 Ocean Science Circle, Savannah, Georgia 31411 (stuart@skio.peachnet.edu)

P. P. Weaver
Southampton Oceanographic Centre, Empress Dock, Southampton SO14 3ZH, England, U.K. (pweaver@soc.soton.ac.uk)

[1] **Abstract:** Alkenone-based proxies are routinely used for paleoceanographic and climatologic reconstructions despite the fact that their calibration to environmental parameters is still a matter of debate. Significant differences are observed among culture calibrations using different strains of alkenone producers, between regional field calibrations within the euphotic zone, and between water column- and core top-based calibrations. The reasons for these discrepancies are not well understood and call for further evaluation. The possibility is raised that several aspects of genetics, physiology, and ecology of alkenone-producing haptophytes may be responsible, and suggestions of future research are proposed.

Keywords: Haptophytes; alkenones; paleothermometer; paleobarometer; bloom dynamics; sediment.

Index terms: Micropaleontology; paleoceanography; ecosystems, structure and dynamics; organic marine geochemistry.

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Theme: Alkenones **Guest Editor:** John Hayes

1. Introduction

[2] Alkenones were discovered over 20 years ago; these compounds are now widely used to reconstruct paleo-sea surface temperatures (SST) and concentrations of dissolved carbon dioxide of the surface mixed layer, [CO_2aq], from their distribution in sediments. However, several issues need to be addressed to increase the accuracy and precision of these proxies. For instance, the global calibration of *Müller et al.* [1998] shows a latitudinal trend between many core top samples and mean annual surface seawater temperature, yet culture calibrations using different strains show large differences from the *Müller et al.* [1998] calibration, as do field calibrations from different oceanographic regions [e.g., *Sikes and Volkman*, 1993]. The reasons for such discrepancies are not well understood, but the observation suggests that aspects of the genetics, physiology, and ecology of alkenone-producing haptophytes may be responsible.

[3] The goal of this working group was thus to identify the possible impact of abiotic and ecological factors on the utility of the alkenone-based proxies. We focused on several questions that were raised in the accompanying position paper, and in the course of our discussions we have identified several lines of research that would enhance our understanding of the links between the generation and preservation of signals in geological records. Our discussions confirm the importance of temperature as the prime determinant of $U_{37}^{k'}$ values, but it seems that it may be possible to extract additional environmental and ecological information from the distributions of alkenones and related compounds in sediments.

2. Recommendations

[4] While it is likely that paleoceanographers will use a global $U_{37}^{k'}$ calibration for some time into the future, we recommend that its use be tempered by the recognition that significant ecological factors are involved in its construction and hence in its interpretation. The global calibration is an empirical relationship based on correlation rather than explicit causality. Critical ecological factors include (1) latitudinal, geographic, and temporal variability in distributions of alkenone-producing species on both modern and paleoceanographic timescales, (2) depth of production, and (3) the seasonality of alkenone production and flux to the underlying sediments. To better constrain the validity of any global (or regional) $U_{37}^{k'}$ calibration and to identify research needed to underpin the development of a workable relationship for paleo-pCO_2 reconstructions, this working group specifically recommends the following:

- Haptophytes should be screened systematically to determine which species are capable of producing alkenones.
- Lipid compositions of alkenone-producing haptophytes should be related to phenotypic and genotypic variations.
- These variations should be related, in turn, to environmental variations, to production patterns, and to geographic distributions of phytoplanktonic lipids.

- Existing databases of $U_{37}^{k'}$ values should be examined to determine whether regional trends can be extracted from the global data set.
- Population dynamics and blooms of alkenone producers should be investigated with special emphasis on seasonal and depth factors that influence the alkenone thermometer or CO_2 barometer.
- Use of multiple proxies should be enhanced so that alkenone-based estimates can be compared to those from complementary indicators (e.g., other biomarkers, distributions and fluxes of coccoliths, and foraminiferal proxies). Precisely equivalent samples should be used in such comparisons.

3. Haptophyte Speciation and Biogeography

[5] Research within the European *Ehux* Project (http://www.soc.soton.ac.uk/SOES/STAFF/tt/eh/index.html) and Coccolithophorid Evolutionary Biodiversity and Ecology Network (CODENET) (http://www.nhm.ac.uk/hosted_sites/ina/CODENET/index.html) programs has focused on many of the questions raised by our working group, and the reader is referred to their Web sites for further information.

3.1. Evolution

[6] Not all coccolithophores or haptophytes produce alkenones. Both plankton data and the micropaleontologic record indicate that in most places throughout the late Neogene the coccolithophore assemblages were dominated by species belonging to the family of the Noelaerhabdaceae, including the genera *Emiliania*, *Gephyrocapsa*, and *Reticulofenestra*. Species of this family are known (*Emiliania* and *Gephyrocapsa*) or believed (*Reticulofenestra*) to be the main alkenone-producing species in the present ocean [*Marlowe et al.*, 1990; *Volkman et al.*, 1995]. The first appearance datum (FAD) of *E. huxleyi* in sediments is a well-established biostratigraphic marker occurring at ~270,000 years B.P. [*Thierstein et al.*, 1977]. This species became dominant in the fossil record in most places after Marine Isotope Stage 5 and in many places not before the Holocene. Consequently, there have been worries about applying the $U_{37}^{k'}$ proxy further back in the geological record. However, similar alkenones are also known from the coccolithophore *Gephyrocapsa oceanica*[1] and from the noncalcifying haptophytes *Isochrysis galbana* and *Chrysotila lamellosa* [*Conte et al.*, 1994b]. *Emiliania*, *Gephyrocapsa*, *Isochrysis*, and *Chrysotila* were all classically combined in the order Isochrysidales on the grounds of possessing a vestigial haptonema in the motile phase. Molecular genetic studies have suggested that several genera originally included in the Isochrysidales are unrelated homeomorphs, sharing only the rather weak character of reduced haptonema. However, a core group of genera including *Emiliania*, *Gephyrocapsa*, and *Isochrysis* does appear to be closely related [e.g., *Edvardsen et al.*, 2000]. Moreover, molecular clock estimates from a distance tree (L. Medlin and A. G. Saez, manuscript in preparation)(available as a CODENET abstract, 1998) would suggest that *Isochrysis* diverged from the *Emiliania*/*Gephyrocapsa* clade some tens of millions of years ago (probably in the Paleogene), and so alkenone biosynthesis can, theoretically, be dated back at least this far.[2] On this basis it is reasonable to speculate that the direct ancestor of *Gephyrocapsa*, *Reticulofenestra*, already produced alkenones. In theory, this would extend alkenone biosynthesis back to the Eocene.

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[1] *Gephyrocapsa oceanica* does not necessarily record realistic temperatures. For instance, at Walvis Ridge the reconstructed temperatures were ~5°C too high [*Müller et al.*, 1997].

[2] Note that the error bar can easily exceed millions of years.

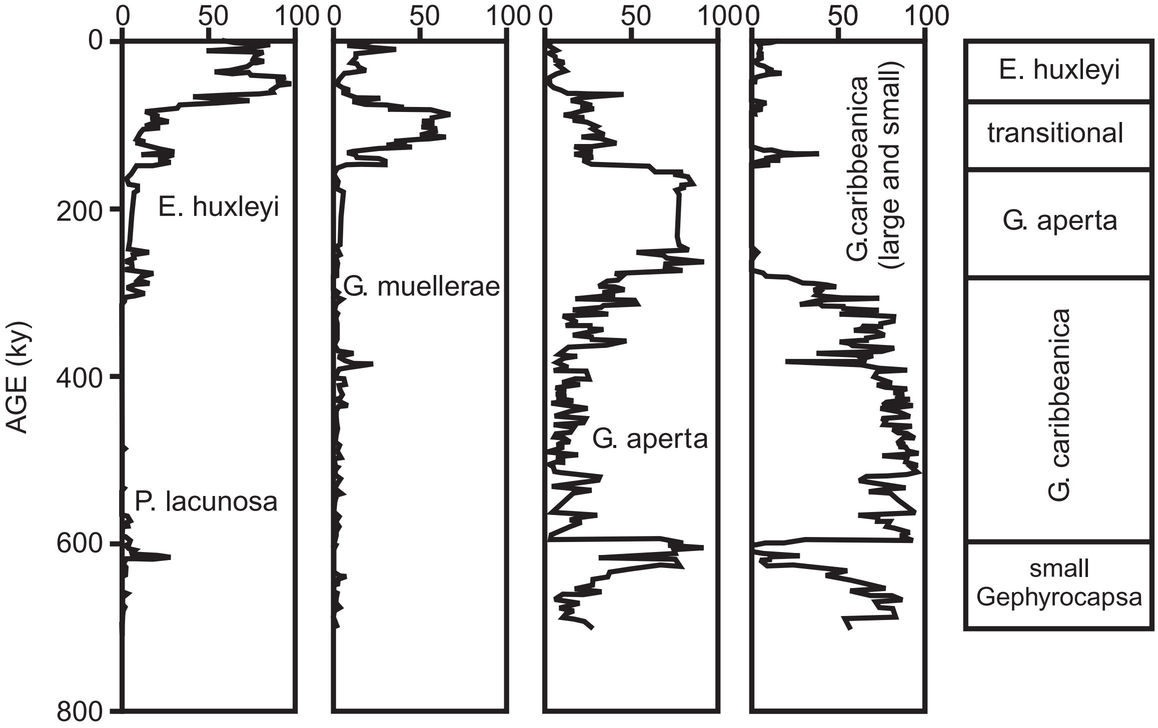

Figure 1. Acme intervals in Deep Sea Drilling Project Hole 610B. The graphs refer to percentage relative abundance of nannoplankton species. Although these data represent a single core, the pattern is very widespread (modified after *Hine and Weaver* [1998]).

[7] The origin of *E. huxleyi* is well established from the fossil record. The genus is descended from other coccolithophore types, some of which are still present in today's ocean. On the basis of coccolith ultrastructure and stratophenetic data (observation of evolutionary lineages) it is believed to have evolved from the Palaeocene genus *Prinsius* through *Toweius*, *Reticulofenestra*, and *Gephyrocapsa* [e.g., *Samtleben*, 1980; *Perch-Nielsen*, 1985; *Young*, 1998]. Other members of the family include *Pseudoemiliania*, *Cyclicargolithus*, and *Dictyococcites*. This group, the Noelaerhabdaceae, has its first occurrence just after the *K–T* boundary, and its origins are rather unsure. The most common interpretation, however, is that it evolved from the Biscutaceae, a common Mesozoic family. If so, divergence from other coccolithophores would be in the Liassic. Thus, on the best available phylogenetic evidence, evolution of alkenone biosynthesis may have evolved at any time from divergence of the Biscutaceae in the Liassic to divergence of the *Isochrysis* clade, probably some time in the Paleogene. Indeed, the oldest reported occurrence of alkenones in the geologic record dates back to the lower Cretaceous [*Farrimond et al.*, 1986].

[8] The dominance of a single species in the fossil record is called an acme zone and can be interpreted as evidence of a "bloom-forming lifestyle." At present we are within the *E. huxleyi* acme zone, and this species dominates in most Holocene assemblages. Gigantic blooms can readily be visualized by satellite imagery. Coccoliths produced by *Gephyrocapsa oceanica* are dominant only in sediments

beneath upwelling areas and from marginal seas [*Wang and Samtleben*, 1983; *Bollmann*, 1997]. Back through time, there is a succession of similar acmes of *Gephyrocapsa* species, each surviving for several tens of thousands of years (Figure 1), and we presume that each of these produced alkenones. Further back in the Neogene, *Reticulofenestra* apparently fills the same niche. Interestingly, the evolution of these acmes does not seem to be related to global climate change (e.g., Milankovitch cycles) but may be the results of varying nutrient regimes [*Bollmann et al.*, 1998; *Gartner*, 1988].

[9] The noncalcifying genera *Isochrysis* and *Chrysotila* almost certainly differ physiologically from the alkenone-producing coccolithophores and so might be expected to produce distinctly different alkenone records. However, while their ecology is very poorly known, they are thought to be predominantly restricted to nonmarine and marginal-marine settings [e.g., *Marlowe et al.*, 1984]. Consequently, they are unlikely to ‘‘contaminate’’ the open marine signal from the Noelaerhabdaceae and may even produce a valuable signal in these environments.

[10] Several aspects of haptophyte evolution need further evaluation in terms of alkenone proxy development. Is alkenone synthesis unique to a group or clade of haptophytes, and if so, where and when did this group or clade separate from other haptophytes? Techniques of molecular phylogeny are now being applied in CODENET research to establish their evolutionary relationships among the haptophytes and to investigate genetic variability which affects the alkenone-temperature relationship among different genera and strains.

[11] Investigations of evolutionary cycles of coccolithophore distributions and the alkenone record [e.g., *Marlowe et al.*, 1990] should be further pursued. When did alkenone synthesis first appear? How do millennial and higher-frequency climatic changes affect coccolithophore species distributions and the alkenone record? Can we apply the $U^{k'}_{37}$ to pre-Quaternary periods of the Earth history?

3.2. Biogeography

[12] General aspects of coccolithophorid biogeography and habitat are well known from taxonomic surveys of the plankton and of bottom sediments [e.g., *Winter et al.*, 1994; *Young et al.*, 1994; *Samtleben et al.*, 1995]. Individual species are cosmopolitan, but with more or less limited latitudinal distributions. Thus three or four broad coccolithophorid zones are recognized [*Okada and Honjo*, 1973; *Winter et al.*, 1994]. These latitudinal zones are thought to reflect temperature tolerance, but even at this level it is apparent that other factors, such as irradiance or mixed layer depth, may be of major significance. For instance, *Coccolithus pelagicus*, which largely defines the high-latitude zone and occasionally occurs at much lower latitudes [e.g., *Pujos*, 1992; *Giraudeau et al.*, 1993], was widespread in the warmer conditions of the late Pliocene [*Young*, 1998]. Similarly, the presence of floral zones associated with equatorial upwelling and the subtropical oligotrophic gyres suggests control by nutrients/trophic level rather than temperature alone [*Molfino and McIntyre*, 1990; *Baumann et al.*, 1999; *Kinkel et al.*, 2000]. *Emiliania huxleyi* and *Gephyrocapsa* are common in all of the biogeographic zones. Provincialism is a more prominent feature of less common species, although the *Emiliania-Gephyrocapsa* group shows assemblage variations at the subspecies level in parallel with the classic latitudinal zones.

[13] There have been very few studies of the ecological factors which determine the biogeography of individual coccolithophore species and their community structure, although paleoceanographers often use coccolith assemblages in sediments as indicators of paleoceanographic

conditions [e.g., *Jordan et al.*, 1996; *Kinkel et al.*, 2000]. The ecology of only a few individual species, notably, *Emiliania huxleyi*, has been studied in detail. Most studies have reported only relative abundances in coccolith assemblages, although there have been a few studies of coccolithophore abundances relative to total phytoplankton [e.g., *Abrantes and Moita*, 1999; *Estrada et al.*, 1999] or of absolute abundances of single species relative to ecological parameters in modern communities [*Takahashi and Okada*, 2000]. Recent work on the biogeography of coccolithophores relative to eutrophication and ecological succession is producing a more coherent if complex picture of coccolithophorid ecology [e.g., *Brand*, 1994; *Young*, 1994].

[14] The facts that coccolithophores are a significant component of the modern phytoplankton, have an exceptional fossil record, and thus a great potential as paleoecological indicators are not recent realizations. Although some of the early work was excellent [e.g., *McIntyre*, 1967], its successes in paleoresearch, as compared to, for example, foraminifers, were limited. This is largely due to the fact that the environmental controls on the presence or absence of a given (sub)species can be so multiphasic that the signals may be difficult to isolate, and hence a major program on coccolithophore ecology seems timely. Total coccolithophore production and calcification is readily derived from coccolith accumulation rates in sediments [*Bollmann et al.*, 1999; *Young and Ziveri*, 2000]. Although many phytoplankton do not produce coccoliths, it constitutes an easily accessible proxy for surface water productivity [e.g., *Kinkel et al.*, 2000].[3] In addition, lipid biomarkers provide an independent record of coccolithophorid production [*Villanueva et al.*, 1998]; pelagic carbonate sedimentation has a major impact on the global carbon dioxide cycle [e.g., *Wollast*, 1994]. This probably goes beyond direct needs of the alkenone community, but initiatives in this direction (e.g., within the CODENET project) could usefully be encouraged.

4. Population Dynamics and Ecology

[15] Paleoceanographers generally assume that the sedimentary alkenone signal reflects the annually averaged sea surface temperature (SST) and/or carbon dioxide concentration. However, ecological studies of *Emiliania huxleyi*, the dominant alkenone-synthesizing species in the modern-day ocean, have shown that this species' productivity, and hence the production of alkenones, is highly seasonal and that a significant portion of the total annual production may occur in short-lived blooms [e.g., *Conte and Eglinton*, 1993; *Ternois et al.*, 1998; *Thomsen et al.*, 1998]. In some areas, significant production may occur below the surface mixed layer within the seasonal thermocline [e.g., *Prahl et al.*, 1993; *Ternois et al.*, 1997; *Bentaleb et al.*, 1999] or in bloom episodes at specific points in the seasonal cycle. Thus it cannot be assumed that sedimentary $U^{k'}_{37}$ values necessarily record mean annual SST (Figure 2). For instance, subsurface alkenone production may bias the $U^{k'}_{37}$ signal toward colder values in comparison to blooms that develop in surface waters. Because it is simpler to understand the factors that determine a signal than to invert the signal and infer the factors (which is what paleoceanographers do), we need a better understanding of how alkenone production varies seasonally and with water depth and of the factors controlling the magnitude and timing of blooms.

[16] The alkenone signal in many regions of the ocean appears to be set during very short periods of intense production (blooms, in which half of the biomass is produced during the last

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[3] Chlorins (proxy for chlorophyll production) are more general, and the analysis of at least some chlorins is easy, fast, and reproducible.

cell doubling). Since high production of coccolithophores is not always detected by satellites, this can be true even in regions not generally regarded as being subject to strong seasonal blooms. In high latitudes, alkenone production is generally limited to the late spring/summer; a shift toward late winter/early spring is observed for low-latitude regions [*Sanders*, 1997] (Figure 2). In some areas, production maxima occur both in spring and in autumn, so that the alkenone temperature signal in the sediments may be biased toward the weighted mean of two production temperatures, which might approximate the annual mean temperature. In some regions, for example, temperate coastal upwelling areas off California [*Herbert et al.*, 1998], the sedimentary $U^{k'}_{37}$ values show surprisingly little influence of seasonality, whereas in other regions, for example, the eastern North Atlantic [*Conte et al.*, 1992], sedimentary $U^{k'}_{37}$ is strongly biased toward a springtime period of maximum production. In some areas, seasonality in production may be low, but interannual variability can be extreme, as was found in a 4-year sediment trap study off Cape Blanc (P. Müller, unpublished data, 2000).

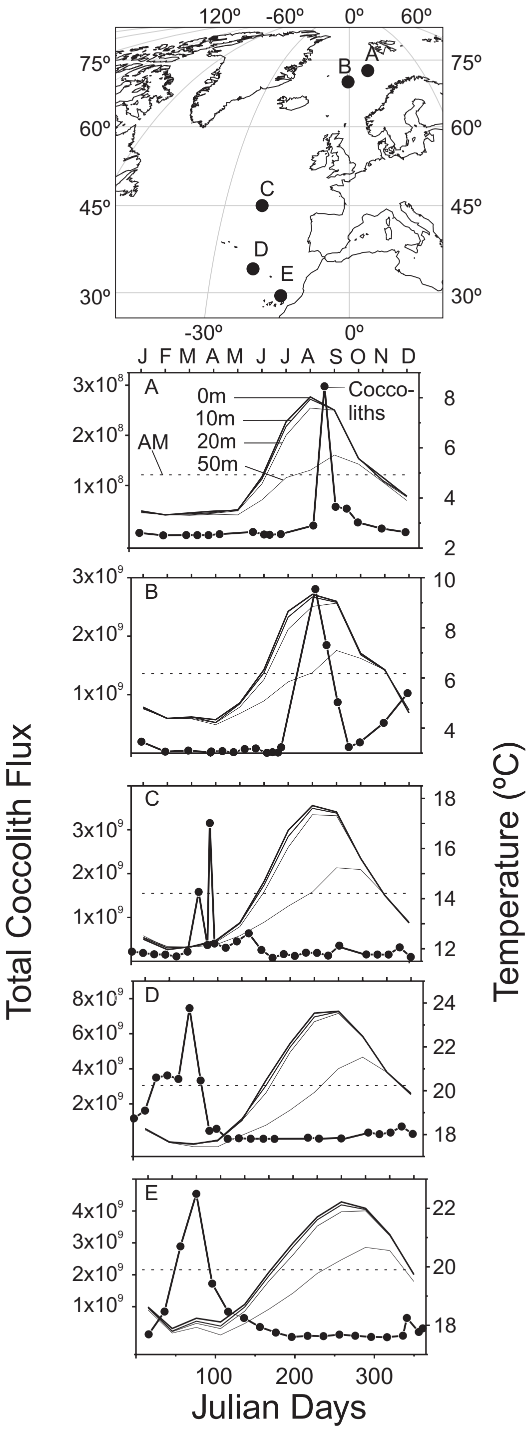

Figure 2. Compilation of a sediment trap transect in the North Atlantic. Trap positions are indicated in the small map on top. A–E show the comparison between the total coccolith flux (solid dots) against the water temperature (°C) at 0, 10, 20, and 50 m (going from the thick to the thin line). The dashed line indicates the annual mean sea surface temperature (SST AM). Temperature data are from *Andruleit* [1997] for sites A and B, *Broerse et al.* [2000] for site C, *Ziveri et al.* [2000] for site D, and *Sprengel et al.* [2000] for site E. Note that at high latitudes the flux maximum occurs at a seawater temperature higher than the annual mean, whereas at low latitudes the opposite is true.

[17] Since Marine Isotope Stage 5, *E. huxleyi* is believed to be the most important alkenone producer in the open ocean. In many regions, production during short-lived bloom periods may account for much of the annual production of alkenones, thus biasing the sedimentary record for $U^{k'}_{37}$ and alkenone $\delta^{13}C$ away from

the annual mean. Hence understanding the ecology and development of *E. huxleyi* blooms is highly relevant to interpretation of the sedimentary alkenone signal. From research conducted to date, primarily in the North Atlantic, it appears that *E. huxleyi* blooms generally develop in stratified waters with mixed layer depths of <30 m [*Nanninga and Tyrrell*, 1996]. The usual timing of the blooms in the high-latitude North Atlantic is in early to middle summer, when surface irradiances are high (for additional information, see *Tyrrell and Taylor* [1996]). Consistent with these observations, *Brand* [1994] noted that *E. huxleyi* is likely to be *r* selected rather than *K* selected,[4] since it has a high maximum growth rate (up to about two doublings per day; I. Zondervan, personal communication, 2000). *Young* [1994] and *Hulbert* [1990] reached similar conclusions in their reviews.

[18] Nutrient conditions are also believed to influence *E. huxleyi* bloom development. Mesocosm experiments in the Norwegian fjords [*Egge and Heimdal*, 1994], and modeling of the results of these experiments [*Aksnes et al.*, 1994], have suggested that *E. huxleyi* may have a competitive advantage over other phytoplankton when inorganic phosphate is limiting but nitrate is still abundant [e.g., *Riegman et al.*, 1998]. Consistent with this hypothesis, it has been shown that there is a greater activity of the enzyme alkaline phosphatase in *E. huxleyi* than in most other phytoplankton and that this enzyme is used to assimilate dissolved organic phosphates (as opposed to dissolved inorganic phosphate). In situ observations of natural blooms have implicated low phosphate as a possible factor leading to blooms, and competition experiments (multispecies chemostat experiments) have obtained greater numbers of *E. huxleyi*, and greater percentages of the total, at high N/P ratios rather than at low N/P ratios [*Riegman et al.*, 1992]. A modeling study of *E. huxleyi* in the NE Atlantic [*Tyrrell and Taylor*, 1996] obtained the most realistic results (model blooms of *E. huxleyi*) when *E. huxleyi* in the model was adapted to low phosphate concentrations and high light intensity.[5]

[19] Low silicate has been advanced as a possible explanation for the timing and distribution of *E. huxleyi* blooms [*Brown and Yoder*, 1994]. Mesocosm studies in the Norwegian fjords have shown that diatoms always bloom (usually to the exclusion of everything else) when silicate is present in concentrations >2 μmol kg^{-1} but are less likely to bloom when silicate concentrations are lower. *Balch et al.* [1991, p. 630] state that "coccolithospheres succeed diatoms in response to increasing stabilization and nutrient depletion of surface waters.. . ." Along the southwestern Norwegian coast, *E. huxleyi* blooms, which color the sea milky green, annually follow the spring diatom bloom [*Heimdal et al.*, 1994]. Coccolithophores such as *E. huxleyi* are also thought to possess a competitive advantage at low concentrations of CO_2 owing to the process of calcification, which produces CO_2 for production of photosynthate [*Dong et al.*, 1993; *Brownlee et al.*, 1995; *Nimer et al.*, 1994]. It follows that *E. huxleyi* is favored when diatoms are limited by silicate (and possibly CO_2) and when a shallow, seasonal mixed layer develops to optimize the light environment.

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[4] Lotka-Volterra equations are based on the logistic curve for each competing species. Two parameters characterize the logistic, *r* (rate of increase) and *K* (saturation density). The competitive ability of organisms can be characterized by the relative importance of *r* and *K* in their life cycles. In some environments, organisms exist near the asymptotic density (*K*) for much of the year; these organisms are subject to *K* selection. In other habitats, organisms rarely approach the asymptotic density but remain on the rising sector of the curve for most of the year; they are subject to *r* selection. All organisms reach some sort of compromise between these two extremes [*Krebs*, 1978].

[5] It should be noted, however, that phosphate is recycled faster than nitrate and thus is probably not the limiting nutrient for marine phytoplankton in general.

[20] Other hypotheses that have been put forward in the past to explain propensity of bloom development are "seeding effects" (the availability of advected cells to provide a seed population for a bloom [e.g., *Birkenes and Braarud*, 1952]) and an ability to thrive under low iron concentrations [*Brand*, 1991]. Some varieties of *Emiliania huxleyi* are known to grow better in media supplemented by thiamine (vitamin B1) [*Carlucci and Bowes*, 1970]. Hence it can be speculated that bloom development requires preconditioning of the water by other blooms, for instance, diatoms.

[21] The importance of blooms in alkenone signal generation may also have implications for the use of alkenones for pCO$_2$ reconstructions. The effect of calcifying coccolithophores on the carbon speciation of seawater depends on the timescales and the state of a bloom [*Holligan et al.*, 1993; *Robertson et al.*, 1994]. On the short term, calcification will lower alkalinity and pH, which will result in a higher pCO$_2$, thus leading to a reduced sink or even a source for CO$_2$ [*Purdie and Finch*, 1994]. In the long run, it is considered to act as a net sink for CO$_2$, since both particulate organic carbon (POC) and particulate inorganic carbon (PIC) are effectively removed from the water column and stored in the sedimentary archive [*Buitenhuis et al.*, 1996; *Crawford and Purdie*, 1997]. It thus seems very likely that the pCO$_2$ recorded during a coccolithophore bloom may be heavily biased by local changes in alkalinity and pH. Indeed, several studies that have used the stable carbon isotope composition of alkenones to reconstruct pCO$_2$ have resulted in trends that differ from those expected from ice-core measurements[6] [*Jasper et al.*, 1994; *Andersen et al.*, 1999] or long-term climate models [*Pagani et al.*, 1999]. This could indicate that calcification status, in addition to cell geometry[7] and growth rate, may need to be estimated in order to successfully use alkenone δ^{13}C in paleo-pCO$_2$ reconstructions.

[22] Temperature as such does not appear to play a significant role in bloom development. As shown in Figure 2, at nutrient-replete high latitudes a bloom is initiated when the light level reaches a certain threshold in summer, when SST is higher. Consequently, a higher temperature than the annual mean can be recorded. In contrast, at lower latitudes, where the light intensity is not limiting, blooms develop when nutrients are brought into the photic (and stratified) layer, generally in late winter to spring, when the SST is below the annual mean. Hence a lower than yearly average SST may be recorded [*Kleijne et al.*, 1989; *Giraudeau et al.*, 1993; *Baumann et al.*, 1999].

[23] The latitudinal study of core top $U^{k'}_{37}$ in the North Pacific by *Ohkouchi et al.* [1999] is a good example of how variations in seasonality and/or depth of production may affect interpretation of sedimentary $U^{k'}_{37}$ (Figure 3). These authors explained the shift toward lower than annual average $U^{k'}_{37}$ temperatures with increasing latitude by a shift toward a deeper depth habitat of alkenone producers. However, the bias toward higher than annual temperatures at high latitudes that they noted cannot be explained solely in terms of subsurface alkenone production. Instead, a seasonal shift of a short-lived alkenone flux (Figure 2) could explain the offsets and would imply a larger latitudinal temperature contrast.[8]

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[6] It should be noted that atmospheric pCO$_2$ reconstructions can be driven by the estimated variations in SST rather than by variations in δ^{13}C of the alkenones.

[7] Cell size of coccolithophores, and especially of the alkenone-producing species, has changed significantly in the geologic record [e.g., *Young*, 1990].

[8] Sedimentation rates for red clay sediments are usually between <1 and 4 mm/kyr [*Chester and Aston*, 1976]; i.e., the possibility of contamination with glacial material in the carbonate free cores cannot be excluded.

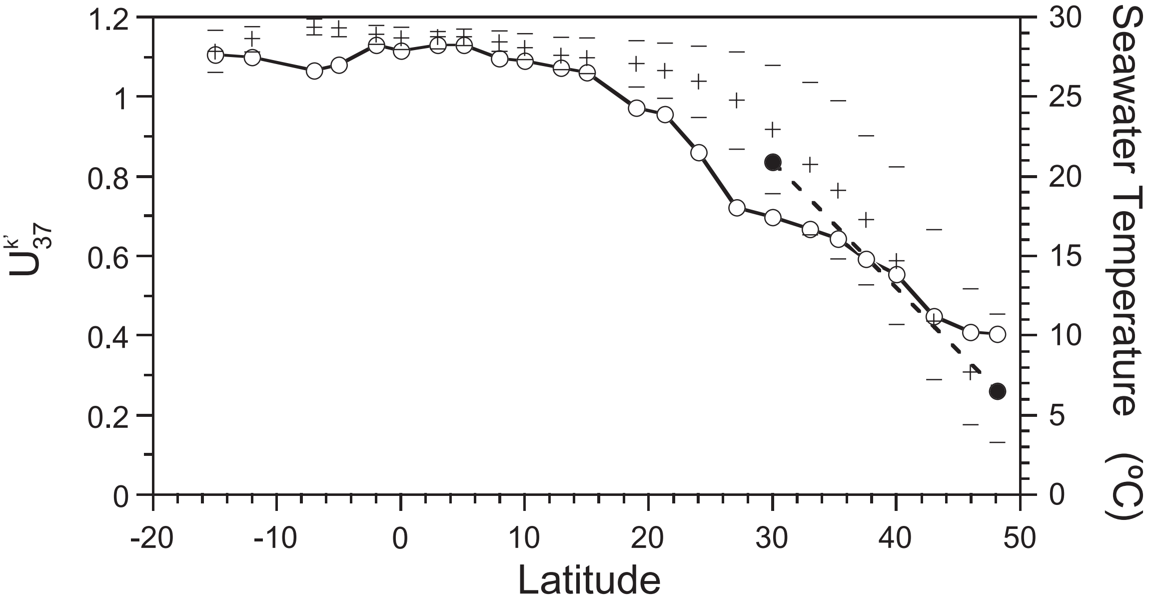

Figure 3. Latitudinal distribution of $U^{k'}_{37}$ values (open symbols and solid line [after *Ohkouchi et al.*, 1999]). The relationship between temperature and $U^{k'}_{37}$ is that reported by *Prahl et al.* [1988]. The average annual temperature (plus signs) and the minimum and maximum temperatures (minus signs) at 20 m depth are according to *Levitus* [1994]. The dashed line represents a hypothetical correction if it is assumed that signal production occurs with a seasonal offset as shown in Figure 2 for the Atlantic (assuming, e.g., that the main fluxes at 50°N and 30°N occur when SST is 3.5°C above and below the annual mean SST, respectively). Such a seasonal shift of a short-lived alkenone flux would imply a larger latitudinal SST contrast.

[24] Can we define a collection of biological and environmental parameters that determines when and where the alkenone thermometer or barometer is "set"? Can regions that deviate significantly from a global calibration be recognized and understood in this context? Are such deviations due to seasonal changes in species composition (Baltic, northern North Atlantic), to high seasonality in alkenone production (temperate to subpolar regions), to changes in depth habitat (notably, the Pacific with its deep chlorophyll maximum), or to a combination of these factors? Is it feasible to work toward a predictive model applicable to paleoreconstructions?

[25] The differences observed among regional field calibrations within the euphotic zone and between regional calibrations and latitudinal (global) core top calibrations [e.g., *Müller et al.*, 1998] call for further evaluation of coccolithophore ecology, on both global and regional scales. Accordingly, we recommend that time series studies of alkenones in both suspended and sinking particles in the euphotic zone and within the water column at key sites should be carried out to cover seasonal as well as interannual variability. These observations should be accompanied by analyses of surface fluff and core tops. Special emphasis should be placed on identifying regions impacted by blooms, their species composition, the environmental parameters which trigger bloom events, and their corresponding seasonal and depth-related variability influencing $U^{k'}_{37}$ and alkenone $\delta^{13}C$ values. The effect of large nutrient, temperature, and salinity gradients (e.g., upwelling, river plumes) in coastal regions on alkenone-

synthesizing species and strains, as well as the physiology and ecology of alkenone biosynthesis, is poorly known and must be further investigated before alkenone records from these areas can be interpreted with confidence.

[26] Included in these studies should be an evaluation of how diagenetic losses may be influenced by seasonality and might further bias the alkenone signal preserved in the sediments. For example, a significant portion of a distinct alkenone production peak may be lost if the benthic community responds rapidly to the corresponding peak in C_{org} flux. Such activity would bring the mean signal back toward the annual "background" production. In essence, this would imply that the signals preserved in the alkenones could reflect the usual state of ocean and not the unique situation during the short bloom period. This would be an advantage in reconstructing the mean annual temperature [cf. *Müller et al.*, 1998] but could complicate the reconstruction of sources and sinks of atmospheric CO_2, which may be driven by events that perturb the system rather than by the average conditions of the water mass.

5. Other Possible Physiological and Environmental Influences on Alkenone Synthesis and Temperature and pCO$_2$ Calibrations

[27] Work with microalgal cultures suggests that environmental variables and changes in the physiological state of the alga can influence alkenone content and composition within the cell [*Conte et al.*, 1995, 1998; *Epstein et al.*, 1998]. For example, *Epstein et al.* [1998] demonstrated a change of 0.1 in $U^{k'}_{37}$ units in a culture of *E. huxleyi* as nitrate plus nitrite concentrations dropped to zero. Alkenone contents increased from about 1 to 15 pg/cell with increasing time in stationary phase. In contrast, changes in pH, [CO_2aq], and alkalinity did not lead to changes in $U^{k'}_{37}$ values in a different strain of this alga [*Riebesell et al.*, 2000]. Changes in light intensity do not seem to affect $U^{k'}_{37}$ values, and *E. huxleyi* does not respond to Fe additions, in terms of either growth rate increases or isotopic composition [*Bidigare et al.*, 1999]. While it has been suggested that salinity could have an effect on alkenone synthesis, increased production of the 37:4 alkenone observed in some lower-salinity coastal regions [e.g., *Conte et al.*, 1994a] might also reflect a change in genetic predisposition, as shown in culture studies using strains from Norwegian fjords [*Conte et al.*, 1995, 1998]. It may be that some of the scatter in $U^{k'}_{37}$ versus temperature calibrations in the field reflects the influence of other environmental factors, as seen in alkenone data from surface waters of the oligotrophic Sargasso Sea (M. H. Conte et al., Calibration of the alkenone temperature signal in western North Atlantic surface waters, submitted to *Geochimica et Cosmochimica Acta*, 2000). On the other hand, the global temperature calibration by *Müller et al.* [1998] is remarkably consistent with annual-average temperatures (except perhaps at the high-temperature end).

[28] Recent research by *Eek et al.* [1999] has provided evidence that environmental conditions may also have a significant influence on carbon isotope fractionation in natural haptophyte populations. In the presence of nitrate the magnitude of the carbon isotope fractionation (ϵ_p) was dependent on the dissolved phosphate concentration normalized to the concentration of dissolved CO_2, but in nitrate-depleted waters the magnitude of carbon isotope fractionation was lower than expected from the ϵ_p versus PO_4/C_e relationship. These results imply that growth conditions approaching nitrogen starvation can affect carbon isotope fractionation in haptophyte algae and hence introduce "considerable uncertainty in estimating the paleo-

$p\mathrm{CO}_2$ record using the alkenone proxy method" [*Eek et al.*, 1999, p. 2874].

[29] From culture experiments, growth rate, cell geometry, and possibly light conditions are now considered important factors in addition to [CO_2(aq)] in determining the isotopic composition of alkenones [e.g., *Popp et al.*, 1998a, 1998b]. Given the variety of coccolith sizes (and presumably cell size) of haptophyte species in the geological record [e.g., *Young*, 1990], we recommend that in any study of δ^{13}C of alkenones in ancient sediments, information on coccolith distribution and species identification be obtained, at least for a representative subset of the samples.

[30] It is difficult to rigorously evaluate the effect of specific environmental factors on alkenone distributions in the natural environment owing to the complex interplay between the multitudes of factors involved, and culture studies have a disadvantage in that culture conditions are not representative of those affecting natural populations. Mesocosm studies [e.g., *Heimdal et al.*, 1994] can bridge the gap between the laboratory and the field to study environmental effects. Recent research at the Alfred Wegener Institute in Bremerhaven, Germany (U. Riebesell, personal communication, 1999), provides a good example of this type of experiment; in their study a strain of *E. huxleyi* was grown in a 1000 L mesocosm using well-defined nutrient and light conditions. All components of the carbon system, including POC, dissolved inorganic carbon (DIC), pH, alkalinity, etc., were measured through the development of the bloom and for several weeks afterward. Samples of microalgae were collected at regular intervals for measurements of carbon isotope fractionation $\mathrm{U}^{\mathrm{k}}_{37}$ and values. Well-defined field studies to examine similar changes during natural blooms are also very valuable but, regrettably, are far more expensive to carry out, and their success depends on the ability to predict both the timing and the location of a bloom, which is still a very difficult task. Further field studies of alkenone production are clearly needed. These need to be well characterized in terms of species, in terms of the depth versus temperature distribution of alkenone production, and in terms of the nutrient and light environment. For ^{13}C studies, independent estimates of alkenone-producer growth rates in the field are needed.

6. Use of Related Biomarkers and Other Molecular Proxies to Constrain Paleoceanographic Reconstructions

[31] Although this workshop has focused on the application of alkenones, specifically, the diunsaturated and triunsaturated C_{37} compounds, as proxies of paleo-SST and $p\mathrm{CO}_2$, it must be remembered that organic carbon contains a much richer molecular composition which contains diverse biological and environmental information. Expansion of molecular stratigraphy beyond the two C37 alkenone compounds which are used in the $\mathrm{U}^{\mathrm{k}'}_{37}$ parameter will not only improve interpretation of the $\mathrm{U}^{\mathrm{k}'}_{37}$ temperature and paleo $p\mathrm{CO}_2$ signal but also more fully exploit the power of molecular stratigraphy in paleoceanographic reconstructions.

[32] A broader approach in molecular proxy development will be especially fruitful in those regions where the relation between alkenone unsaturation and temperature shows higher scatter due to other genetic and/or environmental effects. For example, in cold-water, high-latitude environments, alkenone saturation, which is supposed to be related to temperature only, appears to be influenced by other environmental (salinity?) and/or biological variables independent of temperature [e.g., *Conte et al.*, 1992; *Rosell-Melé et al.*, 1995; *Sikes et al.*, 1997]. Similarly, the $\mathrm{U}^{\mathrm{k}'}_{37}$-temperature rela-

tionship developed for a transect in the Ligurian Sea (Mediterranean) appears to differ significantly from the global calibration [*Ternois et al.*, 1997].[9] To understand these deviations, we need to extract additional environmental information, which requires a broader set of molecular and additional proxies to constrain paleoceanographic reconstructions. Notably, the information obtainable from the related C_{38}, C_{39} ethyl and methyl alkenones, alkenoates, and alkenes may prove to be useful to unravel why for some regions a relatively high scatter in the $U^{k'}_{37}-T$ relation is found. Apart from an improved (paleo) environmental understanding, the analysis of other haptophyte-derived compounds may also provide information on the evolution and speciation of the alkenone producers, as there is more diversity in the fingerprint of these compounds among the alkenone synthesisers. In any case, these compounds could be an important indicator of the possibility of taxon-related shifts in the $U^{k'}_{37}-T$ calibration.

[33] Organic geochemical analysis can also produce records of other biomarkers or compound classes that are produced by phytoplankton. An example is provided by the long-chain diols, which are believed to be produced by a similarly restricted group of organisms (eustigmatophytes) and for which different molecular compositions seem to relate to different present and past environments [*Versteegh et al.*, 1997, 2000]. Utilization of such compounds in conjunction with the alkenones and with others products of haptophytes will add valuable information on paleoecology, which, again, may help to improve the understanding of the alkenone signal with respect to seasonality, nutrients, salinity, and other factors that might influence the alkenone signal. Full utilization of molecular information from other biomarkers in the paleorecord awaits a better understanding of their present-day distributions in relation to phytoplankton species and ecology.

[34] Apart from improving the interpretation of the alkenone temperature record, this effort will greatly enhance the understanding of past environments, not only with respect to temperature. Such a complete understanding may allow alkenone stratigraphy to be applied even more successfully, notably, in high-latitude regions, where the simple correlation of $U^{k'}_{37}$ versus temperature appears to be less well constrained.

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[9] Although the regional, particulate organic matter (POM)-based calibration deviates significantly from the global calibration based on core tops, it was noted that “the temperatures measured in the core top sediments using the general equation are in agreement with the annual average water column temperatures between 0–40 m depth” [*Cacho et al.*, 1999, p. 557].

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