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Molecular proxies for paleoclimatology

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ABSTRACT

We summarize the applications of molecular proxies in paleoclimatology. Marine molecular records especially are proving to be of value but certain environmentally persistent compounds can also be measured in lake sediments, loess deposits and ice cores. The fundamentals of this approach are the molecular parameters, the compound abundances and carbon, hydrogen, nitrogen and oxygen isotopic contents which can be derived by the analysis of sediment extracts. These afford proxy measures which can be interpreted in terms of the conditions which control climate and also reflect its operation.

We discuss two types of proxy; those of terrigenous and those of aquatic origin, and exemplify their application in the study of marine sediments through the medium of ten case studies based in the Atlantic, Mediterranean and Pacific Oceans, and in Antarctica. The studies are mainly for periods in the present, the Holocene and particularly the last glacial/interglacial, but they also include one study from the Cretaceous. The terrigenous proxies, which are measures of continental vegetation, are based on higher plant leaf wax compounds, i.e. long-chain (circa C_{30}) hydrocarbons, alcohols and acids. They register the relative contributions of C_3 vs. C_4 type plants to the vegetation in the source areas. The two marine proxies are measures of sea surface temperatures (SST). The longer established one, ($U^{K}_{37}{}'$) is based on the relative abundances of C_{37} alkenones photosynthesized by unicellular algae, members of the Haptophyta. The newest proxy (TEX_{86}) is based on C_{86} glycerol tetraethers (GDGTs) synthesized in the water column by some of the archaeal microbiota, the Crenarchaeota.

1. Foreword

> “Life is a continual battle to maintain a state of order in a Universe that runs towards disorder. Living systems keep climbing the entropy gradient by obtaining energy from sunlight and food: Life 1, Second Law of Thermodynamics 0 …… except that the game goes into extra time and the Law gets everything in the end” (R. Foster and L. Kreitzman (2004) “Rhythms of Life” Profile Books, 2005, p 97).

Ah! Yes, …… but some of it spends a very long time getting there. A few hardy biomolecules remain in the sedimentary record—persistent ghosts of past life—these provide our biomarker or molecular proxies for paleoclimatology! Like radionuclides, they are often present as mere vestiges of former glory—but still with information to give.

2. Introduction

A typical biomarker molecule is made up of a hundred or so covalently-bound atoms of carbon and hydrogen, sometimes also including few oxygens, nitrogens, etc (for a general introduction to biomarkers, see Killops and Killops, 2004; Eglinton and Pancost, 2004; Peters et al., 2005; Volkman, 2006; Gaines et al., in press). Each molecule measures less than 100 nm across and weighs less than 1000 Da. As such, these biosynthesized molecules are extremely readily dispersed in the environment when released from the precursor organism directly, or upon its death. But their fates are also strongly dependent on “packaging”. Thus dispersion of biomarkers may be greatly influenced by their entrapment within mineral matrices such as shell, teeth, bone etc., or encapsulation in resistant biopolymer matrices such as cell walls, leaf and insect cuticles and pollen grains, or packaging in environmentally ephemeral entities such as fecal pellets, “marine snow” or other detrital debris and colloidal matter (e.g., humic acids). Some compounds possess polar and reactive functional groups—hydroxyls, amino groups, carboxylic acid functions—which adsorb onto or become incorporated covalently into mineral matrices such as clay particles which may themselves travel rapidly in the environment. Additionally, some biomolecules have very low water solubility but high solubility in organic materials and hence may become adsorbed, dissolved or otherwise incorporated in organic particles or organisms in aquatic systems, enabling long-distance transport. This scenario contrasts with the behavior of other proxies such as ^{18}O in planktonic

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foraminifera, where the calcium carbonate is in the form of a shell which is sufficiently large and dense to be deposited rapidly and often permanently from the overlying water column.

The methodologies used for the generation of molecular-proxy data usually start with the use of an organic solvent to extract organic molecules from the sediment, followed by fractionation, purification and then quantitation, either by gas or liquid chromatography (GC and LC, respectively) and/or mass spectrometry (MS). In recent years the range of biomarkers has been dramatically improved by the ability to handle polar molecules, such as acids, alcohols and polyfunctional components, as well as high-molecular-weight components with masses of 1000 Da or more. These developments have opened up new “analytical windows” and revealed novel biomarkers valuable for proxy development (e.g., Hopmans et al., 2000; Talbot et al., 2001). There have also been dramatic increases in sensitivity and specificity through specialized mass spectrometric techniques such as MS/MS and the coupled chromatographic–spectrometric methods such as GC/MS and HPLC/MS. As a result, it is now possible to work with very small sediment samples of the order of milligrams and hence carry out extremely high-resolution sampling of cores.

A second major development which is still moving forward rapidly is compound-specific isotope analysis (CSIA) using continuous-flow isotope ratio MS methodology (e.g., Sessions, 2006). This has been possible for $\delta^{13}C$ for a number of years but now on-line δD measurements are becoming routine, and also increased sensitivity has meant that compound-specific ^{14}C measurements are possible with only micrograms of pure compound.

Molecular-proxy studies are thus becoming more routine. Not only can we use smaller sample sizes but also new proxies are continually emerging. For example, the TEX_{86} proxy based on the polar, relatively high-molecular-weight tetraether lipids was devised only recently (Schouten et al., 2002, 2003) and yet is already in routine use as a sea surface temperature (SST) proxy which can be used on samples of considerable geological age. There is every prospect of more molecular proxies being devised: for example, it is conceivable that there may be microbial biomarkers produced by benthic heterotrophic bacteria or other bottom-dwelling organisms which would provide paleoproxies for bottom-water temperature, extent of oxygenation etc.

In this article we have chosen to concentrate on two types of proxy: first, we discuss terrigenous leaf wax biomarkers synthesized by land plants, which can provide information on continental vegetation. The second type of proxy includes aquatic–marine biomarkers biosynthesized by plankton which can provide information on the photic zone of the ocean. In both cases the proxies are entirely based on molecular measurements and are therefore completely independent of the more conventional proxies based on inorganic or isotopic variations or on abundances of fossil organisms. But, like all proxies, they have their problems and complications resulting from the multiple factors bearing on their abundance and composition. For example, the leaf wax biomarkers transferred from land have to be considered in terms of both the areas of erosion that supply them and the selectivity and rates of transfer and deposition by the transport processes. Furthermore, there is always the question of alteration and attenuation of the signals as a result of decomposition of the molecules. So it is highly desirable to use the same layers from a sediment core to measure multiple proxies, for example, by measuring ^{18}O or Mg/Ca ratios in foraminifera in parallel with molecular SST proxies. Each proxy has differing limitations and advantages so that parallel measurements provide information not only on SST but also on some of the processes involved in the original deposition and in diagenesis. Both terrigenous and marine biomarkers are dependent on climate-related environmental factors such as temperature, CO_2 pressure, light levels etcetera. Thus, the terrestrial vegetation signal relates directly to the climatic conditions controlling both the growth of vegetation and the erosion and transport of the plant waxes—notably temperature, aridity and wind strength. Marine SST is a fundamental parameter in the generation of the wind systems and the hydrological cycle, both in turn directly affecting the continental land masses.

Molecular Jargon Box I

Terrigenous Biomarkers—leaf waxes of land plants as proxies for terrestrial vegetation and climate

The lipid components of the protective waxes that coat the leaf surfaces of almost all land plants are environmentally persistent (Eglinton and Hamilton, 1963). Typically, they are comprised of mixtures of long, straight-chain (i.e., *normal*, *n*-) alkanes, alkanols and alkanoic acids with 24–36 carbon atoms. The alkanes are predominately of odd carbon number and the alkanols and alkanoic acids are of even carbon number. This characteristic odd/even carbon-number distribution is a consequence of the universal polyketide (acetate, malonate) biosynthetic pathway. The odd numbered *n*-alkanes are formed by the loss of a single carbon from the precursor even-numbered *n*-alkanoic acids.

n–alkane $CH_3(CH_2)_nCH_3$,

n–alkanol $CH_3(CH_2)_nCH_2OH$,

n–alkanoic acid $CH_3(CH_2)_nCO_2H$

Their water insolubility, negligible volatility (for compounds with more than 20 carbon atoms), chemical inertness and resistance to biodegradation make them excellent biomarker compounds. They pass into the environment in and on leaf fragments and as aerosols formed by vegetation fires and by wind abrasion. They are often transported long distances by wind and water to be deposited where they can serve as proxy measures of the continental vegetation that biosynthesized them (Fig. 1).

Typically, in using long-chain compounds as biomarker proxies the distributions are described in terms of carbon-number range, carbon number of the most abundant homologue (homologues are compounds in a homologous series that have the same general formula but differ in the number of repeating units they contain), [C_{max}], average chain length [ACL], carbon-number preference index [CPI], and values for stable isotopic abundances [e.g. $\delta^{13}C$, ‰] of individual homologues or their averages. Taking the C_{29} *n*-alkane, nonacosane ($CH_3(CH_2)_{27}CH_3$) as an example, all the atoms are bound together by strong covalent bonds, C–C and C–H, which are very difficult to break without high energy input such as heating at high temperatures, radical attack, or through the highly specific activity of enzymes and other catalysts. Hence, the isotopic contents of carbon and hydrogen incorporated during biosynthesis are relatively inviolate during passage of the intact molecule through the environment and in sediments over geologic time. This type of biomarker is highly conserved.

The $\delta^{13}C$ values of the carbons in the wax molecules depend on that of the ambient atmospheric CO_2, the pathway employed during photosynthesis, e.g. whether it is the C_3 or the C_4 biosynthetic pathway, and on factors (including aridity) that affect the conductance of the plant's stomata. C_3 plants comprise most temperate species, including grasses, trees and shrubs. C_4 species are much less numerous and are typically tropical grasses and sedges. The overall average distributions and isotopic compositions of the *n*-alkanes differ clearly between these two plant types, even though there is considerable interspecific variation within each. Thus, the C_4 grasses on average show the *n*-alkane C_{max} at C_{31} (ACL, 30.7) with $\delta^{13}C$ −22‰, while the C_3 plants peak at C_{29} (ACL, 29.0) with −34‰ (Rommerskirchen et al., 2006b).

Similar characteristics in respect to distributions and isotopic content are also shown by other leaf wax components, such at the *n*-alkanols and *n*-alkanoic acids. Hence, the range of biomarkers which can be used as measures of phytogeography of adjacent continental areas is wider than just the *n*-alkanes. These plant-wax proxies are best used along with other proxies for vegetation dominance—e.g. pollen and phytolith counts, and mineral particle types—in order to develop a robust picture of past vegetation.

C_4 plants can cope better with lower pCO_2, higher temperatures and more arid habitats. The C_4 grasses are the most numerous of C_4 plant types and dominate the huge areas of grassland and savannah which encircle the globe at sub-tropical latitudes in Africa, South America, parts of Australia and India and Pakistan (Still et al., 2003). These zones reflect the distribution of rain-deprived open environments which result from the impact of the prevailing patterns of the earth's weather systems on the continents.

Thus one can use measures such as the leaf wax alkane patterns and the ^{13}C values registered in particulates derived from a given geographical area and deposited elsewhere as proxies for the dominance of C_3 or C_4 plants in the source regions. In turn, these findings can be taken as a reflection of the growth environment and hence the climate controlling it.

The long-chain lipids of plant waxes also show every promise of providing important paleoenvironmental information on hydrologic cycles through their compound-specific hydrogen-isotopic compositions (δD). Just as with the carbon atoms, the covalently bonded hydrogens in the CH_2, CH and CH_3 groups making up the aliphatic chains of the saturated compounds are not exchangeable and retain the δD composition acquired at the time of biosynthesis in the leaf as long as the molecules remain intact. However, rearrangement and isomerisation of the compounds during diagenesis may lead to exchange of the hydrogen atoms. The topic of hydrogen-isotopic exchange is discussed in detail by Sessions et al. (2004).

The δD values of the plant lipids reflect that of the environmental water further modulated by local hydrological processes and by isotope effects associated with biosynthesis. However, recent papers (e.g. Chikaraishi and Naraoka, 2003; Chikaraishi et al., 2004a,b, 2005; Sachse et al., 2004; Smith and Freeman, 2006) show that the isotopic content of the water actually used by plant cells at the site of biosynthesis is also dependent on physiological processes, such as evapotranspiration, operating within the plant (e.g., Barbour et al., 2004). Thus, there will be differences between the isotopic contents of the meteoric water, the soil water and that within the plant. Indeed, it is apparent that in determining the δD of the waxes of plants it is plant physiology rather than the biochemical pathway (e.g., C_3 vs. C_4) which is the main factor. For example, the values for angiosperms typically differ from those of gymnosperms (Smith and Freeman 2006; Sachse et al., 2006). Furthermore, some of these issues can be assessed by parallel $\delta^{13}C$-measurements as angiosperms have different ^{13}C abundances and chain length distributions than gymnosperms. Nevertheless, compound-specific δD data for plant-wax components can be a useful guide to the δD values of the original environmental water used by the plant and hence, serve as indirect palaeoprecipitation/aridity proxies.

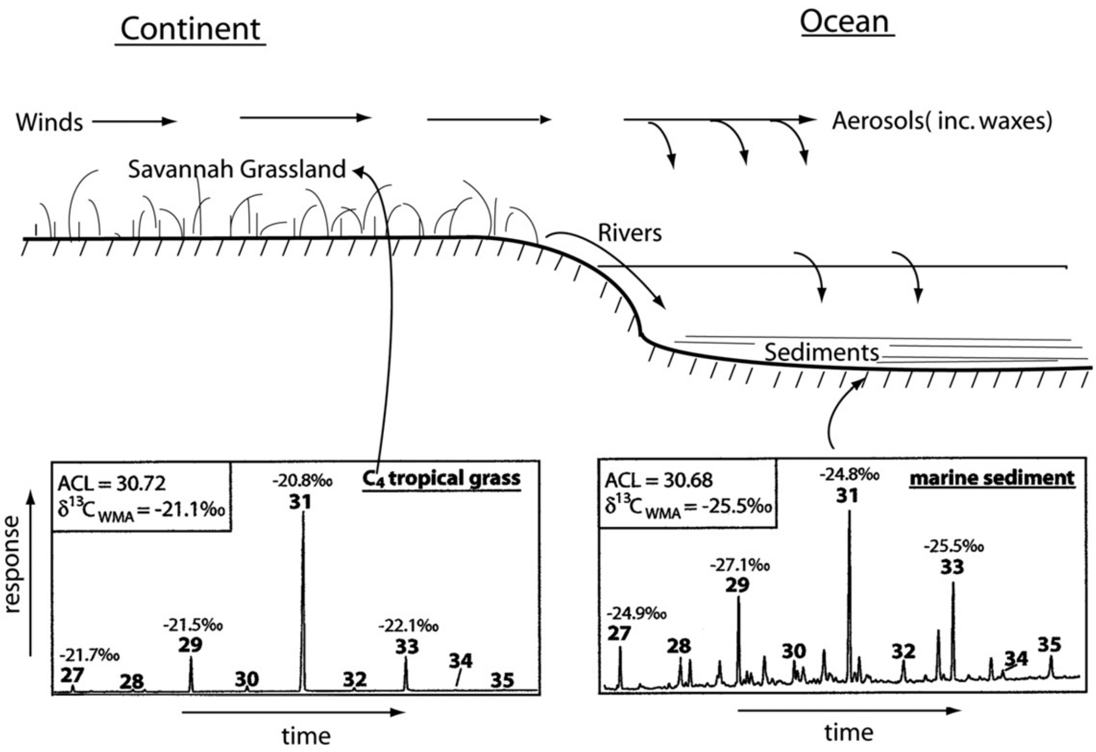


Fig. 1. Plant-wax lipids in ocean sediments. These compounds serve as proxies for continental vegetation since they reach the sediments from the continent by wind and river transport of particulates and dust and smoke aerosols. Typical GC traces are shown for the *n*-alkane fractions [C_{27}–C_{35}] of a C_4 tropical grass and for a marine sediment from the southeast Atlantic. The $\delta^{13}C$ values (in ‰) are marked for each of the prominent odd-carbon-number homologues. The $\delta^{13}C_{WMA}$ (weighted mean average) is also shown for this carbon-number range, together with the Average Chain Length [ACL] (Rommerskirchen et al., 2006a,b). The distribution and isotopic compositions in the marine sediment are in accord with a significant input of *n*-alkanes from the African savannah C_4 grasslands.

3. Terrigenous molecular proxies: biomarkers as tracers of continental paleoclimate in marine sediments

Leaf wax biomarkers preserved in oceanic sediments provide indications of terrestrial phytogeography and hence the continental climate prevailing at the time of biosynthesis of the leaf waxes [see Molecular Jargon Box I].

Solvent extracts of marine sediments from almost anywhere on the ocean floor contain a variety of long-chain lipids. These compounds include hydrocarbons, alcohols, acids, and esters. The hydrocarbons, for example, are mostly straight chain, normal, (*n*-) with a marked odd-over-even carbon-number predominance, and typically with high n-C_{29} and n-C_{31} and low n-$C_{28,30 \text{ and } 32}$ abundances. We now know that most come from the leaf waxes of vegetation on nearby continents and are delivered as aerosols and adsorbed on mineral particles carried by river and wind systems (Fig. 1). Not only are their carbon-number distributions readily recognisable as characteristic of higher plants but also their carbon-isotopic compositions serve as tracers for the photosynthetic pathway used by the parent vegetation. Accordingly, the $\delta^{13}C$ values of sedimentary, long-chain *n*-alkanes can serve as a proxy for the composition of the continental vegetation in the source areas. The vegetation, in turn, reflects regional temperatures, aridity and pCO_2. *n*-Alkanes are resistant to degradation, but suffer from interference from petrogenic hydrocarbons which have low carbon-preference indices (CPIs). Again, which chain lengths are the best choices for a particular site depends on phytogeography. For example, the C_{33} *n*-alkane appears to carry more of the C_4 signal in Africa. This approach has served as the basis for a variety of paleoclimate-related studies over the past 15 yr as illustrated by Case Studies 1 through 5, with further discussion in Case Study 9.

Case Study 1. *Africa and the Southeast Atlantic: Present-day evaluation and validation of terrigenous signals. n-Alkane distributions and $\delta^{13}C$ values as proxy measures of continental coverage by C_3 vs. C_4 plants.*

Examples of the paleoenvironmental records provided by plant waxes are found in studies of marine sediments from the Eastern Atlantic off the African continent. Fig. 2a summarizes aspects of the present-day geography and climate of the region. Sedimentation in the Atlantic Ocean is marked by substantial inputs from a few large rivers such as the Congo and the Niger and by widespread deposition from the highly seasonal dust and smoke plumes carried from the desert, savannah and desiccated lake beds (Eglinton et al., 2002). The wind systems and rainfall distributions are in part driven by SST differences between the different ocean regions (e.g., the equatorial and sub-tropical ocean) in the southeast Atlantic off southwestern Africa. The continental phytogeography (highly simplified in Fig. 2b) reflects the rainfall patterns (Fig. 2a), with the dominant grasslands of the African savannah and desert regions being populated by C_4 plants rather than C_3. Herein lies a major role for molecular distributions and compound-specific stable isotope measurements.

Fig. 2b summarizes available carbon-isotopic compositions ($\delta^{13}C$, ‰) for the n-C_{29} alkane from surface sediments at ~50 sites in the Eastern Atlantic. The color coding of these ocean sites expresses the range in isotopic values. Even at this relatively low coverage, $\delta^{13}C$ values for this single, plant-wax alkane clearly reflect the relative terrigenous inputs from the C_3 vs. C_4 vegetated areas on the adjacent continent (Fig. 2b), if wind trajectories are taken into account (Fig. 2a). Below the equator, the northerly sites (Congo Fan, N. Angola Basin) receive most of their terrestrial material by fluvial supply from the Congo Basin and from the Angolan highlands dominated by C_3 plants. In contrast, off NW Africa and southwards, the dominant contribution is carried by winds as aerosols (dust, smoke) derived from the western and central African hinterland where desert, semi-desert and savanna regions are populated predominantly by C_4 grasses. These distributions are also mirrored by pollen assemblages in these sediments.

The isotopic compositions of other leaf wax biomarkers show similar trends. More detailed mapping, based on more numerous samples, carefully constrained by appropriate ^{14}C dating, would no doubt reveal more specific information on the generation, transport and deposition processes of these terrigenous biomarkers.

Case Study 2. *Southeast Atlantic: A glacial/interglacial comparison for a north–south transect of n-alkane proxy records of C_3 vs. C_4 vegetation on the African continent.*

Molecular Jargon Box II

Marine biomarkers—proxies for past sea surface temperature (SST)

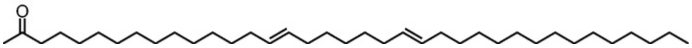
Alkenones and the $U^K_{37}{}'$ index

One of the longest-established biomarker-based proxies is known as the $U^K_{37}{}'$ index (Brassell et al., 1986; Prahl and Wakeham, 1987). It is based on the relative abundances of two compounds, colloquially termed alkenones. The two compounds, each with 37 carbons, differ only in that the $C_{37:2}$ ($C_{37}H_{72}O$) has two carbon–carbon double bonds and the $C_{37:3}$ ($C_{37}H_{70}O$) has three. This SST proxy, expressed as:

$$U^K_{37}{}' = [C_{37:2}]/\{[C_{37:2}] + [C_{37:3}]\}$$

can have values between 0 and 1, roughly corresponding to 0 and 26 °C, respectively, usually assigned as the annual mean SST (mixed-layer temperature):

$$SST = (U^K_{37}{}' - 0.044)/0.033 (\text{Müller et al., 1998})$$

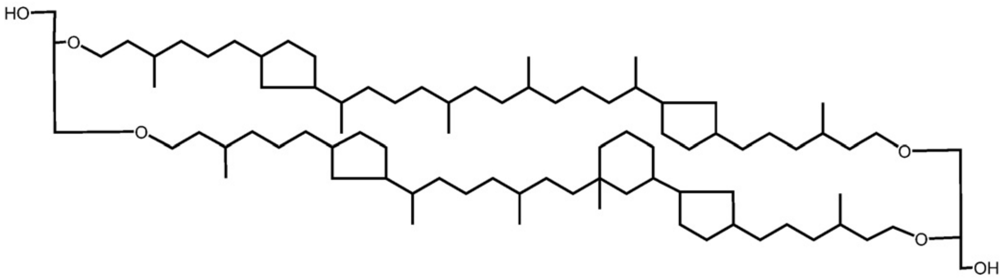


Structure 1: $C_{37:2}$ alkadienone

These long, straight-chain, 37-carbon ketones are biosynthesised by unicellular eukaryotic haptophyte marine algae. Haptophytes are widespread in the photic zone of the modern ocean, being one of the primary producers of pelagic calcium carbonate as minute (micron size), ornate tests (coccoliths). It is still uncertain what role alkenones play in haptophyte physiology, although energy storage seems to be important (Eltgroth et al., 2005), However the number of double bonds they possess is directly related to the growth temperature, with more of the alkenone with three (and also four) double bonds ($C_{37:3}$) rather than two double bonds ($C_{37:2}$), being produced at colder water temperatures. Alkenones have been found in sediments millions of years old and, where present, have been used to reconstruct paleo-SSTs, providing records that are completely independent but complementary to those from other approaches, such as the use of oxygen isotopes. Foraminiferal calcium carbonate shells are not always well preserved whereas the more persistent alkenone molecules have proven to be valuable recorders of Pleistocene and earlier climate change from the poles to the tropics (e.g., Eglinton et al., 2001; Sachs et al., 2001; Sachs and Anderson, 2005; Haug et al., 2005; Zhao et al., 2006; Kienast et al., 2006). Analyses are not limited to determination of alkenone abundances and distributions; it is possible also to determine their stable carbon and radiocarbon radiocarbon-isotopic compositions. The δ^{13}C values have been shown to be related to carbon dioxide concentrations, leading to the development of a 'paleo-pCO_2' proxy (Jasper and Hayes, 1990; Pagani, 2002; Pagani et al., 2005). The interpretation of alkenone carbon-isotopic compositions in terms of pCO_2 is not without controversy, however, as other factors such as algal growth rate have also been shown to influence alkenone δ^{13}C values (Bidigare et al., 1997; Popp et al., 2006). Additionally, alkenone radiocarbon compositions have been used to refine age estimates of marine sediments and in some cases identify long-distance transport of particulates by currents (Ohkouchi et al., 2002; Mollenhauer et al., 2005).

Glycerol Dialkyl Glycerol Tetraether (GDGT) lipids and the TEX$_{86}$ index

The TEX$_{86}$ index is a recent addition to the marine-based biomarker proxies for paleoceanography (Schouten et al., 2002). Once again, the biological sources are single-celled microorganisms, but members of the domain Archaea, rather than the Eucarya. Recently, it has become clear that the Archaea are not restricted to the very narrow range of extreme environments where they were initially characterized. Rather, they are common in many environments and appear to be one of the dominant forms of pelagic picoplankton in the oceans (Karner et al., 2001). Their unusual membrane lipids include a range of C_{86} glycerol dialkyl glycerol tetraethers (GDGTs), such as crenarchaeol (see Structure 2).



Structure 2: Crenarchaeol

The GDGTs vary compositionally in response to growth temperature, and provide an ideal basis for a biomarker proxy. Indeed, the research group at the Royal Netherlands Institute for Sea Research (NIOZ) has shown that the assemblage of GDGT membrane lipids of pelagic Archaea varies with SST; at higher temperatures, these tetraether lipids contain more cyclic groups.

The GDGT molecules appear to be relatively robust diagenetically (Schouten et al., 2002, 2003; Wuchter et al., 2005; Kim et al., 2008). These biomarkers have been found in sediments spanning the last 100 myr, and so they complement the alkenone SST proxy by going back much further in time. Archaeal tetraethers record high (>30 °C) temperatures in Mid-Cretaceous tropical oceans, potentially resolving the cool tropics paradox and providing new insight into greenhouse climates (Schouten et al., 2007). Non-thermophilic Crenarchaeota and their biomarkers are also present in lakes and hence TEX$_{86}$ may be used as a paleothermometer in the study of lacustrine deposits. TEX$_{86}$ is proving of major value in assessing SSTs in the Cretaceous and at the PETM, and shows promise for understanding Cenozoic climate generally (Pearson et al., 2007).

The TEX$_{86}$ proxy has been empirically formulated in terms of the relative abundances of four GDGT compounds which differ mainly in the number of rings and methyl branches they possess. TEX$_{86}$ can be expressed as follows:

$$\mathrm{TEX}_{86} = \{[2] + [3] + [5]\}/\{[1] + [2] + [3] + [5]\}$$

where [1] to [5] represent the amounts of the compounds measured and where [1] represents the amount of the compound with one ring, and so on. The compound [5] is a stereoisomer of crenarchaeol. Empirically derived calibrations have been determined for TEX$_{86}$ against mean annual surface water temperature (T, °C; Powers et al., 2004, 2005; Wuchter et al., 2004, 2005), with the most recent deriving from a global marine sediment core-top survey (Kim et al., 2008) yielding the following:

$$T = -10.78 + 56.2 \times \mathrm{TEX}_{86}$$

Even though the TEX$_{86}$–T correlation suggests that this signal originates from surface waters, there remain unanswered questions, such as just where and when the GDGTs are generated. Pearson et al. (2001) and Ingalls et al. (2006) found that significant amounts of the compounds contributing to the TEX$_{86}$ proxy are made below the mixed layer in the water column. But, then, how does the proxy work? Biologically-mediated consumption and repackaging of materials in the upper water column appears to play an important role in the transmission of GDGTs from surface waters to the sediments (Wuchter et al., 2006). Evidence also indicates that these compounds may be less susceptible to sediment redistribution processes than the alkenones (Mollenhauer et al., 2008), but the infancy of this proxy suggests that caution is in order in its application.

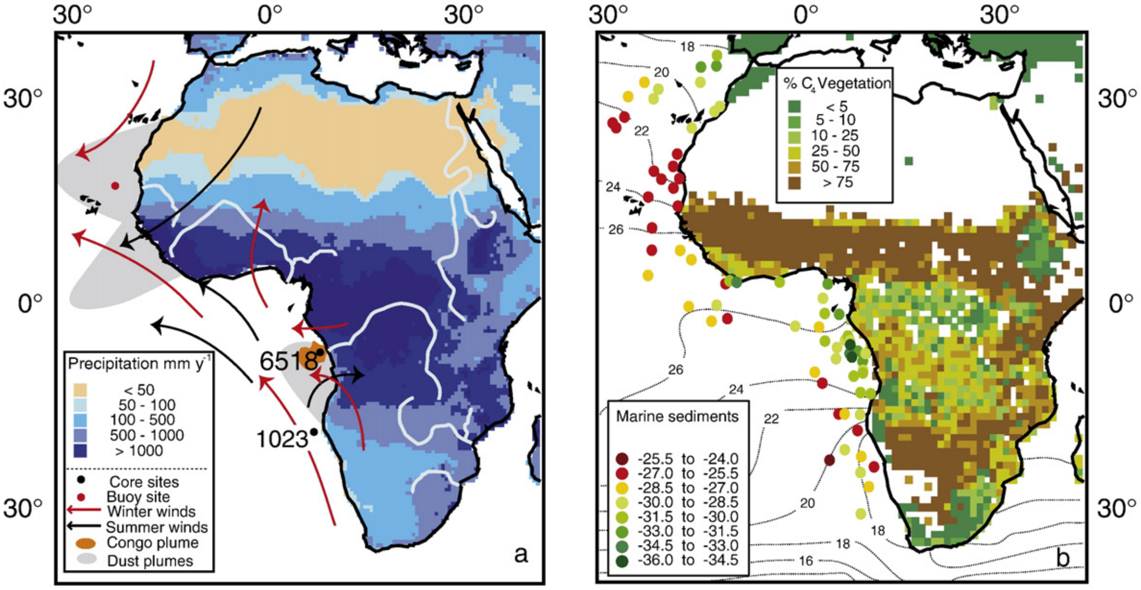


Fig. 2. The African continent and the adjacent Atlantic Ocean. a) Geography and climatological features: Color mapping of the mean annual precipitation rate (mm yr^{-1}; based on Nicholson, 2000). Also shown are the principal rivers (white lines), austral summer winds (black arrows) and austral winter winds (red arrows), the dust plumes, the sediment plume of the Congo River (Schefuss et al., 2004, and sites of dust collection (Eglinton et al., 2002) and sediment coring (GEOB 6518 and 1023; Schefuss et al., 2005). b) Distributions of C_4 plants (% of the continental vegetation) and of compound-specific $\delta^{13}C$ values for n-C_{29} alkane in surface sediments of the East Atlantic (Case Study 1): The color coding for $\delta^{13}C$ (lower box) of the n-C_{29} alkane in the marine sediments ranges from −24 to −36‰. Red/brown (−24 to −27‰) corresponds to high %C_4 and green (−31 to −36‰) to low %C_4. Comparison of this color distribution pattern with that of the precipitation and the transport systems in a) reveals how the $\delta^{13}C$ values of the n-C_{29} alkane in the Atlantic sediments parallel the modeled distribution of C_3 vs. C_4 type vegetation on the continent, color coded from <5 to >75% C_4 (upper box). In this continental distribution of the model C_4 fraction (Still et al., 2003; values below 5% are left blank), the highest C_4 concentrations (brown areas) occur in the tropical and sub-tropical grassland and savannah regions (Huang et al., 2000; Schefuss et al., 2003a, 2004, 2005; Rommerskirchen et al., 2003, 2006b). The SST contours (in °C) are also shown.

A recent study has explored the compound-specific, stable isotope approach for the last glacial–interglacial cycle (Rommerskirchen et al., 2003, 2006a; Fig. 3). It involved core sites off the Southwest African continental margin along a North–South transect from the Congo Fan in the North (4°S) to the Cape Basin in the South (30°S). The cores were sampled to provide 4 time horizons—two glacial (marine isotope stages [MIS] 2 and 6a) and two interglacial (MIS 1 and 5e). Fig. 3 illustrates the N–S transect plots for 8 sites and just two of these time horizons—the Late Holocene at about 4 kyr BP and the Last Glacial Maximum (LGM) at 22 kyr BP. The data document n-alkane (C_{27}–C_{35}) distributions and the corresponding average isotopic compositions. There are clear trends in the plots at both time horizons. The average

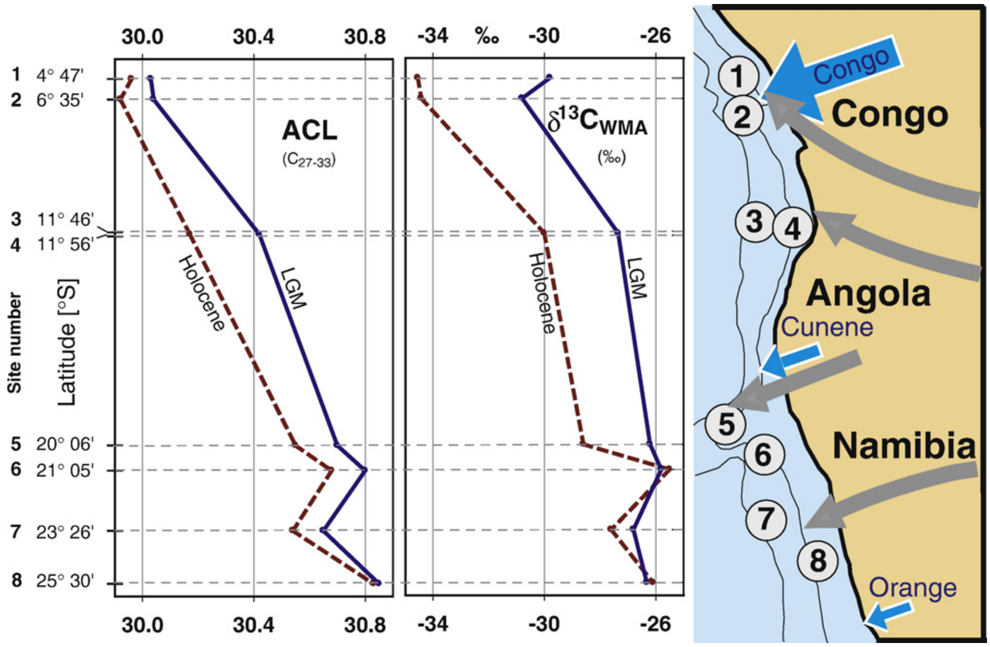


Fig. 3. A biomarker comparison of Late Holocene (ca. 4 kyr BP) and Last Glacial Maximum (LGM; ca. 22 kyr BP) S.E. Atlantic ocean sediments in a N-to-S transect off southern Africa (Case Study 2). n-Alkane Average Chain Length (ACL) and $\delta^{13}C_{WMA}$ (weighted mean average, ‰) are plotted for eight sites. The blue arrows indicate contemporary riverine inputs and the grey arrows prevailing low altitude winds of the Austral winter, which carry smoke, dust, pollen and waxes out to the Atlantic Ocean. Data for the sites 3 and 4 have been combined (Modified and redrawn from Gaines et al. in press). The shifts in ACL and $\delta^{13}C$ values reveal the greater contribution from C_4 grasslands towards the south, as already shown for the Late Holocene in Case Study 1 (Fig. 2b). The C_4 contribution is greater during the LGM, especially at the more northern sites.

chain length (ACL) shifts to higher values and the average $\delta^{13}C$ shifts to less negative values. There are also differences between the Holocene and LGM which are especially marked for the northern sites. This behavior is also seen for the deeper pair of time horizons (MIS 5e and 6a), and can be interpreted in terms of the changing contributions of C_3 vs. C_4 terrigenous leaf waxes to the sites, with the C_4 contributions being marked by higher ACL and heavier $\delta^{13}C$ values. In the northern part of this transect, the data indicate that the C_4 plants make a bigger contribution during glacial times, indicating a northward extension of arid zones dominated by C_4 grass vegetation. These conclusions are concordant with those derived from pollen counts (Rommerskirchen et al., 2006a). Similar variations in plant-wax carbon-isotopic composition have been found to persist through much of the Pleistocene (Schefuss et al., 2003b).

Case Study 3. *Southeast Atlantic during the most recent deglaciation: Plant-wax n-alkane δD values in the Congo Fan follow SST differences in the SE Atlantic and associated precipitation changes in Central Africa.*

An example of the paleoenvironmental applications of compound-specific hydrogen-isotopic (δD) measurements based on *n*-nonacosane is provided in Fig. 4 (Schefuss et al., 2004, 2005). The authors made high-resolution δD measurements for this terrigenous biomarker for the last 18 kyr of marine sedimentation in core GEOB 6518, a near-equatorial Atlantic site off Africa, close to the mouth of the Congo River. They then employed this record (Fig. 4a) as a measure of past variations in rainfall registered by the vegetation in the central African region drained by the Congo. The values of δD for the n-C_{29} alkane varied from −130 to −170‰. Marked negative shifts accompanied the last deglaciation, beginning about 12 kyr BP. Schefuss et al. (2005) proposed that these negative shifts reflect precipitation increases, driven in turn by decreases in the meridional gradient of SSTs (Fig. 4b) between the tropical and sub-tropical South Atlantic (GEOB 6518 &1023, respectively; Fig. 2a). The paleo-SST data were also derived from biomarker measurements (i.e., alkenone $U^{K}_{37}{}'$: See Molecular Jargon Box II). This apparent teleconnection between ΔSSTs in the Atlantic and δD for the n-C_{29} biomarker molecules originating in the mainly C_3 tropical forests can be explained in terms of the controlling effect of regional SSTs on sea-level air pressures and hence the strength of the low altitude wind systems flowing from one region to another. Thus, between 15 and 12.5 kyr BP and between 9 and 3 kyr BP, the low ΔSST (Fig. 4b) is presumed to result in weaker trade winds which would have been less effective in opposing the strong, off-ocean, wet, westerly winds, with consequent increased precipitation in Central Africa. The predicted, strongly negative values for the δD of the resulting meteoric water are then imprinted in the isotopic contents of the hydrogens bonded to the carbon chains of the leaf waxes synthesized by the vegetation of this region and transported on particles to Site 6518. Incidentally, corresponding *n*-alkane $\delta^{13}C$ values in this record did not show any significant changes in C_3/C_4 plant abundance. Each inferential step in reconstruction is subject to uncertainties. In particular, the factors controlling plant-wax δD are incompletely understood. But overall, the interpretations provide an encouraging basis for further studies. They imply that millennial-scale changes in Atlantic thermohaline circulation apparently had a major effect on the continental climate, particularly the hydrologic cycle of Central Africa.

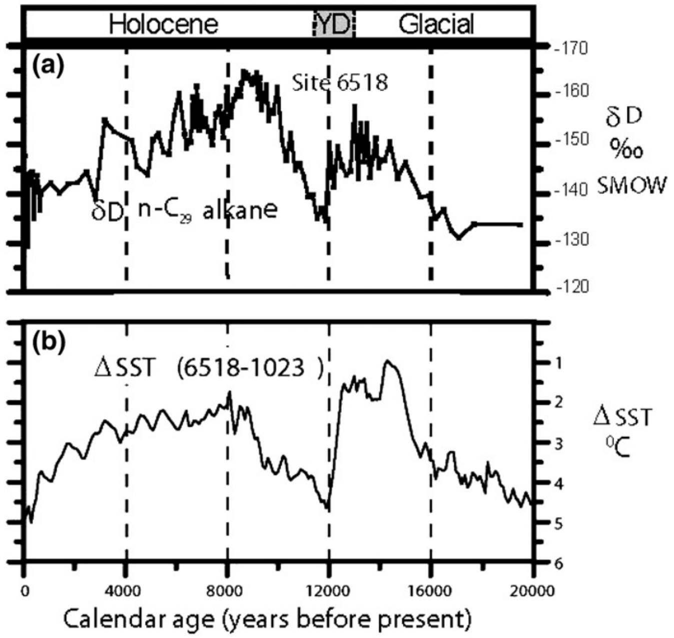


Fig. 4. Compound-specific isotope stratigraphy(δD, ‰), based on *n*-alkane data, for a site near the Congo River outflow (GeoB 6518-1; Fig. 2a), shows trends similar to those in the differences in oceanic SST (ΔSST) for two sites (6518 and 1023) during the past 20,000 yr. (Case Study 3). a) n-C_{29} alkane compound-specific δD record: The values vary over the range −130 to − 170‰ and the trends roughly parallel those of the ΔSST values in the SE Atlantic plotted in b) below. The provisional interpretation is that the precipitation (Fig. 2a) carried into the central African region by the wind systems is controlled in part by the ΔSST of certain latitudinally separated oceanic water masses; lower ΔSST results in increased precipitation and hence more negative δD incorporated in the leaf waxes. b) Alkenone ΔSST record: Differences (plot in °C) between the SST records (obtained from $U^{K}_{37}{}'$ measurements of the C_{37} alkenones) for the more southerly core 1023 as compared with those for the Congo Basin core 6518 (Fig. 2a and b). Figure redrawn from Schefuss et al. (2005).

Case Study 4. *Cariaco Basin: a tropical, anoxic marine basin. Abrupt changes in leaf wax biomarker (n-C_{32} alkanoic acid) $\delta^{13}C$ related to sedimentation changes during the last deglaciation.*

Core PLO7-58PC from the saddle of the Cariaco Basin between the sub-basins (Fig. 5a), contained organic matter-rich (2–5% organic carbon), annually laminated sediments between 15 and 10 kyr BP, constrained by numerous foraminiferal ^{14}C data points. Increased sediment reflectances—lower values of the gray scale—recording diatomaceous, opal-rich laminae, reflect increased trade wind intensity and upwelling and reduced river runoff. In contrast, the darker laminae correspond to increased riverine clastic input. Hughen et al. (2004) and Makou et al. (2007) chose to generate high-resolution, terrigenous vegetation records by using the distributions (ACL) and isotopic compositions ($\delta^{13}C$, δD) of another class of leaf wax-derived biomarkers—the long-chain fatty acids (FA). The biomarker data (Fig. 5b and c) are in accord with increases of C_4-grass inputs during the drier, cooler glacial periods (Last Glacial, Younger Dryas: higher ACL and less negative $\delta^{13}C$) and more C_3-forest vegetation in the warmer, wetter interglacial intervals (Bolling/Allerod, Pre-boreal: lower ACL and more negative $\delta^{13}C$). Fig. 5b also clearly demonstrates that the abrupt changes in the vegetation proxy are tightly coupled with the climatic shifts indicated by the sediment reflectance.

In this case, the terrestrial, leaf wax biomarker signals could have two principal sources: (*i*) local coastal vegetation, for example the extensive belts of mangroves, and the vegetation of the Venezuelan hinterland, carried in by the rivers from the drainage basin, especially during wet periods following long dry spells; or (*ii*) dust borne on the trade winds from NW Africa, especially the strong, drier winds of the glacial periods. Here the waxes would be expected to be a mixture of those derived from contemporary African vegetation and from much older material eroded from soils and lake sediments (Eglinton et al., 2002). Hughen et al. (2004) suspect that any North African biomarker signal is quantitatively overwhelmed by the local riverine and coastal input (Hughen et al., 2004; Makou et al., 2007).

Compound-specific ^{14}C analyses of the long-chain compounds extracted from Cariaco Basin sediments (Drenzek et al., in prep) are in accord with the existence of two end-member pools of compounds which contribute to the sedimentary record: a "pre-aged", circa 2 kyr-old component which makes up the bulk and a "fresh" 10–20 yr-old

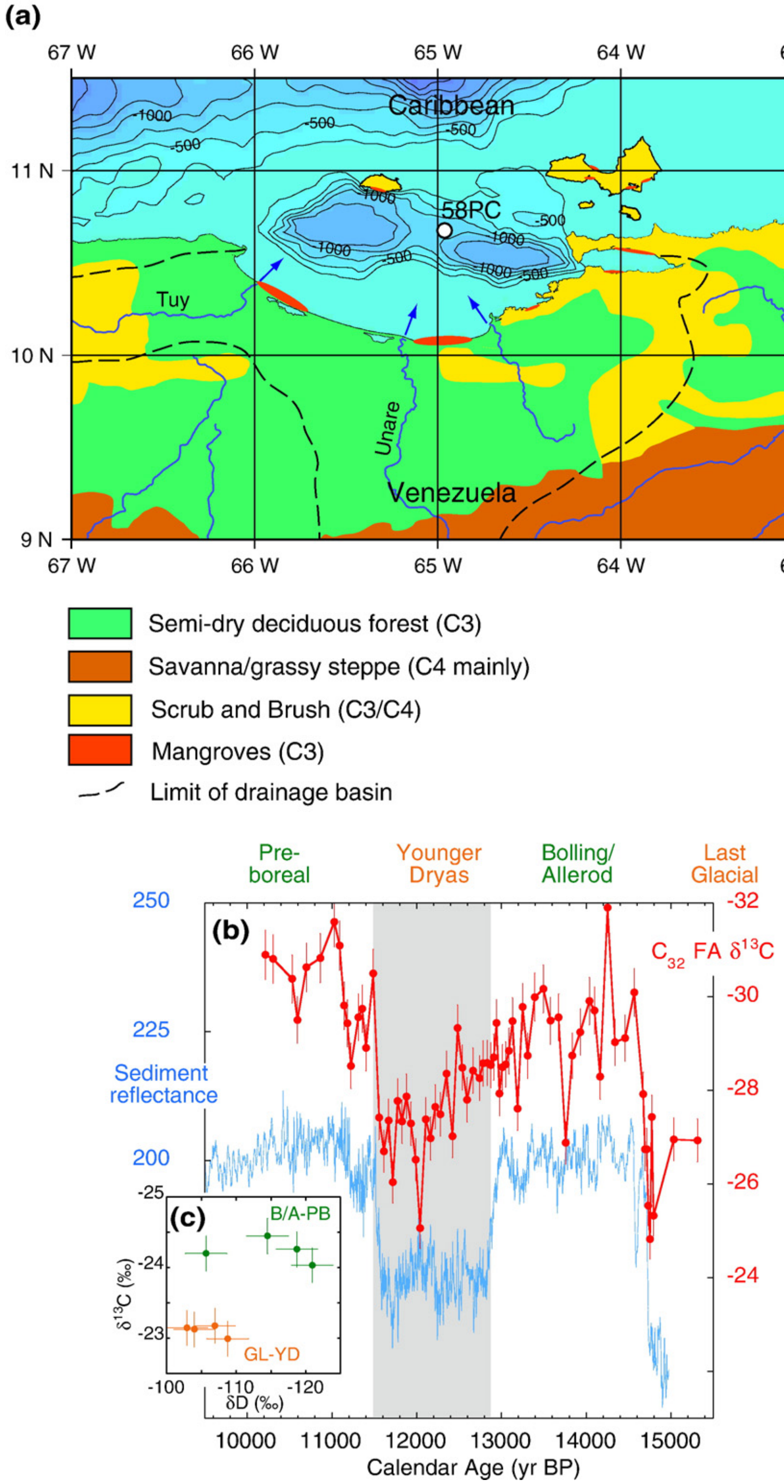


Fig. 5. Rapid (decadal scale) environmental responses of biomarker proxies deposited in an anoxic marine basin. (Case Study 4). a) The Cariaco Basin on the southern coast of the Caribbean (north of Venezuela) is the world's second largest, persistently anoxic, marine basin after the Black Sea. The climate here is strongly influenced by the seasonal migration of the Inter-Tropical Convergence Zone (ITCZ): it varies from strong easterly trade winds in the winter, accompanied by upwelling of nutrient-rich waters and high productivity, especially of diatoms, to weaker trade winds in the summer, with less intense upwelling and lower productivity, mainly of coccolithophorids. The annually varved sediments deposited in the basin are rich in marine-derived organic matter, together with lesser terrigenous components. Pollen records show that the terrigenous source shifted between predominantly dry grasslands in the glacial stadials to wet montane forest during the interstadial times, including the present. The present-day phytogeography of the hinterland has been redrawn from Wikipedia. b) High-resolution biomarker (n-C_{32} n-alkanoic fatty acid (FA), $\delta^{13}C$) and sedimentological data for core PL07-58 PC over the last deglaciation spanning the interval from 15 to 10 kyr BP (Hughen et al., 2004). The red curve is $\delta^{13}C$ of the n-C_{32} FA measured for samples approximately every 70 yr. The blue curve is the sediment reflectivity, measured continuously. The close parallel in the behavior of the $\delta^{13}C$ of the n-C_{32} FA trace and the sediment reflectivity trace (effectively the varve signal) requires that changes in the sedimentation regime are accompanied by changes in the composition of plant-wax input, with increased C_4 contributions in glacial times. Redrawn from Hughen et al. (2004). c) Inset: plot of compound-specific $\delta^{13}C$ against δD values (‰) for weighted mean averages of the long-chain fatty acid fraction ($C_{24,26,28,30,32}$). The eight values available are for the last glacial (GL) and the Younger Dryas (YD) and for the interglacial Bolling-Allerod (B/A) and PreBoreal (PB) intervals. The glacial samples have heavier $\delta^{13}C$ values, corresponding to enhanced C_4 contributions, and heavier δD values indicating drier environments. Redrawn from Makou et al. (2007). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

component which is the minor contributor. This two-component mixing would indicate that most of the leaf waxes reside in soils and in river and coastal sediments for decades to millennia before being finally deposited in the basin. Similar situations have been recorded for Saanich inlet in British Columbia (Smittenberg et al., 2006) and off the Northwest African coast (Eglinton et al., 2002). So how is it that the changes in the biomarker and sediment records are tightly coupled (Fig. 5b)? The abrupt climatic changes evident in the records will have affected both marine sedimentation and land erosion simultaneously and, hence, pulses of leaf waxes, varying in terms of both amount and isotopic content, will have accompanied changes in sedimentation. Given that the leaf wax signal must be considerably smoothed by the mixed-age inputs, the amplitude of the abrupt changes in the $\delta^{13}C$ signal, on the order of 3‰, must be considerably greater, implying dramatic, climate-induced swings from C_3 to C_4 and vice versa. This study highlights the importance of placing temporal constraints on the transmission of molecular-proxy signals into aquatic sediments.

Further application and refinement of this approach, using varved sediment deposits in anoxic basins, should allow detailed investigation of abrupt, climate-induced changes in tropical hydrological cycles. Furthermore, work on terrigenous proxies can be paralleled by high-resolution measurements of distributions and of abundances of marine biomarkers to give new insights into the structures of planktonic communities and their productivities in relation to changing terrigenous input and paleoceanographic conditions.

4. Marine molecular proxies: microbial biomarker tracers of water column conditions and productivity

Paleo-SST is a prime concern in paleoclimatology because the distribution of SST around the contemporary oceans clearly drives the present-day climate engine through the evaporation of water, the generation of the wind systems, and associated subsequent precipitation. Critical factors also include the vertical temperature structure of the water column, especially the upper water column and, more generally, the temperatures of different water masses. These heat sources generate hurricanes, typhoons, monsoon rains and droughts. The transfer of heat from one part of the ocean to the other via both surface and deep currents is therefore crucial. Unfortunately, biomarkers for bottom-water temperatures are yet to emerge.

There are now two biomarker proxies for SST which have been accepted by the paleoceanographic community. They are known as the $U^{K}_{37}{}'$ and TEX_{86} [Molecular-Proxy Box II]. The longer established proxy, $U^{K}_{37}{}'$, is based on the relative abundances of two long-chain (C_{37}) unsaturated ketones which are biosynthesized in considerable quantities by the unicellular marine green algae, *Emiliania huxleyi* and a few other haptophyte species which grow in ocean surface waters. Case Studies 5, 6, and 7 illustrate the use of the alkenones in paleoceanography, and are discussed further in Case Study 10. The newer proxy, TEX_{86}, utilizes the relative abundances of a group of C_{86} glycerol dialkyl glycerol tetraethers (GDGTs), and is illustrated in Case Study 8 and discussed in Case Study 9.

Case Study 5. *Western Mediterranean: High-resolution alkenone records indicate very rapid (centennial scale) influxes of cold, low-salinity waters during the last glacial/interglacial cycle.*

The high-resolution alkenone SST $U^{K}_{37}{}'$ record at ODP site 977A (Fig. 6b; Martrat et al., 2004, 2007) shows many abrupt warming and cooling events which mostly occurred simultaneously with rapid changes in the carbonate $\delta^{18}O$ record of the planktonic foraminiferum *G. bulloides* (Fig. 6a). These events were more common during warming trends. Some of the minima are concurrent with the massive release of icebergs into the North Atlantic–Heinrich events (Fig. 6c, H1-6). That cold, low-salinity waters flowed into the Mediterranean at these times is further supported by well documented, coeval increases in the amounts of the polar planktonic foraminiferum *M. pachyderma*

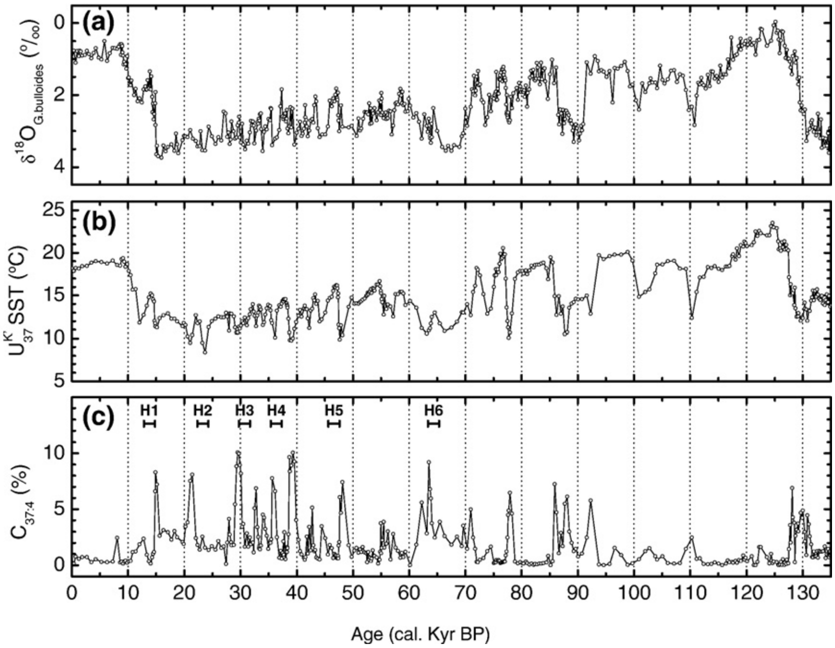


Fig. 6. Paleoenvironmental high-resolution (approx. 400 yr intervals) $\delta^{18}O$ and biomarker proxy records for the last interglacial/glacial cycle at site ODP 977A in the western Mediterranean (redrawn from Martrat et al., 2004, 2007) (Case Study 5). a) The $\delta^{18}O$ plot for the planktonic foraminiferum *Globigerinia bulloides*. This high-resolution curve parallels the smoothed SPECMAP standard isotope curve and has been controlled by ^{14}C ages for the sediments of the last 20 kyr. The record is available for the past 250 kyr but only the last cycle is shown here. b) Annual mean paleo-SST record based on the $U^{K}_{37}{}'$ proxy using $C_{37:2}$ and $C_{37:3}$ alkenone concentrations, in which 26 rapid interstadial and stadial shifts were identified. This high-resolution $U^{K}_{37}{}'$ proxy record reveals the rapidity with which SST can change. c) Relative proportion of the $C_{37:4}$ alkenone to total alkenones. This proxy gives an indication of the advent of cold, low-salinity water at the Iberian margin, presumably flowing in from the North Atlantic. Heinrich Events (H1 etc., abundance of detrital lithics from iceberg discharge) are marked in as they occur at the Atlantic ODP site 980 (55°N off Ireland). The SST drops in the Alboran Sea, ODP 977a, record coincide with some of the H-events but not all: it seems likely that there are some local cold events which are not synchronous with the iceberg discharges in the North Atlantic.

(sinistral), a tetraunsaturated C_{37} alkenone (Fig. 6c), and in arboreal pollen on land. Indeed, there are close similarities between the $U^{K}_{37}{}'$ record and the $\delta^{18}O$ ice core record from the GRIP site on Greenland, pointing to teleconnections between high and mid latitudes in the northern hemisphere.

The power of the alkenone biomarker approach to reveal very rapid SST changes (tens of years) by high-resolution microsampling ($<<$1 gm of sediment) of appropriate cores is well demonstrated in this work. There is a wealth of detail in the biomarker SST records (Fig. 6b,c), but the overall trends show that the climate in southern Europe was predominantly maintained in relatively warm, interglacial, interstadial conditions which were interrupted by much shorter, cold stadials.

Case Study 6. *Bermuda Rise, North Atlantic: Molecular ^{14}C ages from a sediment drift reveal extensive, long-distance, lateral transport of pre-aged alkenones.*

Sediment drifts are often selected as coring sites for paleoclimate studies. In principle, they offer the advantages of rapid sedimentation and hence improved preservation of sedimented organic matter and an expanded age scale which allows high time resolution for the measurement of proxies (e.g., Sachs and Lehman, 1999). However, the term "drift" provides a warning. The high rate of sedimentation is often the result of extensive advection of fine particles from elsewhere, and this allochthonous material may include organic particles and adsorbed or absorbed biomarkers.

This situation was dramatically illustrated when a short box core (extending back to ca 2000 yr BP) from the sediment drift on the Bermuda Rise was analysed in detail (Fig. 7; Ohkouchi et al., 2002, submitted for publication). Alkenones extracted from horizons which had been radiocarbon dated using the $CaCO_3$ of large, rapidly sedimented, planktonic foraminifera yielded compound-specific ^{14}C ages that were up to 7000 yr older than those of the calcareous microfossils. Similarly discordant ages were found for the total organic carbon and for the fine-carbonate fractions. Various mixing models are possible but these age offsets down core must be explained by large allochthonous contributions, often exceeding 50%. Thus, the $U^{K}_{37}{}'$ record (Fig. 7b) is influenced by advection of "old, cold" alkenones biosynthesized several thousand years prior by algae growing in more northern, colder waters. These must have been subsequently sedimented, eroded, transported and finally re-deposited along with fine calcium carbonate (Fig. 7a) and organic debris at the Bermuda Rise at the time of deposition of the planktonic foraminifera. As a result, Ohkouchi et al. (2002) found that the sediments at 2 cm core depth, dated as the Little Ice Age (ca 100–350 Cal yr BP) contained alkenones of ~5000 yr ^{14}C age (Fig. 7c). There is likely to be more than one original source for these transported alkenones, all with much colder surface waters (Ohkouchi et al., 2002, submitted for publication; McCave, 2002). Case Study 7 further illustrates this point.

Case Study 7. *Bermuda Rise, North Atlantic: Additional constraints on alkenone provenance from compound-specific δD measurements.*

Recently, δD measurements on the alkenones (C_{37} and C_{38} combined) have provided a new perspective (Fig. 7d; Englebrecht and Sachs, 2005). First, a hydrogen-isotopic depletion of circa. −193‰ relative to the ambient sea water was determined for alkenones in surface particles filtered from the sub-polar and sub-tropical Northwest Atlantic, where there is an approximately 20‰ δD isotopic N to S gradient in surface waters (Fig. 8c). Engelbrecht and Sachs then used this isotopic contrast as a tool to calculate that 60–100% of the alkenones in the Late Holocene sediments on the Bermuda Rise had been produced elsewhere, in cold and deuterium depleted sub-polar waters to the NW of the Rise (see Fig. 8b,c). Furthermore, using both $U^{K}_{37}{}'$ and δD as two parameters which have to be reconciled, they proposed a variable mix of sediment from at least three sources—the Nova Scotian margin, the Laurentian Fan and the sub-polar NE Atlantic.

The end result for this and other sites (Mollenhauer et al., 2003, 2005; Mollenhauer and Eglinton, 2007) is that, due to sediment

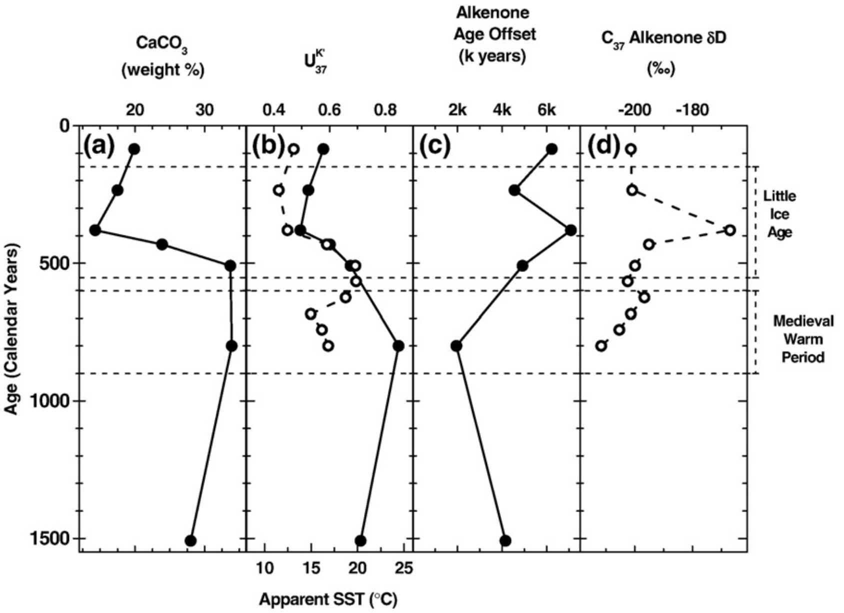


Fig. 7. Temporal offsets in alkenone records for the last 1.5 kyr of a Late Holocene core (OCE 326) from the Bermuda Rise in the North Atlantic (Ohkouchi et al., 2002). (Case Study 6). (a) Weight % calcium carbonate (fine fraction); (b) The $U^{K}_{37}{}'$ alkenone record, which indicates a major temperature swing over the last thousand years that is matched in part by the $U^{K}_{37}{}'$ record (open circles) in a second core from the same site (Englebrecht and Sachs, 2005); (c) Age offsets (^{14}C kyr) of the alkenones with respect to those of the carbonate of the foraminiferum, *G. ruber* at the same depth horizons; (d) δD values for the C_{37} alkenones in the second core (Englebrecht and Sachs, 2005). The age offset data (c), based on radiocarbon ages of alkenones as compared to those of the autochthonous foraminiferal fossils, clearly show that advection of "old and cold" alkenone biomarkers from distant northerly sites has occurred extensively, though variably, at the Bermuda Rise site. The alkenone δD data (d) also indicate contributions from distant sources for these biomarkers, especially during the Little Ice Age.

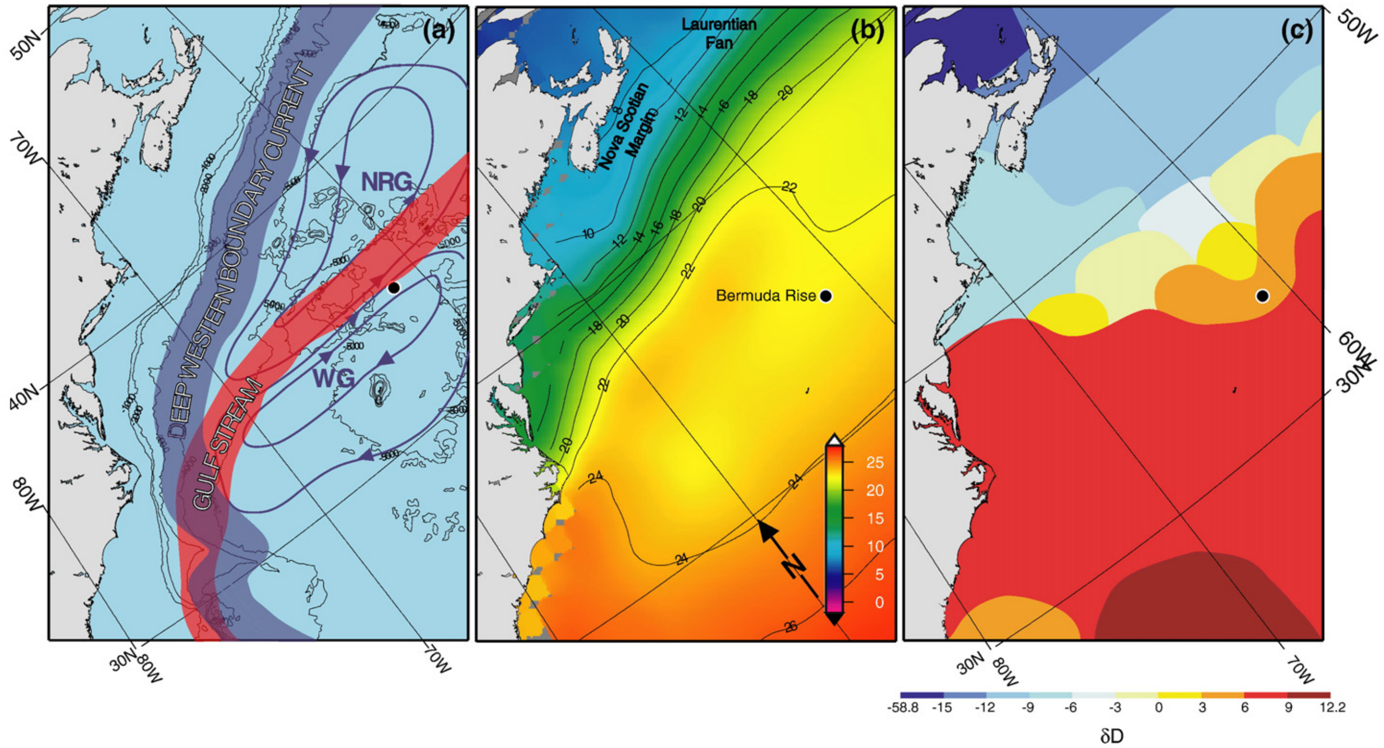


Fig. 8. The North American continental margin and the Bermuda Rise in the North West Atlantic Ocean (Case Studies 6, 7): hydrographic features and δD values for surface waters. (a) Bathymetry, major deep water and surface currents, and known abyssal circulation areas (Northern Recirculation Gyre, NRG; Worthington Gyre, WG; based on figures in Ohkouchi et al., submitted for publication; Englebrecht and Sachs, 2005 and McCave, 2002); (b) Annual mean sea surface temperatures (SST), measured for 2001; (c) Schematic of surface water δD values (colored areas), which reveal the influence of massive fresh water influxes from the St. Lawrence and other northern sources (Based on δ^{18}O data prepared by G. Schmitt; see Englebrecht and Sachs, 2005). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

drifting and/or focusing, the parallel use of proxy records to infer past conditions for the overlying surface ocean can be problematic at sites with high deposition rates. The potential for long-range transport of biomarker compounds in, or adsorbed on, tiny particles or even carried in the body mass of migrant animals is clearly a complication in their use as paleoenvironmental tools. But conversely, when the

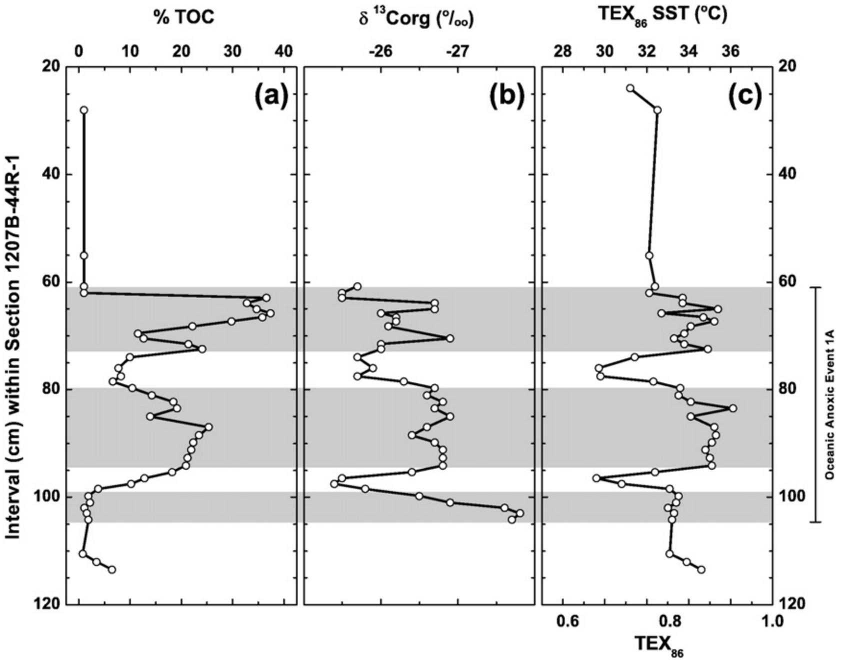


Fig. 9. The Lower Aptian oceanic anoxic event (OAE 1A, circa 120 Ma) at ODP site 1207 on the Shatsky Rise in the tropical Pacific (Dumitrescu et al., 2006) (Case Study 8). Records for organic carbon and the TEX_{86} SST proxy. The high organic OAE-1A interval of the core is marked; it was sampled at approx. 1 cm. intervals. (a) Total organic carbon, TOC (%); (b) δ^{13}Corg. (‰); (c) TEX_{86} and its SST°C equivalent. TEX_{86} reveals SSTs in the 30–36 °C range. The %TOC and the TEX_{86} records indicate that two remarkable periods of decreased carbon burial were accompanied by lower SSTs during the OAE-1A interval. Redrawn from Dumitrescu et al. (2006).

underlying processes are better understood, proxies using appropriate molecular biomarkers might provide new information on the past operation of natural transport systems, such as migrating biota, melt water pulses, drifting surface water masses, benthic storms and abyssal currents. Careful analyses of compound-specific isotopic compositions and extensive use of ^{14}C and other means of dating will be needed to unravel the complexity behind the leads and lags in proxy records.

Case Study 8. *Lower Aptian (120 Ma): Marine Biomarker TEX$_{86}$ records high SST (ca. 35 °C) during Oceanic Anoxic Event 1A.*

This example of the use of the TEX$_{86}$ proxy [Molecular Jargon Box II] goes back to 120 Ma by examining sediments deposited during a major perturbation in the global carbon cycle, the first of the Oceanic Anoxic Events (OAE) in the Cretaceous, when widespread organic-rich sediments were preserved under oxygen-deficient conditions (Dumitrescu et al., 2006). The core selected was of Lower Aptian age, drilled on the Shatsky Rise in the NW Pacific (ODP Site 1207). In the OAE 1A interval, the high organic content (4–40%) of the characteristic black shale (Fig. 9a) was accompanied by a positive excursion of circa. 2‰ in δ^{13}C bulk organic carbon (δ^{13}Corg, Fig. 9b) and high, TEX$_{86}$-derived, SSTs of 30–36 °C (Fig. 9c). However, there were two prominent cooling episodes of approximately 4 °C during OAE 1A. The authors point out that these intriguing episodes of instability in the burial of organic carbon and in δ^{13}C and SST during this interval of extreme warmth must reflect major climatic perturbations triggered by changes in the global carbon cycle. Forster et al. (2007) found similar cooling events for OAE 2.

Another very prominent example of high-resolution molecular stratigraphy with TEX$_{86}$ is from the Integrated Ocean Drilling Program expedition 302 which cored the Paleocene/Eocene thermal maximum (PETM) at high latitudes in the Arctic Basin (Sluijs et al., 2006). Low latitude studies had previously documented the PETM as a brief period of several thousand years duration when widespread extreme climatic warming occurred. The total absence of both carbonate and alkenones in the sediments meant that TEX$_{86}$ was the only paleotemperature proxy available. Using TEX$_{86}$, Sluijs et al. (2006) showed that the annual mean SSTs in these Arctic waters increased from approximately 18 °C to over 23 °C during the PETM event. They conclude that much higher than modern concentrations of greenhouse gases (CH_4 and/or CO_2) must have been responsible, a salutary warning in view of the current extremely rapid upward trend in pCO_2.

5. Biomarker proxies: problems and challenges

We have illustrated the use of biomarker molecules as proxy measures in paleoceanography and paleoclimatology in Case Studies 1 to 8. All proxies depend on assumptions, and biomarkers are no exception. However, biomarkers can provide information not otherwise available from other proxies. Moreover, the sensitivity and speed of the current methodology has resulted in biomarker proxies achieving wide applicability particularly in high-temporal-resolution stratigraphy and in detailed geographic mapping at specific time horizons. Questions remain for any biomarker study, some of which are apparent in the preceding examples, such as the spatial and temporal relationships embedded in the acquired data. For example, do any leads or lags accurately reflect differences in residence times in intermediate reservoirs such as soils, river and coastal sediments, or marine water masses? Certainly, plant waxes can be transported from continent to ocean in days to weeks (Conte and Weber, 2002)—but molecular ^{14}C data have revealed that compounds can reside for hundreds or thousands of years in soils (Eglinton et al., 2002). There is also ^{14}C evidence for long biomarker transit times during fluvial transport (Drenzek et al., 2007) and during ocean transport (cf. Case Studies 6 and 7).

Additional questions include: (*i*) What precisely is being measured, and are there several sources for the compounds concerned? (*ii*) Which environmental processes govern the input of compounds; notably through production, dispersal, and sedimentation? (*iii*) Once sedimented, are the compounds then immobile and what do we know of the chronostratigraphy? In other words, is the proxy measuring a single well-defined event? (*iv*) Are the compounds concerned really persistent or does diagenesis control or seriously bias the molecular stratigraphic record? Indeed, a highly persistent compound may constitute something of a double-edged sword—that is, the more robust the molecule, the better the record, but the more likely it will be to survive transport and advection and hence provide anachronistic signals elsewhere!

In the following two case studies we have shown how different processes may determine the origin and history of biomarkers and hence affect their application as proxies.

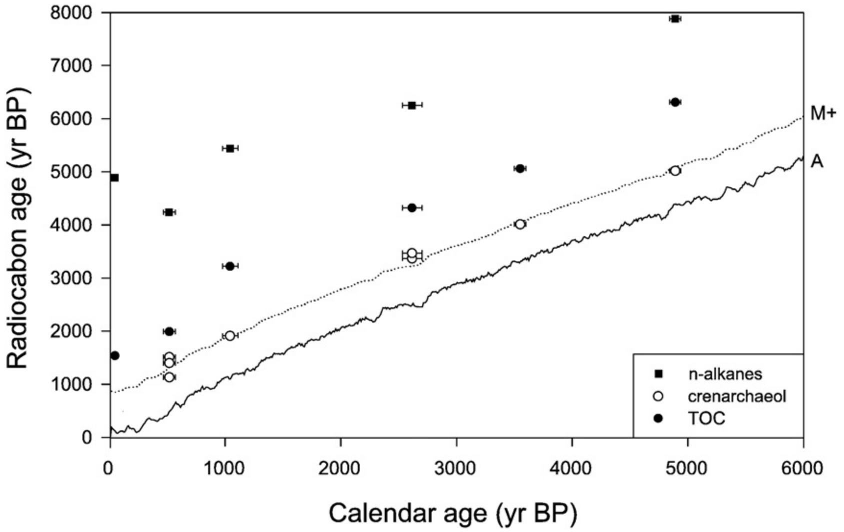


Fig. 10. ^{14}C age calibration of *n*-alkane and crenarchaeol biomarkers in varved Holocene sediments from Saanich Inlet, British Columbia (Case Study 9). Radiocarbon ages of TOC and compound-specific radiocarbon analyses (CSRA) for high-carbon-number *n*-alkanes and for crenarchaeol isolated from 6 horizons in a 44-meter core from ODP hole 1034C are plotted against sediment calendar ages determined by counting annual varves. Also shown is the atmospheric calibration curve (A) as well as marine calibration curve (+401 yr reservoir age, M+). Crenarchaeol evidently provides a valid indicator for calendar age of recent sediment horizons. In contrast, the *n*-alkane data must reflect mean reservoir storage ages in soils prior to their erosion and deposition in the basin (based on Smittenberg et al., 2004).

Case Study 9. *Saanich Inlet, Pacific Northwest Coast: Compound-specific ^{14}C measurements afford molecularly-based chronologies for varved Holocene sediments.*

Case Study 9 illustrates the value of annually varved sediments deposited under anoxic conditions in providing a chronological test bed. Here, compound-specific ^{14}C measurements were used to understand the nature and timing of the sedimentary processes involved (Fig. 10; Smittenberg et al., 2004).

Shallow sills largely isolate the deeper waters (237 m) of this fjord on Vancouver Island from the northeast Pacific Ocean. High *in situ* primary production and rapid sedimentation rates promote quasi-permanent anoxia of the water column below 200 m, resulting in the deposition of annually varved, organic carbon-rich sediments over the last 6 kyr. Hence, ^{14}C ages of individual biomarkers in a sediment interval can be compared with calendar ages derived by direct varve counting (Fig. 10). Smittenberg et al. (2004) selected crenarchaeol as an important biolipid biosynthesized by marine archaeal picoplankton in the water column. Although it is not used in the TEX_{86} proxy because of its quantitative dominance, crenarchaeol [Molecular Jargon Box II] is a major component of the GDGT biolipid assemblage synthesized by the Archaea. Its age characteristics will, therefore, also apply to the TEX_{86} compounds. The calibrated ages of the crenarchaeol deposited over the last 6 kyr all fall on virtually the same line as the calendar ages of the visually counted varves after the marine reservoir effect is accounted for (Fig. 10). Smittenberg et al. (2004) therefore propose crenarchaeol as an ideal biomarker for use in molecular ^{14}C dating of time horizons in young marine sediments.

In contrast, significant age offsets are found with both the TOC and the long-chain *n*-alkanes, the latter reflecting the age of the plant-wax debris eroded into the fjord from the surrounding land. Closer examination of the age relationships indicated an increasing offset towards the present day, and this trend has been interpreted as a consequence of increasing build-up of refractory terrestrial organic matter in soils during the Holocene (Smittenberg et al., 2006).

Case Study 10. *Ace Lake, Antarctica: Holocene sediment record of Haptophyte productivity explored with genomics and biomarker proxies.*

Case Study 10 demonstrates a novel way of looking at the origin of lipid biomarker signals by undertaking parallel genomic analyses on the same core samples, illustrating the exciting conjunction which has developed recently between molecular biology and lipid biogeochemistry. This approach holds great promise for improved understanding of the sedimentary record of the relatively recent past. Genes, the discrete DNA segments which direct the biosynthesis of individual proteins and other key biomolecules, represent the ultimate molecular biomarkers in terms of their information content. Genes have now been shown to be capable of surviving for thousands of years when sedimentary conditions are favourable, even when the parent huge DNA macromolecule has been extensively fragmented (Coolen and Overmann, 1998). Such conditions, namely burial in permanently cold, anoxic and light-free sediments, have been found, for example, for Holocene DNA in Ace Lake—a small lake in Eastern Antarctica. These workers identified fossil ribosomal DNA (18S rDNA) of different species of haptophyte green algae and compared the abundances with the concentrations of specific haptophyte lipid biomarkers, namely the alkenones and alkenoates, all in the same sedimentary horizons of the core (Coolen et al., 2004). This is the first DNA-based identification of species of fossil microorganisms

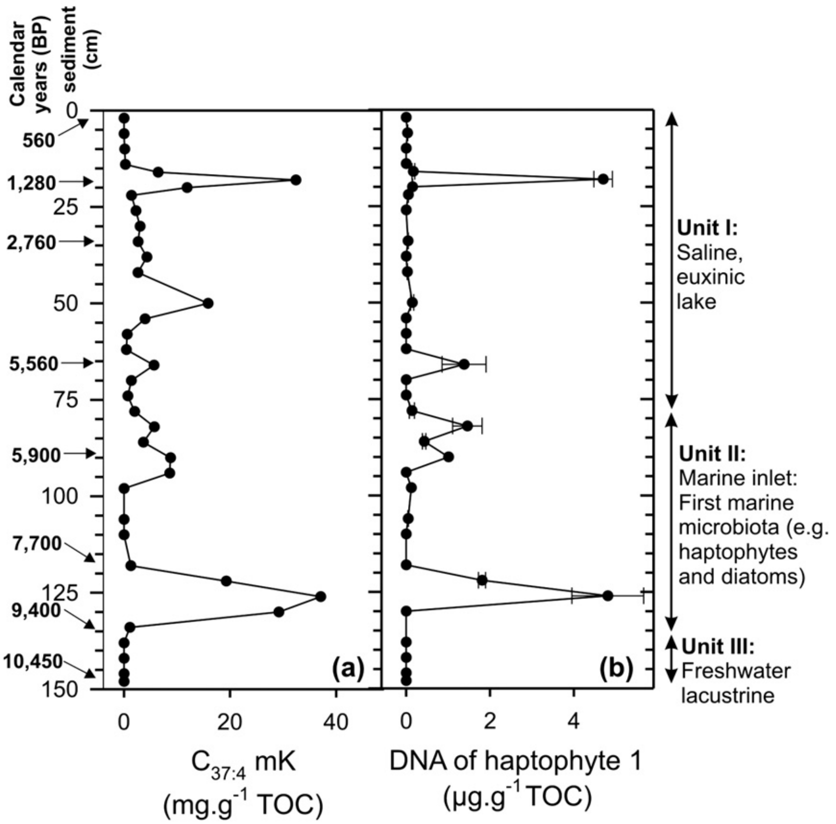


Fig. 11. A Holocene, high-resolution record of sedimentation of two very different types of algal biomarker (rDNA and alkenones) in an Antarctic lake. The 150-cm core, which records the last ~10,500 yr of sedimentation at the depocenter (25 m) of Ace Lake (68.5°S, 75.5°E), was analyzed for lipids and haptophyte 18S rDNA at 2 cm. intervals (circa. 130 y resolution). Ages expressed in calendar years result from radiocarbon ages of TOC together with calibration based on atmospheric $\Delta^{14}C$ (modified from Coolen et al., 2004). Changes in haptophyte 1 DNA abundances (b) closely match those of the $C_{37:4}$ methyl ketone (a), for which it must be the principal source. (a) Quantity of $C_{37:4}$ alkenone (methyl series; mg g^{-1} TOC) with depth. $C_{37:4}$ is produced by haptophyte phylotypes 1–4 (Quantitation was determined by lipid extraction, fractionation and GCMS analysis); (b) Quantity of 18S rDNA specific to haptophyte phylotype 1 (microgram g^{-1} TOC). Determined by real time PCR, using primers selective for 18S rDNA of haptophytes.

to be coupled with the distributions of the key lipid biomarkers they produced. Changes in species composition accompanied changes in alkenone distribution. Thus, the differing amounts of 18S rDNA of haptophyte species 1, which became dominant in the marine period when the lake was a coastal inlet (Unit II), provided a good match (Fig. 11b) for the abundance profile of the $C_{37:4}$ methyl alkenones (Fig. 11a). Also of particular interest is the finding that the six novel haptophyte sequences, all closely related to *Isochrysis galbana* as revealed by the DNA data, changed in their relative abundances when the salinity of the lake changed. In effect, the alkenone distribution patterns were recording changes in the population of haptophyte species rather than the physiological responses of a single species. There is a clear message here for future lipid biomarker studies—to link up with molecular biological analyses wherever possible. This Ace Lake paper points the way to combined DNA–biolipid studies of other anoxic marine sediments and sapropel horizons. Indeed, since this study, past haptophyte communities have been analyzed, based on the combined preserved DNA and lipid biomarkers, in Holocene sulfidic sediments of the Black Sea (Coolen et al., 2006) and Late Holocene lakes in Greenland (D'Andrea et al., 2006). More recently, ancient DNA of green sulfur bacteria as well as their specific carotenoids were recovered from Holocene and even Late-Pleistocene eastern Mediterranean sapropels (Coolen and Overmann, 2007). There are many other depositional settings that may prove amenable to this approach, but care will be needed to distinguish between signals due to living and fossil populations of microorganisms.

6. Future developments in molecular paleoclimatology

6.1. Methodological developments

The study of biomarkers is rapidly evolving as novel analytical techniques continue to be developed for characterization of minute quantities of organic compounds in sedimentary matrices. A necessary corollary is that these developments should be accompanied by faster and more powerful methods for the reduction of, and signal extraction from, multivariate data sets. As for other approaches to paleoclimatology, the development of multiple molecular-proxy records is essential to bolster interpretations and to broaden our understanding of present and past environmental change.

A key driver for paleoclimatology is the development of high-resolution chronostratigraphic records. For biomarker proxies, this necessarily involves increased sensitivity, speed and automation of the analyses (e.g., Harris and Maxwell, 1995; McDuffee et al., 2004; Matrat et al., 2007; Makou et al., submitted for publication). Paleoclimate archives hitherto virtually untapped from a biomarker perspective include speleothems, ice cores, coral skeletons, and tree-rings, and these will also become more accessible as measurement techniques improve in sensitivity.

A goal must also be to retrieve more organism-specific information on past climate conditions from biomarker records. In this context, the measurement of multiple isotopes on individual molecular species holds great promise. Currently, there are only a few studies using ^{13}C, ^{14}C and D conjointly for single compounds, as very different quantities of samples are needed for the measurements. However, as the sensitivity and ease of these measurements improves this situation will undoubtedly change. Moreover, isotopes of other elements that are currently not routinely measured at the molecular level (e.g., ^{18}O, ^{15}N, and ^{34}S) may prove useful (e.g., Sachs and Repeta, 2000; Werne et al., 2004). Similarly, with a few exceptions, intramolecular compound-specific isotope measurements (i.e., analyses of the distribution of isotopes within a molecular structure) are analytically challenging and presently rarely attempted, but may ultimately prove of value.

6.2. Major questions

In this review we have focused on two important parameters that biomarker proxies have proven of value in constraining sea surface temperature and C_3 vs. C_4 vegetation distributions on land. These two examples highlight a key attribute of molecular proxies—namely the ability to recover information from a single sedimentary archive on responses of both marine and terrestrial biospheres to climate variability.

As methodologies evolve, and as our understanding of biomarker signals increases, the applicability of biomarkers will no doubt expand to address other aspects of the climate system. Indeed, the literature already contains examples of nascent molecular proxies. The potential to derive estimates of past mean terrestrial temperature using a suite of tetraether lipids of soil microbes similar to the GDGTs used to assess paleo-SST has recently been demonstrated (Weijers et al., 2007). Molecular proxies based on sea-ice diatom isoprenoid lipids have also been proposed as a measure of past sea-ice extent (Belt et al., 2007; Massé et al., 2008). The utility and applications of biomarkers may only be limited by our imagination. For example, given the evidence for long-range transport of molecules in water bodies, could molecular proxies be used to assess past trajectories and vigor of deep ocean currents? Do lipids synthesized by deep-dwelling microbial communities carry signatures of the waters they grow in—such as temperature and oxygen content? Can lipids from vascular plants be sufficiently specific so as to pinpoint geographic patterns of long-range dust transport and hence the strength, direction and persistence of paleowind systems? Similarly, could molecular proxies of vegetation fires (e.g., levoglucosan; Elias et al., 2001) inform on regional and global variations in past aridity? To what extent can we use biomarkers to better understand the response of both oceanic and terrestrial biomes to past changes in hydrography and nutrient supply?

Above all, we need to search for more process-specific and organism-specific biomarkers. Some organism-specific biomarkers must already be documented in the existing “libraries” of sedimentary compounds, but to recognize them we need improved knowledge of just how organisms relate to specific environments through their physical, chemical or metabolic capabilities. Detailed studies of the organic compounds in the contemporary biosphere are essential if we are to properly “ground-truth” the biomarker approach for systematic paleoclimatic exploitation. Commonly, proxy values at core tops are compared to conditions in the overlying water column but there are inherent problems. Down-core signals can differ from those observed at the sediment surface. Careful research is needed to uncover the underlying reasons, but such detailed studies of these complex situations are likely to move the science forward in new and useful ways.

What of the long term? A radically new wave of advancement is already in train as organic geochemists seek to interpret the biolipid distributions of organisms in terms of genomics, proteomics, metabolomics, microbial ecology and evolutionary studies. Indeed, John Hayes in his 2002 Goldschmidt Lecture (Hayes, 2004) points to “the convergence of three lines of enquiry: studies of lipid biomarkers (isotopic and structural), microbial physiology and ecology, and microbial genomics”. He concludes: “this synergy promises to revolutionize our understanding of the evolution of the carbon cycle over the course of Earth history.” We believe he has a good point!

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