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5. Analysis of Lipid Biomarkers in Sediments from the Benguela Current Coastal Upwelling System (Site 1084)[1]

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ABSTRACT

The major biomarker compounds in surface (0.95 meters below seafloor [mbsf]) and deep (579.92 mbsf) sediment samples from the Benguela Current coastal upwelling system off Lüderitz, Namibia (Leg 175 Hole 1084A), have been identified and quantified. Lipids of marine origin (especially long-chain alkenones) dominate the solvent-soluble extracts of both samples with minor constituents of terrestrially derived lipids. The paleoenvironmental significance of the more labile biomarker distributions (sterols) is limited by losses from depth-related diagenetic transformations. These losses may have led to the relative enrichment of the more refractory biomarkers (alkenones) with depth.

INTRODUCTION

Identification and quantification of major lipid biomarkers in deep-sea sediments have been features of many Ocean Drilling Program (ODP) and Deep Sea Drilling Project (DSDP) studies. Compilation of this data has allowed molecular stratigraphic studies to elucidate the origin of sedimentary organic matter and the influence of water-column and postdepositional diagenesis and to determine various proxy signals of paleoenvironmental parameters (e.g., Brassell et al., 1981, 1986a; ten Haven et al., 1990, 1992; Farrimond et al., 1990; Poynter et al., 1989; Repeta et al., 1992).

Coastal upwelling systems provide environments well suited to biomarker analysis owing to elevated photic zone primary productivity,

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causing high sedimentation rates of organic matter–rich material. Preservation of the organic matter may be enhanced by rapid incorporation into the sedimentary matrix, limiting the length of time labile lipids are exposed to oxygen (Hartnett et al., 1998; Müller and Suess, 1979). Upwelling regimes of the Atlantic and Pacific Oceans and the Arabian Sea have been studied for their biomarker distributions in previous ODP and DSDP Legs (see ten Haven et al., 1992, for a review). The Benguela Current system (BCS) represents the eastern boundary of the South Atlantic gyre and is analogous to the eastern boundary currents off California, Peru, and northwest Africa. Cold, nutrient-rich South Atlantic Central Water is upwelled in the BCS off Namibia owing to the southeasterly trade wind–driven Ekman transport (Dowsett and Willard, 1996; Shannon, 1985). The BCS was previously studied for organic molecular parameters during DSDP Legs 40 and 75. These and other studies of the BCS have tended to concentrate on sediments deposited on Walvis Ridge and in Walvis Bay (e.g., Boon and de Leeuw, 1979). The Walvis sediments are displaced northward from the intense upwelling cells that occur off Lüderitz, where filaments of cold, nutrient-rich waters from the coastal upwelling area extend well off shore and mix with low-productivity oceanic water, forming a zone of year-round high phytoplankton productivity (Lutjeharms and Stockton, 1987). Site 1084 is located within the zone of year-round high phytoplankton productivity (25°31′S, 13°2′E, North Cape Basin), and the high organic carbon contents and high sedimentation rates have led to suboxic conditions (Wefer, Berger, Richter, et al., 1998).

Micropaleontological, geochemical, and molecular reconstructions of the late Neogene history of the BCS indicate that the intensity of upwelling has fluctuated in accordance with the oscillations of the global climate system (Hinrichs et al., 1999; Kirst et al., 1999; Summerhayes et al., 1995) with an underlying trend toward intensification since the mid-Pliocene (Berger et al., 1998; Diester-Haass et al., 1992; Hay and Brock, 1992; Lange et al., 1999; Marlow et al., 2000; Meyers, 1992).

In this study we have analyzed two samples from upper and lower cores of Hole 1084A for lipid biomarkers. The biomarker data allow a preliminary assessment of how the intensification of upwelling and depth/time-dependent diagenetic transformations may have influenced the input and preservation of the major lipid biomarkers present in the sediments. In addition, identifying and quantifying the major biomarkers for Hole 1084A will add to the inventory of data for further molecular stratigraphic studies.

EXPERIMENTAL METHODS

Extraction and Bulk Parameters

Sediments were stored at <0°C prior to freeze-drying and homogenization. Aliquots of the dry sediment were taken for total carbon (TC) and sulfur (TS) analysis using a Leco carbon analyzer. A further aliquot of dry sediment was fired to remove organic carbon (500°C for 24 hr) and carbon content determined to give total inorganic carbon (TIC). It is assumed that all inorganic carbon consists of calcite so that $CaCO_3$ = TIC × 8.3334. Organic carbon content (C_{org}) was determined by difference (C_{org} = TC – TIC). Further aliquots of dry sediment (~3 g) had a known quantity of an internal standard (*n*-C_{36} alkane) added for later quantification and were extracted into dichloromethane/methanol

(3:1) (6 × 3 mL extractions) with ultrasonication (15 min). Samples were centrifuged following each extraction and decanted. Combined extracts were dried under N_2 onto silica (0.5 g; 70–230 mesh) ready for column chromatography.

Compound Class Fractionation

Column chromatography was conducted on each sample after the methods of Peltzer et al. (1984). The column was packed with deactivated (5%) silica (7 g of 70–230 mesh in a 9-mm internal diameter [ID] column) in hexane. Four fractions were collected following elution with (1) hexane (20 mL), (2) hexane/toluene (4:1; 30 mL), (3) hexane/ethyl acetate (37:3; 40 mL), and (4) hexane/ethyl acetate (4:1; 40 mL). Excess solvent was removed by rotary evaporation and fractions were transferred in dichloromethane to vials, dried under N_2, and stored at ~4°C until analysis.

Lipid Analysis

Fractions 1–3 were analyzed directly without prior derivatization. Fraction 4 contained alcohol and acid moieties that were derivatized to their trimethylsilyl ethers with bis-(trimethylsilyl) trifluoroacetamide (BSTFA) in dichloromethane (100 µL of each at 70°C for 2 hr in N_2-purged vials). Quantification was made by gas chromatography with on-column injection and flame ionization detection (GC-FID) using an HP1 fused silica capillary column (60 m × 0.32 mm ID). Hydrogen was used as a carrier gas and the oven temperature program was 45° to 145°C at 10°C/min and 145° to 305°C at 4°C/min. Data acquisition and integration were made with an Atlas data system. Gas chromatography-mass spectrometry was performed using a Hewlett-Packard 5972 quadrapole mass spectrometer. Split-splitless injection was used with an HP1 fused silica capillary column (30 m × 0.32 mm ID; the subsequent loss of resolution by using a shorter column was compensated by minimizing column bleed above 280°C). Helium was used as a carrier gas with the same oven-temperature program as used for GC-FID. The mass spectrometer was operated in electron impact (ionizing energy of 70 eV; ion source temperature of 250°C) with a scan time (m/z 50–600) of 1 s. Compound identification was made by comparing mass spectra with authentic standards, literature sources, and relative retention times.

Mass accumulation rates were calculated as in Emeis et al. (1995) from gamma-ray attenuation porosity evaluator–derived dry-bulk densities (from Wefer, Berger, Richter, et al., 1998) and linear sedimentation rates (calculated from the biostratigraphic age model in Wefer, Berger, Richter, et al., 1998).

RESULTS AND DISCUSSION

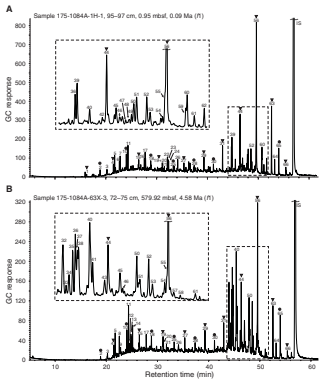
ODP labels, depths, ages, and the bulk geochemical properties with their corresponding mass accumulation rates for each sample are given in Table T1.

Hydrocarbons

The hydrocarbons eluted in Fraction 1 and their distributions are illustrated in the gas chromatograms in Figure F1. Identities and quanti-

T1. Sample identification and bulk properties, p. 22.

F1. Gas chromatograms from the surface and deep sample of Fraction 1, p. 16.

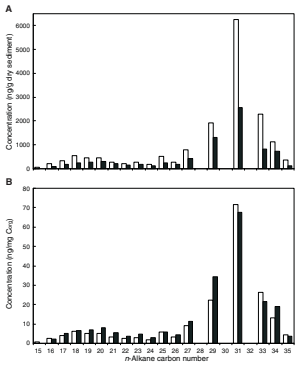


ties of the compounds corresponding to the numbered peaks are listed in Table T2. The dominant series of compounds in both samples are *n*-alkanes with a bimodal distribution (Fig. F2A) biased toward higher chain lengths (*n*-C_{25} to *n*-C_{35}). Even-number homologues of the longer chain *n*-alkanes are conspicuously absent in any detectable amount. Such an odd-over-even predominance is indicative of a terrestrial higher plant origin (Eglinton et al., 1962). The source of this terrigenous signal is likely to be continental Africa through eolian transport owing to the trajectory of the dominant along-shore trade winds and the absence of any major fluvial input directly affecting Site 1084 (Gagosian et al., 1981, 1987; Simoneit et al., 1977). The higher abundances of *n*-alkanes in the near-surface sample relative to the mid-Pliocene sample could be a result of increased trade wind transport of eolian material. However, such an interpretation is complicated by the aridification and expansion of the Namib Desert associated with the intensification of upwelling leading to a decline in the abundance of terrestrial higher plants (Dowsett and Willard, 1996). The contribution of *n*-alkanes to the total organic matter (as mass per milligram of C_{org}) (Fig. F2B) is similar for each sample, indicating that the input of terrigenous organic carbon to the site may not have increased coincident with the increase in trade wind strength.

Pristane (Pr) and phytane (Ph) are present in both samples, with a Pr:Ph ratio of <1 (0.95 mbsf = 0.77 and 579.92 mbsf = 0.54). Studies have suggested that values less than unity may indicate anoxic phytol diagenesis (Didyk et al., 1978). However, various factors restrict this interpretation (ten Haven et al., 1987), and the ratio may have been influenced by direct bacterial inputs (Han and Calvin, 1969; Risatti et al., 1984). A C_{25} isoprenoid (2,6,10,15,19-pentamethyleicosane) is also present in both samples. This compound is a biomarker for methanogenic bacteria (Brassell et al., 1981) and was identified in sediments underlying the upwelling system off northwest Africa (ten Haven et al., 1989). The series of 3-methyl and 5-methyl branched alkanes found in the surface sample may also be indicative of an archaebacterial input (Brassell et al., 1981; Kenig et al., 1995; Shiea et al., 1990). An unsaturated compound in this series and monounsaturated isoprenoids (pristene and phytene isomers) in the deeper sample suggests that the depositional environment may have been less reducing than for the surface sample. Moreover, the presence of these compounds in the deep sample suggests that thermal maturation has not progressed significantly at depth in Hole 1084A (Van Graas et al., 1981). No compounds from the series of highly branched isoprenoid (HBI) alkanes or alkenes were identified in either sample. It is possible that the HBI compounds are present in low concentrations and/or coelute with other compounds. These compounds have been identified in several marine diatom species (Belt et al., 1996; Johns et al., 1999; Sinninghe Damsté et al., 1999; Volkman et al., 1994; Wraige et al., 1997) and in a variety of marine sediments (see Rowland and Robson, 1990, for a review). Their absence in Hole 1084A sediments is conspicuous owing to micropaleontological evidence for large inputs of diatoms (Lange et al., 1999). Sulfur incorporation has been shown to be a rapid mode of diagenetic removal of the HBI alkenes (Kohnen et al., 1990; Sinninghe Damsté et al., 1989a), but their solvent extractable diagenetic products appear to be absent from both samples (other organic sulfur compounds are discussed below). The absence of HBI compounds was also noted in the diatomaceous sediments underlying the coastal upwelling regime of the

T2. Nomenclature, concentrations, and accumulation rates of compounds in Fraction 1, p. 23.

F2. Profiles of *n*-alkanes in surface and deep samples, p. 17.



Peru margin (ten Haven et al., 1990) and the central Arabian Sea (Prahl et al., 2000). This latter study showed that significant quantities of HBIs were exported from the water column, but they were not detected in the underlying surface sediments. However, Schouten et al. (2000) have reported a series of HBI polyenes in surface samples from the Arabian Sea although absolute quantities were not given.

The relative abundance of steroidal hydrocarbons to *n*-alkanes increases in the deeper sample, indicating a depth/time-dependent transformation from their sterol and/or steroidal ketone precursors (Mackenzie et al. 1982; Peakman and Maxwell, 1988; Brassell et al., 1984). Limited double-bond isomerization to ster-4-enes and ster-5-enes suggests that the sediments have undergone diagenetic transformation. The absence of fully saturated steranes indicates that the sediments remain thermally immature at depth (Gagosian and Farrington, 1978; ten Haven et al., 1989). Unsaturated and ββ isomers of the bacterially derived hopanoidal hydrocarbons (Ourisson et al., 1984) are present in both samples as well as the diagenetically rearranged αβ/βα isomers. The distribution of these hydrocarbons per gram of dry sediment and per gram of C_{org} does not indicate any clear trend toward increasing thermal maturity with depth (Ensminger et al., 1977; Brassell and Eglinton, 1983; Farrimond et al., 1986a). The distribution of fernene isomers (also of bacterial origin) between the surface and deep samples is similar to that observed in the upwelling sediments off northwest Africa (ten Haven et al., 1989). The distribution of fernenes appears to follow progressive isomerization from the Δ^7 to the thermodynamically more stable Δ^8 and $\Delta^{9(11)}$ isomers with depth.

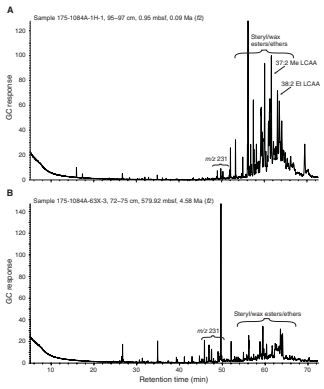
Organic Sulfur Compounds

Two C_{20} isoprenoid thiophenes were identified in Fraction 1 of both samples (Table T2). These compounds have been found in many marine sediments, including previous studies form the Walvis Ridge DSDP studies (Brassell et al., 1986b; ten Haven et al., 1992). The thiophenes are formed during the early stages of diagenesis in the water-column and surface sediments (Brassell et al., 1986b; Kohnen et al., 1991a). Their biological precursors are likely to be phytenyl moieties that react with reduced inorganic sulfur species (H_2S and hydrogen polysulfides) to form the sulfur incorporated thiophenes (Brassell et al., 1986a; Sinninghe Damsté et al., 1989b). The greater abundance of the thiophenes in the deeper sample suggests a more anoxic/reducing environment during deposition. This interpretation contradicts the information on depositional setting given by the presence of the unsaturated hydrocarbons in the deep sample. However, interpretation of the distribution of the thiophenes in the solvent extractable fraction is complicated by the potentially more significant form of sulfurization via sulfur bridges into the bound macromolecular fraction (Kohnen et al. 1991a, 1991b, 1991c).

Wax Esters and Sterol Ethers/Esters

Fraction 2 was dominated by high molecular-weight compounds that were tentatively identified from their relative GC retention times and mass spectra as wax esters and compounds containing sterol moieties probably as alkyl ethers and/or esters (Fig. F3). The exact structures of the sterol compounds were difficult to identify owing to the absence

F3. Gas chromatograms from the surface and deep sample of Fraction 2, p. 18.



of a significant molecular ion in their electron impact mass spectra. Such compounds have been identified in sediments deposited under the upwelling cells of Walvis Bay (Boon and de Leeuw, 1979), the Peru margin (ten Haven et al., 1990), and the Arabian Sea (Schouten et al., 2000). The source of these wax and sterol ethers/esters has been assigned to zooplankton grazing on algal sterols (Wakeham, 1982). However, the noticeable occurrence of these compounds in sediments underlying waters with high abundances of diatoms and the disparity between the sterol moiety of the ethers compared to the free sterols studied by Schouten et al. (2000) has led these authors to suggest that diatoms may be the direct source of sterol ethers. Further analyses using chemical ionization mass spectrometry (Lusby et al., 1984) and saponification are required for full structural characterization. The highest abundances of the ethers/esters are in the surface sample, including the long-chain (C_{37} and C_{38}) alkyl alkenoates (see **"Long-Chain Alkenones and Alkenoates"** below). The presence of a series of unknown compounds eluting prior to the wax/sterol esters in Fraction 2 was noted. These compounds are dominant in the deep sample. Their mass spectra contain a large base peak at m/z 231, with no apparent molecular ion or any other characteristic fragment ions.

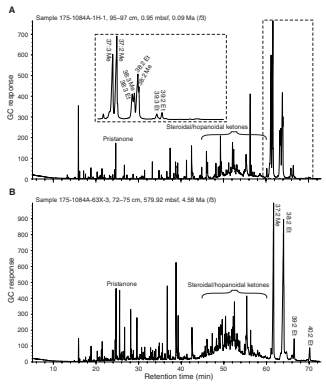
Steroidal/Hopanoidal Ketones

Uncharacterized ketone-substituted steroid and hopanoid compounds eluted in Fraction 3 (Fig. **F4**). Steroid ketones have previously been identified in the sediments from the BCS (Gagosian and Smith, 1979), where their origin was suggested to be a diagenetic intermediate in the microbiologically/chemically mediated degradation of stenols to sterenes. However, a direct input from dinoflagellates is also possible (Harvey et al., 1988).

Long-Chain Alkenones and Alkenoates

The long-chain alkenones are ubiquitous in marine sediments (Brassell, 1993) and have been found to be among the largest components of the extractable lipids in upwelling sediments (ten Haven et al., 1989, 1990; Hinrichs et al., 1999; Farrimond et al., 1990). These compounds are the most abundant lipids in Fraction 3 (Fig. **F4**) and have concentrations and accumulation rates considerably higher than any other compound in any of the fractions (Table **T3**). The C_{37}–C_{39} alkenones and alkenoates are biomarkers for the haptophyte algae (Volkman et al., 1980; Marlowe et al., 1984; Conte et al., 1994), notably the ubiquitous coccolithophorids *Emiliania huxleyi* and *Gephyrocapsa oceanica*. In this respect, it would appear that haptophyte algae have been dominant members of the plankton at Site 1084 throughout the past 4.5 m.y. (Marlow et al., 2000). The highest accumulation rate is found in the surface sample (1.8 mg/cm²/k.y. compared to 0.6 mg/cm²/k.y. in the deep sample). The concentration of alkenones relative to C_{org} becomes enriched in the deep sample (1.44 mg/g C_{org} compared to 0.97 mg/g C_{org} in the surface sample) as a likely result of the preferential preservation of the alkenones relative to other more labile organic compounds. The observation that alkenone abundances are significant in a variety of marine sediments predating the first occurrence of *E. huxleyi* at 268 ka (Thierstein et al., 1977) suggests that alkenones have been biosynthesized by phylogenetic ancestors throughout the late Neogene and possi-

F4. Gas chromatograms from the surface and deep sample of Fraction 3, p. 19.



T3. Nomenclature, concentrations, and accumulation rates of compounds in Fraction 3, p. 25.

bly earlier (Emeis et al., 1995; Dzvonik, 1996; Farrimond et al., 1986b; Herbert and Schuffert, 1998; Marlowe et al., 1990; Müller et al., 1997; Rullkötter et al., 1998). The C_{40} di-unsaturated alkenone was tentatively identified in the deep sample, as the molecular ion was particularly weak. Full characterization will be possible with chemical (NH_3) ionization mass spectrometry (Rosell-Melé et al., 1995a). This compound has previously been reported in Cretaceous black shales (Farrimond et al., 1986b). The di- and tri-unsaturated C_{37} alkenones (37:2 Me and 37:3 Me) are commonly used for reconstructing paleo–sea surface temperatures (SST) owing to the observation that the ratio of 37:2 Me/(37:2 Me + 37:3 Me) = $U^{K}_{37}{}'$ has a linear relationship with growth temperature and can be accurately calibrated to the SST through core-top studies and cultures (Brassell et al., 1986a; Müller et al., 1998; Prahl and Wakeham, 1987; Prahl et al., 1988; Rosell-Melé et al., 1995b). The $U^{K}_{37}{}'$ and SST estimates for the two samples are given in Table **T3.** The $U^{K}_{37}{}'$ value for the surface sample corresponds to the cooling interval following the thermal optimum of marine oxygen isotope Stage 5 (Marlow et al., 2000). Interpretation of a complete time series of $U^{K}_{37}{}'$ -derived SST for the 4.5-m.y. period between the surface and deep sample reported here suggests that the elevated SST for the deep sample probably reflects a combination of increased global temperatures and less intense upwelling relative to the late Pleistocene (Marlow et al., 2000).

Long-Chain Alkyl-1,n-diols and Alkyl-1-ol-n-ones

Mid-chain (1,15) C_{30}–C_{32} diols and keto-ols were first reported in Black Sea sediments, and their source was postulated to be of cyanobacterial origin (de Leeuw et al., 1981). A series of alkyl diols were subsequently identified in marine and freshwater eustigmatophyte algae (Volkman et al., 1992; Volkman et al., 1999). However, compositional differences between the positional isomers found in cultures and sediments suggest that eustigmatophyte algae are not the major source of these compounds and the source organisms are still as yet unknown (Versteegh et al., 1997). Contrary to other published results for upwelling sediments (ten Haven et al., 1992; McCaffrey et al., 1991), including BCS sediments (Hinrichs et al., 1999), alkyl diols were not readily identifiable in either of the samples. However, a series of alkyl keto-ols were easily identifiable in large quantities from their mass spectra, with large fragment ions at m/z = 130, 143, and M^{+}–15. The surface sample contains a significantly larger quantity of keto-ols, a wider diversity of chain lengths, and a monounsaturated compound. The distribution of the 1,15-C_{30} keto-ol and 1,15-C_{32} keto-ol in the surface sample may be related to the surface water conditions at the time of production (Versteegh et al., 2000). The normalized ratio of the two saturated ket-ols defined by Versteegh et al. (1997) as [100 × (1,15-C_{30} keto-ol)]/[([1,15-C_{30} keto-ol) + (1,15-C_{32} keto-ol)] is ~72%. This ratio is similar to that found by Versteegh et al. (2000) in sediments from the Southern Angola Basin (11°35′S, 11°41′E) corresponding to the same time interval and these authors speculate a relationship to surface water salinity. Owing to the possible compound-environment relationship for the keto-ols, it is difficult to determine whether the different distributions and absolute quantities between the surface and deep samples are caused by diagenetic alteration or changes in the surface water conditions.

n-Alcohols and *n*-Acids

Straight-chain alcohols and acids eluted in Fraction 4 (Fig. F5). Three even-chain–length alcohols (C_{18}, C_{22}, and C_{26}) were present in the surface sample, but only the C_{18} homologue was found in the deep sample. An even-over-odd predominance was also reported in Peru margin upwelling sediments (Farrimond et al., 1990), implying an input derived from higher plants (Kolattukudy, 1976; Gagosian et al., 1981, 1987) most probably through eolian transport.

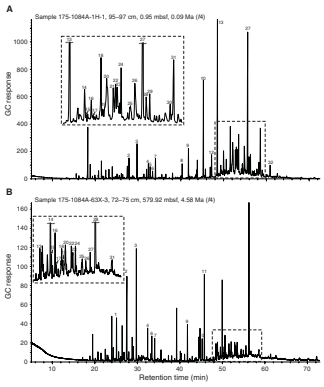
Fatty acids formed a significant fraction of the polar compounds (Table T4), with the surface sample having the largest overall abundance. An absolute quantitative interpretation of the fatty acid distribution is limited by the absence of an acidification step during the preparative procedures. The distribution of fatty acids in both samples is bimodal with maxima at C_{16} and C_{26} (Fig. F6). However, the dominant maxima are different for each sample, with the surface sample biased toward longer chain lengths and the deep sample biased toward shorter chain lengths with a uniformly low abundance of long-chain fatty acids. A $C_{18:1}$ mono-unsaturated acid was identified in both samples. The biological source of fatty acids is varied (Volkman et al., 1998; Gagosian et al., 1981, 1987). Fatty acids at Site 1084 are most likely derived from a mixture of autochthonous inputs from microalgae and bacteria and to a lesser extent from eolian transport. Similar distributions have been described for other late Quaternary sediments from the BCS (Hinrichs et al., 1999).

Steroidal Alcohols

Sterols (C_{27}–C_{30}) eluted in Fraction 4 (Fig. F5) and were identified from their relative retention times and comparison with published mass spectra (Brassell, 1980; McEvoy, 1983). All sterols are significantly more abundant per gram C_{org} in the surface sample relative to the deep sample (Table T4) as a possible result of the progression of diagenetic transformation in the deep sample and from increasing productivity following the intensification of upwelling since the mid-Pliocene. The interpretation of sterols as source indicators for surface BCS sediments is complicated by strong diagenetic degradation during transport through the oxygenated water column (Hinrichs et al., 1999).

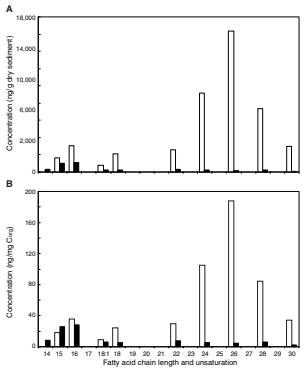
The 4-desmethyl C_{27} sterols cholest-5-en-3β-ol and 5α-cholestan-3β-ol are present in both samples, with the former being the most abundant single sterol in the deep sample. The stanol can have both a biological (e.g., dinoflagellates) and diagenetic (from the unsaturated sterol) origin (Robinson et al., 1984; Mackenzie et al., 1982). The C_{28} sterols 24-methylcholestα-5,22-dien-3β-ol and 24-methy-5α-l-cholest-22-dien-3β-ol are present in both samples. The unsaturated compound is found in diatoms, haptophytes, and cryptophytes (Goad et al., 1983; Volkman, 1986; Volkman et al., 1998). The C_{29} sterols are difficult to interpret as source markers owing to their presence in both marine algae and higher plants (Volkman et al., 1998), although a marine origin is most likely in this case (e.g., diatoms and raphidophytes). The C_{29} sterols are the most abundant sterols in the surface sample but are depleted in the deep sample. A similar observation in BCS sediments was interpreted as diagenetic loss and/or reduced biological supply (Hinrichs et al., 1999). C_{30} sterols were present in both samples, including the 4-methylsterols 4α,23,24-trimethyl-5α-cholest-22-en-3β-ol (dino-

F5. Gas chromatograms from the surface and deep sample of Fraction 4, p. 20.



T4. Nomenclature, concentrations, and accumulation rates of compounds in Fraction 4, p. 26.

F6. Profiles of fatty acids in surface and deep samples, p. 21.



sterol) and 4α,23,24-trimethyl-5α-cholest-8(14)-en-3β-ol, which have been used as biomarkers for dinoflagellates (Boon et al., 1979; Robinson et al., 1984).

CONCLUSIONS

The lipid distribution in sediments from the surface and base of Hole 1084A (late Pleistocene and mid-Pliocene, respectively) are dominated by marine microalgal biomarkers comprised primarily of long-chain alkenones originating from haptophyte algae. Terrigenous inputs of *n*-alkanes and *n*-alkanols are minor components of the GC-amenable lipids, but their presence suggests a terrigenous input most likely via eolian transport in trade winds running off and along the coast of continental southern Africa.

Direct interpretation of lipid abundances in relation to changes in paleoproductivity between the mid-Pliocene and late Pleistocene is complicated by evidence of increased diagenetic transformations in the deep sample. These changes may have caused an apparent enrichment of refractory lipids relative to C_{org} (e.g., *n*-alkanes and long-chain alkenones) compared to the more labile lipids (e.g., sterols). This observation would suggest that the labile functionalized compounds present in the surface sediment have become diagenetically depleted in the deeper sediment. Their diagenetic byproducts are evident in the deep sample as increased relative abundances of steroidal/hopanoidal hydrocarbons. The distribution of compounds that might indicate the extent of early diagenesis (unsaturated hydrocarbons and thiophenes) appear contradictory. This observation may be explained by the incorporation of functionalized lipids into the geomacromolecular-bound fraction throughout the diagenetic process and illustrates a potential limitation in studying only the free solvent extractable lipids.

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Figure F1. Gas chromatograms from the (**A**) surface and (**B**) deep sample of Fraction 1 containing hydrocarbons and organic sulfur compounds identified in Table T2, p. 23. Circles indicate even chain–length *n*-alkanes, and triangles indicate odd-chain–length *n*-alkanes.

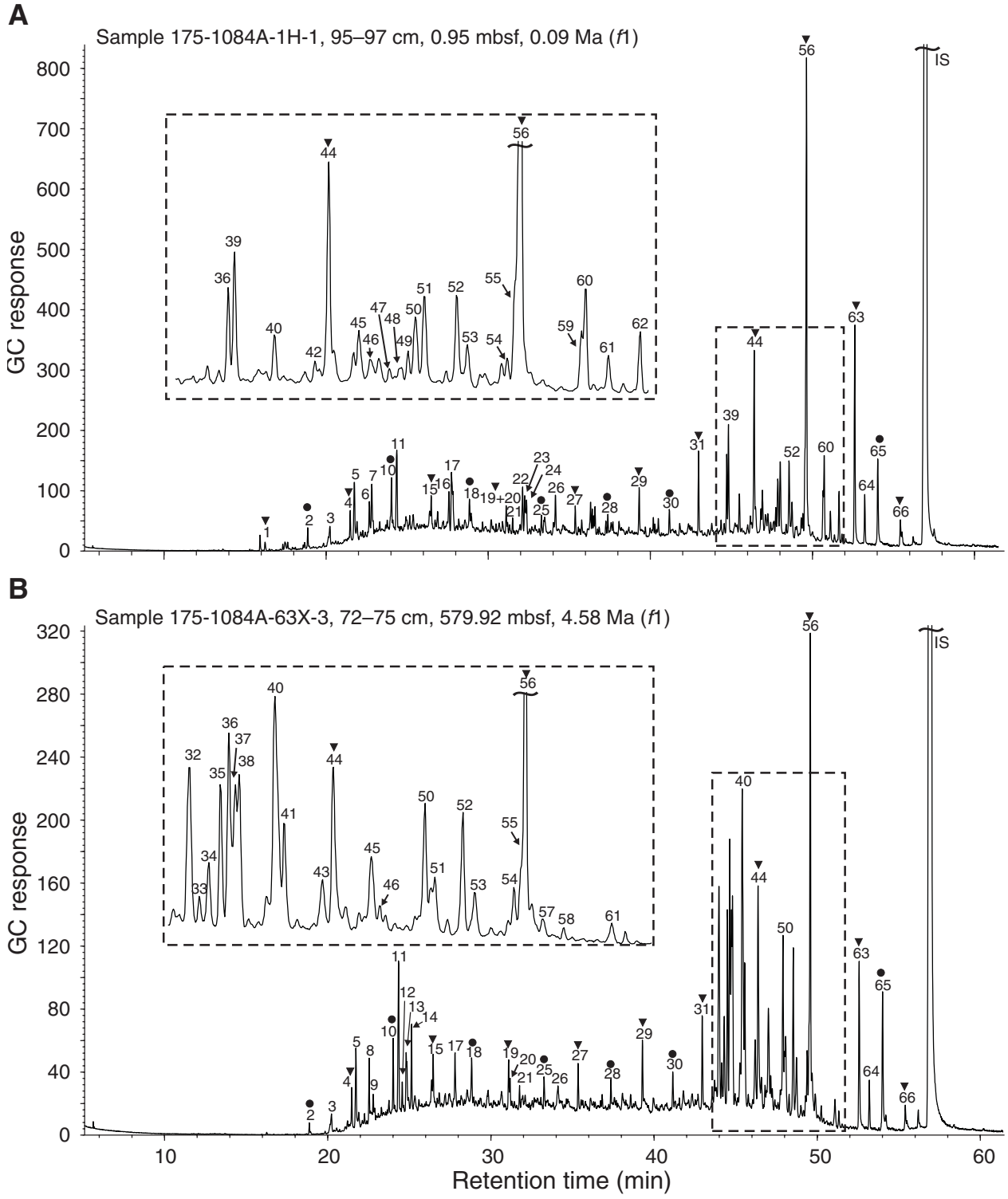

Figure F2. Profiles of *n*-alkanes in surface (open) and deep (solid) samples expressed as (**A**) absolute concentration per gram dry sediment and (**B**) relative abundance to C_{org}.

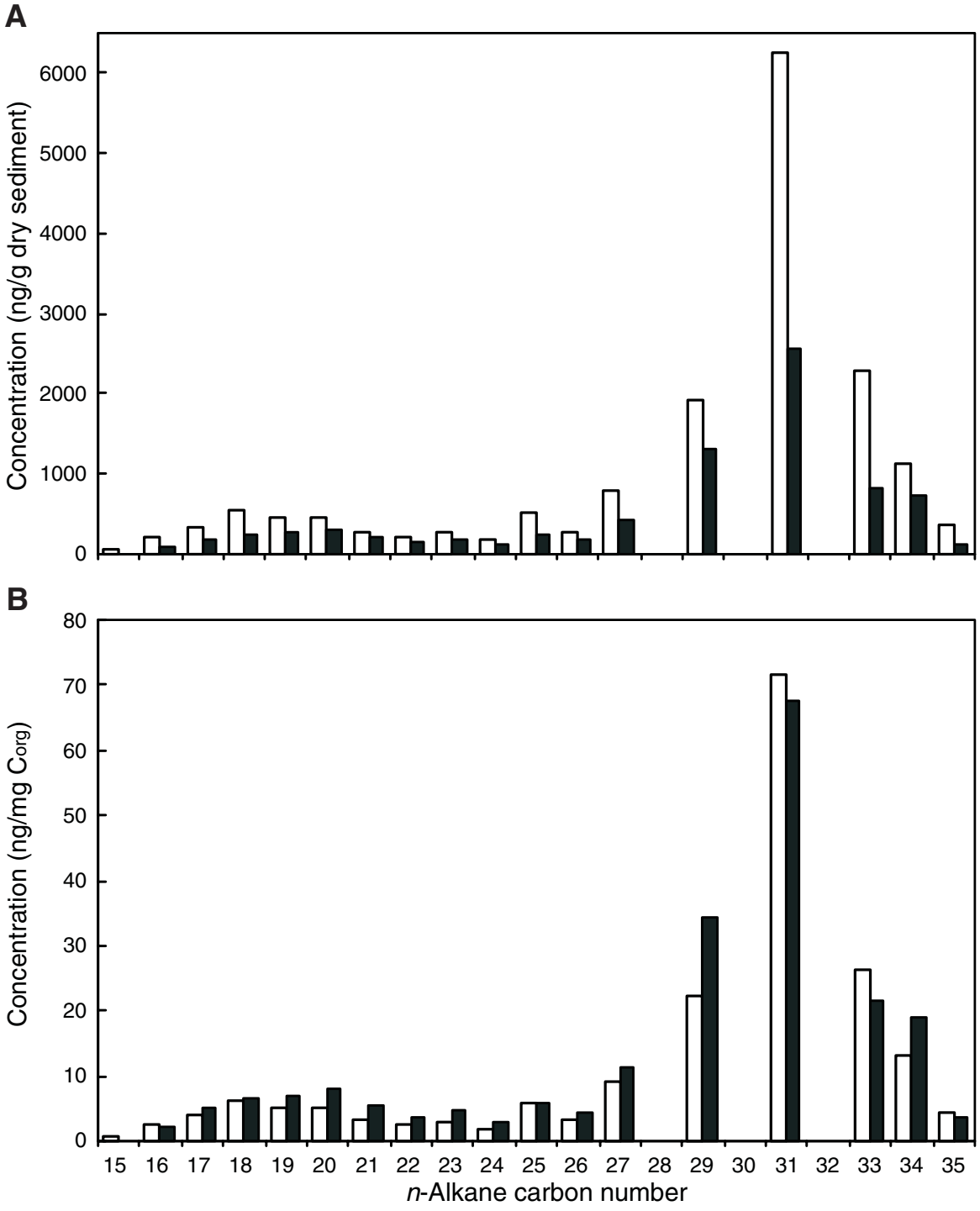

Figure F3. Gas chromatograms from the (**A**) surface and (**B**) deep sample of Fraction 2 containing wax and steryl esters/ethers.

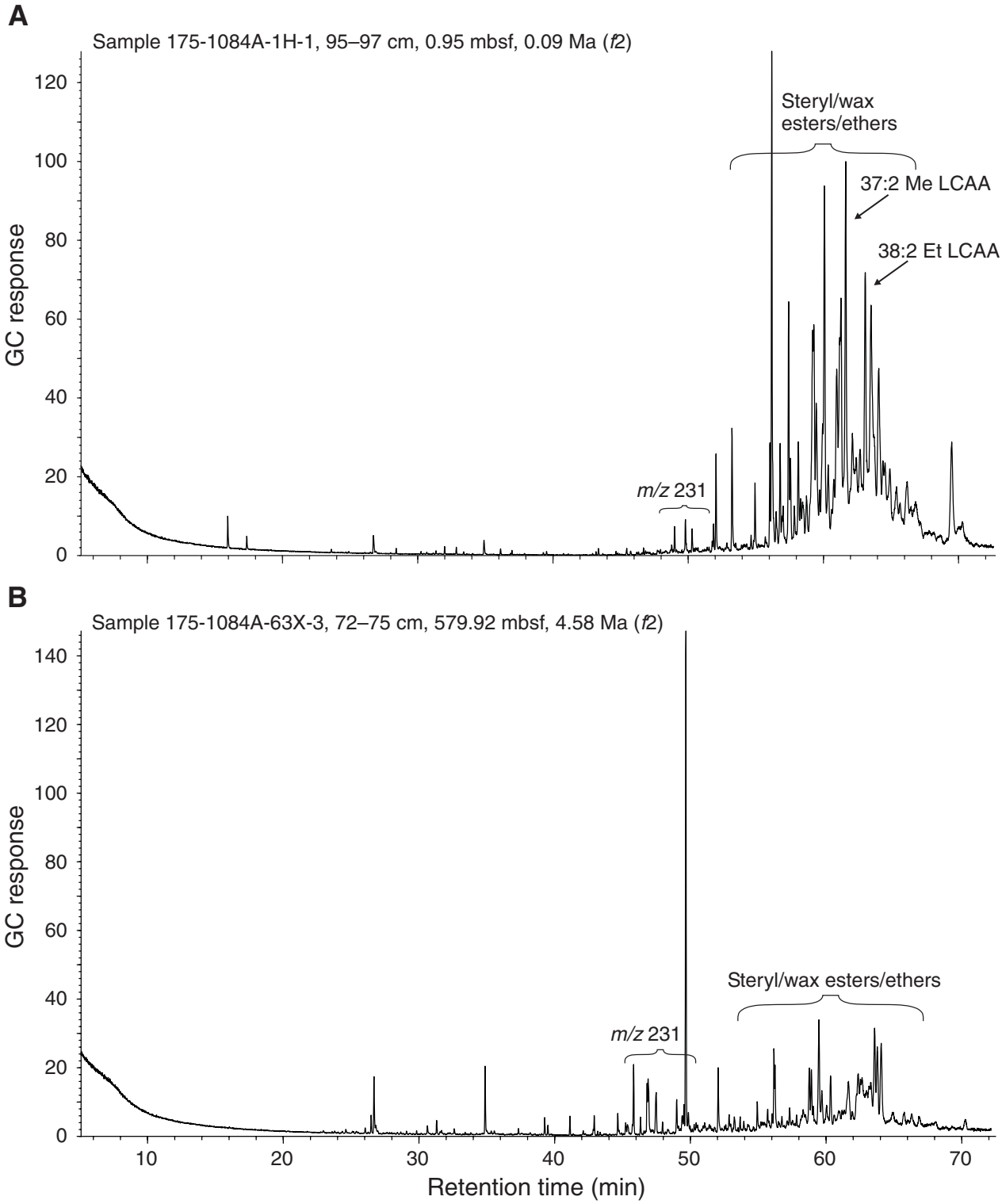

Figure F4. Gas chromatograms from the (**A**) surface and (**B**) deep sample of Fraction 3 containing steroidal/hopanoidal ketones and long-chain alkenones identified in Table T3, p. 25. Note that the surface sample was diluted 2× relative to the deep sample to avoid overloading the gas chromatograph.

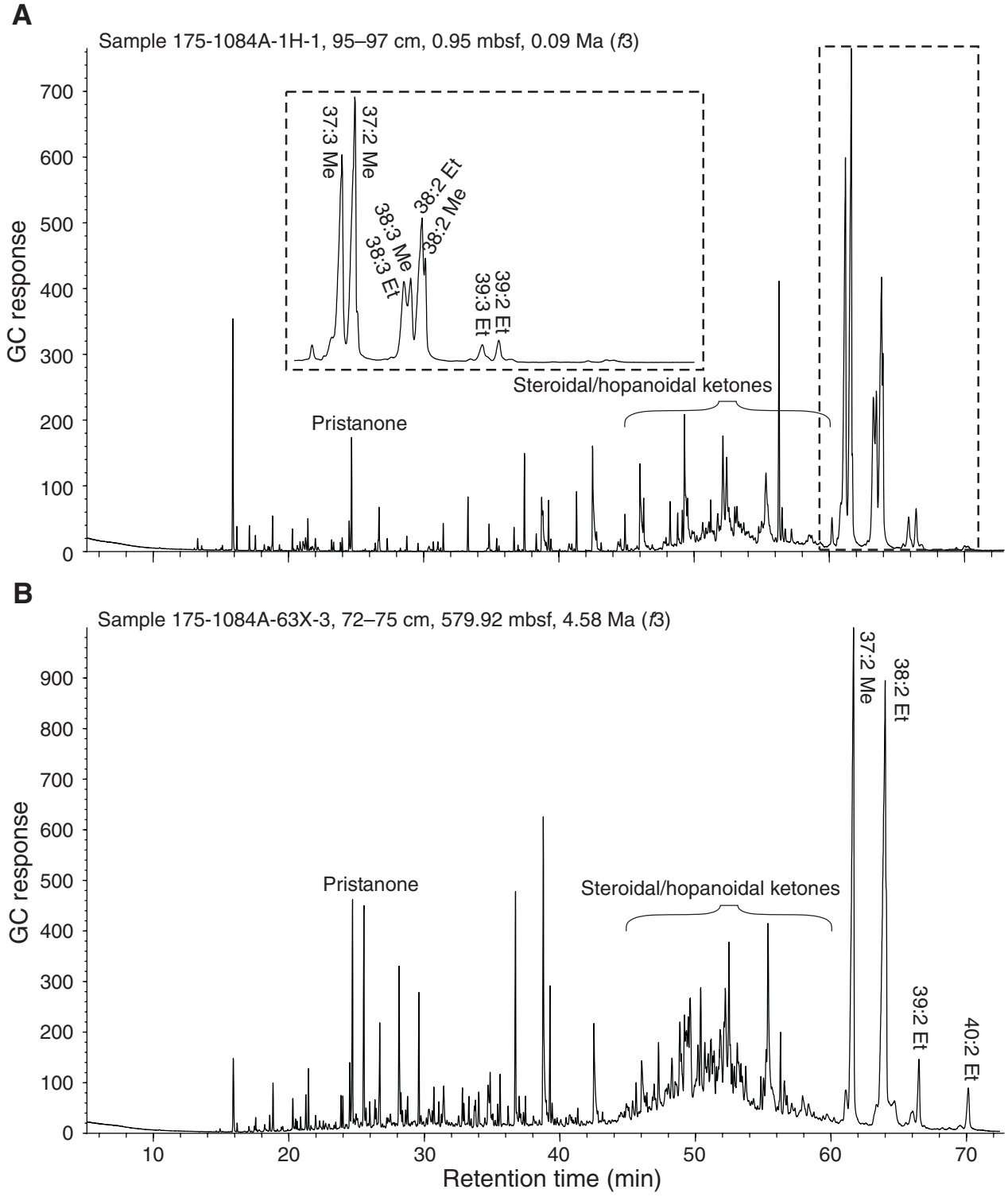

Figure F5. Gas chromatograms from the (**A**) surface and (**B**) deep sample of Fraction 4 containing polar compounds identified in Table T4, p. 26. Note that the surface sample was diluted 2× relative to the deep sample to avoid overloading the gas chromatograph.

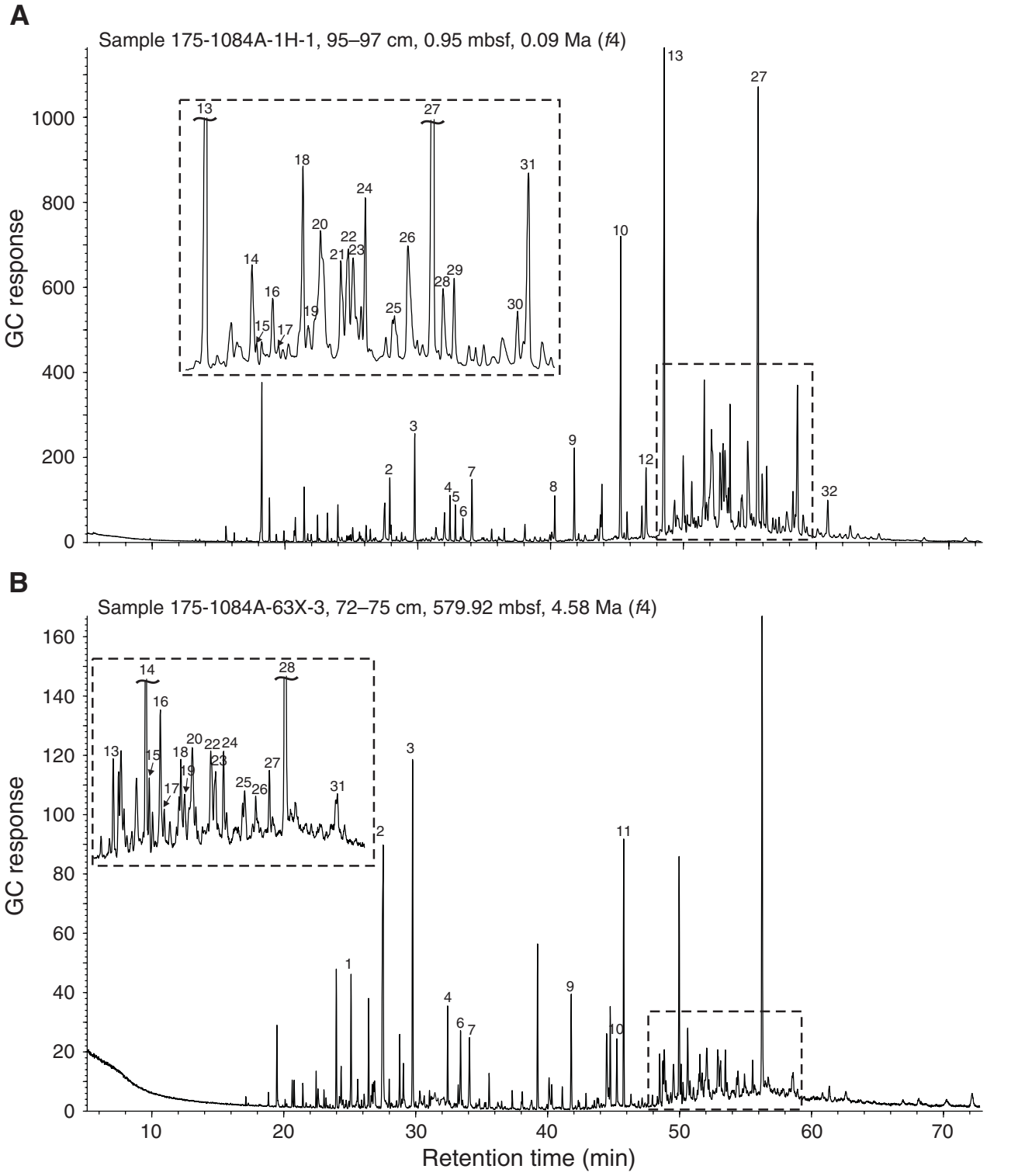

Figure F6. Profiles of fatty acids in surface (open) and deep (solid) samples expressed as (**A**) absolute concentration per gram dry sediment and (**B**) relative abundance to C_{org}.

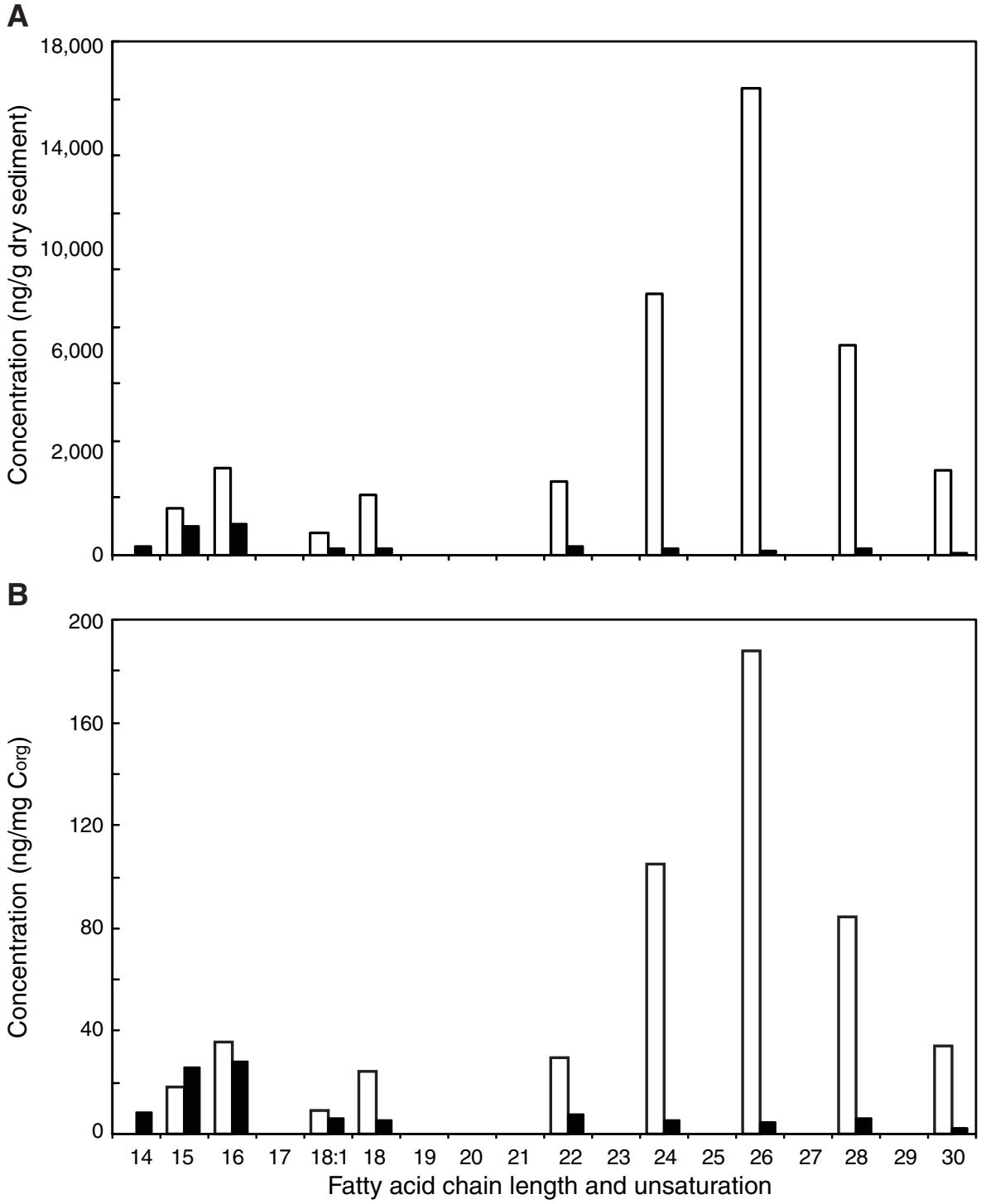

Table T1. Sample identification and bulk properties.

Core, section, interval (cm)	Lithologic subunit	Depth (mbsf)	Age (Ma)*	Sedimentation rate (cm/k.y.)*	$CaCO_3$ (wt%)	C_{org} (wt%)	MAR $CaCO_3$ ($g/cm^2/k.y.$)	MAR C_{org} ($g/cm^2/k.y.$)	TS (wt%)
175-1084A-1H-1, 95-97	IA	0.95	0.093	28.6	22.6	8.7	4.75	1.83	0.85
175-1084A-63X-3, 72-75	IV	579.92	4.58	11.4	20.2	3.8	2.37	0.45	1.07

Note: * = ages and sedimentation rates are calculated from the biostratigraphic age model of Wefer, Berger, Richter, et al. (1998).

Table T2. Nomenclature, concentrations, and accumulation rates of compounds identified in organic solvent extract Fraction 1 (see Fig. F1, p. 16) of (**A**) Sample 175-1084A-1H-1, 95–97 cm, and (**B**) Sample 175-1084A- 63X-3, 72–75 cm.

		Concentration (ng/g)		Concentration (ng/mg C_{org})		MAR (µg/cm^2/k.y.)	
Peak*	Compound	A	B	A	B	A	B
1	*n*-C_{15} alkane	60	—	0.7	—	1.3	—
2	*n*-C_{16} alkane	211	88	2.4	2.3	4.4	1.0
3	Norpristane	249	173	2.9	4.6	5.2	2.0
4	*n*-C_{17} alkane	343	188	3.9	4.9	7.2	2.2
5	Pristane	748	395	8.6	10.4	15.7	4.6
6	3-methylheptadecane	383	—	4.4	—	8.0	—
7	5-methylheptadecane	697	—	8.0	—	14.6	—
8	Pristene isomer	—	235	—	6.2	—	2.8
9	5-methylheptadecene	—	125	—	3.3	—	1.5
10	*n*-C_{18} alkane	543	245	6.2	6.4	11.4	2.9
11	Phytane	968	725	11.1	19.1	20.3	8.5
12	Phytene isomer	—	113	—	3.0	—	1.3
13	Phytene isomer	—	217	—	5.7	—	2.6
14	Phytene isomer	—	306	—	8.0	—	3.6
15	*n*-C_{19} alkane	444	263	5.1	6.9	9.3	3.1
16	3-methylnonadecane	485	—	5.6	—	10.2	—
17	5-methylnonaadecane	774	339	8.9	8.9	16.3	4.0
18	*n*-C_{20} alkane	450	310	5.2	8.1	9.5	3.6
19	*n*-C_{21} alkane	277	214	3.2	5.6	5.8	2.5
20	3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene	90	137	1.0	3.6	1.9	1.6
21	3-(4,8,12-trimethyltridecyl)-thiophene	—	103	—	2.7	—	1.2
22	3-methylheneicosane	548	—	6.3	—	11.5	—
23	5-methylheneicosane	487	—	5.6	—	10.2	—
24	C_{22} cyclic alkane	355	—	4.1	—	7.5	—
25	*n*-C_{22} alkane	212	141	2.4	3.7	4.5	1.6
26	C_{25} isoprenoid	492	214	5.7	5.6	10.3	2.5
27	*n*-C_{23} alkane	268	184	3.1	4.8	5.6	2.2
28	*n*-C_{24} alkane	168	114	1.9	3.0	3.5	1.3
29	*n*-C_{25} alkane	520	229	6.0	6.0	10.9	2.7
30	*n*-C_{26} alkane	278	169	3.2	4.4	5.9	2.0
31	*n*-C_{27} alkane	797	430	9.2	11.3	16.8	5.0
32	Unknown with base *m/z* 231	—	1461	—	38.4	—	17.1
33	Cholesta-4,22-diene	—	250	—	6.6	—	2.9
34	Unknown with base *m/z* 231	—	530	—	14.0	—	6.2
35	Unknown with base *m/z* 231	—	893	—	23.5	—	10.5
36	Cholest-4-ene	796	1387	9.2	36.5	16.7	16.3
37	Unknown with base *m/z* 231	—	888	—	23.4	—	10.4
38	Cholest-5-ene	—	1025	—	27.0	—	12.0
39	Squalene	1111	—	12.8	0.02	3.3	0.0
40	24-methylcholesta-4,22-diene	524	2375	6.0	62.5	11.0	27.9
41	24-methylcholesta-5,22-diene	—	757	—	19.9	—	8.9
42	27ß(H) or 17ß(H) hopane	375	—	4.3	0.0	7.9	0.0
43	Unknown sterene	—	525	—	13.8	—	6.2
44	n C_{29} alkane	1936	1308	22.2	34.4	40.7	15.3
45	24-methylcholest-4-ene	350	704	4.01	8.5	7.4	8.3
46	24-methylcholest-5-ene	614	114	7.1	3.0	12.9	1.3
47	24-ethylcholesta-4,22-diene	413	—	4.7	—	8.7	—
48	24-ethylcholesta-5,22-diene	366	—	4.2	—	7.7	—
49	C_{30} hopene	335	—	3.9	—	7.0	—
50	24-ethylcholesta-4-diene	830	1021	9.5	26.9	17.5	12.0
51	24-ethylcholesta-5-diene	1062	454	12.2	12.0	22.3	5.3
52	Δ17(21)- C_{30} hopene	1054	891	12.1	23.4	22.1	10.5
53	Unknown sterene	—	457	0.0	12.0	0.0	5.4
54	17α(H),21ß(H)-C_{30} hopane	301	370	3.5	9.7	6.3	4.3
55	Δ13(18)- C_{30} hopene	—	—	—	—	—	—
56	*n*-C_{31} alkane	6244	2562	71.76	67.43	131.24	30.05
57	Δ^8 fernene	—	232	—	6.10	—	2.72
58	$\Delta^{9(11)}$ fernene	—	88	—	2.31	—	1.03
59	C_{30} hopene	528	—	6.07	—	11.09	—
60	Δ^7 fernene	965	—	11.09	—	20.28	—
61	17ß(H),21ß (H)- C_{30} hopane	418	209	4.80	5.51	8.78	2.45
62	C_{30} hopene	636	—	7.31	—	13.37	—
63	*n*-C_{33} alkane	2294	822	26.37	21.63	48.23	9.64
64	17α(H),21 _ (H)- C_{31} hopane	585	256	6.72	6.75	12.29	3.01
65	*n*-C_{34} alkane	1133	721	13.03	18.99	23.83	8.46

Table T2 (continued).

Peak*	Compound	Concentration (ng/g)		Concentration (ng/mg C_{org})		MAR (μg/cm^2/k.y.)	
		A	B	A	B	A	B
66	*n*-C_{35} alkane	373	137	4.29	3.61	7.85	1.61
67	*n*-C_{36} alkane (internal standard)	—	—	—	—	—	—

Notes: * = peak assignments refer to gas chromatograms in Figure F1, p. 16. — = not detected.

Table T3. Nomenclature, concentrations, and accumulation rates of compounds identified in organic solvent extract Fraction 3 (see Fig. F4, p. 19) of (**A**) Sample 175-1084A-1H-1, 95–97 cm, and (**B**) Sample 175-1084A-63X-3, 72–75 cm, with $U^{K}_{37}{}'$ and SST values.

		Concentration (ng/g)		Concentration (ng/mg C_{org})		MAR (µg/cm^2/k.y.)	
Notation*	Compound	A	B	A	B	A	B
Alkenones							
37:3 Me	Heptatriaconta-8,15,22-trien-2-one	18,870	1,569	217	41	397	18
37:2 Me	Heptatriaconta-15,22-dien-2-one	24,500	21,214	282	558	515	249
38:3 Et	Octatriaconta-9,16,23-trien-3-one	8,674	—	100	—	182	—
38:3 Me	Octatriaconta-9,16,23-trien-2-one	6,369	—	73	—	134	—
38:2 Et	Octatriaconta-16,23-dien-3-one	14,580	29,067	168	765	307	341
38:2 Me	Octatriaconta-16,23-dien-2-one	4,670	704	54	19	98	8
39:3 Et	Nonatriaconta-10,17,24-trien-3-one	1,632	352	19	9	34	4
39:2 Et	Nonatriaconta-17,24-dien-3-one	1,834	—	21	—	39	—
40:2 Et	Tetraconta-18,25-dien-3-one†	—	1,798	—	47	—	21
Alkenoates							
37:2 Me	Methyl hexatriaconta-14,21-dienoate	2,251	—	26	—	47	—
37:2 Et	Ethyl hexatriaconta-14,21-dienoate	1,658	—	19	—	35	—
Total		85,038	54,705	977	1,440	1,788	642
$U^{K}_{37}{}'$		0.565	0.931				
SST‡ (°C)		15.8	26.9				

Notes: * = notation scheme as in gas chromatograms in Figures F3, p. 18, and F4, p. 19. † = tentative assignment of unsaturation position is following general alkenone homology. ‡ = calculated from the calibration equation of Müller et al. (1998). — = not detected.

Table T4. Nomenclature, concentrations and accumulation rates of compounds identified in organic solvent extract Fraction 4 (see Fig. F5, p. 20) of (**A**) Sample 175-1084A-1H-1, 95–97 cm, and (**B**) Sample 175-1084A-63X-3, 72–75 cm.

		Concentration (ng/g)		Concentration (ng/mg C_{org})		MAR (µg/cm^2/k.y.)	
Peak*	Compound	A	B	A	B	A	B
1	*n*-C_{14} alkanoic acid	—	304	—	8.0	—	3.6
2	*n*-C_{15} alkanoic acid	1,615	983	18.6	25.9	33.9	11.5
3	*n*-C_{16} alkanoic acid	3,087	1,083	35.5	28.5	64.9	12.7
4	*n*-C_{18} alcohol	1,109	264	12.7	7.0	23.3	3.1
5	Phytol	831	—	9.6	—	17.5	—
6	*n*-$C_{18:1}$ alkenoic acid	799	229	9.2	6.0	16.8	2.7
7	*n*-C_{18} alkanoic acid	2,106	211	24.2	5.6	44.3	2.5
8	*n*-C_{22} alcohol	1,284	—	14.8	—	27.0	—
9	*n*-C_{22} alkanoic acid	2,585	301	29.7	7.9	54.3	3.5
10	*n*-C_{24} alkanoic acid	9,124	209	104.9	5.5	191.8	2.5
11	*n*-C_{22} hydroxy *n*- alkanoic acid methyl ester?	—	399	—	10.5	—	4.7
12	*n*-C_{26} alcohol	3,020	—	34.7	—	63.5	—
13	*n*-C_{26} alkanoic acid	16,330	163	187.7	4.3	343.2	1.9
14	Cholest-5-en-3ß-ol	4,032	667	46.3	17.5	84.8	7.8
15	5-cholestan-3ß-ol	802	105	9.2	2.8	16.9	1.2
16	24-methylcholesta-5,22-dien-3ß-ol	2,935	268	33.7	7.0	61.7	3.1
17	24-methyl-5_-cholest-22-dien-3ß-ol	1,005	70	11.6	1.9	21.1	0.8
18	*n*-C_{28} alkanoic acid	7,376	229	84.8	6.0	155.0	2.7
19	24-methylcholestan-3ß-ol	2,267	148	26.1	3.9	47.6	1.7
20	23,24-dimethylcholest-22-en-3ß-ol	1,236	268	14.2	7.1	26.0	3.1
21	24-ethylcholesta-22-en-3ß-ol	5,003	—	57.5	—	105.2	—
22	23,24-dimethylcholestan-3ß-ol	5,145	148	59.1	3.9	108.1	1.7
23	24-ethylcholestan-3ß-ol	4,709	120	54.1	3.2	99.0	1.4
24	4α,23,24-trimethyl-5_-cholest-22-en-3ß-ol	4,416	155	50.8	4.1	92.8	1.8
25	*n*-C_{30} alkanoic acid	2,984	99	34.3	2.6	62.7	1.2
26	4α,23,24-trimethyl-5_-cholest-8(14)-en-3ß-ol	7,454	101	85.7	2.6	156.7	1.2
27	C_{30} alkan-15-one-1-ol	19,000	123	218.4	3.2	399.4	1.4
28	Unknown	3,487	1,273	40.1	33.5	73.3	14.9
29	Unknown	2,972	164	34.2	4.3	62.5	1.9
30	$C_{32:1}$ alken-15-one-1-ol	2,502	—	28.8	—	52.6	—
31	C_{32} alkan-15-one-1-ol	7,234	—	83.1	—	152.1	—
32	C_{32} ßß hopanol	2,157	—	24.8	—	45.3	—

Note: * = peak assignments refer to gas chromatograms in Figure F5, p. 20. — = not detected.