Wefer, G., Berger, W.H., and Richter, C. (Eds.)
Proceedings of the Ocean Drilling Program, Scientific Results Volume 175

10. Marine and Terrigenous Lipids in Southeast Atlantic Sediments (Leg 175) as Paleoenvironmental Indicators: Initial Results[1]

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ABSTRACT

Lipid compositions of sediments recovered during Ocean Drilling Program Leg 175 in the eastern South Atlantic reflect a variety of oceanographic and climatological environments. Most of the identified lipids can be ascribed to marine sources, notably haptophytes, eustigmatophytes, dinoflagellates, archaea, and diatoms. Elevated concentrations of cholesterol suggest zooplankton herbivory, characteristic for sites influenced by upwelling. At these sites, sulfurized highly branched isoprenoids from diatoms are also present in high amounts. Sterols, sterol ethers, hopanoids, and midchain hydroxy fatty acids could also be detected. Terrigenous lipids are *n*-alkanes, fatty acids, *n*-alcohols, and triterpenoid compounds like taraxerol and β-amyrine. *n*-Alkanes, fatty acids, and *n*-alcohols are derived from leaf waxes of higher land plants and transported to the sea by airborne dust or fresh water. Triterpenoid compounds are most probably derived from mangroves and transported solely by rivers. Lipid compositions below the Congo low-salinity plume are strongly influenced by terrigenous material from the Congo River. Elevated organic carbon contents and predominantly marine lipid distributions at the Angola margin may indicate a highly productive plankton population, probably sustained by the Angola Dome. Sedimentary lipids in the Walvis Basin contain an upwelling signal, likely transported by the Benguela Current. Sedimentary lipids off Lüderitz Bay and in the southern Cape Basin are dominated by plankton

[1] Schefuss, E., Versteegh G.J.M, Jansen, J.H.F, and Sinninghe Damsté, J.S., 2001. Marine and terrigenous lipids in southeast Atlantic sediments (Leg 175) as paleoenvironmental indicators: initial results. *In* Wefer, G., Berger, W.H., and Richter, C. (Eds.), *Proc. ODP, Sci. Results,* 175, 1–34 [Online]. Available from World Wide Web: <http://www-odp.tamu.edu/publications/175_SR/VOLUME/CHAPTERS/SR175_10.PDF>. [Cited YYYY-MM-DD]

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Initial receipt: 21 February 2000
Accepted: 14 September 2000
Web publication: 10 April 2001
Ms 175SR-228

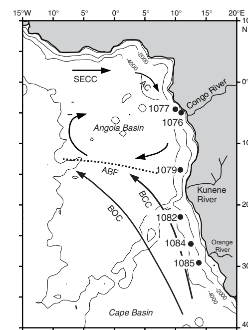
lipids in high to intermediate amounts, reflecting persistent and seasonal upwelling, respectively.

INTRODUCTION

The eastern South Atlantic plays an important role in the global heat transport system (Berger and Wefer, 1996). It contains one of the largest upwelling systems worldwide and receives clastic and organic material from the second largest river in the world. The oceanographic environments include a tropical region strongly affected by river discharge, a tropical oceanic region, and a region influenced by coastal upwelling. It should thus be possible to distinguish all these depositional settings by specific assemblages of terrigenous and marine components. Lipid biomarker compositions provide information on different types of terrigenous lipid sources and a detailed view on marine plankton groups contributing to the sedimentary organic matter. Furthermore, the biomarkers in marine sediments can supply information on early diagenetic reactions in the sediments and paleoceanographic conditions (Brassell, 1993).

For these purposes, a detailed molecular organic geochemical overview study was performed on two to three samples each from Ocean Drilling Program (ODP) Sites 1076, 1077, 1079, 1082, 1084, and 1085 in the southeast Atlantic Ocean (Fig. F1). The study is intended to be solely inventory; samples were chosen randomly from different sediment depths in each core (Table T1). Therefore, only restricted paleoceanographic interpretations can be drawn from the results. The concentrations of single compounds and lipid classes are used to compare the different oceanographic environments with respect to terrigenous, phytoplanktonic, and zooplanktonic lipids. An attempt is made to give an overview for each site about the lipid biomarkers present and their potential use as paleoceanographic indicators. Earlier organic geochemical investigations of sediments from this particular ocean area (e.g., Boon, 1978) provided valuable background information.

F1. Site locations and generalized surface hydrography, p. 23.



Oceanographic Setting

In the present-day eastern South Atlantic, the South Equatorial Countercurrent in the north feeds the warm southward-flowing waters of the Angola Current (AC) (Fig. F1). At ~15°S–17°S, these waters converge with the cold northward-flowing Benguela Coastal Current and are deflected to the northwest. A sharp frontal zone, the Angola-Benguela Front (ABF), is established and extends to a distance of up to 1000 km off the coast (Meeuwis and Lutjeharms, 1990). The ABF effectively forms a barrier for surface ocean transport, as does the Walvis Ridge for deep water.

The cyclonic gyre in the Angola Basin is overlain by the low-salinity plume of the Congo River at ~5°S. Sites 1076 and 1077 are located below the Congo plume. Riverine input, coastal upwelling, and incursions of open ocean waters influence this environment. Site 1076 is the shallowest location and should record the strongest interaction of river discharge and coastal upwelling. Site 1077 is at larger water depth and is presumably more influenced by open-ocean conditions.

In the eastern Angola Basin, the cyclonic circulation causes shoaling of the thermocline and supply of nutrients to the photic zone. Site 1079 is located on the Angola margin and is neither directly influenced by

rivers nor situated under a coastal upwelling cell (Lutjeharms and Stokton, 1987). Productivity benefits from a seasonal supply of nutrients from the Angola Dome.

In the south, the Benguela Current is fed by the South Atlantic Current and the Agulhas Current. At ~30°S, the Benguela Current splits into the Benguela Oceanic Current, the main current in northwestern direction, and the Benguela Coastal Current, flowing as a sluggish, wide current along the continental margin. These currents are driven by the predominantly southerly and southeasterly winds (Shannon, 1985). Off the coast of South Africa and Namibia, these winds drive coastal upwelling of cold, nutrient-rich South Atlantic Central Water (Shannon, 1985). Productivity reaches high values of >180 g $C/m^2/yr$ (Berger, 1989). Site 1082 is located in the Walvis Basin, outside recent upwelling activity. Since filaments of cold, nutrient-rich waters extend up to 600 km offshore (Lutjeharms and Stokton, 1987) where they mix with low-productivity waters sustaining intermediate productivity, Site 1082 most probably records an upwelling signal transported by filaments and eddies. Site 1084 is situated close to the upwelling cell in Lüderitz Bay. At this site, persistent upwelling of South Atlantic Central Water (Shannon, 1985) causes high productivity and high rates of sedimentary accumulation of phytoplankton biomass (Brown et al., 1991). Site 1085 is located in the southern part of the Cape Basin near the continent. Besides seasonal upwelling activity, this site may also record terrigenous supply from the Orange River.

MATERIAL AND METHODS

Samples

The samples investigated were taken during the expedition on board the *JOIDES Resolution* and kept frozen until analysis. Because the sampling was done on board, no detailed sampling strategy was applied. Sample information is given in Table T1.

T1. Summary of samples analyzed, p. 31.

Extraction and Fractionation of Soluble Organic Matter

Sediment samples were lyophilized and finely ground in an agate mortar and subsequently serially extracted ultrasonically using three 40-mL aliquots of methanol (MeOH), three 40-mL aliquots of dichloromethane (DCM):MeOH (1:1, v/v), and three 40-mL aliquots of DCM, each for 5 min. For each sample, the extracts were combined and concentrated with a rotary evaporator at 35°C. Salts were removed by washing with double-distilled H_2O in a separatory funnel and extraction of the lipids with three aliquots of DCM. For total lipid analysis, known aliquots of the extracts with an added amount of standard (2,3-dimethyl-5-1′,1′-d_2-hexadecyl-thiophene) were methylated with diazomethane after drying with anhydrous Na_2SO_4. Before silylation with bis(trimethyl-silyl)trifluoro-acetamide in pyridine (1 hr at 60°C), very polar compounds were removed on a silica gel column eluted with ethyl acetate. Before fractionation, extracts were mixed with known amounts of thiophene and chroman standards and separated on a 4-cm column packed with activated Al_2O_3. Apolar fractions were collected by elution with four column volumes of hexane:DCM (9:1, v/v) and polar fractions by stripping the column with MeOH:DCM (1:1, v/v).

One sample, 175-1084A-12H-6, 140–143 cm, was further separated by thin-layer chromatography (TLC). The plate was developed with diisopropylether:acetic acid (96:4, v/v) to 75% of the height of the plate and redeveloped with petroleum ether 40–60:ether:acetic acid (89:10:1, v/v) (Skipski et al., 1965). Eight fractions were scraped off the TLC plate and ultrasonically extracted using three aliquots of hexane for TLC fractions 1 and 2 and three aliquots of ethyl acetate for other fractions. Fractions were cleaned on a small column filled with nonactivated alumina by elution with hexane:DCM (9:1, v/v) and subsequently methylated and silylated before analyses. The polar fraction of Sample 175-1084A-12H-6, 140–143 cm, was desulfurized with Raney nickel (Sinninghe Damsté et al., 1988) followed by hydrogenation.

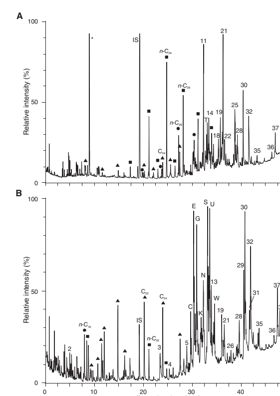
Instrumental Analyses

Gas chromatography (GC) was performed on a Hewlett Packard 5890 series II chromatograph equipped with an on-column injector and fitted with a fused silica capillary column (25 m × 0.32 mm) coated with CP Sil 5 (film thickness = 0.12 µm). Helium was used as the carrier gas, and the oven was programmed from 70°C to 130°C at 20°C/min, followed by 4°C/min to 320°C (10 min hold time). Effluents were detected using a flame ionization detector (FID). GC-mass spectrometry (GC-MS) was performed using the same type of gas chromatograph with the same conditions described above. The chromatographic column was directly inserted into the electron impact ion source of a VG Autospec Ultima mass spectrometer operated with an ionization energy of 70 eV and scanned over a mass range of *m/z* 50–800 with a cycle time of 1.8 s. Compound identifications are based on comparison of relative GC retention times and mass spectra with those in the literature. Quantification of long-chain alkenones, alkyldiols, and biphytanediols was performed by integration of their peak areas and those of internal standards in FID chromatograms. Data were acquired and integrated using Atlas analytical software. Other biomarkers were quantified using characteristic fragment ion abundances in mass chromatograms. Resulting abundance values were converted to concentrations by compound-specific correction factors determined in samples in which these compounds could be identified in FID traces. The relative precision of the entire analytical procedure, based on duplicate sediment extractions, was between 10% and 15%. Concentrations are calculated in micrograms per gram of total organic carbon (TOC). TOC contents were measured after decalcification of samples on a Carlo Erba NA-1500 elemental analyzer using flash combustion at 1050°C. Standard deviations of duplicate measurements were better than 0.3%.

RESULTS AND DISCUSSION

Figure F2 shows the chromatograms of two total lipid fractions (Samples 175-1077A-9H-2, 75–77 cm, and 175-1084A-12H-6, 140–143 cm), with compounds listed in Tables T2 and T3. A wide variety of biomarkers from both terrestrial plants and marine sources such as algae, (cyano) bacteria, and archaea is present in the samples. These biomarkers will be discussed according to compound class.

F2. Total ion chromatograms of the total lipid fractions, p. 24.



T2. Compounds identified in selected samples, p. 32.

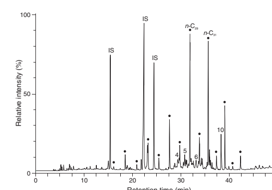
T3. Steroids identified in selected samples, p. 33.

Terrigenous Lipids

n-Alkanes

n-Alkanes in the studied sediments range in carbon number from 18 to 35, with C_{25}–C_{33} *n*-alkanes the most dominant homologues (Fig. F3). A strong odd-over-even carbon number predominance (carbon preference index [CPI]) (CPI_{25-33} = 3–10) (Table T4) was observed in all samples, indicating a predominantly terrigenous origin of the *n*-alkanes. These distributions resemble those of *n*-alkanes from leaf waxes of higher plants (Kolattukudy, 1976; Eglinton and Hamilton, 1967) and in eolian dust samples (Gagosian et al., 1981, 1987; Simoneit et al., 1977), supporting a terrigenous origin.

F3. Total ion chromatogram of the apolar fraction, p. 25.

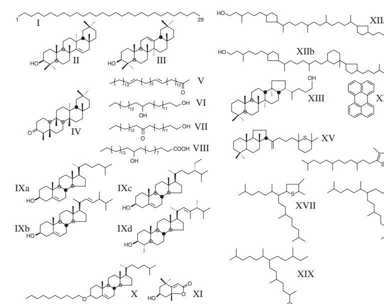


Concentrations of *n*-alkanes in sediments from Sites 1076 and 1077 are much higher than in sediments from the southern sites (see Table T4). These differences can probably be related to the different oceanographic and climatologic settings for both regions. The northern sites (1076, 1077, and to a minor extent also 1079) receive river input of terrigenous organic matter, whereas the terrigenous compounds in the southern sites are mainly transported via the wind and diluted by a high production of marine lipids resulting from upwelling activity. The variations in concentrations of leaf wax components at the southern sites possibly result from changes in the strength and direction of the trade winds, influencing the strength of marine upwelling and, therefore, the relative dilution of terrigenous by marine lipids.

T4. Concentrations of quantified biomarker lipids and compound indices, p. 34.

At the northern sites (Sites 1076, 1077, and 1079), the *n*-alkane distributions maximize at *n*-nonacosane (*n*-C_{29}, structure I) (see Fig. F4 for structures). In samples from Sites 1082, 1084, and 1085, *n*-untriacontane (*n*-C_{31}) is most abundant. The chain length distributions of the *n*-alkanes could thus reflect different sources of the terrigenous compounds in both regions. The average chain length (ACL) of the C_{25}–C_{33} *n*-alkanes changes from ~29.6 in the northern sediments to ~30.4 at the southern sites (Table T4). It has been suggested that plants produce longer-chain compounds in warmer climates (e.g., Poynter et al., 1989). The observed shift in our limited data set contradicts this interpretation. At present, vegetation in southern Africa consists predominantly of savanna-type grasslands, whereas in the more northern, tropical parts, lowland rainforest and Afromontane forest dominate. Therefore, an influence of vegetation type on chainlength of terrigenous leaf lipids seems more likely. Leaf lipids derived from grasslands may on average have longer chain lengths than do leaf lipids from plants in rainforests (Cranwell et al., 1973). Obviously, the limited sample number of this study prevents any further conclusions on this subject, which will be addressed in future research.

F4. Compound structures of biomarker lipids, p. 26.



Fatty Acids and *n*-Alcohols

Fatty acids in the sediments range in carbon number from C_{16} to C_{30} with only small amounts of C_{16}–C_{18} fatty acids. *n*-Alcohols occur in the carbon number range of C_{20}–C_{30}. The highest concentrations of fatty acids and *n*-alcohols occur in the sediments close to the Congo River, where also the largest variation could be detected (Table T4). The lowest concentrations of both compound classes are present in the sediments from the Walvis Basin (Site 1082). Even carbon numbered long-chain compounds dominate the distributions of both compound groups. The dominance of the long-chain compounds, together with the observed

strong even-over-odd carbon number predominance (for both classes, $CPI_{22–28}$ = 5–11), indicates a terrigenous origin for fatty acids and *n*-alcohols. Series of long-chain fatty acids and *n*-alcohols with a strong even carbon number predominance are characteristic constituents of surface waxes of higher plants (Kolattukudy, 1976). Therefore, the biological source of these compounds is closely related to that of the leaf wax–derived *n*-alkanes. Similar to the *n*-alkanes, the high concentrations of fatty acids and wax alcohols in the Congo plume sediments suggest a predominant fluvial supply, whereas the smaller amounts at other sites are more readily explained to be derived from dust (Gagosian et al., 1981, 1987; Simoneit et al., 1977). An algal origin of the long-chain fatty acids, however, cannot be completely excluded (Volkman et al., 1998). Marine microalgae are not a major source of long-chain *n*-alcohols but may contain minor amounts of these compounds (for a review see Volkman et al., 1998). However, the strong covariance of the concentrations of fatty acids and *n*-alcohols with the concentrations of *n*-alkanes, together with their high CPI values, indicate that autochthonous sources of fatty acids and *n*-alcohols are of minor importance. Higher plant leaf waxes are the main source.

Pentacyclic Triterpenoids

Two pentacyclic triterpenoid alcohols were detected in samples from Sites 1076, 1077, and 1079 (see Fig. F2). They were identified as taraxerol (taraxer-14-en-3β-ol; Structure II in Fig. F4) and β-amyrine (olean-12-en-3β-ol; Structure III in Fig. F4) by comparison with mass spectra published by Killops and Frewin (1994) and relative retention times. The largest quantities were found in sediments located below the Congo River plume (Sites 1076 and 1077) and a smaller amount in sediments from the Angola margin (Site 1079). In samples from the Congo, the triterpenoid concentrations varied strongly, and they were below the detection limit in samples from the southern Sites 1082, 1084, and 1085. Another triterpenoid compound present in trace amounts in samples from Sites 1076, 1077, and 1079 is friedelan-3-one (Structure IV in Fig. F4), a triterpenoid ketone.

All three pentacyclic triterpenoids (Structures II–IV in Fig. F4) are widespread in higher plants (Beaton et al., 1955) and therefore represent a terrigenous source. Their occurrence has been reported in several marine sediments (e.g., Brassell and Eglinton, 1983; Volkman et al., 1987). β-Amyrine has been isolated from several species of mangroves, including some species of *Rhizophora* (Ghosh et al., 1985). In *Rhizophora mangle*, it was found to be a major component of the epicuticular wax of the leaves, whereas taraxerol was largely bound in the cutin fraction of the leaves (Frewin et al., 1993; Killops and Frewin, 1994). Another mangrove species, *Avicennia germinans*, contains smaller amounts of β-amyrine and taraxerol (Killops and Frewin, 1994). At present, the dominant mangrove species in the Congo area is *Rhizophora racemosa* (Moguedet, 1980). We suggest therefore, that this species, or its predecessor, is the major source of β-amyrine and taraxerol in the sediments. The strong variation in triterpenoid content between the samples could thus give an indication of the proximity and the extent of mangrove vegetation in the Congo area.

Interestingly, none of the pentacyclic triterpenoid compounds could be detected in sediments from sites south of the ABF. This is in agreement with the present restriction of mangrove swamps to humid, tropical environments north of the ABF. Furthermore, it strongly favors the

hypothesis of fluvial rather than atmospheric transport of mangrove lipids. The northward-flowing Benguela Coastal Current could limit southward transport of lipids at the ABF.

Marine Lipids

Long-Chain Alkenones

All sediment samples contain C_{37} and C_{38}, and to a lesser extent C_{39} and di- and triunsaturated methyl and ethyl ketones (Structure V in Fig. F4) (de Leeuw et al., 1980). The highest concentrations of these compounds were found in samples from Site 1084 (up to 1400 µg/g TOC), but the highest variability was detected in samples from Site 1076, where the maximum concentration was slightly smaller. Concentrations of alkenones in sediments from other sites are much smaller in range and absolute amount. These lipids are exclusively biosynthesized by haptophyte algae like *Emiliania huxleyi* and *Gephyrocapsa* spp. (Volkman et al., 1980, 1995; Marlowe et al., 1984) and were detected in numerous marine sediments (e.g., Brassell et al., 1986a), including the South Atlantic. Changes in coccolithophorid assemblages seem not to have affected alkenone production (Müller et al., 1997). Sedimentary alkenone concentrations have also been used as an indicator for marine primary production (Villanueva et al., 1998; Schubert et al., 1998; Hinrichs et al., 1999). The $U^{k}_{37}{}'$ index, the ratio of the diunsaturated to the sum of the di- and triunsaturated C_{37} alkenones, is extensively used in paleoceanography as a temperature proxy. It has been shown that the $U^{k}_{37}{}'$ index is strongly correlated to sea-surface temperature (e.g., Brassell, 1993). The calculated sea-surface temperature estimates using the temperature calibration for the South Atlantic by Müller et al. (1998) are given in Table T4. The lowest sea-surface temperature is reconstructed for samples from below the upwelling activity. This suggests upwelling of cold South Atlantic Central Water as the main cause. Highest temperatures and largest temperature variability were detected for samples from Site 1082 in the Walvis Basin. Because of our limited data set, we regard any suggestion on the cause of this large range of temperatures as highly speculative. Alkenone concentrations are generally elevated during times of lower sea-surface temperatures (Table T4). This observation indicates that haptophyte algae are strongly dependent on upwelling events, which decrease sea-surface temperature and increase nutrient concentrations.

Alkyl Diols and Alkyl Keto-ols

Long-chain saturated C_{28}–C_{32} alkyl diols (Structure VI in Fig. F4) were detected in all samples. The highest concentrations were found in samples from Sites 1076 and 1077, off the mouth of the Congo River (Table T4). Samples from Sites 1082 and 1085 contain only small amounts of these compounds (cf. Fig. F2), whereas samples from Sites 1079 and 1084 have intermediate quantities. The highest variability in alkyl diol content was also detected in samples from Site 1076. The major sources are probably microalgae of the class Eustigmatophyceae (Volkman et al., 1992; Volkman et al., 1999). The high concentrations of alkyl diols in sediments underlying the Congo River plume may point to a contribution by freshwater eustigmatophyte algae in the low-salinity waters (Volkman et al., 1999), although marine eustigmatophytes of the genus *Nannochloropsis* are also known to contain alkyl diols (Volkman et al.,

1992). Alkyl diols have been reported to occur in sediments from various areas (de Leeuw et al., 1981; see review in Versteegh et al., 1997). Remarkably, samples from the Congo area predominantly contain the C_{30} homologue, whereas the C_{28} compound is the dominant alkyl diol in sediments from the southern upwelling region. A similar change was detected for the isomeric composition of the diols. 1,15-Isomers dominate diol distributions from sites north of the ABF, whereas sediments south of the ABF contain smaller amounts of the 1,15-diols but more of 1,14-diols. Versteegh et al. (2000) reported the same change in isomer composition in surface sediments and in sediments from the oxygen isotope Stage 5–6 transition from this area. The differences are most likely to be explained by different algal communities living under contrasting temperature and nutrient conditions.

C_{30} and C_{32} alkyl keto-ols (Structure VII in Fig. F4) are present in all samples. Their amounts do not exceed trace levels, except in sediments from Site 1079 on the Angola margin. In these sediments, the C_{30} and C_{32} alkyl keto-ols are major components. By comparison of chain length and isomer distributions of diols and keto-ols, Versteegh et al. (1997) concluded that both compound classes are diagenetically independent. Therefore, the high amounts of keto-ols in Angola margin sediments seem to reflect a specific planktonic source of an as-yet-unidentified nature.

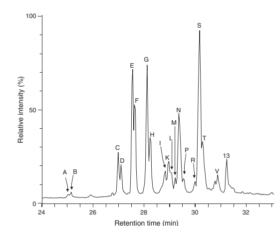
Midchain Hydroxy Fatty Acids

In sediments from Site 1084, C_{26} and C_{28} midchain hydroxy fatty acids are present in relatively large amounts. At Site 1082, they occur in trace amounts, whereas they could not be detected at other sites. Both compounds are dominated by the 12-hydroxy-isomer. The C_{28} 12-hydroxy fatty acid (Structure VIII in Fig. F4) has already been detected in organic matter–rich sediments, like Mediterranean sapropels (ten Haven et al., 1987), sediments from the Oman margin (ten Haven and Rullkötter, 1991), those from the Arabian Sea (Versteegh et al., 1997; Prahl et al., 2000), and from K/T boundary sediments (Yamamoto et al., 1996). Their phytoplanktonic origin was indicated by occurrence in sediment trap samples from high productive Arabian Sea waters (Prahl et al., 2000). Midchain hydroxy fatty acids have been reported from the genus *Nannochloropsis* (Gelin et al., 1997) but only homologues $\geq C_{30}$. Therefore, organisms different from the *Nannochloropsis* investigated must have been the source of the detected compounds in the investigated South Atlantic sediments. Because these compounds could only be identified in sediments from Sites 1082 and 1084, which are potentially influenced by upwelling, an origin from planktonic organisms living at high nutrient availability seems likely.

Steroids

A range of C_{26}–C_{30} sterols was detected. An overview of compounds identified in the TLC-5 fraction of Sample 175-1084A-12H-6, 140–143 cm (Fig. F5), is given in Table T3. The sterol distribution is dominated by only few components: cholesta-5-en-3β-ol (cholesterol; Structure IXa in Fig. F4), 24-methylcholesta-5,22-dien-3β-ol (Structure IXb in Fig. F4), 24-ethylcholest-5-en-3β-ol (Structure IXc in Fig. F4), and 4α,23,24-trimethylcholest-22-en-3β-ol (dinosterol; Structure IXd in Fig. F4). All other detected sterols contribute only minor to trace amounts. The ste-

F5. Partial total ion chromatogram of the TLC-5 fraction, p. 27.



rol content is highest in sediments from drill sites under upwelling cells (Sites 1084 and 1085) where phytoplankton primary production is high. Sediments from the Congo (Sites 1076 and 1077) and the Walvis Basin (Site 1082) contain minor quantities of sterols, and only trace amounts were detected in samples from the Angola margin (Site 1079). A conclusive interpretation of sterol distributions is complicated by the multiple sources of most sterols (Volkman, 1986).

Cholesta-5-en-3β-ol (cholesterol) in marine sediments is derived from a variety of planktonic organisms, including haptophyte algae (Volkman, 1986). Zooplankton was found to be a major source of cholesterol in the Peru upwelling system through dietary alteration of phytosterols (Volkman et al., 1987). Therefore, the intermediate to high abundance of cholesterol in the samples from Site 1084 probably indicates extensive grazing of primary marine biomass by zooplankton.

The occurrence of the C_{28} sterol 24-methylcholesta-5,22-dien-3β-ol in sediments is often ascribed to a diatom lipid contribution. However, it was also detected in cultures of dinoflagellates (Teshima et al., 1980; Goad and Withers, 1982) and haptophytes (Volkman et al., 1998) and detected in the water column after massive blooms of *Emiliania huxleyi* (Conte et al., 1995). Its occurrence in sediment samples from Sites 1082, 1084, and 1085, all characterized by a substantial long-chain alkenone content (i.e., 80–1400 µg/g TOC) (Table **T4**), thus cannot be used to specifically indicate remnants of diatom biomass. More likely, a combined contribution of haptophytes and diatoms was responsible for the relatively high content of 24-methylcholesta-5,22-dien-3β-ol.

Another C_{28} sterol proposed as a marker compound for diatoms is 24-methylcholesta-5,24(28)-dien-3β-ol because of its elevated concentrations in some centric diatom species (Volkman et al., 1998), although it also occurs in marine dinoflagellates (Nichols et al., 1984). It was only detected in minor amounts in samples from Site 1084 and was below the detection limit in all other samples. Specific diatom occurrence from sterol distributions is, therefore, only indicated at the site of the most substantial upwelling intensity.

Another major sterol is 24-ethylcholest-5-en-3β-ol, together with its stanol analog (24-ethyl-5α-cholestan-3β-ol) present in smaller amounts. Both are commonly associated with terrestrial higher plants, in which they are the dominant sterols (Huang and Meinschein, 1976). In environmental settings, where terrigenous material is scarce, the main contributors likely are microalgae like diatoms and xantophyceae (Volkman et al., 1998). The source of these compounds in samples containing high concentrations of long-chain *n*-alkanes may have been terrestrial higher plant detritus as in the samples from the Congo area. In samples from upwelling sites, which contain minor or neglectable amounts of other terrigenous lipids, marine phytoplankton sources seem more likely.

The occurrence of 4α,23,24-trimethylcholest-22-en-3β-ol (dinosterol), accompanied by a range of other 4-methyl sterols, is ascribed to dinoflagellates. Dinosterol is almost uniquely produced by dinoflagellates (Boon et al., 1979b; Robinson et al., 1984), with minor quantities occurring in diatoms (Volkman et al., 1993). High concentrations of dinosterol were found in samples from Sites 1076, 1079, and 1084, with the highest variability in the Congo Fan sediments. Dinoflagellates, therefore, are considered to have significantly contributed to the marine extractable lipids in the Congo plume and in the upwelling cells, although the detection as a major lipid does not necessarily imply that dinoflagellates were dominant constituents of the phytoplankton com-

munity in these environments. Other less abundant sterols are less specific and may be derived from a variety of algal sources (cf. Volkman, 1986).

In the apolar fractions of samples from the upwelling Sites 1084 and 1085, and to a lesser extent also in samples from Sites 1079 and 1082, series of sterenes, steradienes, and steratrienes are present. The most abundant compounds are C_{27} and C_{28} homologues. They are diagenetic transformation products of sterols. Their formation proceeds via microbiologically mediated reduction and/or dehydration of sterols (Gagosian and Farrington, 1978; review in de Leeuw and Baas, 1986).

Sterol Ethers

In samples from Sites 1084 and 1085, relatively large amounts of sterol ethers are present; they occur in minor amounts at Site 1079. They commonly consist of C_{27} and C_{28}, Δ^5 and $\Delta^{5,22}$ steroid moieties, ether bound to a nonyl or decyl moiety (Structure X shows the C_{27} Δ^5 decyl ether in Fig. **F4**). These compounds have been identified by comparison with mass spectra reported by Schouten et al. (2000a). Their distributions show distinct differences from the sterol distributions. Steroid moieties larger than C_{28}, or stanol analogs, could not be detected. A diagenetic origin of sterol ethers from alkylation of the sterols therefore seems unlikely. The occurrence of sterol ethers has earlier been reported for Walvis Bay diatomaceous ooze (Boon and de Leeuw, 1979a), and from sediments from the Miocene Monterey formation and the Arabian Sea (Schouten et al., 2000a). All these settings, including the samples under consideration, are known to receive a large amount of organic matter from diatoms, from which these compounds could be derived. It is assumed that the sterol ethers either represent primary biosynthetic products or are derived from zooplankton feeding on specific source organisms. Copepods are known to convert algal sterols to steryl chlorin esters (Talbot et al., 1999). In that case, algal sterols were converted with equal efficiency to steryl esters, resulting in the same ratio for sterols and steryl esters. We suggest that the formation of sterol ethers could take place by a similar mechanism during herbivory, although no sterol ether-producing organism has yet been identified.

Loliolide and *iso*-Loliolide

An omnipresent compound pair in all investigated samples is loliolide (Structure XI in Fig. **F4**) and its isomer, *iso*-loliolide. They are the dominant lipids in the TLC-8 fraction of Sample 175-1084A-12H-6, 140–143 cm. Highest concentrations in samples from Site 1084 are followed by slightly lower contents in samples from Sites 1076 and 1079. At Site 1076 the highest variability was detected. Loliolide and *iso*-loliolide are known as end products of anaerobic degradation of fucoxanthin (Klok et al., 1984; Repeta, 1989). Fucoxanthin is the major carotenoid in diatoms and haptophytes. Loliolide and *iso*-loliolide were earlier reported from sediments receiving abundant marine phytoplankton biomass, like the Mediterranean sapropels (ten Haven et al., 1987), the Namibian margin (Klok et al., 1984), and the Peruvian shelf (Repeta, 1989). The elevated concentrations of loliolide and *iso*-loliolide in the sediments from Sites 1076, 1079, and 1084 therefore indicate a large carotenoid contribution from diatoms and/or haptophyte algae at these sites. Furthermore, it is concluded that anaerobic degradation of carotenoids to loliolides has taken place in the sediments.

Biphytane Diols

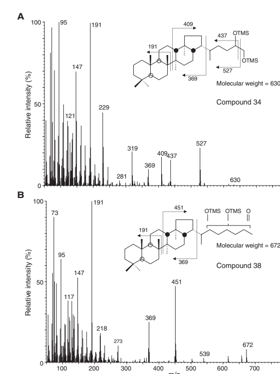
Two C_{40} cyclic biphytanediols were detected in the TLC-5 fraction of Sample 175-1084A-12H-6, 140–143 cm. By comparison with published mass spectra, they were identified as the C_{40} dicyclic (Structure XIIa in Fig. F4) (Schouten et al., 1998) and C_{40} tricyclic biphytanediol (Structure XIIb in Fig. F4) (Schouten et al., 2000b). Investigations of all samples showed that those lipids are present in highest concentrations and with the largest variation in samples from Site 1084. Although these compounds have not yet been identified in organisms, they were encountered in various sediments from, for example, the Indian Ocean, Arabian Sea, Angola Basin, Walvis Bay, and Madeira Abyssal Plain (Schouten et al., 1998, 2000a). From the structural similarities with sedimentary C_{40} ether-bound biphytanes, it was proposed that biphytane diols are biosynthesized by archaea (Hoefs et al., 1997; Schouten et al., 1998). The presence of intact archaeal tetraether lipids was proven for Sample 175-1084A-25X-3, 20–23 cm, by high performance liquid chromatography following the methodology described by Hopmans et al. (2000). Their high abundance in water-column samples of the Black Sea and the Cariaco Basin and in surface sediments from the Indian Ocean (Hoefs et al., 1997) suggests that they are already produced in the water column. The carbon skeleton structure of the sedimentary $C_{40:3}$ biphytane diol (and ether-bound biphytane) differs from that of thermophilic archaea (Schouten et al., 1998). Therefore, it is assumed that these compounds derive from nonthermophilic archaea (Hoefs et al., 1997). Possibly, the pelagic archaea are associated with low-oxygen conditions (Hoefs et al., 1997).

Hopanoids

Small amounts of hop-17(21)-ene and *neo*-hop-13(18)-ene were detected in all samples. These compounds are present in slightly elevated concentrations in samples from Sites 1082, 1084, and 1085, influenced by upwelling. For *neo*-hopenes, a direct biological origin was suggested (J.S. Sinninghe Damsté et al., unpubl. data), but hop-17(21)-ene is likely to be derived from diploptene by isomerization during early diagenesis.

Extended hopanoids identified in the sediments are 17β,21β(H)-*homo*-hopane, 17β,21β(H)-*homo*-hopan-31-ol, 17β,21β(H)-*dihomo*-hopan-32-ol (Structure XIII in Fig. F4), a C_{33} hopane-diol, and a C_{35} hopane-keto-diol. The latter two compounds were tentatively identified by their mass spectra (Fig. F6). They are present in all investigated samples but occur in highest amounts in samples from the Congo Fan (Sites 1076 and 1077). Common precursors of hopanoid compounds are bacteriohopanepolyols (Rohmer et al., 1989). Hopanoids are exclusively biosynthesized by prokaryotes as membrane rigidifiers and can be considered the bacterial counterparts of steroids in cell membranes of algae (Rohmer et al., 1989). Recently, it has been inferred that extended hopanoids in sediments are predominantly derived from cyanobacteria and much less from heterotrophic bacteria or bacterial reworking (Schoell et al., 1994; Summons et al., 1999). Sediments located under the Congo plume are therefore considered to receive a larger cyanobacterial contribution than the other sediments investigated.

F6. Mass spectrum of compounds from the TLC-6 fraction, p. 28.



Wax Esters

Wax esters identified in the TLC-1 fraction of Sample 175-1084A-12H-6, 140-143 cm, range from C_{32} to C_{40} and have exclusively saturated fatty acid and alcohol moieties. The fatty acid moieties range from C_{14} to C_{24} and the alcohol moieties from C_{16} to C_{24}. For both counterparts, the C_{16}, C_{18}, and C_{20} homologues are quantitatively the most important ones. Wax esters are minor components of the total extractable organic matter and they could only be detected in the TLC fraction. Besides their occurrence in leaf waxes of higher plants (Kolattukudy, 1976), wax esters were reported to occur in pelagic marine animals, especially copepods. Copepods contain relatively large amounts of wax esters as energy reserves (Sargent et al., 1976). The storage of wax esters in copepods is connected to intermittent food supply with periods of starvation. The occurrence of wax esters in sediments from Site 1084 thus could be potentially indicative of zooplankton lipids at upwelling-influenced sites.

Perylene

In the TLC-2 fraction of Sample 175-1084A-12H-6, 140–143 cm, perylene (Structure XIV in Fig. **F4**) was identified as a major compound. It is the only detected polycyclic aromatic hydrocarbon in all samples. It was earlier identified in Namibian shelf sediments by Wakeham et al. (1979). Perylene was reported to be most abundant in anoxic diatomaceous sediments (Louda and Baker, 1984). Although the actual precursor compound is still unknown, in situ diagenetic formation of perylene under anoxic conditions is commonly assumed (Silliman et al., 1999). Venkatesan's (1988) conclusion that diatoms are the most likely source of a precursor compound fits well with our finding of perylene in sediments below the Lüderitz upwelling cell. Besides suggesting an origin from diatom lipids, the presence of perylene is related to a large abundance of labile organic matter, leading to a strong oxygen consumption in the sediments.

Organic Sulfur Compounds

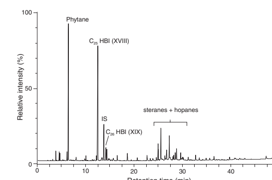
Two tricyclic triterpenoid thianes were detected in minor amounts in the apolar fractions of samples from Site 1084. By comparison with mass spectra reported by Werne et al. (2000), they were identified as monounsaturated malabaricane thianes (Structure XV in Fig. **F4**).

A sulfur compound present in trace amounts in sediments from Sites 1084 and 1082 was identified as a C_{20} isoprenoid thiophene, 3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene (Structure XVI in Fig. **F4**). Its occurrence in sediments from Walvis Bay was reported earlier (Brassell et al., 1986b; ten Haven et al., 1990). Sulfur incorporation into phytol-derived phytadienes leads to the formation of isoprenoid thiophenes (Brassell et al., 1986b). Source organisms of phytol are chlorophyll-producing photoautotrophic algae.

Several isomers of highly branched isoprenoid (HBI) thiolanes were detected in sediments from Site 1084 and, in much lower amounts, from Site 1082. They were identified as C_{25} monounsaturated and saturated HBI thiolanes (Structure XVII in Fig. **F4**) by comparison with published mass spectra (Kohnen et al., 1990). These compounds derive from the reaction of inorganic sulfur species with specific double bonds of the precursor HBI polyenes during early diagenesis (Kohnen et al.,

1990). Precursor compounds of the HBI thiolanes are HBI polyenes biosynthesized by specific diatom species like *Rhizosolenia setigera* and *Haslea* sp. (Volkman et al., 1994; Belt et al., 1996; Sinninghe Damsté et al., 1999). Desulfurization of the polar fraction of Sample 175-1084A-12H-6, 140–143 cm, released C_{25} (Structure XVIII in Fig. F4) and C_{26} HBI (Structure XIX in Fig. F4) compounds (Fig. F7) in quantities similar to those of the long-chain alkenones. The C_{26} HBI compound most probably originates from the same diatom species as the C_{25} HBI (Rospondek et al., 1997). The presence of these compounds in samples from Site 1084 therefore indicates an important contribution of diatom lipid material to sediments deposited in upwelling-influenced environments. Rapid sulfur incorporation into alkenes may account for the absence of unsulfurized HBI compounds in samples from Site 1084 (cf. Werne et al., 2000; Kohnen et al., 1990).

F7. Total ion chromatogram of the apolar fraction of the desulfurized and hydrogenated polar fraction, p. 29.



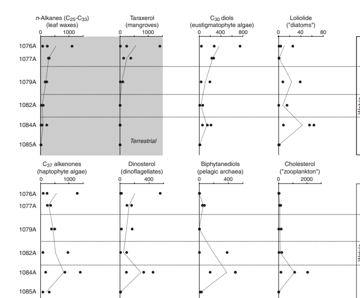
This rapid formation of organosulfur compounds is in line with the high rate of sulfate reduction in the uppermost meters of sediment at Sites 1082 and 1084 (Wefer, Berger, Richter, et al., 1998), suggesting a high abundance of labile organic matter and low-oxygen conditions at these locations. In other sediments, organic sulfur compounds were not detected. The formation of organic sulfur compounds at other locations could possibly be inhibited by a higher availability of reactive iron.

Site Summaries

The majority of biomarker lipids in sediment samples drilled during Leg 175 in the eastern South Atlantic are of marine, autochthonous origin. Terrigenous lipids, detected in minor but varying amounts, were transported into the marine environment via dust or fresh water. Their contribution to the sedimentary lipid material could be used as a measure of the relative importance of terrigenous vs. marine organic matter deposition in each setting. Because of the limited number of samples in this study and their different ages, paleoceanographic interpretations are restricted. The study is solely intended to provide an inventory and underline the potential of detailed biomarker analyses for paleoceanographic purposes.

Figure F8 shows the concentrations of selected biomarkers or compound classes to illustrate the lipid composition at each site, as summarized below.

F8. Concentrations of quantified biomarker lipids, p. 30.



Site 1076

Site 1076 is the shallow-water drill site in the lower Congo Basin. The sediments contain the highest amounts of terrigenous lipids of all investigated samples (Table T4; Fig. F8). The concentrations of *n*-alkanes, derived from leaf waxes of higher plants, and taraxerol, most probably derived from mangroves, show strong variations between the samples (Fig. F8). This suggests a dependence of the concentrations of terrigenous lipids on fluctuations in river discharge, similar to the late Quaternary (Jansen et al., 1984; van der Gaast and Jansen, 1984; Jansen, 1990; Schneider et al., 1997). Long-chain alkenone concentrations in samples from Site 1076 display a strong variability with elevated concentrations when sea-surface temperatures were low (Table T4). This is in agreement with the results from the late Quaternary of stronger coastal upwelling during cold times with low river discharge (Jansen and van Iperen, 1991). On average, samples from Site 1076 contain the highest concentrations of alkyl diols and intermediate amounts of dinosterol

and loliolide. These compounds also exhibit strong variability in concentrations, suggesting that the production of eustigmatophytes, dinoflagellates, and diatoms covaried with river discharge of nutrients or coastal upwelling. The presence of large amounts of eustigmatophyte-derived lipids may indicate a significant contribution by eustigmatophyte algae from brackish waters. Cholesterol is present in trace amounts and biphytanediols are absent. Zooplankton herbivory and pelagic archaea are therefore suggested to have been of minor importance.

Site 1077

Site 1077 is the intermediate-depth drill site on the Congo Fan. Samples from this location have the lowest organic carbon content of all investigated sediments. The content of terrigenous lipids, *n*-alkanes, and taraxerol is lower than in the sediments from Site 1076 but still elevated compared to the more southern sites (Table **T4**). On average, concentrations of alkenones, loliolide, alkyl diols, and dinosterol are lower than at Site 1076 (Table **T4**). Slightly higher concentrations were detected for biphytanediols and cholesterol (Table **T4**). This suggests that haptophyte algae, diatoms, eustigmatophytes, and dinoflagellates on average were less important as primary producers. In contrast, archaea generally contributed slightly higher amounts to the lipid material (Fig. **F8**). This change agrees, despite the limited sample numbers, with a zonation of plankton groups depending on the proximity to the river mouth (van Iperen et al., 1987; Ufkes et al., 1998). The influence of fluviatile nutrients (on diatoms) and river-induced upwelling (on haptophytes) thus would be much smaller at Site 1077 than at Site 1076.

Site 1079

Samples from Site 1079 on the Angola margin contain intermediate concentrations of alkenones, loliolide, dinosterol, cholesterol, and alkyl diols. Terrigenous lipids (e.g., *n*-alkanes and taraxerol) are present in low but significant amounts in both samples (Table **T4**). A direct supply of river-transported terrigenous lipid material seems unlikely because of the lack of rivers draining into this area. However, alongshore transport from the Kunene River might carry terrigenous lipids to this site. The composition of marine lipids, with alkenones, loliolide, and dinosterol as the major components, is, except for the high content of alkyl keto-ols, not significantly different from the lipid composition of sediments in the Congo area. The elevated sedimentary organic carbon contents of these samples therefore probably result from a similar plankton community, with haptophyte algae, diatoms, dinoflagellates, and unidentified, keto-ol-producing microalgae as main lipid producers. The supply of nutrients from subsurface waters, likely involving the Angola Dome nearby, may sustain high productivity.

Site 1082

Sediments at Site 1082 in the Walvis Basin were reported to receive abundant biological material from displaced upwelling filaments (Wefer, Berger, Richter, et al., 1998). The elevated organic carbon content of the studied samples (Table **T1**) may therefore reflect a strong phytoplankton signal. Most commonly, upwelling induces high diatom productivity. Only low amounts of loliolide are present in the sedi-

ments. However, HBI thiolanes clearly indicate a significant supply of diatom-derived lipid material. The average concentration of alkenones in the sediments is relatively high (Fig. F8). Biphytanediols are present in significantly elevated amounts, in contrast to the more northern sites. Other biomarkers only contribute small to minor quantities. Especially the terrigenous lipid contribution is very low: the concentrations of *n*-alkanes are low, and taraxerol is absent (Table T3). The *n*-alkanes at this location are most probably predominantly wind derived, whereas mangrove lipids are probably absent in the samples because of the lack of coastal mangrove vegetation in this area and because of the ABF in the north inhibiting southward transport.

Site 1084

Investigated sediments from Site 1084 off Lüderitz Bay contain the highest amount of organic carbon of all studied samples (up to 13%) (Table T1). Sediments from this site should contain the most pronounced coastal upwelling signal because of their close vicinity to the Lüderitz upwelling cell (Wefer, Berger, Richter, et al., 1998). This is well expressed in the lipid geochemistry of these samples. Sediment from Site 1084 contains the highest concentrations of biphytanediols, long-chain alkenones, loliolide, and cholesterol. Alkyl diols and dinosterol are present in elevated amounts (Table T4; Fig. F8). The presence of other plankton-derived compounds, like midchain hydroxy fatty acids, sterols, sterol ethers, hopanoids, isoprenoid thiophenes, and sulfurized HBIs, also indicates the importance of plankton biomass contribution. The investigated sediments from Site 1084 contain the highest amounts of phytoplankton, pelagic archaea, and zooplankton markers of all investigated samples. Land-derived lipids are present only in trace amounts. The *n*-alkanes exhibit only small concentrations. Taraxerol, like at Site 1082, is absent. Of all studied samples, the sediments from Site 1084 contain the most diverse upwelling-derived lipids. The organic geochemical phytoplankton signals are much more pronounced than at Site 1082.

Site 1085

Site 1085 is located in the southern Cape Basin, situated under a seasonal upwelling regime. Its sediments show less pronounced upwelling signals than those at Site 1084. The contribution of marine-derived compounds, like alkenones, loliolide, alkyl diols, and dinosterol, is on average smaller than at Site 1084 and in the same range as at Site 1082. The presence of elevated amounts of sterols and sterol ethers, however, suggests phytoplankton production with subsequent zooplankton grazing. The sediments from Site 1085 contain only trace quantities of *n*-alkanes, indicating negligible transfer of material from the nearby Orange River. Taraxerol could not be detected in this setting, which agrees with the present absence of mangrove vegetation in southern Africa. The lipid compositions of sediments from Site 1085 resemble those of sediments from Site 1082. Both settings receive their biological signal from seasonal upwelling or mixing of upwelled, nutrient-rich waters with low-productivity surface waters, in contrast to the persistent year-round upwelling at Site 1084.

CONCLUSIONS

The lipid biomarker content in selected sediments from several sites along the southwestern African margin reflects different marine environments. The majority of the extracted lipids in all samples is of marine origin, with varying contributions of terrigenous lipids. It should be noted that the limited sample number restricts detailed paleoceanographic interpretations and that this study is solely intended to be an inventory. Conclusions are summarized as follows:

1. In general, two main areas can be distinguished, separated by the ABF. Elevated concentrations of terrigenous lipids and lipids from eustigmatophyte algae were only observed north of the ABF, whereas lipids from archaea and zooplankton are only present in significantly elevated amounts south of it.
2. The sediments below the Congo River freshwater plume received a large contribution of lipids from terrestrial higher plants and mangroves. The contribution of terrigenous lipids is suggested to decrease with increasing distance from the river mouth. At the shallower site, marine lipids were mainly derived from haptophyte algae, diatoms, dinoflagellates, and eustigmatophyte algae. Lipids of these algae were less abundant in samples from the deeper site, whereas the contribution from pelagic archaea and zooplankton were slightly higher. The changes in lipid composition with distance from the river mouth suggest variation of plankton communities with reduction of river influence.
3. The investigated sediments on the Angola margin received a small amount of terrigenous lipids. A highly productive plankton community of haptophyte algae, diatoms, dinoflagellates, and unidentified, keto-ol-producing microalgae probably caused the elevated sedimentary organic carbon contents. Supply of nutrients from the nearby Angola Dome may sustain high productivity.
4. Walvis Basin sediments received an upwelling signal transported by the Benguela Current. Major contributors of marine lipids were haptophyte algae and pelagic archaea. Diatom lipids were detectable in low concentrations as sulfurized compounds.
5. Persistent coastal upwelling off Lüderitz Bay is well reflected in the sedimentary lipids. The investigated samples contain the highest lipid contributions of pelagic archaea, haptophyte algae, dinoflagellates, diatoms, and zooplankton. Anoxic sedimentary conditions were most probably caused by a large supply of labile organic matter.
6. In the southern Cape Basin, sediments probably received plankton material from seasonal upwelling, indicated by their content of sterols and sterol ethers. Their marine lipid content is comparable to the lipids of the sediments in the Walvis Basin. The nearby Orange River did not cause elevated concentrations of terrigenous lipids in the investigated samples.

ACKNOWLEDGMENTS

The authors thank M. Baas and Dr. H. Kinkel for technical assistance. Financial support by the Netherlands Organization of Scientific Research (NWO/ALW) is gratefully acknowledged. Helpful comments by

Prof. J. Rullkötter and an anonymous reviewer greatly improved the manuscript. ODP is thanked for providing samples. This is publication No. 3470 of the Netherlands Institute for Sea Research (NIOZ).

REFERENCES

Beaton, J.M., Spring, F.S., Stevenson, R., and Stewart, J.L., 1955. Triterpenoids, Part XXXVII: The constitution of taraxerol. *J. Chem. Soc.,* 2131–2137.

Belt, S.T., Cooke, A.T., Robert, J.-M., and Rowland, D., 1996. Structural characterisation of widespread polyunsaturated isoprenoid biomarkers: a C_{25} triene, tetraene and panaene from the diatom *Haslea ostrearia* Simonsen. *Tetrahedron Lett.,* 27:4755–4758.

Berger, W.H., 1989. Global maps of ocean productivity. *In* Berger, W.H., Smetacek, V.S., and Wefer, G. (Eds.), *Productivity of the Oceans: Present and Past:* New York (Wiley), 429–455.

Berger, W.H., and Wefer, G., 1996. Central themes of South Atlantic circulation. *In* Wefer, G., Berger, W.H., Siedler, G., Webb, D.J. (Eds.) *The South Atlantic: Present and Past Circulation:* Berlin (Springer-Verlag), 1–11.

Boon, J.J., 1978. Molecular biogeochemistry of lipids in four natural environments [Ph.D. thesis]. Delft Univ.

Boon, J.J., and de Leeuw, J.W., 1979a. The analysis of wax esters, very long midchain ketones and sterol ethers isolated from Walvis Bay diatomaceous ooze. *Mar. Chem.*, 7:117–132.

Boon, J.J., Rijpstra, W.I.C., de Lange, F., de Leeuw, J.W., Yoshioka, M., and Shimizu, Y., 1979b. Black Sea sterol: a molecular fossil for dinoflagellate blooms. *Nature,* 277:125–127.

Brassell, S.C., 1993. Applications of biomarkers for delineating marine paleoclimatic fluctuations during the Pleistocene. *In* Engel, M.H., and Macko, S.A. (Eds.), *Organic Geochemistry: Principles and Applications:* New York (Plenum), 699–738.

Brassell, S.C., and Eglinton, G., 1983. Steroids and triterpenoids in deep-sea sediments as environmental and diagenetic indicators. *In* Bjorøy, M., et al. (Eds.), *Advances in Organic Geochemistry 1981:* Chichester (Wiley), 684–697.

Brassell, S.C., Eglinton, G., Marlowe, I.T., Pflaumann, U., and Sarnthein, M., 1986a. Molecular stratigraphy: a new tool for climatic assessment. *Nature,* 320:129–133.

Brassell, S.C., Lewis C.A., de Leeuw, J.W., de Lange, F., and Sinninghe Damsté, J.S., 1986b. Isoprenoid thiophenes: novel products of sediment diagenesis? *Nature,* 320:160–162.

Brown, P.C., Painting, S.J., and Cochrane, K.L., 1991. Estimates of phytoplankton and bacterial biomass and production in the northern and southern Benguela ecosystem. *S. Afr. J. Mar. Sci.,* 11:537–564.

Conte, M.H., Eglinton, G., and Madureira, L.A.S., 1995. Origin and fate of organic biomarker compounds in the water column and sediments of the eastern North Atlantic. *Philos. Trans. R. Soc. London B,* 348:169–178.

Cranwell, P.A., 1973. Chain-length distribution of *n*-alkanes from lake sediments in relation to post-glacial environmental change. *Freshwater Biol.,* 3:259–265.

de Leeuw, J.W., and Baas, M., 1986. Early-stage diagenesis of steroids. *In* Johns, R.B. (Ed.), *Biological Markers in the Sedimentary Record:* Amsterdam (Elsevier), 101–123.

de Leeuw, J.W., Rijpstra, W.I.C., and Schenck, P.A., 1981. The occurrence and identification of C_{30}, C_{31} and C_{32} alkan-1,15-diols and alkan-15-one-1-ols in Unit I and Unit II Black Sea sediments. *Geochim. Cosmochim. Acta,* 45:2281–2285.

de Leeuw, J.W., van de Meer, F.W., Rijpstra, W.I.C., and Schenck, P.A., 1980. On the occurrence and structural identification of long chain ketones and hydrocarbons in recent and subrecent sediments. *In* Douglas, A.G., and Maxwell, J.R., *Advances in Organic Geochemistry, 1979:* Oxford (Pergamon Press), 219–227.

Eglinton, G., and Hamilton, R.J., 1967. Leaf epicuticular waxes. *Science,* 156:1322–1335.

Frewin, N.L., Killops, S.D., van Bergen, P.F., de Leeuw, J.W., and Collinson, M.E., 1993. Preservation potential of biomacromolecules of higher plant cuticules in Florida Bay. *In* Øygard, K. (Ed.), *Organic Geochemistry: Poster Sessions from the 16*th

International Meeting on Organic Geochemistry, Stavanger: Oslo (Falch Hurtigtrykk), 566–569.

Gagosian, R.B., and Farrington, J.W., 1978. Sterenes in surface sediments from the southwest African shelf and slope. *Geochim. Cosmochim. Acta,* 42:1091–1101.

Gagosian, R.B., Peltzer, E.T., and Merrill, J.T., 1987. Long-range transport of terrestrially derived lipids in aerosols from the south Pacific. *Nature,* 325:800–803.

Gagosian, R.B., Peltzer, E.T., and Zafiriou, O.C., 1981. Atmospheric transport of continentally derived lipids to the tropical North Pacific. *Nature,* 291:312–314.

Gelin, F., Volkman, J.K., de Leeuw, J.W., and Sinninghe Damsté, J.S., 1997. Midchain hydroxy long-chain fatty acids in microalgae from the genus *Nannochloropsis. Phytochemistry,* 45:641–646.

Ghosh, A., Misra, S., Dutta, A.K., and Choudhury, A., 1985. Pentacyclic triterpenoids and sterols from seven species of mangrove. *Phytochemistry,* 24:1725–1727.

Goad, L.J., and Withers, N., 1982. Identification of 27-nor-(24R)-24-methylcholesta-5,22-dien-3β-ol and brassicasterol as the major sterols of the marine dinoflagellate *Gymnodinium simplex. Lipids,* 17:853–858.

Hinrichs, K.-U., Schneider, R.R., Müller, P.J., and Rullkötter, J., 1999. A biomarker perspective on paleoproductivity variations in two Late Quaternary sediment sections from the Southeast Atlantic Ocean. *Org. Geochem.,* 30:341–366.

Hoefs, M.J.L., Schouten, S., de Leeuw, J.W., King, L.L., Wakeham, S.G., and Sinninghe Damsté, J.S., 1997. Ether lipids of planktonic archaea in the marine water column. *Appl. Environ. Microbiol.,* 63:3090–3095.

Hopmans, E.C., Schouten, S., Pancost, R.D., van der Meer, M.T.J., and Sinninghe Damsté, J.S., 2000. Analysis of intact tetraether lipids in archaeal cell material and sediments by High Performance Liquid Chromatography/Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Rapid Commun. Mass Spectrom.,* 14:585–589.

Huang, W.Y., and Meinschein, W.G., 1976. Sterols as source indicators of organic materials in sediments. *Geochim. Cosmochim. Acta,* 40:323–330.

Jansen, J.H.F., 1990. Glacial-interglacial oceanography of the southeastern Atlantic Ocean and the paleoclimate of west central Africa. *In* Lanfranchi, R., and Schwartz, D. (Eds.), *Paysages Quaternaires de l'Afrique Centrale Atlantique:* Paris (Editions ORSTOM), 110–123.

Jansen, J.H.F., and Van Iperen, J.M., 1991. A 220,000-year climatic record for the east equatorial Atlantic Ocean and equatorial Africa: evidence from diatoms and opal phytoliths in the Zaire (Congo) deep-sea fan. *Paleoceanography,* 6:573–591.

Jansen, J.H.F., van Weering, T.C.E., Gieles, R., and van Iperen, J., 1984. Middle and late Quaternary oceanography and climatology of the Zaire-Congo fan and the adjacent eastern Angola Basin. *Neth. J. Sea Res.,* 17:201–249.

Killops, S.D., and Frewin, N.L., 1994. Triterpenoid diagenesis and cuticular preservation. *Org. Geochem.,* 21:1193–1209.

Klok, J., Baas, M., Cox, H.C., de Leeuw, J.W., and Schenck, P.A., 1984. Loliolides and dihydroactinidiolide in a recent marine sediment probably indicate a major transformation pathway of carotenoids. *Tetrahedron Lett.,* 25:5577–5580.

Kohnen, M.E.L., Sinninghe Damsté, J.S., Kock-van Dalen, A.C., ten Haven, H.L., Rullkötter, J., and de Leeuw, J.W., 1990. Origin and diagenetic transformations of C_{25} and C_{30} highly branched isoprenoid sulphur compounds: further evidence for the transformation of organically bound sulphur during early diagenesis. *Geochim. Cosmochim. Acta,* 54:3053–3063.

Kolattukudy, P.E., 1976. *Chemistry and Biochemistry of Natural Waxes:* New York (Elsevier).

Louda, J.W., and Baker, E.W., 1984. Perylene occurrence and possible sources in deep-ocean sediments. *Geochim. Cosmochim. Acta,* 48:1043–1058.

Lutjeharms, J.R.E., and Stockton, P.L., 1987. Kinematics of the upwelling front off southern Africa. *S. Afr. J. Mar. Sci.,* 5:35–49.

Marlowe, I.T., Brassell, S.C., Eglinton, G., and Green, J.C., 1984. Long-chain unsaturated ketones and esters in living algae and marine sediments. *In* Schenck, P.A., de Leeuw, J.W., and Lijmbach, G.W.M. (Eds.), *Advances in Organic Geochemistry 1983.* Org. Geochem., 6:135–141.

Meeuwis, J.M., and Lutjeharms, J.R.E., 1990. Surface thermal characteristics of the Angola-Benguela Front. *S. Afr. J. Mar. Sci.,* 9:261–279.

Moguedet, G., 1980. Le milieu de mangrove au Congo. *In* Blasco, F., Caratini, C., Fredou, A., Giresse, P., Moguedet, G., Tissot, C., and Weiss, H. (Eds.), *Mangroves d'Afrique et Asie.*Cent. Nat. Rech. Sci., 5–19.

Müller, P.J., Cepek, M., Ruhland, G., Schneider, R.R., 1997. Alkenone and coccolithophorid species changes in late Quaternary sediments from the Walvis Ridge: implications for the alkenone paleotemperature method. *Palaeogeogr., Palaeoclimatol., Palaeoecol.,* 135:71–96.

Müller, P.J., Kirst, G., Ruhland, G., von Storch, I., and Rosell-Melé, A., 1998. Calibration of the alkenone paleotemperature index (U^{k}_{37}′) based on core-tops from the eastern South Atlantic and the global ocean (60°N–60°S). *Geochim. Cosmochim. Acta,* 62:1757–1772.

Nichols, P.D., Jones, G.J., and de Leeuw, J.W., 1984. The fatty acid and sterol composition of two marine dinoflagellates. *Phytochemistry,* 23:1043–1047.

Poynter, J.G., Farrimond, P., Robinson, N., and Eglinton, G., 1989. Aeolian derived higher plant lipids in the marine sedimentary record: links with palaeoclimate. *In* Leinen, M., and Sarnthein, M. (Eds.), *Palaeoclimatology and Palaeometeorology: Modern and Past Patterns of Global Atmospheric Transport:* Dordrecht (Kluwer Academic Press), 435–462.

Prahl, F.G., Dymond, J., and Sparrow, M., 2000. Annual biomarker record for export production in the central Arabian Sea. *Deep-sea Res.,* 47:1581–1604.

Repeta, D.J., 1989. Carotenoid diagenesis in recent marine sediments. II. Degradation of fucoxanthin to loliolide. *Geochim. Cosmochim. Acta,* 53:699–707.

Robinson, N., Eglinton, G., Brassell, S.C., and Cranwell, P.A., 1984. Dinoflagellate origin for sedimentary 4α-methylsteroids and 5α(H)-stanols. *Nature,* 308:439–441.

Rohmer, M., Boivier-Nave, P., and Ourisson, G., 1989. Distribution of hopanoid triterpenes in prokaryotes. *J. Genetic Microbiol.,* 130:1137–1150.

Rospondek, M.J., Köster, J., and Sinninghe Damsté, J.S., 1997. Novel C_{26} highly branched isoprenoid thiophenes and alkane from the Menilite Formation, Outer Carpathians, SE Poland. *Org. Geochem.,* 26:295–304.

Sargent, J.R., Lee, R.F., and Nevenzel, J.C., 1976. Marine waxes. *In* Kolattukudy, P.E. (Ed.), *Chemistry and Biochemistry of Natural Waxes:* Amsterdam (Elsevier), 49–92.

Schneider, R.R., Price, B., Müller, P.J., Kroon, D., and Alexander, I., 1997. Monsoon-related variations in Zaire (Congo) sediment load and influence of fluvial silicate supply on marine productivity in the east equatorial Atlantic during the last 200,000 years. *Paleoceanography,* 12:463–481.

Schoell, M., Schouten, S., Sinninghe Damsté, J.S., de Leeuw, J.W., and Summons, R.E., 1994. A molecular organic carbon isotope record of Miocene climate changes. *Science,* 263:1122–1125.

Schouten, S., Hoefs, M.J.L., Koopmans, M.P., Bosch, H.-J., and Sinninghe Damsté, J.S., 1998. Structural characterization, occurrence and fate of archaeal ether-bound acyclic and cyclic biphytanes and corresponding diols in sediments. *Org. Geochem.,* 29:1305–1319.

Schouten, S., Hoefs, M.J.L., and Sinninghe Damsté, J.S., 2000a. A molecular and stable carbon isotopic study of lipids in late Quaternary sediments from the Arabian Sea. *Org. Geochem.,* 31:509–521.

Schouten, S., Hopmans, E.C., Pancost, R.D., and Sinninghe Damsté, J.S., 2000b. Widespread occurrence of structurally diverse tetraether membrane lipids: Evidence for the ubiquitous presence of low-temperature relatives of hyperthermophiles. *PNAS,* 97:14421–14426.

Schubert, C.J., Villanueva, J., Calvert, S.E., Cowie, G.L., von Rad, U., Schulz, H., Berner, U., and Erlenkeuser, H., 1998. Stable phytoplankton community structure in the Arabian Sea over the past 200,000 years. *Nature,* 394:563–566.

Shannon, L.V., 1985. The Benguela ecosystem, Part I: Evolution of the Benguela, physical features and processes. *Annu. Rev. Oceanogr. Mar. Biol.,* 23:105–182.

Silliman, J.E., Meyers, P.A., and Eadie, B.J., 1999. Perylene: an indicator of alteration processes or precursor materials? *Org. Geochem.,* 29:1737–1744.

Simoneit, B.R.T., Chester, R., and Eglinton, G., 1977. Biogenic lipids in particulates from the lower atmosphere over the eastern Atlantic. *Nature,* 267:682–685.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., de Leeuw, J.W., and Schenck, P.A., 1988. Origin of organic sulphur compounds and sulphur containing high molecular weight substances in sediments and immature oils. *In* Matavelli, L., and Novelli, L. (Eds.), *Advances in Organic Geochemistry 1987*. Org. Geochem., 13:593–606.

Sinninghe Damsté, J.S., Rijpstra, W.I.C., Schouten, S., Peletier, H., van der Maarel, M.J.E.C., and Gieskes, W.W.C., 1999. A C_{25} highly branched isoprenoid alkene and C_{25} and C_{27} *n*-polyenes in the marine diatom Rhizosolenia setigera. *Org. Geochem.,* 30:95–100.

Skipski, V.P., Smolowne, A.F., Sullivan, R.C., and Barclay, M., 1965. Separation of lipid classes by thin-layer chromatography. *Biochim. Biophys. Acta,* 106:386–396.

Summons, R.E., Jahnke, L.L., Hope, J.M., and Logan, G.A., 1999. 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. *Nature,* 400:554–557.

Talbot, H.M., Head, R.N., Harris, R.P., and Maxwell, J.R., 1999. Steryl esters of pyrophaeophobide b: a sedimentary sink for chlorophyll b. *Org. Geochem.,* 30:1403–1410.

ten Haven, H.L., Baas, M., de Leeuw, J.W., and Schenck, P.A., 1987. Late Quaternary Mediterranean sapropels, I. On the origin of organic matter in sapropel S_7. *Mar. Geol.,* 75:137–156.

ten Haven, H.L., and Rullkötter, J., 1991. Preliminary lipid analyses of sediments recovered during Leg 117. *In* Prell, W.L., Niitsuma, N., et al., *Proc. ODP, Sci. Results,* 117: College Station, TX (Ocean Drilling Program), 561–569.

ten Haven, H.L., Rullkötter, J., Sinninghe Damsté, J.S., and de Leeuw, J.W., 1990. Distribution of organic sulfur compounds in Mesozoic and Cenozoic sediments from the Atlantic and Pacific Oceans and the Gulf of California. *In* Orr, W.L., and White, C.M. (Eds.), *Geochemistry of Sulfur in Fossil Fuels*. ACS Symp. Ser., 613–632.

Teshima, S.I., Kanazawa, A., and Tago, A., 1980. Sterols of the dinoflagellate Noctiluca milialis. *Mem. Fac. Fisher. Kagoshima Univ.,* 29:319–326.

Ufkes, E., Jansen, J.H.F., and Brummer, G.-J.A., 1998. Living planktonic foraminifera in the eastern South Atlantic during spring: indicators of water masses, upwelling and the Congo (Zaire) River Plume. *Mar. Micropaleontol.,* 33:27–53.

van der Gaast, S.J., and Jansen, J.H.F., 1984. Mineralogy, opal, and manganese of Middle and Late Quaternary sediments of the Zaire (Congo) deep-sea fan: origin and climatic variation. *Neth. J. Sea Res.,* 17:313–341.

van Iperen, J.M., van Weering, T.C.E., Jansen, J.H.F., and van Bennekom, A.J., 1987. Diatoms in surface sediments of the Zaire deep-sea fan (SE Atlantic Ocean) and their relation to overlying water masses. *Neth. J. Sea Res.,* 21:203–217.

Venkatesan, M.I., 1988. Occurrence and possible sources of perylene in marine sediments: a review. *Mar. Chem.,* 25:1–27.

Versteegh, G.J.M., Bosch, H.-J., and de Leeuw, J.W., 1997. Potential paleoenvironmental information of C_{24} to C_{36} midchain diols, keto-ols and mid-chain hydroxy fatty acids: a critical review. *Org. Geochem.,* 27:113.

Versteegh, G.J.M., Jansen, J.H.F., de Leeuw, J.W., and Schneider, R.R., 2000. Mid-chain diols and keto-ols in SE Atlantic sediments: a new tool for tracing past sea surface water masses? *Geochim. Cosmochim. Acta,* 64:1879–1892.

Villanueva, J., Grimalt, J.O., Labeyrie, L., Cortijo, E., Vidal, L., and Turon, J.-L., 1998. Precessional forcing of productivity in the North Atlantic Ocean. *Paleoceanography,* 13:561–571.

Volkman, J.K., 1986. A review of sterol markers for marine and terrigenous organic matter. *Org. Geochem.,* 9:83–99.

Volkman, J.K., Barrett, S.M., and Blackburn, S.I., 1999. Eustigmatophyte microalgae are potential sources of C_{29} sterols, C_{22}–C_{28} *n*-alcohols and C_{28}–C_{32} *n*-alkyl diols in freshwater environments. *Org. Geochem.,* 30:307–318.

Volkman, J.K., Barrett, S.M., Blackburn, S.I., Mansour, M.P., Sikes, E.L., and Gelin F., 1998. Microalgal biomarkers: a review of recent research developments. *Org. Geochem.,* 29:1163–1179.

Volkman, J.K., Barrett, S.M., Blackburn, S.I., and Sikes, E.L., 1995. Alkenones in *Gephyrocapsa oceanica:* implications for studies of paleoclimate. *Geochim. Cosmochim. Acta,* 59:513–520.

Volkman, J.K., Barrett, S.M., and Dunstan, G.A., 1994. C_{25} and C_{30} highly branched isoprenoids in laboratory cultures of two marine diatoms. *Org. Geochem.,* 21:407–414.

Volkman, J.K., Barrett, S.M., Dunstan, G.A., and Jeffrey, S.W., 1992. C_{30}–C_{32} alkyl diols and unsaturated alcohols in microalgae of the class Eustigmatophyceae. *Org. Geochem.,* 18:131–138.

————, 1993. Geochemical significance of the occurrence of dinosterol and other 4-methyl sterols in a marine diatom. *Org. Geochem.,* 20:7–15.

Volkman, J.K., Eglinton, G., Corner, E.D.S., and Forsberg, T.E.V., 1980. Long-chain alkenes and alkenones in the marine coccolithophorid *Emiliania huxleyi. Phytochemistry,* 19:2619–2622.

Volkman, J.K., Farrington, J.W., and Gagosian, R.B., 1987. Marine and terrigenous lipids in coastal sediments from the Peru upwelling region at 15°S: sterols and triterpene alcohols. *Org. Geochem.,* 11:463–477.

Wakeham, S.G., Schaffner, C., Giger, W., Boon, J.J., and de Leeuw, J.W., 1979. Perylene in sediments from the Namibian Shelf. *Geochim. Cosmochim. Acta,* 43:1141–1144.

Wefer, G., Berger, W.H., and Richter, C., et al., 1998. *Proc. ODP, Init. Repts.,* 175 [CD-ROM]. Available from: Ocean Drilling Program, Texas A&M University, College Station, TX 77845-9547, U.S.A.

Werne, J.P., Hollander, D.J., Behrens, A., Schaeffer, P., Albrecht, P., and Sinninghe Damsté, J.S., 2000. Timing of early diagenetic sulfurization of organic matter: a precursor-product relationship in Holocene sediments of the anoxic Cariaco Basin, Venezuela. *Geochim. Cosmochim. Acta,* 64:1741–1751.

Yamamoto, M., Ficken, K., Baas, M., Bosch, H.-J., and de Leeuw, J.W., 1996. Molecular paleontology of the earliest Danian at Geulhemmerberg (the Netherlands). *Geol. Mijnbouw,* 75:255–267.

Figure F1. Site locations and generalized surface hydrography (after Wefer, Berger, Richter, et al., 1998). SECC = South Equatorial Counter Current, AC = Angola Current, ABF = Angola Benguela Front, BCC = Benguela Coastal Current, BOC = Benguela Oceanic Current.

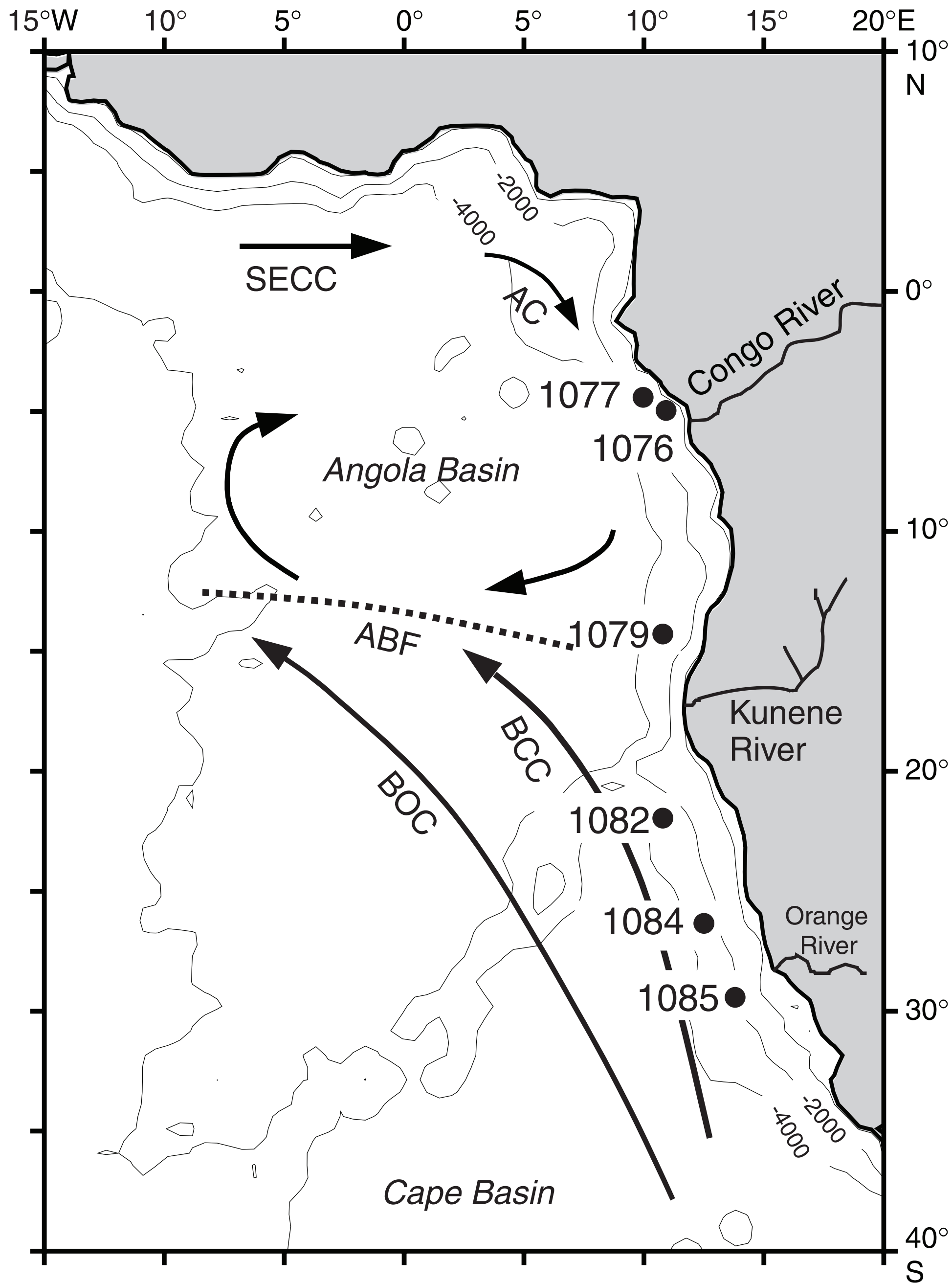


Figure F2. Total ion current (TIC) chromatogram of the total lipid fraction of (**A**) Sample 175-1077A-9H-2, 75–77 cm, and (**B**) Sample 175-1084A-12H-6, 140–143 cm. Numbers indicate compounds listed in Table T2, p. 32. Letters indicate sterols listed in Table T3, p. 33. Triangles = fatty acids, circles = *n*-alkanes, squares = *n*-alcohols. IS = internal standard. * = contamination.

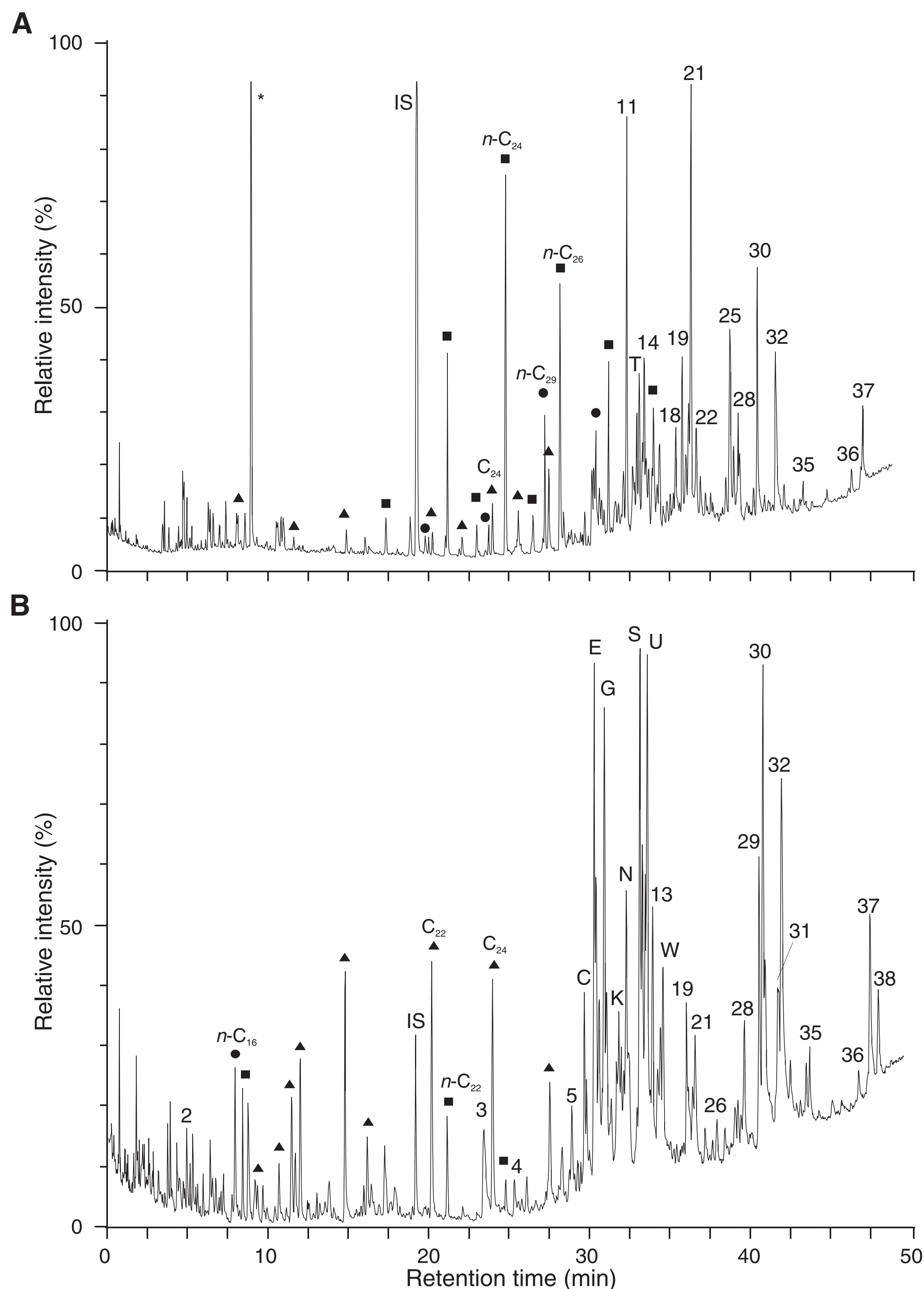


Figure F3. TIC chromatogram of the apolar fraction of Sample 175-1076A-15-2, 75–77 cm. Numbers refer to compounds listed in Table T2, p. 32. Circles = *n*-alkanes. IS = internal standard.

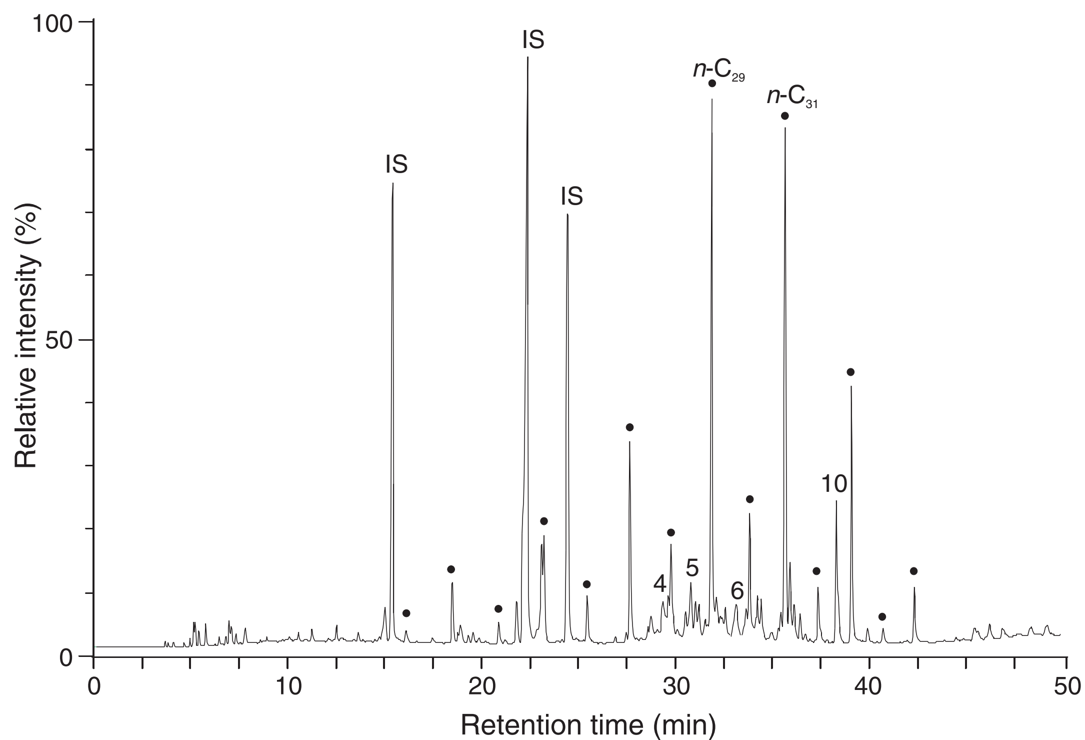


Figure F4. Compound structures of identified biomarker lipids.

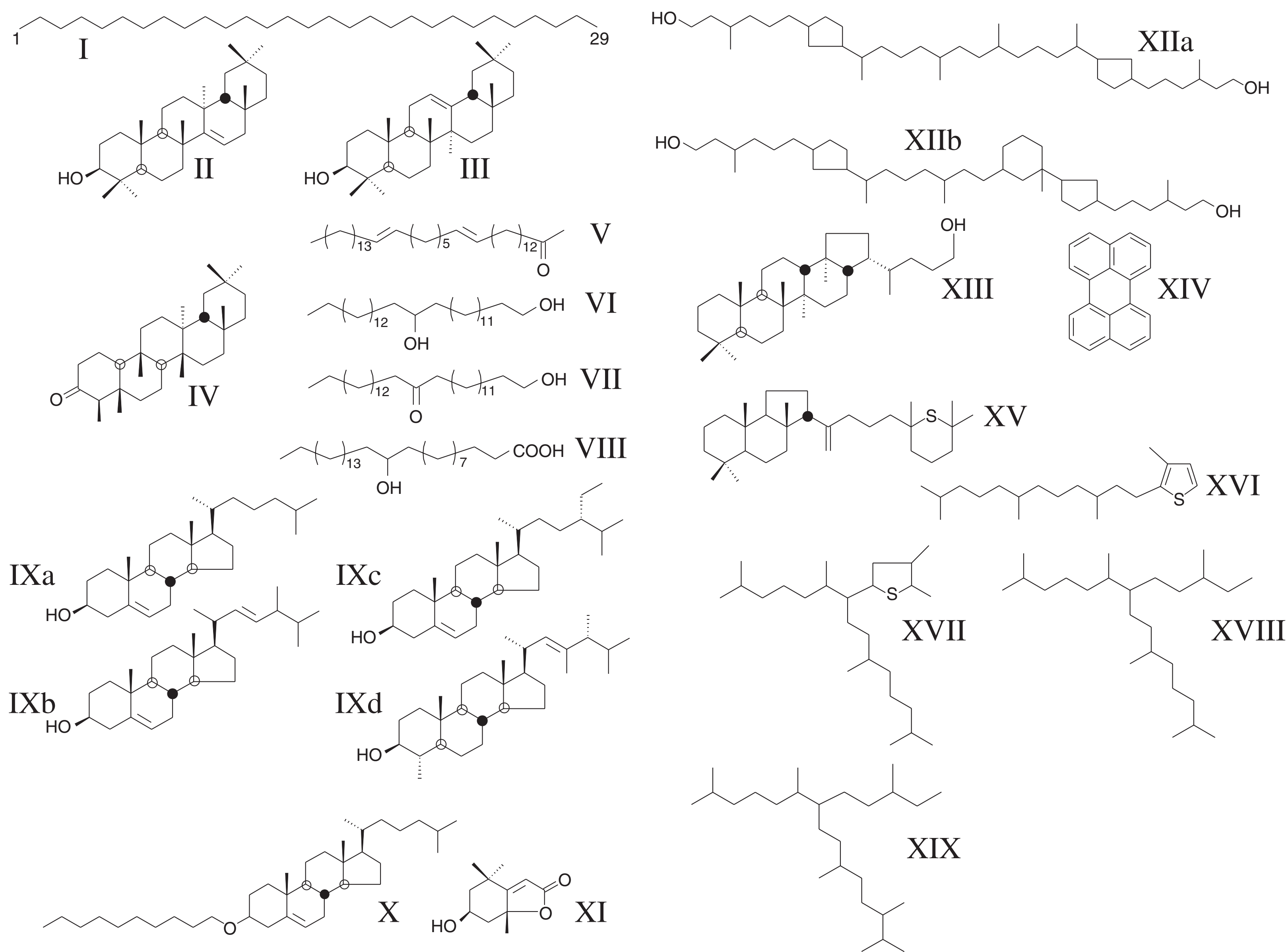


Figure F5. Partial TIC chromatogram of the TLC-5 fraction of Sample 175-1084A-12-6, 140–143 cm. Letters refer to steroids listed in Table T3, p. 33.

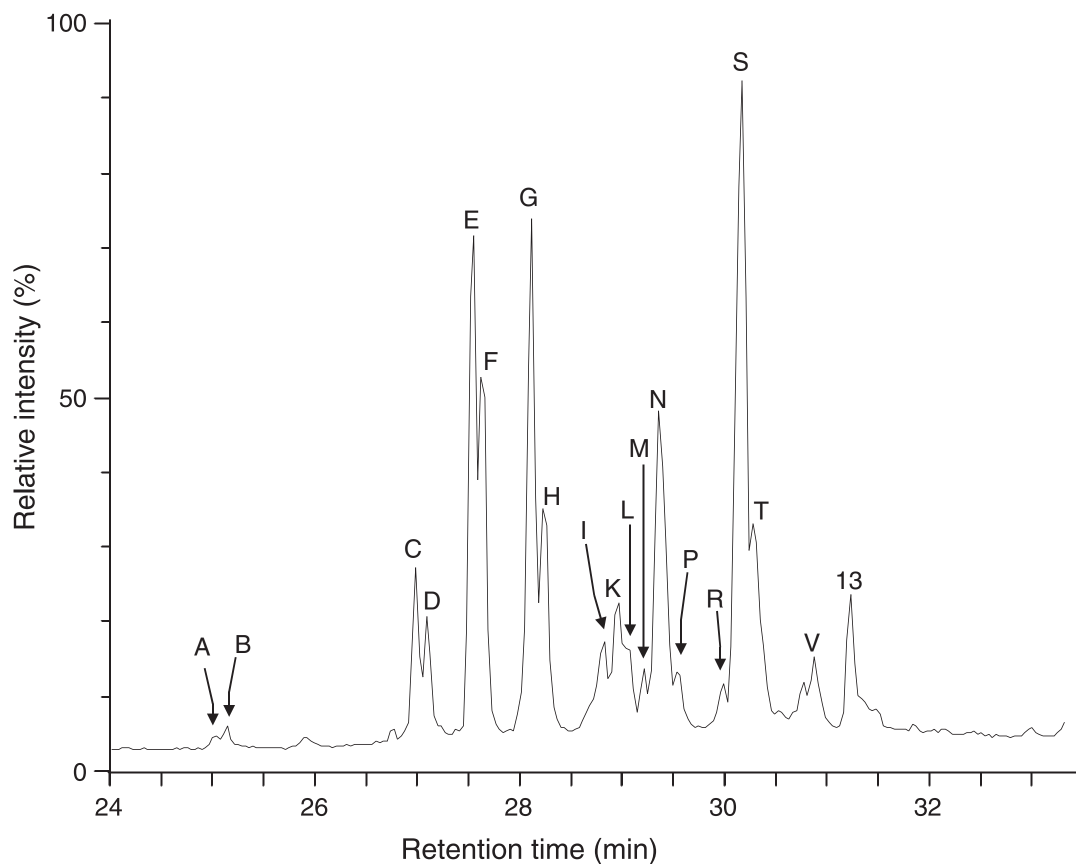


Figure F6. A. Mass spectrum of compound 34, tentatively identified as *trihomo*-hopane-32,33-diol (as TMS ether). **B.** Mass spectrum of compound 38, tentatively identified as *pentakishomo*-hopane-keto-diol (as TMS ether). Both compounds are present in the TLC-6 fraction of Sample 175-1084A-12-6, 140–143 cm.

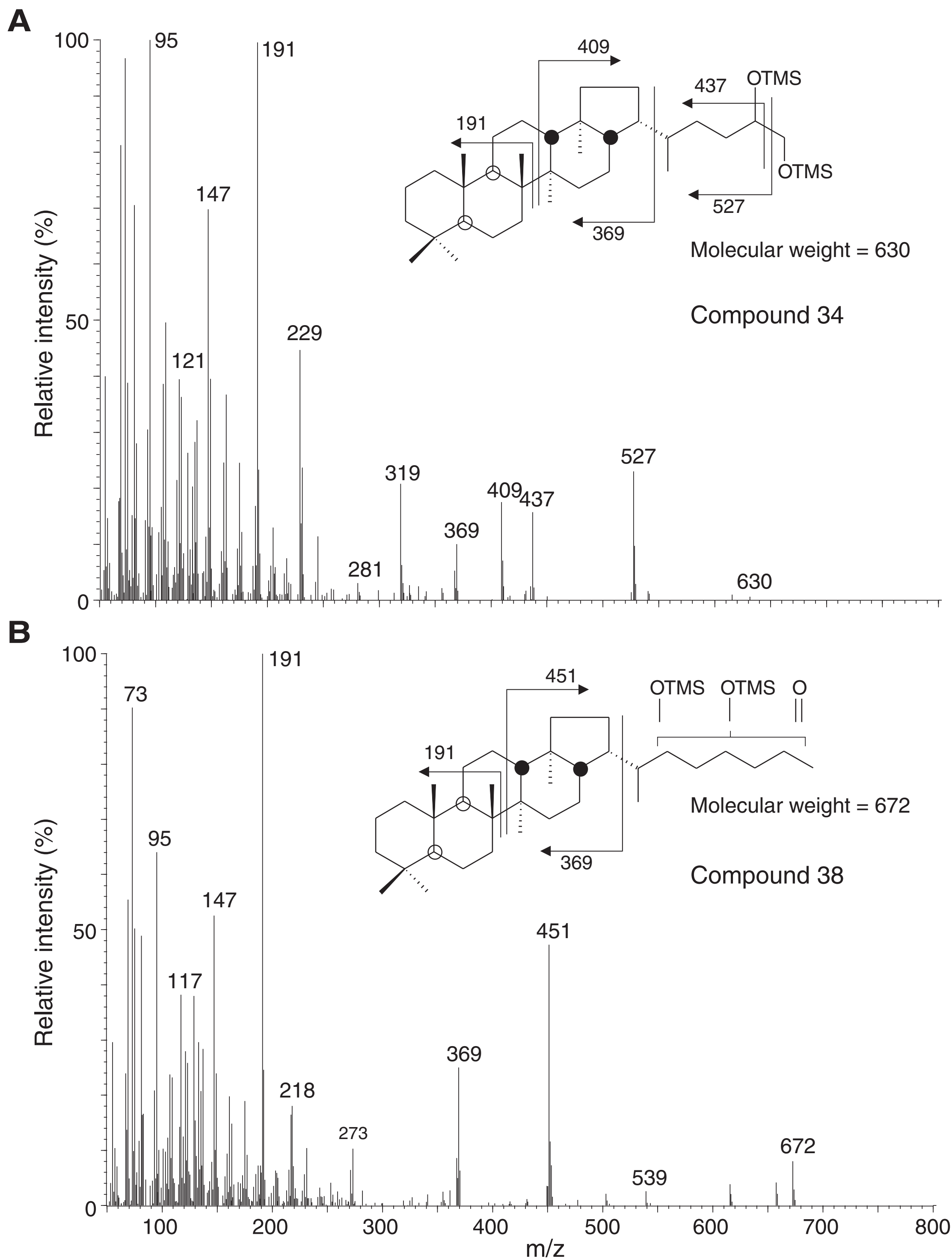


Figure F7. TIC chromatogram of the apolar fraction of the desulfurized and hydrogenated polar fraction of Sample 175-1084A-12-6, 140–143 cm. IS = internal standard.

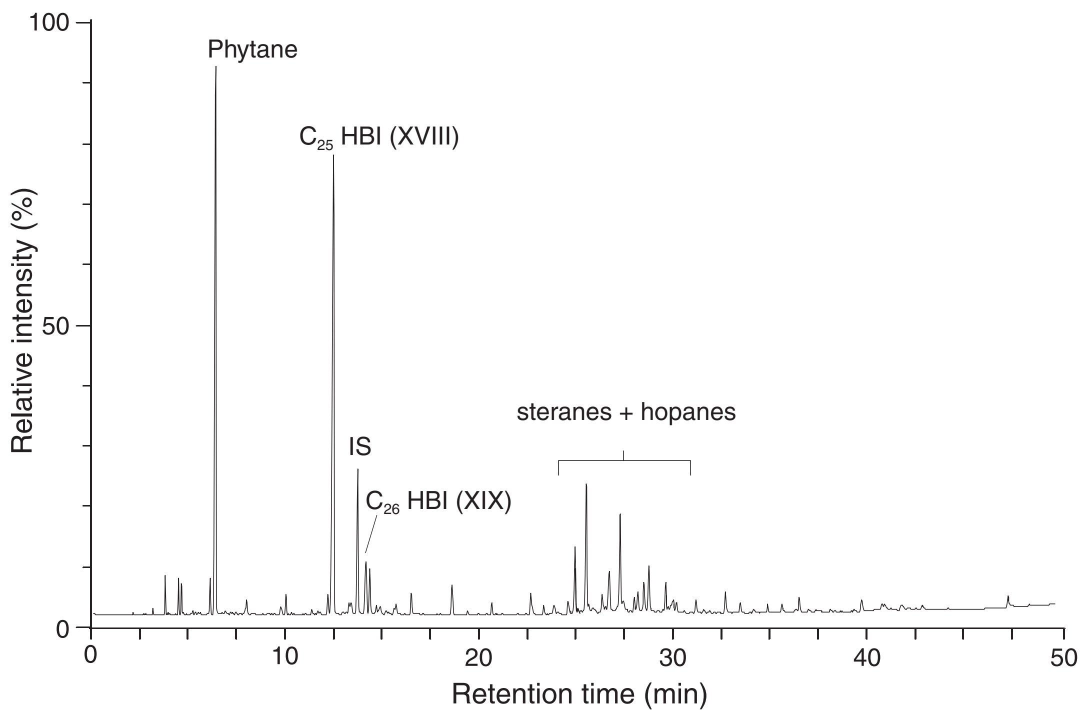


Figure F8. Concentrations of quantified biomarker lipids (in micrograms per gram of TOC). Averages of concentrations of each site are connected by a stippled line.

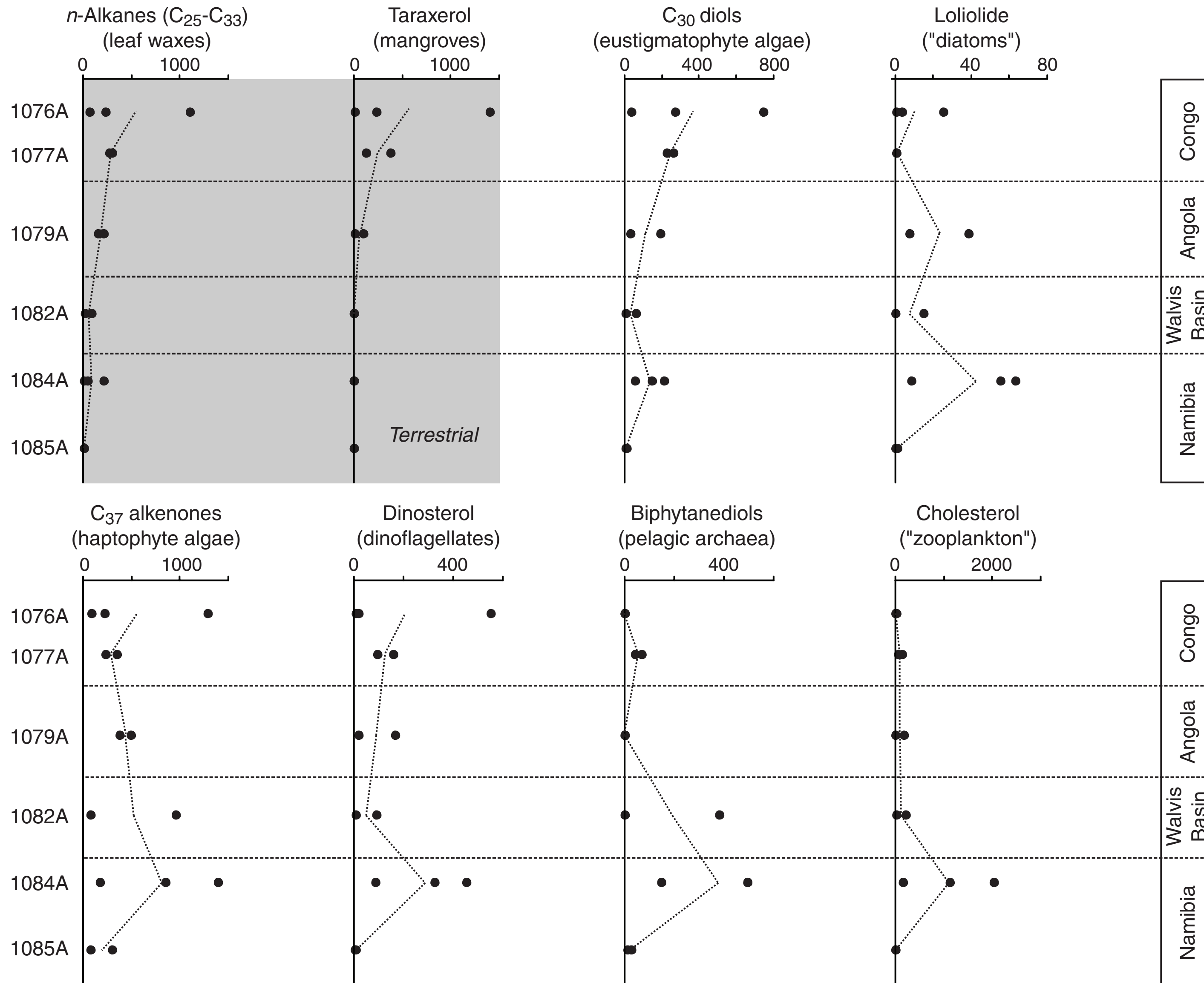


Table T1. Summary of samples analyzed.

Core, section, interval (cm)	Location	Water depth (m)	Depth (mcd)	TOC (wt%)	Age (Ma)
175-1076A-	11°6.1′E, 5°4.1′S	1402			
4H-2, 75-77			30.51	3.06	0.15
7H-2, 75-77			61.16	1.74	0.25
15H-2, 75-77			142.08	1.90	1.0
175-1077A-	10°26.2′E, 5°10.8′S	2394			
9H-2, 75-77			79.13	1.83	0.7
13H-2, 75-77			118.47	1.15	0.9
175-1079A-	13°18.5′E, 11°55.8′S	749			
2H-4, 46-49			10.26	2.50	0.1
13H-4, 46-49			117.65	2.97	0.7
175-1082A-	11°49.2′E, 21°5.6′S	1280			
6H-1, 105-108			51.86	10.69	0.65
53X-3, 27-30			503.63	8.50	5.0
175-1084A-	13°1.7′E, 25°30.8′S	1990			
12H-6, 140-143			120.72	12.82	0.7
25X-3, 20-23			242.60	11.61	1.4
51X-3, 20-23			493.00	5.12	3.2
175-1085A-	13°59.4′E, 29°22.5′S	1713			
11X-3, 20-23			102.40	8.10	2.2
50X-3, 20-23			489.56	7.32	10

Notes: TOC = total organic carbon. All data except TOC data are from Wefer, Berger, Richter, et al. (1998).

Table T2. Compounds identified in selected samples, Leg 175.

Number	Compound	Structure
1	*Iso*-loliolide	
2	Loliolide	XI
3	Perylene	XIV
4	C_{27} steradiene	
5	C_{27} sterene	
6	Hop-17(21)-ene	
7	*Neo*-hop-13(18)-ene	
8	Fern-9(11)-ene	
9	12-hydroxy-hexacosanoic acid	
10	17ß,21ß(H)-*homo*-hopane	
11	Taraxer-14-en-3ß-ol (taraxerol)	II
12	Olean-12-en-3ß-ol (ß-amyrin)	III
13	12-hydroxy-octacosanoic acid	VIII
14	4α,23,24-trimethylcholest-22-en-3ß-ol (dinosterol)	IXd
15	Octacosane-1,14-diol	
16	Friedelan-3-one	IV
17	4α,23,24 trimethyl-5α-cholestan-3ß-ol (dinostanol)	
18	Hopan-22-ol (diplopterol)	
19	Glyceroldipentadecylether	
20	*n*-Triacontan-1-ol-x-one; x = 13, 15	VII
21	Triacosane-1, x-diol; x = 13, 14, 15	VI
22	*n*-Untriacontan-1-ol-x-one; x = 13, 15	
23	Untriacontane-1, x-diol; x = 13, 14, 15	
24	*n*-Dotriacontan-1-ol-x-one; x = 13, 15	
25	Dotriacontane-1,15-diol	
26	17ß,21ß(H)-*homo*-hopan-31-ol	
27	17ß,21ß(H)-*dihomo*-hopanoic acid	
28	17ß,21ß(H)-*dihomo*-hopan-32-ol	XIII
29	$C_{37:3}$ methyl ketone	
30	$C_{37:2}$ methyl ketone	V
31	$C_{38:3}$ methyl + ethyl ketones	
32	$C_{38:2}$ methyl + ethyl ketones	
33	$C_{38:3}$ alkene-3-ol	
34	*Trihomo*-hopan-32,33-diol	
35	$C_{39:2}$ ethyl ketone	
36	C_{40} dicyclic biphytanediol	XIIb
37	C_{40} tricyclic biphytanediol	XIIa
38	*Pentakishomo*-hopane-keto-diol	

Notes: Stucture number relates to the structures shown in Figure **F4,** p. 26. Identified compounds are shown on the TICs in Figures **F2,** p. 24, and **F3,** p. 25.

Table T3. Steroids identified in selected samples.

Peak number	Compound	Structure
A	24-*nor*-cholesta-5,22-diene-3ß-ol	
B	24-*nor*-5α-cholest-22-ene-3ß-ol	
C	Cholesta-5,22-diene-3ß-ol	
D	5α-cholest-22-ene-3ß-ol	
E	Cholest-5-ene-3ß-ol	IXa
F	5α-cholestan-3ß-ol	
G	24-methylcholesta-5,22-diene-3ß-ol	
H	24-methyl-5α-cholest-22-ene-3ß-ol	
I	24-methylcholesta-5,24(28)-dien-3ß-ol	
K	24-methylcholest-5-ene-3ß-ol	
L	24-methyl-5α-cholestan-3ß-ol	
M	23,24-dimethylcholest-5,22-diene-3ß-ol	IXb
N	23,24-dimethyl-5α-cholest-22-ene-3ß-ol	
O	4,24-dimethyl-5α-cholest-22-ene-3ß-ol	
P	24-ethylcholesta-5,22-diene-3ß-ol	
Q	24-ethyl-5α-cholest-22-ene-3ß-ol	
R	23,24-dimethylcholest-5-ene-3ß-ol	
S	24-ethylcholest-5-ene-3ß-ol	IXc
T	24-ethyl-5α-cholestan-3ß-ol	
U	4α,23,24-trimethylcholest-22-ene-3ß-ol	IXd
V	24-ethyl-5α-cholest-24-ene-3ß-ol	
W	4α,23,24-trimethyl-5α-cholestan-3ß-ol	
X	4α-methyl-24-ethylcholestan-3ß-ol	

Notes: Identified compounds are shown on the TICs in Figures F2, p. 24, and F5, p. 27. Structure number relates to the structures shown in Figure F4, p. 26.

Table T4. Concentrations of quantified biomarker lipids and compound indices.

Core, section, interval (cm)	C_{25}–C_{33} *n*-alkanes	$CPI_{alk27-31}$	ACL_{25-33}	C_{20}–C_{30} fatty acids	C_{20}–C_{30} *n*-alcohols	C_{37} alkenones	$U^{k'}_{37}$	Temperature (°C)	Taraxerol	Loliolide	Dinosterol	Cholesterol	C_{30} diol	Biphytanediols
175-1076A-														
4H-2, 75-77	64	6.0	29.5	29	59	90	0.79	22.5	6.0	0.7	18	5.4	34	ND
7H-2, 75-77	230	3.8	29.6	40	81	230	0.93	26.9	230	3.6	8.0	9.7	270	ND
15H-2, 75-77	1100	10.4	29.6	550	1100	1300	0.73	20.8	1400	25	550	25	740	ND
175-1077A-														
9H-2, 75-77	280	7.0	29.7	330	720	350	0.86	24.6	120	0.4	96	130	260	43
13H-2, 75-77	300	4.2	29.6	960	780	230	0.89	25.7	380	0.6	160	67	220	69
175-1079A-														
2H-4, 46-49	210	7.4	29.9	47	94	490	0.78	22.2	12	39	19	6.8	29	ND
13H-4, 46-49	150	6.0	30.4	150	310	370	0.85	24.4	99	7.5	170	180	190	ND
175-1082A-														
6H-1, 105-108	90	8.4	31.0	39	78	960	0.58	16.4	ND	15	89	210	60	380
53X-3, 27-30	18	5.6	30.3	7.5	15	80	0.95	27.4	ND	ND	7.9	10	5.2	ND
175-1084A-														
12H-6, 140-143	210	3.1	30.4	170	350	1400	0.55	15.4	ND	63	450	1100	150	500
25X-3, 20-23	44	NA	NA	180	360	850	0.58	16.1	ND	56	320	2000	210	500
51X-3, 20-23	13	NA	NA	68	140	180	0.74	21.2	ND	8.5	86	150	53	150
175-1085A-														
11X-3, 20-23	12	6.9	30.4	8.6	17	300	0.68	19.3	ND	0.9	5.6	5.6	8.7	27
50X-3, 20-23	13	5.1	30.2	9.5	19	80	0.84	24.0	ND	ND	9.0	5.8	4.5	12

Notes: NA = not applicable because concentration was too low, ND = not detected. Lipid concentration is given in micrograms per gram of TOC.

CPI (carbon preference index) = $0.5 \times \Sigma(X_i+X_{i+2}+..+X_n)/\Sigma(X_{i-1}+X_{i+1}+..+X_{n-1}) + 0.5 \times \Sigma(X_i+X_{i+2}+..+X_n)/\Sigma(X_{i+1}+X_{i+3}+..+X_{n+1})$.

ACL (average chain length) = $\Sigma(i \times X_i)/\Sigma X_i$.

$U^{k'}_{37}$ (ketone unsaturation index) = $C_{37:2}/(C_{37:2}+C_{37:3})$.

Temperature was calculated using the equation from Müller et al. (1998): $U^{k'}_{37} = 0.033T + 0.044$.