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Organic Geochemistry 37 (2006) 539–557

Organic Geochemistry

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Well preserved Palaeogene and Cretaceous biomarkers from the Kilwa area, Tanzania

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Received 11 August 2005; received in revised form 1 December 2005; accepted 4 January 2006
Available online 6 March 2006

Abstract

We have investigated the biomarker composition of sediments ranging in age from 30 to 70 Ma from the Kilwa area of Tanzania. They are dominated by material of terrestrial (*n*-alkanols, *n*-alkanoic acids, *n*-alkanes and triterpenoids) and bacterial [hopanoids and a dipentadecyl glycerol diether (DGD)] origin with only a minor contribution of marine origin (crenarchaeol and some algal steroids). This indicates a marine setting dominated by higher plant input, which most likely stimulated sedimentary microbial activity, including sulfate reduction.

The lipid composition, specifically the presence of bacteriohopanepolyols (BHPs) and the stereochemistry of hopanoids, suggests a low degree of thermal maturity. Many biomarkers have still retained functionality even after 30–70 million years. This is in good agreement with the exceptional preservation of foraminifera and nannofossils and can probably be attributed to the very low sediment permeability and burial depth.

There is a clear distinction in the biomarker distributions between the Oligocene-age sediments collected at the end of the peninsula near Kilwa Masoko and the older sediments collected from elsewhere, indicating differences in depositional environment. Sediments from the end of the peninsula have higher branched and isoprenoid tetraether index values, indicating a relatively higher terrestrial input. They also contain two tentatively assigned C_{28} hopenes (28,30-dinorneohop-13(18)-ene and 28,30-dinorhop-17(21)-ene), (aromatic) des-*A*-triterpenes, des-*E*-hopenes, aromatic pentacyclic triterpenoids, C_{33} DGD, archaeol and BHPs, which are absent from or only present in small amounts in the other sediments. These differences likely reflect an evolution of the depositional area from a relative open shelf environment with substantial water depth to a shallower setting during the early Oligocene.
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0146-6380/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.orggeochem.2006.01.003

1. Introduction

A major limitation in organic geochemical palaeoclimate research is the quality of the organic material (OM) preserved in the sedimentary record. In general, a relatively small fraction (<5%) of the OM produced by primary producers is stored in the sediment. During geological time, this material can be significantly altered due to increasing subsurface temperature (e.g. Tissot and Welte, 1984; Peters and Moldowan, 1993). This causes the loss of diagnostic structural characteristics and makes the sediment less valuable for palaeoclimate research. Besides this alteration of OM, recent research has also shown that other material such as foraminiferal shells can be greatly affected by diagenesis, with the introduction of diagenetic calcite upon recrystallisation occurring on a μm-scale (Schrag et al., 1995; Schrag, 1999; Pearson et al., 2001). Consequently, there is a growing appreciation among geochemists of a need for sediments which exhibit very good to excellent preservation.

The mudstones of southern coastal Tanzania are well preserved late Cretaceous and Palaeogene tropical sediments (Pearson et al., 2001). They are, for instance, known to yield exceptionally well-preserved planktonic foraminifer shells (Ramsay, 1962; Blow and Banner, 1962; Pearson et al., 2001; Stewart et al., 2004). The shells seem to be protected by relatively impermeable clays and shallow maximum burial depth, circumstances which could also lead to good OM preservation. The composition and thermal maturity of the OM are unknown, as is the information the biomarker distribution can provide about the depositional environment. The aim of this study was to assess the composition and preservation of extractable lipids and their biogeochemical significance in southern coastal (Kilwa area) sediments deposited in a tropical marine environment between 70 and 30 million years ago.

2. Materials and methods

2.1. Study area and sampling

Large outcrops of Cretaceous marine sediment occur along the Tanzanian coastal region south of Dar-es-Salaam (Kent et al., 1971). In contrast, the overlying Palaeogene deposits are less widespread. The most extensive outcrop is a continuous strip between Kilwa and Lindi, in the south of the country (Kent et al., 1971; Schlüter, 1997; Fig. 1), with the predominant lithology being marine clays or claystones, often punctuated by thin carbonate or siliciclastic turbidites (Kent et al., 1971). For a tectonic history of the Kilwa area, see Pearson et al. (2004).

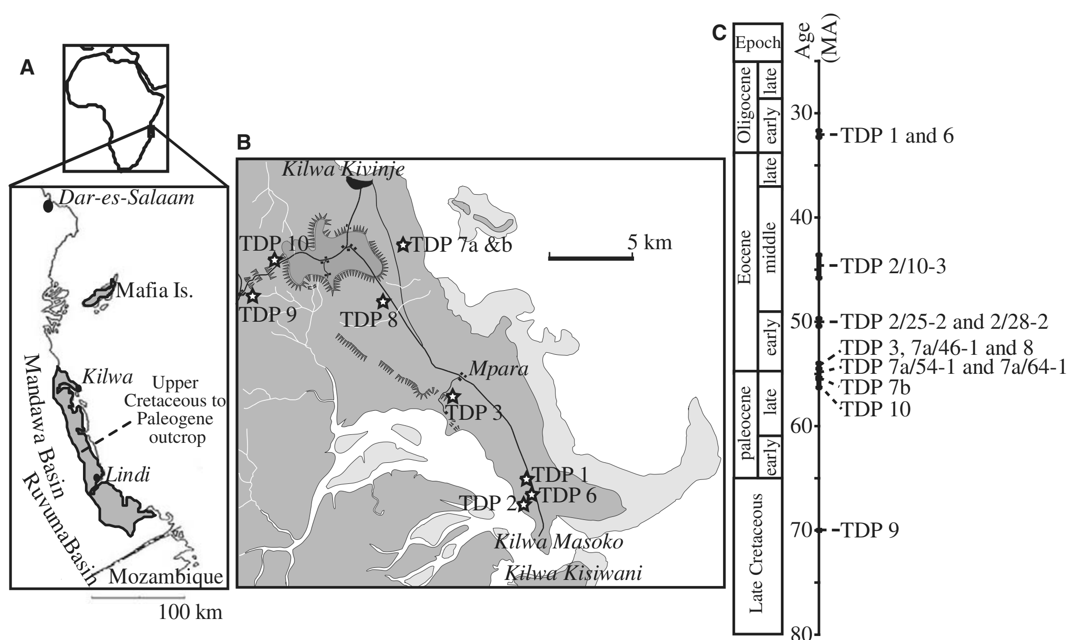


Fig. 1. Maps of (A) study area in Southern Tanzania in relation to Upper Cretaceous and Palaeogene outcrop, (B) detailed location map for TDP sites 1–3 and 6–10 on the Kilwa peninsula and (C) ages of samples.

Table 1
Sample location and bulk geochemical data

Sample[a]	Depth (m)	Location	Age (Ma)[b]	$CaCO_3$ (%)	TS[c] (%)	TOC[d] (%)	TN[e] (%)
TDP 1/11-1, 39–50 cm	36.79–36.90	8°54.516′S, 39°30.397′E	31.7–32.3	3.2	1.0	0.8	0.07
TDP 1/20-1, 23–32 cm[g]	64.44–64.53		31.7–32.3	2.5	1.2	1.2	0.11
TDP 6/4-1, 50–60 cm	55.39–55.49	8°54.672′S, 39°30,426′E	31.7–32.3	3.7	0.5	1.6	0.07
TDP 2/10-3, 16–30 cm	21.06–21.20	8°55.277′S, 39°30.219′E	45.8–43.6	10.5	0.5	0.5	n.d.[f]
TDP 2/25-2, 53–60 cm[g]	70.76–70.98		50.4–49.7	21.4	0.5	0.2	n.d.[f]
TDP 2/28-2, 6–20 cm	61.83–61.90		50.4–49.7	12.2	0.2	0.4	0.02
TDP 3/4-1, 84–93 cm[g]	14.74–14.82	8°51.585′S, 39°27.655′E	54.5–54.0	6.0	0.1	0.3	0.02
TDP 3/16-2, 73–85 cm	49.13–49.25		54.5–54.0	1.5	1.1	0.2	0.04
TDP 7a/46-1, 30–40 cm[g]	79.50–79.60	8°46,437′S, 39°25.709′E	54.5–54.0	8.2	0.2	0.5	0.05
TDP 8/11-1, 24–34 cm	20.19–20.29	8°48.771′S, 39°26.207′E	54.5–54.0	11.4	0.1	0.7	0.03
TDP 7a/54-1, 26–36 cm	90.61–90.71	8°46.437′S, 39°25.709′E	55.35–54.5	5.9	0.1	0.9	0.03
TDP 7a/64-1, 68–82 cm	101.13–101.27		55.35–54.5	10.2	0.5	0.1	0.05
TDP 7b/50-1, 30–40 cm	119.35–119.42	8°46.422′S, 39°25.711′E	55.5–55.35	15.2	0.7	0.5	0.04
TDP 10/13-2, 10–20 cm	27.05–27.15	8°47.157′S, 39°22.501′E	56.3–55.5	5.0	0.3	0.7	0.04
TDP 10/26-1, 92 cm to TDP 10/26-2, 07 cm	59.72–59.87		56.3–55.5	3.3	0.3	0.5	0.06
TDP 9/28-3, 10–20 cm	50.15–50.25	8°48.106′S, 39°21.271′E	Approximately 70	11.4	0.1	0.6	0.04

[a] A typical sample identifier refers to site, core number, section number and depth in cm from top of section.
[b] Pearson et al. (2004).
[c] TS, total sulfur.
[d] TOC, total organic carbon.
[e] TN, total nitrogen.
[f] n.d., not detectable.
[g] Samples used for BHP analysis.

Drilling was conducted at 8 sites (TDP 1–3 and 6–10, Fig. 1 and (Table 1; Pearson et al., 2004) using truck-mounted rigs, with a core diameter of ~5 cm, using water and mud circulation to avoid organic contamination. For a complete core description, see Pearson et al. (2004). Samples for organic geochemical analysis were taken well below the zone of surface oxidation, at least 10 m, and the zone of contamination by modern terrestrial OM and kept frozen at −20 °C.

2.2. Extraction and fractionation

Sixteen samples, at least one from every site and ranging in age from 32 to 70 Ma (Fig. 1C), were chosen (Table 1). Between 50 and 70 g of each freeze-dried, crushed sample were extracted using a Soxhlet apparatus with dichloromethane/methanol (DCM/MeOH, 2:1, v/v) for 24 h, and the total lipid extracts (TLEs) were concentrated using rotary evaporation. An aliquot of the TLE was treated with activated (2 N HCl) copper to remove elemental sulfur and a mixture of three standards (11.0 μg of androstane, 12.0 μg of hexadecan-2-ol and 44.3 μg of hexadecyl-1-octadecanoate) was added. Subsequently, the aliquot was separated into three fractions using bond-elut column chromatography (Strata NH_2; 5 μm, 70A; Kim and Salem, 1990), eluting with DCM/isopropanol (2:1 v/v; 12 ml; "neutral lipid fraction"), 2% acetic acid in diethyl ether (12 ml; "acid fraction") and MeOH (12 ml; "phospholipid fraction"). Further analyses were only performed on the neutral lipid and acid fractions. The neutral lipid fraction was further separated into three fractions using a column packed with (activated) Al_2O_3 by elution with hexane (3 ml; "saturated hydrocarbon fraction"), hexane/DCM (9:1 v/v; 3 ml; "aromatic hydrocarbon fraction") and DCM/MeOH (1:1 v/v; 3 ml; "polar fraction"). The saturated hydrocarbon, aromatic hydrocarbon, polar and acid fractions were analysed using gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS) and, in the case of the saturated hydrocarbon fractions, GC–isotope ratio MS (GC–IRMS). Prior to analysis, the acid fractions were derivatized with BF_3 in MeOH to convert acids to methyl esters. Subsequently, very polar compounds were removed by column chromatography over silica gel with ethyl acetate as eluent. These fractions and the polar fractions were dissolved in pyridine with bis(trimethylsilyl)trifluroacetamide (BSTFA) and heated (70 °C; 60 min) to convert alkanols to trimethylsilyl ethers. Blanks were run to ensure that no contamination

was introduced during the extraction and separation procedures.

Analysis of the intact glycerol dialkyl glycerol diethers or GDGTs was carried out using a method comparable to that reported by Hopmans et al. (2004). In short, the TLE was separated into four fractions using a column packed with Al_2O_3 and eluting with hexane/DCM (9:1, v/v; 3 column volumes) to give the apolar fraction, hexane/DCM (1:1 v/v; 3 column volumes) for the ketone fraction, DCM/MeOH (95/5 v/v; 3 column volumes) to give the GDGT fraction and DCM/MeOH (1/1 v/v; 3 column volumes) to for the residual polar fraction. The tetraether lipid fraction was dissolved in a mixture of hexane/isopropanol (99:1, v/v; HPLC grade) and sonicated for 5 min. If there was any precipitate left, the mixture was centrifuged and the supernatant was used for further analysis. Consequently, the solvent mixture/supernatant was filtered using a 0.45 μm pore size, 4 mm diameter PTFE filter attached to a 5 or 10 ml syringe. The filtered fractions were analysed using high-performance liquid chromatography–atmospheric pressure chemical ionisation–MS (HPLC–APCI-MS).

Four samples from TDP 1, 2, 3 and 7a (Table 1) were selected for bacteriohopanepolyol (BHP) analysis which was carried out as described in full elsewhere (Innes et al., 1997; Farrimond et al., 2000). Freeze-dried, powdered samples (ca. 10 g) were extracted with $CHCL_3$/MeOH (180 ml; 2:1 v/v) using a Gerhardt Soxtherm apparatus. After evaporation to dryness, an internal standard (5α-androstanol; 0.15 μg/mg extract) was added and the total extract was split into aliquots for derivatisation targeted at different specific hopanoid functionalities prior to analysis (see Innes et al., 1997). One aliquot was treated with periodic acid and sodium borohydride to convert the BHPs to more readily analysable terminal alcohols (Rohmer et al., 1984; Innes et al., 1997). These were subsequently acetylated (acetic anhydride/pyridine, 4 ml; 1:1 v/v; 50 °C for 1 h), as was a second aliquot of the total extract for the detection of hopanols and the more GC-amenable intact BHPs. Analyses were performed using GC/MS and HPLC–APCI multistage ion trap mass spectrometry (HPLC–APCI-MS^n).

2.3. Instrumental analysis

GC was performed using a Hewlett–Packard 5890 instrument, equipped with an on-column injector. A fused silica capillary column (50 m × 0.32 mm) coated with CP-Sil-5 (film thickness 0.12 μm) was used with H_2 as carrier gas and the effluent was monitored with a flame ionisation detector. The samples were injected at 50 °C and the oven was programmed to 130 °C at 20 °C/min and then at 4 °C/min to 300 °C at which it was held isothermally for 20 min.

GC/MS was performed using a Thermoquest Finnigan TRACE GC, equipped with an on-column injector and He as carrier gas, interfaced to a Thermoquest Finnigan TRACE MS operated with electron ionisation at 70 eV and scanning from m/z 50 to 650 using a cycle time of 1.7 scan s^{-1}. The interface was set to 300 °C with the ion source at 240 °C. The same columns, conditions and temperature programme were used as for GC analysis. Compounds were identified by comparison of mass spectra and retention times with those reported in the literature.

GC–IRMS analysis was performed using a Finnigan MAT Delta S isotope ratio monitoring mass spectrometer. The same column conditions and temperature programme were used as above. The $\delta^{13}C$ values (vs. VPDB standard) were obtained from at least two analyses and the results were averaged to obtain a mean value and to estimate the reproducibility (<5% deviation in the measurements).

HPLC–APCI-MS analysis of the GDGTs was performed using an HP1100 series LC–MS equipped with an auto-injector. The same column, flow rate and gradient conditions were used as those described by Hopmans et al. (2004). Detection was achieved using APCI-MS of the eluent with the same conditions as decribed by Hopmans et al. (2004). Relative GDGTs were detected via single ion monitoring of the $[M + H]^+$ ions (dwell time 237 ms) and quantified by integration of the peak areas.

GC/MS analysis of the BHPs was performed using a Hewlett–Packard 5890 II GC system (split/splitless injector; 350 °C) linked to a Hewlett–Packard 5972 mass-selective detector (electron energy 70 eV; filament current 220 μA; source temperature 270 °C; multiplier voltage 2000 V; interface temperature 350 °C). The column, column conditions and temperature programme were the same as those described in Talbot et al. (2005). Hopanoids were identified from full scan (m/z 50–700) analysis of selected samples, by comparison with authentic standards and published spectra and by relative retention times.

HPLC–APCI-MS^n analysis of the BHPs was performed as reported in full elsewhere (Talbot et al., 2003a,b). Reversed-phase HPLC analysis of acetylated extracts (injected in MeOH:propan-2-ol,

60:40 v/v) was accomplished using a Surveyor HPLC system and the HPLC–APCI-MS^n analysis was performed using a Finnigan LCQ ion trap mass spectrometer equipped with an APCI source operated in the positive ion mode. HPLC–MS settings were similar to those described by Talbot et al. (2005).

C, H and N abundances were determined with a Carlo Erba EA 1108. The amounts of carbon (present as carbonate) and sulfur were determined with a Coulomat 702 (Strohlein). The total organic carbon (TOC) was determined by subtracting the amount of carbon present as carbonate from the total amount of carbon. All values reported are averages of duplicate measurements and have an average reproducibility of ±0.2%.

3. Results

3.1. Bulk analyses

The TOC and total nitrogen (TN) contents of the Kilwa TDP sediments range from 0.1% to 1.6% and 0.02% to 0.11% (Table 1), respectively, with substantially higher average values for the TDP 1 and 6 sediments. The total sulfur (TS) content ranges from 0.1% to 1.2%, with substantially higher values for the TDP 1 sediments (Table 1). The carbonate content ranges from 1.5% to 21.4% (Table 1).

3.2. Extractable organic matter

3.2.1. Saturated hydrocarbon fraction

Hydrocarbon fractions are all dominated by a homologous series of C_{16}–C_{35} *n*-alkanes with a predominance of the odd-numbered homologues (Fig. 2). The most abundant homologue varies among the sediments; the C_{31} *n*-alkane is dominant in the TDP 1, 6 and 9 sediments, whereas either the C_{29} or C_{27} homologue is the most abundant *n*-alkane in the others (Table 2). This difference is reflected in the ratio of the C_{31} *n*-alkane to the C_{29} *n*-alkane (Table 2), with higher values in the TDP 1, 2, 6 and 9 sediments. In contrast, this difference is not clear from the average chain length (ACL; Table 2). The carbon preference index (CPI) of the *n*-alkanes also varies, with values ranging from 2.9 in a TDP 2 sample to 5.6 in a TDP 6 sample (Table 2). The weighted mean $\delta^{13}C$ values of the C_{27}, C_{29} and C_{31} *n*-alkanes range from −28.9‰ to −32.2‰ (Table 2), with the most depleted values occurring in TDP 1 and 6 sediments. In addition, the *n*-alkane-based proxy P_{aq} used to differentiate emergent/terrestrial and submerged freshwater/marine organic material, as defined by Ficken et al. (2000), shows values between 0.16 and 0.37 (Table 2).

Substantial amounts of hopanes and hopenes are also present in all the samples (Fig. 3). The hopanes have a comparable distribution in all the samples, with 17β(H),21β (H)-homohopane (C_{31}ββ hopane; I) being predominant, except in TDP 1 sediments. Indeed, in these samples 17α(H),21β(H)-homopane (C_{31}αβ hopane) is the most abundant hopane and occurs exclusively with the 22R configuration. The hopenes have a comparable distribution pattern in most of the samples, ranging from C_{27} to C_{31} with the C_{30} hop-17(21)-ene (II) being the most abundant component (Fig. 3). Such distributions are comparable to those found, for instance, in sediments from the DSDP 416A and DSDP 530A (Brassell et al., 1980; Brassell and Farrimond, 1986). However, the sediments from TDP 1, 2 and 6 have a completely different hopene distribution. The homologous hopene series in these samples are dominated by hopenes that elute between the C_{27} and the C_{29} homologue and are absent from the other samples (Figs. 2 and 3). Based on their molecular ion ($M^{+\cdot} = 382$), these two compounds are clearly dinorhopenes; comparison of their mass spectra with those of hopenes observed in Cenomian/Turonian Black shales from DSDP site 144 (Sinninghe Damsté, 1997) suggests that they are 28,30-dinorneohop-13(18)-ene and 28,30-dinorhop-17(21)-ene.

In addition, substantial amounts of des-*A*-triterpenes, with des-*A*-lupane (III) being the most abundant component, and des-*E*-hopenes are present in the TDP1 and 6 samples (Fig. 4). These compounds are absent from or only present in trace amounts in the other sediments. Also present in all samples, but in substantially lower amounts, are sterenes, mainly 24-ethylcholest-5-ene (IV; Fig. 2).

3.2.2. Aromatic hydrocarbon fraction

Components in these fractions are only present in substantial amounts in the TDP 1 and 6 samples. The aromatic hydrocarbon fraction from the TDP 6 sediment (Fig. 5A) is dominated by a series of aromatic pentacyclic triterpenoids, ranging from A-ring monoaromatics to pentacyclic aromatic picene derivatives (V). Also present are substantial amounts of aromatic des-*A*-triterpenes, such as des-*A*-26,27-dinorlupa-5,7,9,11,13-pentaene (VI) and a number of unidentified compounds showing relatively intense fragment ions at *m*/*z* 218, 203 and 189, most

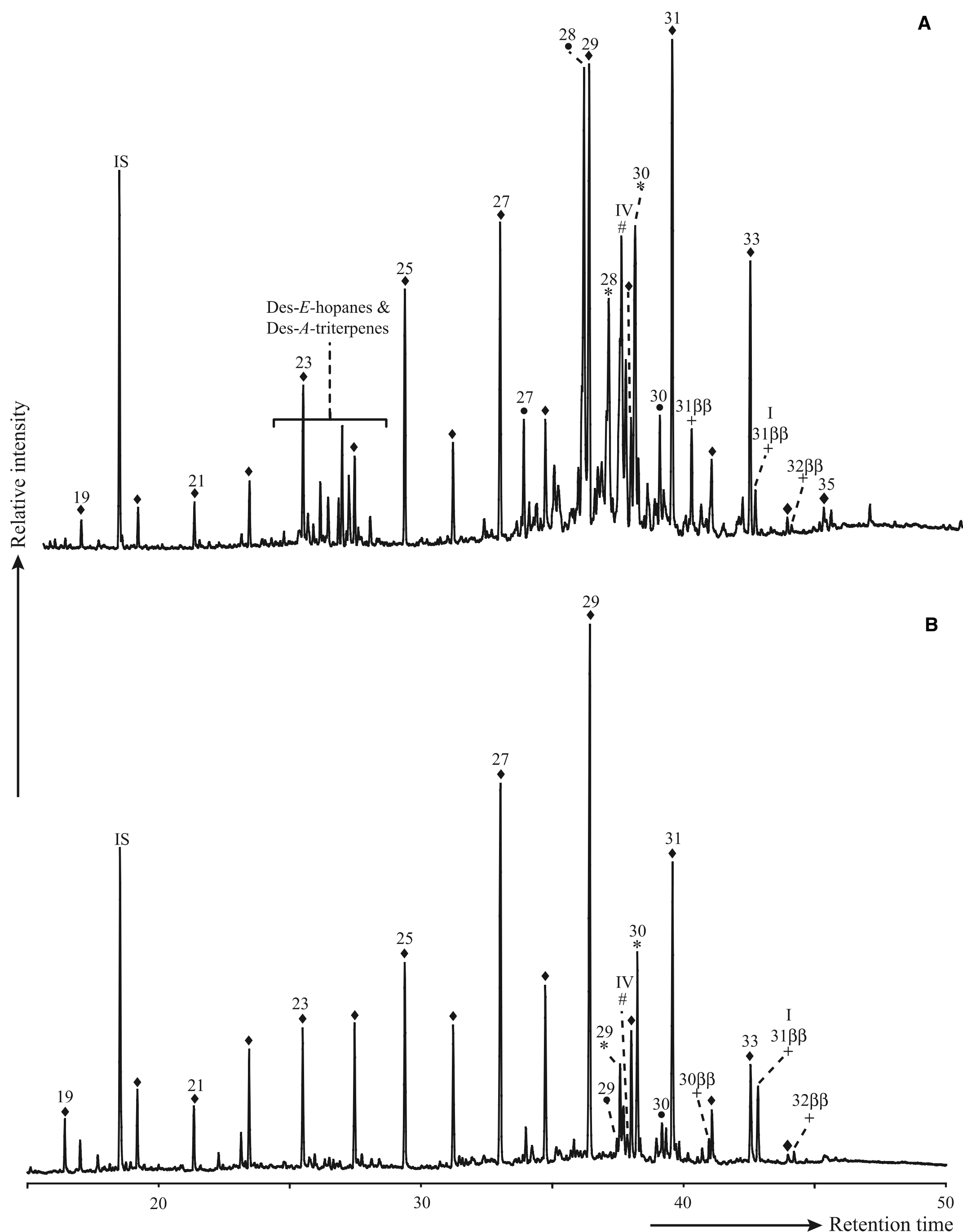


Fig. 2. Total ion current chromatograms of saturated hydrocarbon fractions from sample: (A) TDP 1/20-2, 14–23 cm and (B) TDP 3/16-2, 73–85 cm, illustrating differences in biomarker composition between a younger sample collected at the end of the peninsula near Kilwa Masoko and an older sample collected elsewhere. ♦, *n*-alkanes; ●, hop-13(18)-enes; *, hop-17(21)-enes; +, hopanes; sterenes; IS, internal standard. Numbers indicate carbon chain length, αβ or ββ indicate stereochemistry of hopanes at C-17 and C-21, and roman numerals refer to compounds in appendix.

likely having a triterpenoid structure. The TDP 1 sediments also contain substantial amounts of aromatic pentacyclic triterpenoids. In contrast, aromatic pentacyclic triterpenoids and aromatic des-*A*-triterpenes are absent from or present in only small amounts in the other samples.

Table 2
Distributions and stable carbon isotopic compositions of *n*-alkanes and distributions of hopanes and hopenes in Kilwa TDP sediments

Sample	*n*-Alkanes						Hopanes	Hopenes
	C_{max}[a]	31/(29 + 31)[b]	ACL_{27-33}	CPI	P_{aq}	$\delta^{13}C_{wm}$ (‰)[c]	$31\beta\beta/(31\alpha\beta + 31\beta\beta)$[e]	C_{max}[a]
TDP 1/11-1, 39–50 cm	31	0.6	30.6	4.4	0.16	n.d.[d]	0.32	30 17(21)
TDP 1/20-1, 23–32 cm	31	0.6	30.0	4.6	0.30	−30.5	0.33	28 13(18)
TDP 6/4-1, 50–60 cm	31	0.5	29.7	5.6	0.21	−32.2	0.60	28 13(18)
TDP 2/10-3, 16–30 cm	29	0.5	30.1	2.9	0.37	n.d.[d]	0.82	28 13(18)
TDP 2/25-2, 53–60 cm	29	0.4	29.4	3.4	0.26	−28.9	0.80	28 13(18)
TDP 2/28-2, 6–20 cm	29	0.5	29.9	4.1	0.21	−29.6	0.83	28 13(18)
TDP 3/4-1, 84–93 cm	29	0.3	29.4	3.8	0.29	−29.4	0.92	30 17(21)
TDP 3/16-2, 73–85 cm	29	0.4	29.2	3.1	0.33	n.d.[d]	0.85	30 17(21)
TDP 7a/46-1, 30–40 cm	29	0.4	29.4	4.4	0.23	−29.0	0.83	30 17(21)
TDP 8/11-1, 24–34 cm	29	0.3	29.6	4.2	0.34	−29.0	0.90	30 17(21)
TDP 7a/54-1, 26–36 cm	29	0.3	28.9	4.5	0.30	−30.0	0.84	30 17(21)
TDP 7a/64-1, 68–82 cm	29	0.4	29.4	4.2	0.21	−29.5	0.88	30 17(21)
TDP 7b/50-1, 30–40 cm	29	0.4	29.1	4.4	0.24	−29.8	0.74	30 17(21)
TDP 10/13-2, 10–20 cm	27	0.4	28.9	4.5	0.22	−30.3	0.90	30 17(21)
TDP 10/26-1, 92 cm to TDP 10/26-2, 07 cm	29	0.4	29.3	4.0	0.23	−30.1	0.87	30 17(21)
TDP 9/28-3, 10–20 cm	31	0.5	29.6	4.8	0.30	−29.0	0.74	30 17(21)

ACL (average chain length) and CPI (carbon preference index) calculated following the method of Schefuß et al. (2003) and P_{aq} following the method of Ficken et al. (2000).
[a] Carbon number of *n*-alkane or hopene homologue with highest abundance.
[b] Ratio of concentration of C_{31} *n*-alkane to sum of concentrations of C_{29} and C_{31} *n*-alkanes.
[c] Weighted mean of $\delta^{13}C$ values of C_{27}, C_{29} and C_{31} *n*-alkanes.
[d] n.d., not determined.
[e] Ratio of concentration of C_{31} ββ hopane (I) to sum of concentrations of C_{31} αβ and ββ hopanes.

The aromatic hydrocarbon fractions of TDP 1 samples also contain high relative amounts of C_{25}–C_{35} *n*-alkan-2-ones, especially the C_{29} *n*-alkan-2-one, with a predominance of the odd-numbered homologues (Fig. 5B). However, TDP 1 and 6 sediments do not contain mid-chain ketones, whereas they are present in trace amounts in a number of TDP 7a, 7b, 8 and 9 sediments.

3.2.3. Polar fraction

All polar fractions contain a homologous series of C_{16}–C_{32} *n*-alkanols, dominated either by the C_{28} or C_{30} homologue (Table 3) and a predominance of the even numbered homologues (Fig. 6A). The *n*-alkanol ACLs are comparable for all samples, with values ranging between 26.5 and 27.9 (Table 3). In a number of samples (e.g. TDP 6), triterpenoids, especially friedelan-3-one (VII) and α- and β-amyrin, are the most abundant compounds (Fig. 6A). Trace to substantial amounts of hopanoids, predominantly homohopan-29-one (VIII) and bishomohopan-31-one (Fig. 6A), and trace to minor amounts of steroids, especially 4,24-dimethylcholestan-3-one (IX) and 23,24-dimethyl-5α-cholestan-3-one or 24-ethyl-5α-cholestan-3-one, are also present in all samples (Fig. 7).

In addition, only in the TDP 1, 2 and 6 samples, are the C_{33} dipentadecyl glycerol diether (DGD, where the pentadecyl moieties are *anteiso* branched; X) and archaeol (XI) present, although in relatively low amounts (Fig. 6A).

3.2.4. Acid fraction

Almost all acid fractions are dominated by a homologous series of C_{16}–C_{34} *n*-alkanoic acids, with either C_{24} or C_{28} member being the most abundant (Table 3), showing an even-over-odd carbon number predominance (Fig. 6B). The ACLs are comparable for all samples, with values between 27.9 and 29.4 (Table 3). Also present in all samples is an abundant homologous series of C_{22}–C_{32} ω-hydroxy alkanoic acids, with the C_{22} member being the most abundant, showing a predominance of the even numbered homologues (Fig. 6B). In TDP 2, 3 and 7a, the C_{22} ω-hydroxy alkanoic acid is the most abundant compound present. Also present are triterpenoic acids, especially 3,4-seco-friedelan-3-oic acid (XII; Fig. 6B). In all the samples, except the TDP 6

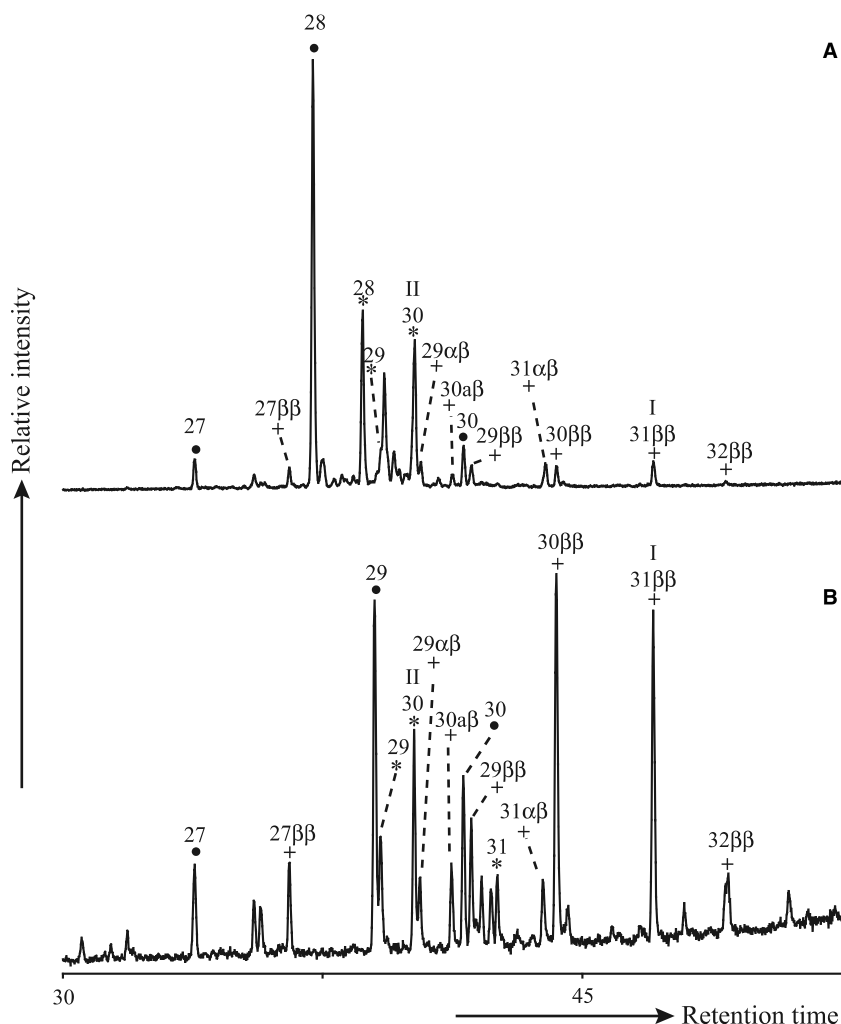


Fig. 3. Partial m/z 191 mass chromatograms of saturated hydrocarbon fractions from sample: (A) TDP 6/4-1, 50–60 cm and (B) TDP 7a/54-1, 26–36 cm, illustrating differences in hopane and hopene distribution between a younger sample collected at the end of the peninsula near Kilwa Masoko and an older sample collected elsewhere. ●, hop-13(18)-enes; ✻, hop-17(21)-enes; +, hopanes. Numbers indicate carbon chain length, αβ or ββ indicate stereochemistry of hopanes at C-17 and C-21 and roman numerals refer to the compounds in appendix.

sediment, these compounds are present in substantially lower amounts than the *n*-alkanoic acids. However, in the case of the TDP 6 sediments, the concentrations of these triterpenoic acids are substantially higher, with 3,4-seco-friedelan-3-oic acid being the most abundant compound (Fig. 6B). In addition, hopanoic acids, mainly 17β(H),21β(H)-bishomohopanoic acid (XIII), are also abundant in most of the samples.

3.2.5. GDGTs

A number of the sediments contain substantial amounts of intact glycerol dialkyl glycerol diethers (GDGTs), including both non-isoprenoidal branched GDGTs (XIV–XVI) and isoprenoidal GDGTs (XVII–XX; Fig. 8). The TDP 1 and 6 sediments contain much higher relative abundances of branched GDGTs than the other Kilwa TDP sediments (Fig. 8). This difference is clearly reflected in the BIT index (Hopmans et al., 2004; Table 3), which is substantially higher for the TDP 1 and 6 sediments (between 0.73 and 0.85) than for the other sediments (between 0.22 and 0.58).

3.2.6. BHPs

GC/MS and HPLC–APCI-MS^n analyses of the acetylated total extracts of the selected TDP 1 and 2 samples (Table 1) indicate predominantly the presence of acetylated 32,35-anhydrobacteriohopanetetrol (anhydroBHT, XXI; Fig. 10A and B;

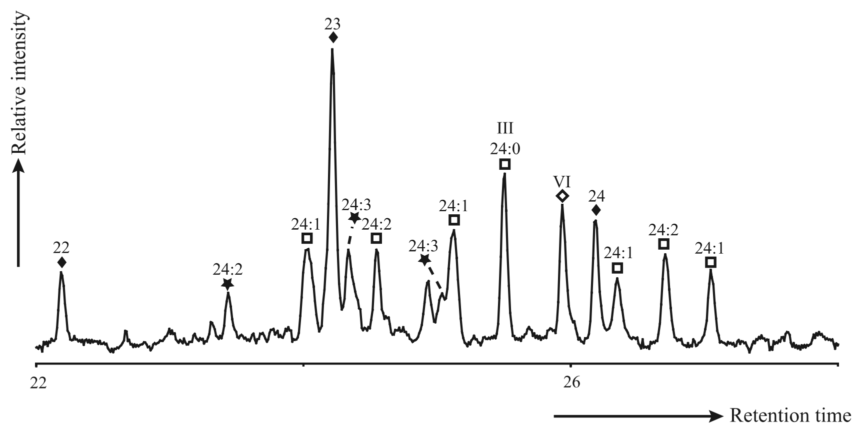


Fig. 4. Total ion current chromatograms showing distribution of des-*A*-tritepenes and des-*E*-hopenes in saturated hydrocarbon fraction from sample TDP 6/4-1, 50–60 cm. ♦, *n*-alkanes; ★, des-*A*-triterpenes; □, des-*E*-hopenes. Numbers before colon indicate carbon chain length, numbers after colon indicate number of double bonds and roman numerals refer to compounds in appendix.

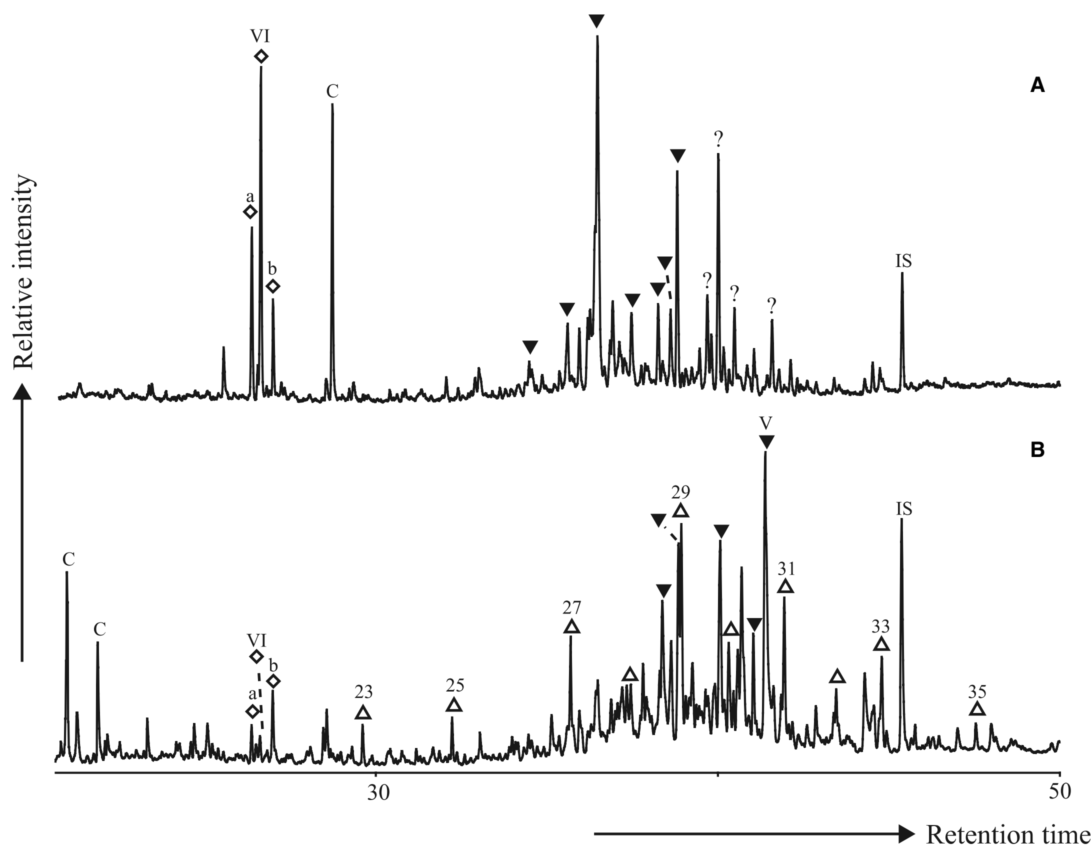


Fig. 5. Total ion current chromatograms of the aromatic hydrocarbon fraction from sample: (A) TDP 6/4-1, 50–60 cm and (B) TDP 1/20-1, 23–32 cm. ◊, aromatic des-*A*-triterpenes; ▼, aromatic pentacyclic triterpenoids; △, *n*-alkanones; ?, unknown; a, des-*A*-26,27-dinoroleana-5,7,9,11,13-pentaene (Trendel et al., 1989; bin Abas et al., 1995); b, des-*A*-26,27-dinorlupa-5,7,9,11,13-pentaene (Freeman et al., 1994); IS, internal standard and C, contaminant. Numbers indicate carbon chain length and roman numerals refer to compounds in appendix.

Bednarczyk et al., 2005). Relatively small amounts of two isomers of 31-hydroxyanhydroBHT (XXII; Talbot et al., 2005) are also present. The presence of these three BHPs was confirmed by the identification of their transformation products (XXIII and XXIV; Talbot et al., 2005) and C_{32} hopanol, after

Table 3
Distributions of *n*-alkanoic acids and *n*-alkanols and BIT indices for Kilwa TDP sediments

Sample	*n*-Alkanoic acids		*n*-Alkanols		BIT
	C_{max} [a]	ACL_{24-32}	C_{max} [a]	ACL_{26-30}	
TDP 1/11-1, 39–50 cm	28	27.6	28	27.9	0.82
TDP 1/20-1, 23–32 cm	28	27.2	28	28.1	0.73
TDP 6/4-1, 50–60 cm	24	25.8	28	27.9	0.85
TDP 2/10-3, 16–30 cm	28	27.9	30	29.0	n.d.[b]
TDP 2/25-2, 53–60 cm	n.d.[b]	n.d.[b]	30	29.2	n.d.[b]
TDP 2/28-2, 6–20 cm	n.d.[b]	n.d.[b]	30	29.4	0.22
TDP 3/4-1, 84–93 cm	24	26.7	30	28.9	0.50
TDP 3/16-2, 73–85 cm	n.d.[b]	n.d.[b]	30	28.8	0.31
TDP 7a/46-1, 30–40 cm	24	26.7	28	28.4	n.d.[b]
TDP 8/11-1, 24–34 cm	24	26.4	30	29.0	n.d.[b]
TDP 7a/54-1, 26–36 cm	28	27.2	28	28.2	0.37
TDP 7a/64-1, 68–82 cm	28	27.4	28	28.6	0.58
TDP 7b/50-1, 30–40 cm	28	27.1	28	28.5	n.d.[b]
TDP 10/13-2, 10–20 cm	24	26.8	28	28.3	n.d.[b]
TDP 10/26-1, 92 cm to TDP 10/26-2, 07 cm	28	27.2	28	28.5	0.44
TDP 9/28-3, 10–20 cm	24	26.5	28	28.4	n.d.[b]

ACL (average chain length) calculated following the method of Schefuß et al. (2003) and BIT (branched and isoprenoid tetraether) following the method of Hopmans et al. (2004).
[a] Carbon number of homologue with highest abundance.
[b] n.d., not determined.

treatment with periodic acid and sodium borohydride (Fig. 9C and D). In contrast, no BHPs were observed in the acetylated total extracts of the selected TDP 3 and 7a samples and their transformation products were not detected after treatment with periodic acid/sodium borohydride.

4. Discussion

4.1. Origin

Organic geochemical analyses of all the sediments reveal a predominance of biomarkers such as C_{16}–C_{35} *n*-alkanols, C_{16}–C_{34} *n*-alkanoic acids and C_{22}–C_{32} ω-hydroxy alkanoic acids (all with even-over-odd predominance), C_{16}–C_{25} *n*-alkanes and C_{25}–C_{35} *n*-alkan-2-ones (with an odd-over-even predominance) and triterpenoids that are typical of higher plants (Eglinton and Hamilton, 1963, 1967; Pant and Rastogi, 1979; Halloway, 1982; Mahato et al., 1988; Wolff et al., 1989; Trendel et al., 1989; Ten Haven et al., 1992; Freeman et al., 1994; Leif and Simoneit, 1995), indicating a predominance of terrestrially derived material. This is in agreement with the palynology, which indicates the presence of substantial plant debris (Pearson et al., 2004). The $\delta^{13}C$ values of the *n*-alkanes range from −29‰ to −32‰ (Table 2), also indicating an origin from higher plant waxes. In addition, the P_{aq} values range from 0.16 to 0.37 (Table 2), comparable to those reported for terrestrial/emergent derived material (Ficken et al., 2000; Mead et al., 2005), again confirming the predominance of terrestrially derived material. The CPIs of the *n*-alkanes range from 3.1 to 5.6 (Table 2), slightly lower than those typically observed for extant plants (>5). This is most likely caused by a minor input of *n*-alkanes with low CPI, but such values are commonly observed in sediments and our values are still consistent with a predominantly higher plant origin. The majority of the terrestrial material is probably transported by fluvial processes (Bird et al., 1995). However, wax particles are also easily sloughed off the surface of leaves by wind and can become airborne (Simoneit, 1977). Substantial amounts of homologous series of long-chain *n*-alkanes, *n*-alkanols and *n*-alkanoic acids have been observed in dust samples (Cox et al., 1982; Eichmann et al., 1979; Gagosian et al., 1981; Schefuß et al., 2003) and, consequently, an input of aeolian origin cannot be excluded.

Besides these terrestrial biomarkers, substantial amounts of bacterial biomarkers such as hopanes, hopenes, hopanoic acids, hopanols and C_{33} DGD are present (Ourisson et al., 1979; Pancost et al., 2001a). These are all typically produced by bacteria during the decay of organic matter, with the hopanoids indicative (although not exclusively so; cf.

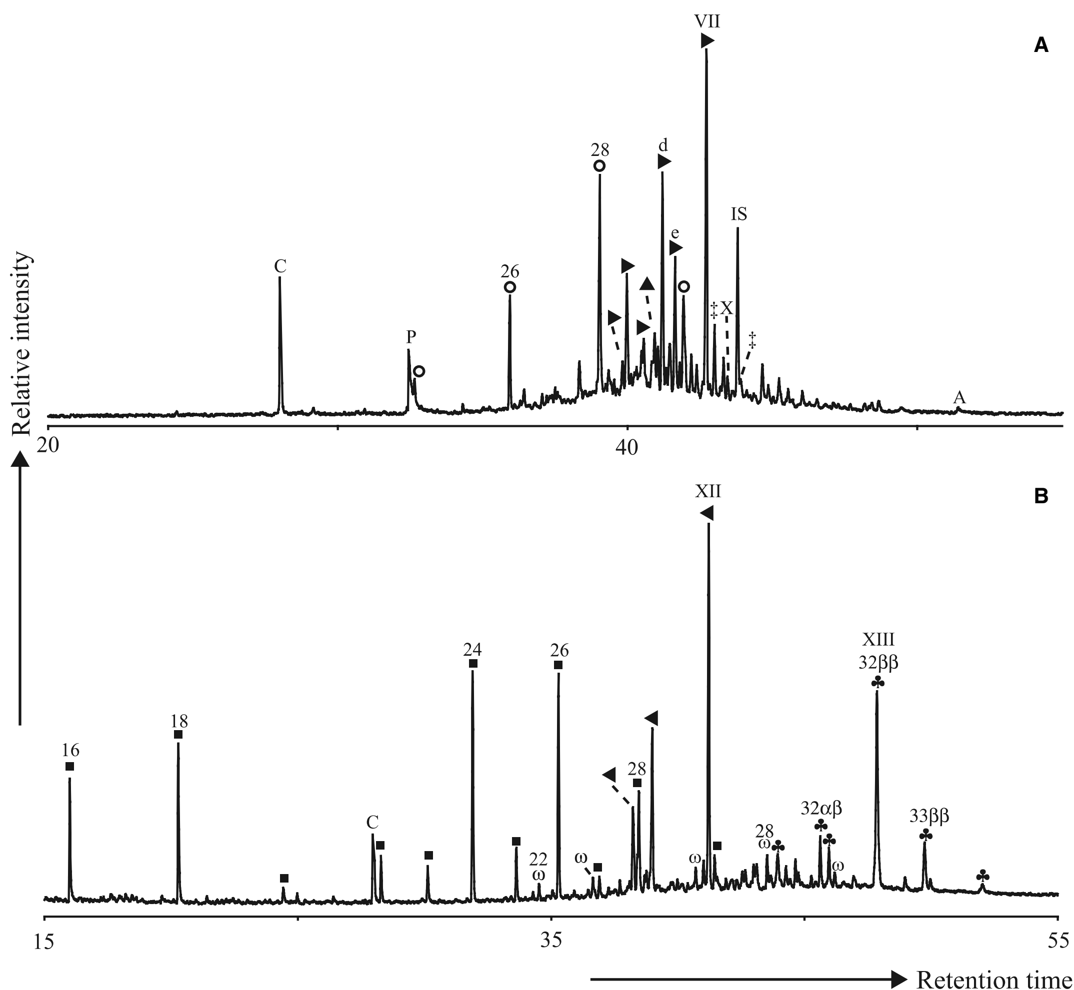


Fig. 6. Total ion current chromatograms of: (A) polar fraction and (B) acid fraction from sample TDP 6/4-1, 50–60 cm. ○, *n*-alkanols; P, polycyclic aromatic hydrocarbons (PAH); ►, triterpenoids; ▲, steroids; ‡, hopanoids; A, archaeol; ■, *n*-alkanoic acids; *ω*, *ω*-hydroxy alkanoic acids; ♣, hopanoic acids; ◄, triterpenoic acids; d, α-amyrin; e, β-amyrin; IS, internal standard; C, contaminant. Numbers indicate carbon chain length, αβ or ββ indicate stereochemistry and roman numerals refer to compounds in appendix.

Thiel et al., 2003; Sinninghe Damsté et al., 2004; Hartner et al., 2005) of aerobic heterotrophs and the C_{33} DGD of sulfate reducing bacteria (SRB). Hence, detection of both C_{33} DGD and archaeol in TDP 1, 2 and 6 indicates the presence of both SRB and archaea (Kates et al., 1993; Koga et al., 1993; Pancost et al., 2001a) which could represent a similar type of consortium as that recently found in cold seeps where methane is oxidized under anaerobic conditions, with sulfate serving as the terminal electron acceptor (e.g. Pancost et al., 2001a,b; Hinrichs et al., 2000; Teske et al., 2002). Compared to other compounds present in the polar fraction, archaeol is not abundant (Fig. 6A). Consequently, no reliable $\delta^{13}C$ value, which would give evidence for the use of methane as carbon source could be obtained. In addition, in contrast to our samples, archaeol is generally more abundant in cold seeps compared to other compounds present in the polar fraction. We therefore suggest that these compounds likely derive from sedimentary heterotrophic sulfate reducers and methanogens involved in the degradation of organic matter, as inferred for the same compounds in Amazon sediments (Boot et al., 2006). Besides these bacterial biomarkers, substantial amounts of (aromatic) des-*A*-triterpenes, des-*E*-hopenes and aromatic triterpenoids occur in TDP 1 and 6 sediments (Figs. 2, 5 and 6). Both the loss of the A or E ring and aromatization are thought to be mediated by microbial activity

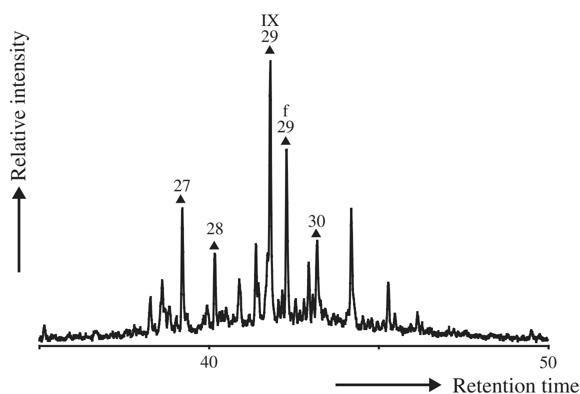


Fig. 7. Partial m/z 231 mass chromatogram, showing methyl steroid distribution of polar fraction from sample TDP 2/10-3, 16–30 cm. ▲, methyl steroids; numbers indicate carbon chain length; f, 24-ethyl-cholestane-3-one or 23,24-dimethylcholestan-3-one; roman numerals refer to compounds in appendix.

(Greiner et al., 1976; Corbet et al., 1980; Lohmann, 1988; Wolff et al., 1989; Trendel et al., 1989; Freeman et al., 1994; Logan and Eglinton, 1994) and the occurrence of these compounds is further evidence for sedimentary microbial activity (Lohmann, 1988; Logan and Eglinton, 1994; Hauke et al., 1993).

Biomarker evidence for a marine input, despite the abundance of foraminifera and coccoliths (Pearson et al., 2004), is limited to steroids and crenarchaeol. The former are present in relatively low abundance and also probably partly derive from terrestrial sources. However, the presence of 4,24-dimethylcholestan-3-one and other 4-methyl steroids is probably indicative of a dinoflagellate input (Withers et al., 1978; Volkman et al., 1990, 1999), consistent with palynological analysis (Pearson et al.,

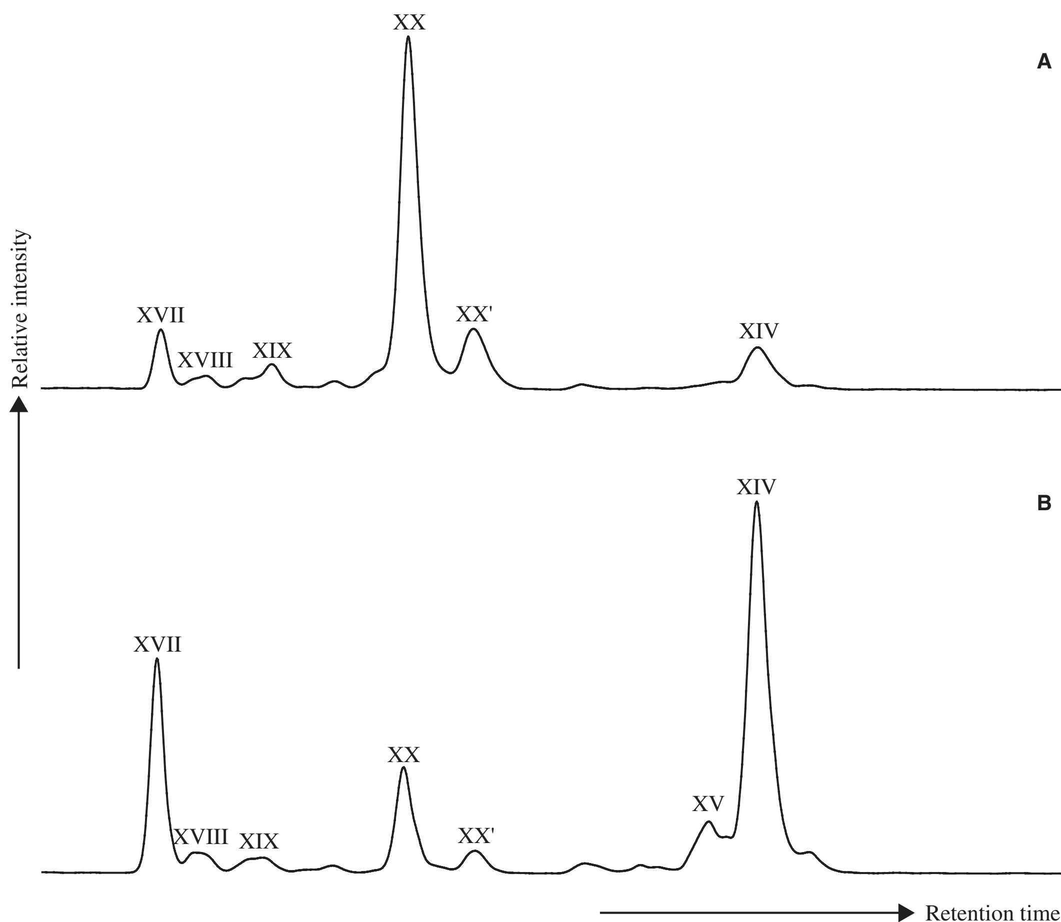


Fig. 8. HPLC/MS base peak chromatograms of tetraether lipids in sample: (A) TDP 2/28-2, 6–20 cm, and (B) TDP 6/4-1, 50–60 cm, illustrating differences GDGT distribution between a younger sample collected at end of the peninsula near Kilwa Masoko and an older sample collected elsewhere. Roman numerals refer to compounds in appendix and compound XX′ is an isomer of XX.

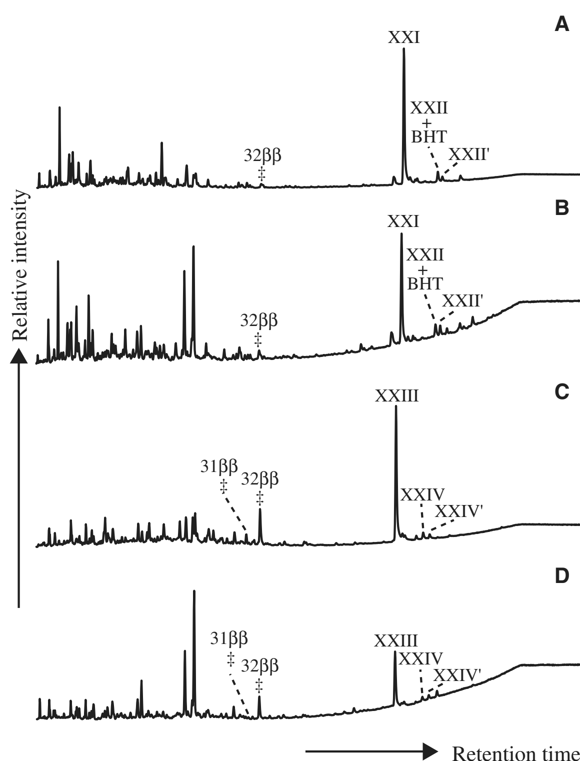


Fig. 9. Partial *m*/*z* 191 mass chromatograms of acetylated total extracts from sample: (A) TDP 1/20-1, 23–32 cm and (B) TDP 2/25-2, 53–60 cm and acetylated periodic acid cleavage products from sample (C) TDP 1/20-1, 23–32 cm and (D) TDP 2/25-2, 53–60 cm, showing the presence of bacteriohopanepolyols in samples collected at end of the peninsula near Kilwa Masoko. ‡, hopanoid; BHT, bacteriohopane-32,33,34,35-tetrol. ββ indicates stereochemistry of hopanoid at C-17 and C-21 and roman numerals refer to compounds in appendix. Compounds XXII′ and XXIV′ are isomers of XXII and XXIV, respectively.

2004), although a contribution from diatoms (Volkman et al., 1993) or prymnesiophytes (Volkman et al., 1990) is also possible.

Isoprenoidal and branched GDGTs most likely have a mixed origin from both marine and terrestrial sources (Sinninghe Damsté et al., 2000; Schouten et al., 2000; Hopmans et al., 2004; Weijers et al., 2004). However, crenarchaeol (XX) is likely derived from marine crenarchaeota and provides further evidence for a marine input; their presence in sediments that are otherwise dominated by terrestrial inputs has been reported previously. Schouten et al. (2000, 2002) indeed found substantial amounts of marine crenarchaeol (XX) in sediments from the Wadden Sea and the North Sea, which are otherwise dominated by terrestrial biomarkers (van Dongen et al., 2000).

The low amounts of marine-derived material could indicate that terrestrially derived material dominates over the OM of marine origin. Alternatively, it cannot be excluded that the oxic conditions experienced by transport through the water column led to an enrichment in the more refractory terrestrial biomarkers relative to the more labile marine biomarkers (Haddad et al., 1992; Harvey, 1994; Santos et al., 1994; Canuel and Martens, 1996; Colombo et al., 1997; Budge and Parrish, 1998; van Dongen et al., 2000). In summary, these OM assemblages clearly indicate a marine setting dominated by higher plant inputs, likely related to fluvial transport processes. The delivery of high amounts of terrestrial organic matter likely stimulated sedimentary microbial activity, including sulfate reduction and possibly methanogenesis.

4.2. Preservation

Decay and diagenesis of organic matter involve the loss of diagnostic (functional group) characteristics of the original biological compounds (Mackenzie et al., 1982; Maxwell and Wardroper, 1982; Brassell et al., 1984; de Leeuw et al., 1989). Most of the changes occur rapidly, initially in the water column, followed by further decay in the microbially active upper zones of the sediment. This diagenetic alteration is often characterised by the loss of a range of different functionalities in the compounds preserved. Thus, the presence of not only relatively large amounts of compounds such as *n*-alkanoic acids, *n*-alkanols and ω-hydroxy alkanoic acids in the sediments of the Kilwa area, but also the occurrence of intact BHPs in TDP 1 and 2 sediments, after such a long period of time (up to 50 Ma), indicates exceptional preservation of organic matter. Although BHPs have a widespread occurrence in the sedimentary record, the only sediments older than 10 Ma in which these compounds have been observed thus far are Upper Jurassic sediments from the Gorodische outcrop (Bednarczyk et al., 2005), oil shales which also show excellent preservation of OM (Carrillo-Hernandez et al., 2003).

Beside the preservation of functional groups, the stereochemistry of bacterially derived hopanoids suggests little or no thermal alteration. Bacteria synthesize hopanoids with the a 17β(H),21β(H) – stereochemistry (or ββ hopanoids). However, sediment extracts often contain 17α (H),21β(H)-hopanes (αβ hopanes) and 17β(H),21α(H)-hopanes (βα hopanes), formed by thermally induced isomerisation (Peters

and Moldowan, 1993, and references therein). In the Kilwa sediments, with the exception of TDP 1 samples, hopanes retaining the natural ββ configuration are dominant (Fig. 3 and Table 2). The presence of relatively high amounts of αβ-hopanes in the TDP 1 sediments suggests higher thermal maturity. However, this is in contradiction with the occurrence of compounds indicative of low maturity, such as BHPs. Furthermore, the absence of αβ 22S hopanoid isomers, (van Duin et al., 1997), suggests that αβ-hopanes derive either from soil bacteria known to contain αβ-hopanes (Rosa-Putra et al., 2001) or from an 'early' acid catalysed isomerisation process comparable to that occurring in peat (Quirk et al., 1984; Pancost et al., 2003). Hence, (part of) these hopanes may have a terrestrial origin.

In summary, the lipid composition, especially the presence of BHPs, and the predominance of hopanes with the natural ββ configuration, all indicate that the sediments in the Kilwa area are generally very immature. This is consistent with inferences that these sediments have never been deeply buried (e.g. Pearson et al., 2004). Moreover, the clays have a very low porosity and are largely impermeable to migrating fluids, preventing the OM from (bio)degradation. The excellent preservation of both organic matter and planktonic and benthic foraminifera shells (Pearson et al., 2001, 2004) in these sediments makes them valuable for tropical palaeoclimate studies.

4.3. Differences between samples

All the sediments have a generally comparable distribution of biomarker sources, with a predominance of biomarkers from terrestrial sources, substantial amounts of bacterial biomarkers and low amounts of marine-derived biomarkers. In addition, the lithological composition indicates that all the sediments are dominated by the same silty claystone assemblage (Pearson et al., 2004). However, there are significant differences between the specific biomarker distribution patterns in the two sets of sediments. The first set consists of the TDP 1, 2 and 6 sediments, collected from the end of the Kilwa peninsula near Kilwa Masoko (Fig. 1) and ranging in age from 30 to 50 Ma. The second set includes the other sediments, all of which are older (up to 70 Ma old). There are substantial differences in the relative amounts of the terrestrial lipids, as shown, for instance, by the BIT index (Table 3), but most of the differences appear within the microbial biomarkers. First, in contrast to most samples, which contain the commonly observed C_{27}, C_{29}, C_{30} and C_{31} hop-17(21)-enes and hop-13(18)-enes, the hopenes from the Kilwa peninsula sediments are dominated by the tentatively identified dinorhopenes (Fig. 3). Second, the Kilwa peninsula sediments contain substantial amounts of (aromatic) des-*A*-triterpenes, des-*E*-hopanes, aromatic pentacyclic triterpenoids and BHPs, which are absent from or present in relatively low amounts in the other sediments. Third, archaeol and the C_{33} DGD, indicators for methanogens and SRB, respectively, are only present in the sediments from the Kilwa peninsula (NB archaeol is not a specific biomarker for methanogens and occurs in other archaea, such as hyperthermophiles and hypersaline archaea, although the latter are unlikely biological precursors in this case).

An explanation for these differences could be that the younger sediments from the Kilwa peninsula are less degraded than those from other sites. Thus, the presence of more labile functionalized compounds, such as archaeol, C_{33} DGD and BHT, in the younger sediments might not reflect a difference in the palaeodepositional environment. However, differential degradation would not explain the differences in BIT ratios or the presence/absence of compounds such as the tentatively identified dinorhopenes. Thus, we suggest that the differences record variations in depositional conditions between the two sample sets.

Potential differences in depositional conditions include the nature or quantity of terrestrial organic matter inputs and/or the redox state within the water column or sediments from the basin. Nowadays, the Kilwa area is partly characterized by large amounts of mangrove vegetation and palynology indicates a past contribution of mangroves (Pearson et al., 2004). It is possible that the differences observed between the two sample sets could be due to different proportional inputs from mangroves and/or submerged freshwater/marine derived organic material and strictly terrestrial higher plants. Although there was a higher proportion of terrestrial material in the younger Kilwa peninsula sediments and despite the fact that a difference in terrestrial organic matter source cannot be completely excluded, the absence of mangrove biomarkers, such as taraxerol and its degradation products (Versteegh et al., 2004) together with the relatively low P_{aq} (Table 2) makes a variation in contributing mangroves and/or submerged sources unlikely.

Alternatively or additionally, recent research suggests that the depositional environments of the two sample sets were different (Pearson et al., 2004). The

planktonic to benthic foraminifer ratios (*P*:*B* ratios) indicate that the sediments of the second sample set were deposited in an open shelf environment with a substantial water depth. In contrast, the depth of the water column of the younger Kilwa peninsula sediments, inferred from the *P*:*B* ratios, is less clear to evaluate. The *P*:*B* ratios in the TDP 2 sediments also indicate an open shelf environment with a substantial water depth, whereas the *P*:*B* ratios in TDP 1 and 6 sediments indicate a relatively more shallow, anoxic, possibly estuarine or deltaic, setting (Pearson et al., 2004). This shallower environment would probably be associated with a relatively higher influx of terrestrially derived organic matter, and consequently a relatively high BIT index (Hopmans et al., 2004). A shallower water column depth would also imply a shorter exposure to oxidative degradation and thus better preservation. This could, for instance, partly explain the differences in biomarker assemblages brought about by microbial transformation, such as the (aromatic) des-*A*-triterpenes in the TDP 1 and 6 sediments, formed by microbial alteration of precursor compounds of higher plant origin. In addition, anoxic conditions would favour sulfate reduction and possibly methanogenesis, explaining the presence of compounds such as C_{33} DGD and archaeol. Thus, it appears that the depositional environment shifted from a relatively open shelf environment with a substantial water depth to a shallower setting.

Regardless of the precise differences in depositional environment, they could have been caused by temporal evolution of the system or simply reflect the geographical variability between the sites. As mentioned above, the sediments from the first set were all drilled on the end of the peninsula relatively close to Kilwa Masoko, whereas the other sites were drilled further north (Fig. 1 and Table 1). However, the distances between the sampling sites are most likely too short to cause differences which would have persisted over tens of millions of years. Instead, we suggest that the change from a relatively open shelf environment with a substantial water depth to a shallower setting was caused by temporal evolution of the depositional environment.

5. Conclusions

Organic geochemical analysis of sediments from the Kilwa area, Tanzania, reveals biomarkers of predominantly terrestrial and bacterial origin. Evidence for marine productivity is limited to crenarchaeal marine GDGTs and algal steroids, present in relatively low abundances and, in the case of the steroids, also probably partly derived from terrestrial sources. These organic matter assemblages suggest a marine setting dominated by higher plant inputs likely related to fluvial processes. The delivery of high amounts of terrestrial organic matter likely stimulated sedimentary microbial activity, including sulfate reduction.

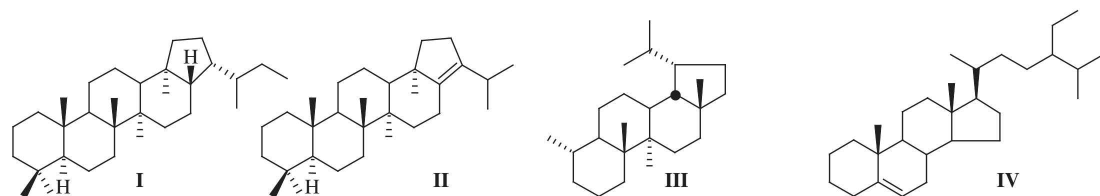
The lipid preservation generally reflects an immature thermal history. Many biomarkers have still retained functionality even after 30–70 million years. This is in good agreement with the exceptional preservation of foraminifera and nannofossils in these sediments and can probably be attributed to the very low permeability and burial depth. This excellent preservation also indicates that the sediments could be useful for tropical palaeoclimate studies.

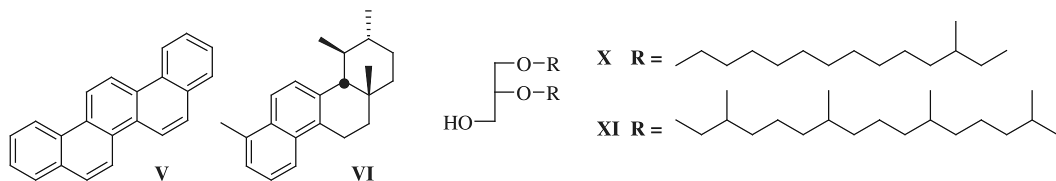
Within the sample set there is a clear distinction between relatively young sediments collected on the end of the peninsula (TDP 1, 2 and 6) and the rest of the sample set, indicating differences in depositional environment. These differences likely reflect an evolution of the depositional area from an open marine environment to a more shallow setting over time.

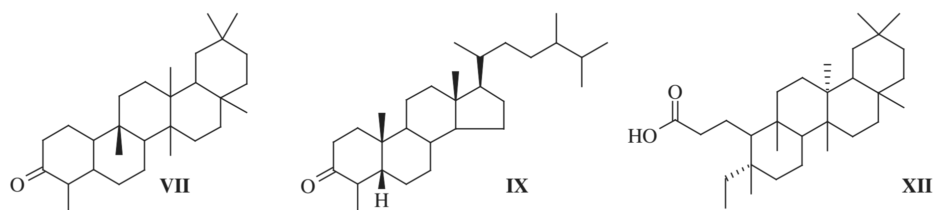
Acknowledgements

This project was funded by the UK Natural Environment Research Council (NERC) through Grant NER/A/S/2001/01213. The authors thank Dr. P. Schaeffer and Prof. Dr. J.S. Sinninghe Damsté for their assistance in the identification of the Des-*A*-triterpenes and Des-*E*-hopenes and C_{28} hopenes, respectively. In addition, we thank Drs. T. Elliot, C.J. Nicholas and J.M. Singano and the other members of the Tanzania Petroleum Development Corporation for scientific and logistic support, Drs I. Bull and R. Berstan for technical assistance, NERC for funding the Bristol node of the Life Sciences Mass Spectrometry Facility (Agreement No. F14/6/13/01; http://www.chm.bris.ac.uk/lsmsf/index.html) and for provision of funding (HMT). We are also grateful to Mr. P. Donohoe (Newcastle) for technical assistance with GC–MS, The Science Research Infrastructure Fund (SRIF) from HEFCE for funding the purchase of the ThermoFinnigan LCQ ion trap mass spectrometer and Mr. M. Woltering and Dr. E. Hopmans (NIOZ) for technical assistance with GDGT analysis. Finally, we thank Prof. G. Wolff and Dr. J. Werne for reviewing the manuscript.

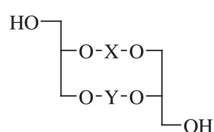
Appendix







XIV X = a, Y = a
XV X = a, Y = b
XVI X = b, Y = b
XVII X = c, Y = c
XVIII X = c, Y = d
XIX X = d, Y = d
XX X = e, Y = f



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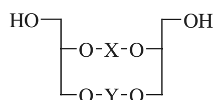

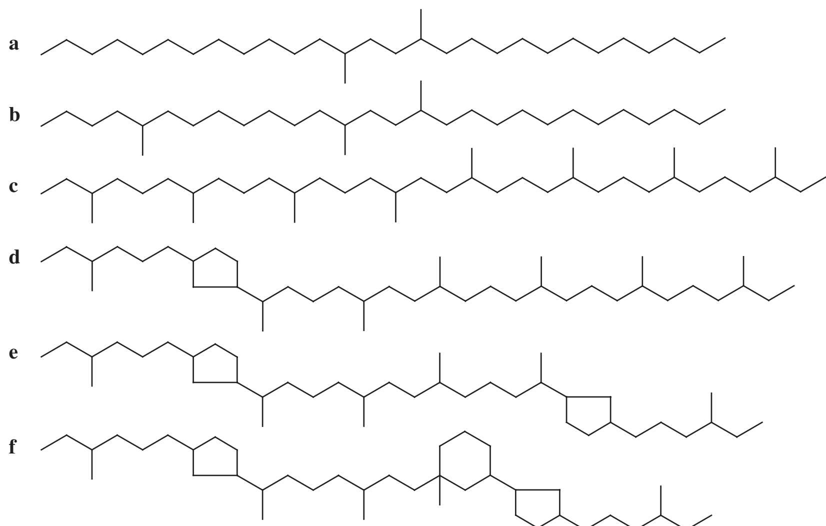

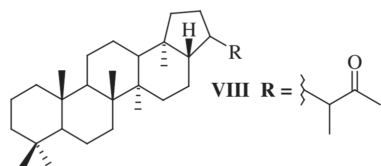

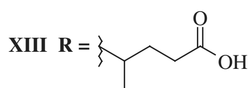

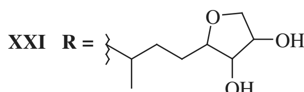

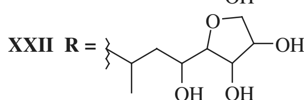

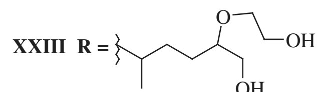

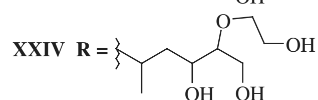

Associate Editor—**P. Schaeffer**

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