PRESENCE OF GEOCHEMICAL PENTACYCLIC TRITERPANES IN A CRETACEOUS SEDIMENT FROM THE BORNU BASIN, NORTHEAST NIGERIA

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Abstract

The Chad basin belongs to a series of Cretaceous and later rift basins in Central and West Africa whose origin is related to the opening of the Atlantic. Despite the lack of outcrops in the area, works on the evolution and the stratigraphy of the Bornu basin have been published by many researchers. Most of these studies were based on boreholes and exploratory oil wells data as well as correlation from the adjoining basins like the upper Benue trough. The stratigraphic succession in the Bornu basin commenced in the Albian with deposition of the Bima Sandstones resting unconformably on the Precambrian basement. It is a sparsely fossiliferous, poorly sorted, medium to coarse-grained feldspathic sandstone known regionally, as the "Continental Intercalaire". The sample was collected from ditch-cutting from Kasade-1 well. GC-MS analysis was undertaken of a waxy, paraffinic, low-sulphur source rock from Bornu Basin, apparently deriving mainly from bacterially reworked terrestrial organic matter deposited in a lacustrine environment. In addition to the regular C_{27}-C_{35} hopanes, a number of pentacyclic triterpanes was identified in the range C_{29}-C_{32}. These components appeared to be members of at least two homologous series, one of which has been previously postulated to be 18α (H)-neohopanes. A further, previously unreported, series is characterized by a relatively intense molecular ion response during GC-MS analysis. A bacterial origin is suggested for these pentacyclic triterpane series, the presence of which may reflect a particular set of sedimentological conditions.

Keywords: Biomarkers, Pentacyclic triterpane, Sterane, Depositional environment Lacustrine, Bornu Basin.

Introduction

The Bornu basin constitutes the southeastern section of the Chad basin, which is a large structural depression common to five countries namely Cameroon, Central Africa, Niger, Nigeria and Chad. The Chad basin belongs to a series of Cretaceous and later rift basins in Central and West Africa whose origin is related to the opening of the Atlantic (Burke, 1976; Benkhelil, 1989; Fairhead andBlinks, 1991; Genik, 1993; Hartley and Allen, 1994; Obaje et al., 2004). Representing about one-tenth of the Chad basin, the Bornu basin covers the whole of Bornu State, part of Yobe, Bauchi and Gombe States in Nigeria (Fig. 1).

It is the most studied among the Nigerian inland basins. The vast amount of data generated over the years is being evaluated to assist in designing a proper roadmap for future exploration programme. Twenty three (23) exploratory oil wells have so far been drilled by the Nigerian National Petroleum Cooperation (NNPC) through its frontier exploration service (NAPIMS) and only gas shows were encountered. Nigeria is the sixth world oil producer with its large reserve of the Niger Delta. Today, any oil company has full confidence to invest in the Niger Delta.

The Nigeria inland basins are therefore classified as high risk areas. However with the recent discovery of oil in Sudan and Chad in similar basins as the Bornu basin, exploration in the Nigerian inland basins can be encouraged.

In the absence of sourced oil samples, information on sources of organic material and depositional environment was sought from organic geochemical analysis of the potential source rocks. Biomarker analysis can provide much useful information (e.g., Mackenzie, 1984; Mello et al., 1988; Pu and Baisheng, 1988; Aichner et al., 2010b).
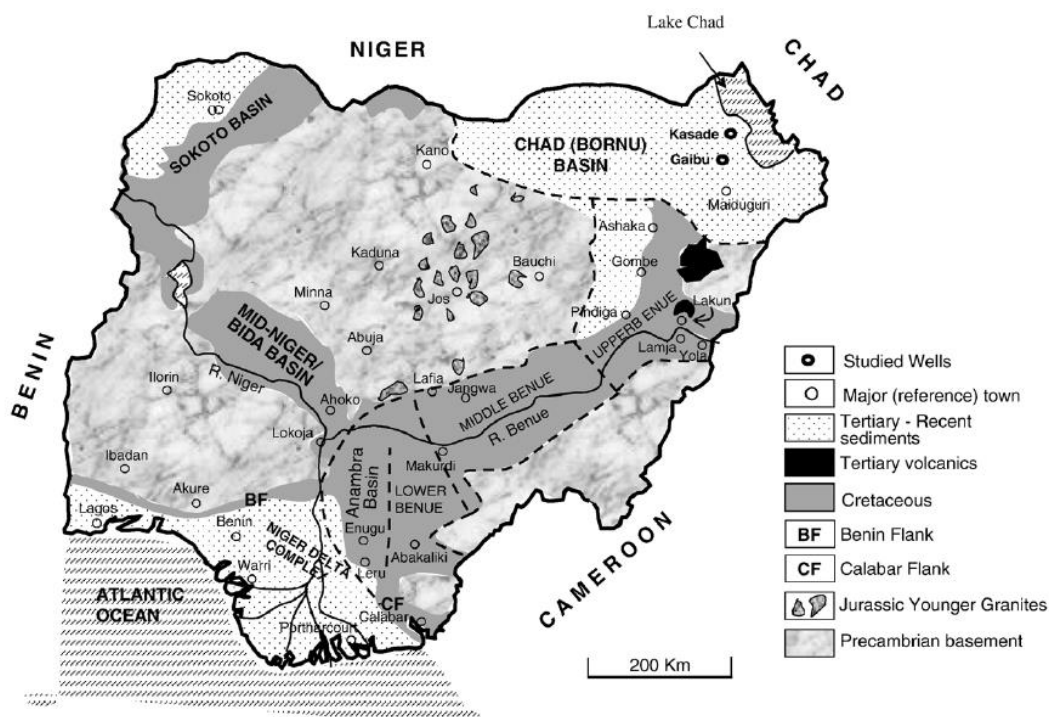
Fig. 1: Sketch geological map of Nigeria showing the location of the Nigerian sector of the Chad Basin and the relationship to other inland basins (modified from Obaje et al., 2004).

For example, among the triterpenoidal hydrocarbons a number of source and depositional environment indicators has been recognized. In addition to the ubiquitous C_{27}-C_{35} bacteriohopanes (Ourisson et al., 1979; Cvejic et al., 2000; Barbanti et al., 2011), there are some further groups of bacterially derived hydrocarbons, which also appear to be characteristic of restricted depositional environments. These comprise C_{32}-C_{35} benzohopanes (Hussler et al., 1984) and their saturated counterparts (Connan and Dessort, 1987; Douka et al., 2001; Duan et al., 2004), and the C_{27}-C_{35} D-ring aromatic 8, 14-secohopanoids (Hussler et al., 1984; Eickhoff et al., 2014).

Bacterially derived methylated and demethylated hopane series have been found to be less widely distributed than the regular hopanes, and can prove useful for correlation purposes. The demethylated species, which have been observed in non-biodegraded oils as well as in certain heavily biodegraded oils, may result from specific types of bacteria, while the methylated series may reflect particular sedimentological conditions as well as certain bacterial types (Howell et al., 1984; Seifert and Moldowan, 1986; Hu et al., 2012).

Non-hopanoidal triterpanes are generally less widely distributed than hopanes, and can provide useful information. Gammacerane, a C_{30} pentacyclic triterpane with a six-membered E-ring, probably of protozoan origin, appears to become quantitatively important with the development of hypersaline conditions, (Powell, 1986; Katz and Liu, 2014). Many other C_{30} species possessing a six membered E-ring (e.g., friedelane, taraxerane, ursane) represent terrestrial higher plant inputs (e.g., Simoneit, 1986; Rˇezanka et al., 2010). An important member of this group is 18α(H)-oleanane, which derives from higher plant oleanenes and appears to reflect a near-shore depositional environment (e.g., Ekweozor, 1979; Hoffmann et al., 1984; Villanueva et al., 2014).

The following account reports the detection of presence of pentacyclic triterpanes in the sample from well Kasade-1 in the Bornu Basin. These components are discussed in the context of the sources of organic material and the depositional environment inferred from organic geochemical analyses.

Stratigraphic Setting

The Bornu basin is the Nigerian sector of the Chad basin (Fig. 1). The Chad basin belongs to the Western Central Africa Rift (WCARS) system that was formed in response to the mechanical separation of the African crustal blocks in the Cretaceous (Genik, 1992). Despite the lack of outcrops in the area, works on the evolution and the stratigraphy of the Bornu basin have been published by many researchers among which are Carter et al. (1963), Matheis (1976), de Klasz (1978), Petters and Ekweozor (1982), Wright et al. (1985), Avbovbo et al. (1985), Genik (1992), Okosun (1992, 1995), Olugbemiro et al. (1997), and Obaje et al. (2004) among others. Most of these studies were based on boreholes and exploratory oil wells data as well as correlation from the adjoining basins like the upper Benue trough.
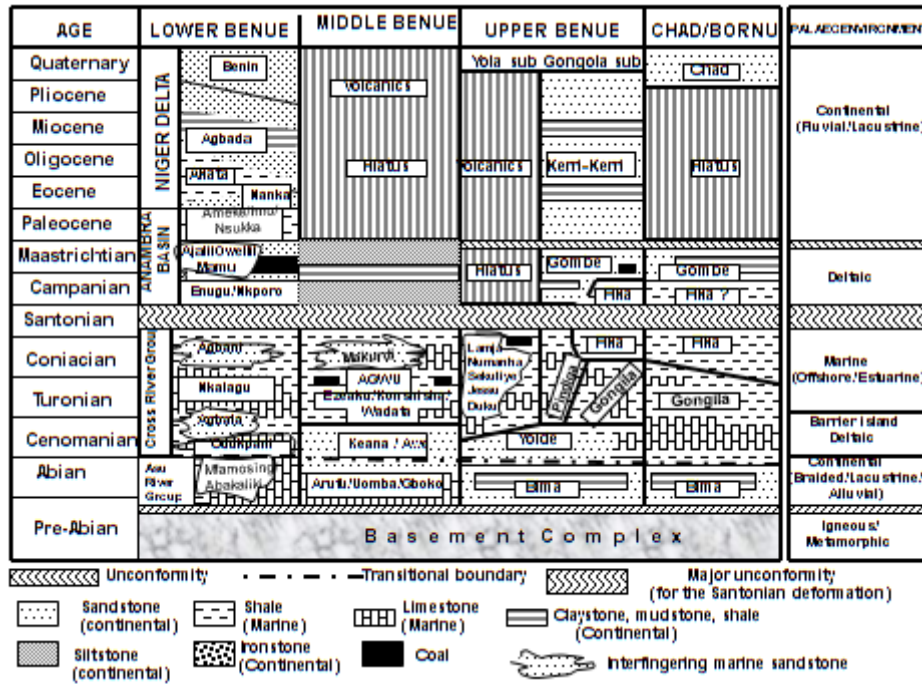
Fig. 2: Stratigraphic successions in the Benue Trough, the Nigerian sector of the Chad Basin and the relationship to the Niger Delta (Obaje et al., 2006).

The stratigraphic succession in the Bornu basin commenced in the Albian with deposition of the Bima Sandstones resting unconformably on the Precambrian basement (Fig. 2). It is a sparsely fossiliferous, poorly sorted, medium to coarse-grained feldspathic sandstone known regionally, as the "Continental Intercalaire" (Wright et al., 1985). The Bima Sandstone is overlain by the GongilaFormation, which is composed of calcareous shales and sandstones deposited in a shallow-marine environment.

The deposition of this formation is taken to mark the onset of the marine incursion into the Chad basin in the Turonian (Olugbemiro et al., 1997; Obaje et al., 2004). The Fika (Shale) Formation overlies the Gongila Formation and was deposited during the continued marine transgression in the Turonian–Coniacian. During the Maastrichtian, the Gombe Sandstone was deposited on top of the Fika Formation in an estuarine/deltaic environment. It contains intercalation of siltstones, shales, and claystones but not the coal seams reported from the upper Benue trough (Obaje et al., 1999, 2004). The Tertiary period was characterized by the deposition of the Keri–Keri Formation outside the Bornu basin. Hence, the uppermost Pliocene-Pleistocene period Chad Formation lies unconformably on top of the Gombe Sandstone. The Chad Formation, which obscures older sediments consists of fluviatile and lacustrine clays and sands, with lenses of diatomite up to a few meters thick (Wright et al., 1985).

Materials and Methods

The ditch-cutting sample collected from Kasade-1 well was sieved-washed, dried and pulverized. The sample was solvent extracted by means of an Accelerated Solvent Extractor (ASE) using *iso*hexane and acetone in a 9:1 ratio.

Isolation of hydrocarbon fractions

Hexane (1 ml) was added to a sample of extract (100 mg), the mixture was agitated, and centrifuged (10 min at 3000 rpm) and the supernatant liquid was removed from the precipitated aspaltenes. Resins (i.e., polar NSO compounds) were then removed from the hexane-soluble fraction by column chromatography on alumina (Merck ®, Brockman activity I), the total hydrocarbon fraction being eluted with dichloromethane (three times the volume of the alumina). The eluate was reduced to dryness on a rotary evaporator.

Various fractions were obtained from the total hydrocarbons fraction by TLC on silica gel (Merck ® *60G,* 0.4 mm, pre-eluted for 24 h with dichloromethane prior to re-activation) and elution with hexane. Bands were isolated by reference to standards: total aliphatics R_f> tri-decylbenzene; total aromatics $R_f \leq$ tri-decylbenzene; mono/triaromatic steroidal hydrocarbons phenanthrene $\leq R_f <$ eicosane. Branched/cyclic saturate fractions were obtained from aliphatic hydrocarbon fractions by urea adduction.

GC and GC-MS analysis

Hydrocarbon fractions were analysed using a Carlo Erba ® Mega 5360 gas chromatograph (GC) fitted with a splitless injector and a FID. A 25 m×0.25 mm i.d., 0.25 μm WCOT 5% phenylmethylsilicone (bonded) fused silica column (Durabond ®, DB-5) was used with helium carrier gas (2.2 kg cm^{-2} – approximately 1.2 ml min^{-1}). Samples were injected in hexane solution (1.0 μl). A typical temperature programme for the GC was: 1 min at 60°C, then an increase to 300°C at 8 ° min^{-}1, followed by 20 min at 300°C. Quantification of components was achieved using a Laboratory Data Control ® (LDC) 308 integrator. Gas chromatography-mass spectrometry (GC-MS) analyses were performed using the same GC, but using a cooled, on-column injector.

Samples in hexane solution (0.5 μ) were injected onto a 30 reX0.32 mm i.d. WCOT fused silica column, with the column effluent being taken through to the ion volume of a Finnigan ® INCOS 50 quadrupole mass spectrometer (MS) via a flow restrictor in the form of approximately 1 m of uncoated fused silica (0.2 mm i.d., Scientific Glass Engineering ®).

Bonded stationary phases (0.17 μm coatings; Hewlett Packard ®) were either methylsilicone (for aliphatic fractions) or 5% phenylmethylsilicone (for aromatic

fractions). Helium carrier gas was used (0.7 kg cm^{-2} – approximately 2.4 ml min^{-1}). The temperature programme of the GC was a rise of 6 ^{o}min^{-1} over the range 80-300°C. The MS was operated in electron impact (EI) mode under the following conditions: emission current 800 μA, electron energy 30 eV, transfer-line temperature 270°C, ion source temperature 100°C. GC-MS analyses involved either wide mass ranges (45-500 amu) for major component identification, or selected ion monitoring (SIM) for biomarker hydrocarbon distributions, both at scan rates not exceeding 1 s scan^{-1}

Elemental analysis

Sulphur, nickel and vanadium levels were measured by direct aspiration (following 2:1 dilution with white spirit) into the source of an ICP emission spectrophotometer.

Results and Discussion

Bulk geochemical characteristics

General data on the extract from Kasade-1 well(hereafter called Oil Kasade-1)are given in Table I. Its waxy consistency and low sulphur content are consistent with generation from a lacustrine source rock containing terrestrial plant material (Hedberg, 1968; Tissot and Welte, 1984).

In addition the aromatic hydrocarbon content is low (14% of total hydrocarbons), and *n*-alkanes account for a substantial proportion of saturates (81%), suggesting a paraffinic classification. The oil is light in terms of its ^{13}C content (Table 1), which could reflect generation from terrestrial organic material (Schoell, 1984; Sinninghe Damste' et al., 2014). In a plot of aromatic versus saturated hydrocarbon δ^{13}C values, oil Kasade-1lies fractionally above the waxy line of Sofer (1984; van Winden et al., 2012). Similar isotopic data have been noted for Chinese oils derived fromfreshwater lacustrine environments (e.g. Philpet al., 1989).

Ni and V levels are extremely low for oil Kasade-1, as found in generally low-sulphur oils from detritalsand-shale series (Tissot and Welte,1984). As these metals are usually associatedwith the resin and asphaltene fractions of oils(Tissot and Welte, 1984), their low levels inoil Kasade-1 are, at least in part, due to the lowabundance of resins and asphaltenes. Theavailability of metal ion species during diagenesisis also important, in which Eh/pHconditionsplay a dominant role, and which can beevaluated from V/(V+Ni) values (Lewan,1984; Hu et al., 2012). This ratio for oil Kasade-1 corresponds toLewan's Regime II, examples of which, again with low sulphur, are oils from Tertiary reservoirs in eastern Nigeria (Lewan, 1984).

GC analysis of aliphatic and aromatic hydrocarbons

n-Alkanes predominate in the total hydrocarbons chromatogram (Fig. 3). Superimposed on a non-specific catagenetic distribution is a higher plant contribution,characterized by an odd/even predominance>*n*-C_{20} (carbon preference index--CPI--1.12, Table 1) (Eglinton and Hamilton, 1967).Minor contributions from alkylnaphthaleneswere discernible (Fig. 3). A Pr/Ph ratio of 4.51suggests that the organic matter from which oil Kasade-1was derived may have been deposited inrelatively oxidizing conditions (Didyk et al.,1978), although the limitations of the ratio inthis application are acknowledged (Ten Havenet al., 1987). A Pr/Ph ratio of > 1 suggeststhat hypersalinity did not develop (Powell,1986), and there was no indication of hypersalinityfrom biomarker distributions (Ten Haven et al., 1985; Powell, 1986). In addition,Pr/Ph values > 3, as found for Kasade-1,havebeen shown to be characteristic of oils derivedfrom lacustrine facies associated with floodplains and coal-bearing sequences (Powell,1986). Such oils are derivedfrom organic matter of higher plant originwhich has undergone some oxidation priorto preservation, and are typified by oils fromthe Eromanga Basin of Australia (Powell,1986; Volkman, 2014).

Table 1: Gross composition data and biomarker parameters for source rock sample from well Kasade-1

Parameter	Value	Parameter	Value
As proportion of extract:		GC-MS analysis[S]:	
Asphaltenes (%)	28	Terpenoidal maturity ratios:	
Resins (%)	4	Ts/(Ts+Tm) (%)	62
Hydrocarbons (%)	68	30αβ/(30αβ+ 30αβ)(%)	91
S (%)	0.1	32αβS / (32αβS + 32αβR) (%)	55
Ni (ppm)	0.06		
V (ppm)	0.6	Steroidal maturity ratios:	
V/(V+Ni) (%)	~90	29 ααS / (29ααS + 29ααR) (%)	69
$\delta^{13}C$ whole extract (‰)	-30.9	29ββ/ (29ββ+ 29αα) [6] (%)	62
$\delta^{13}C$ sats (‰)	-31.44		
$\delta^{13}C$ aromatics (‰)	-29.53	Terpenoidal source ratios:	
		29αβ/ (29αβ+ 30αβ) (%)	39
As proportion of hydrocarbons:		23-3/(23-3+24-4) (%)	45
saturates (%)	86	23-3/(23-3 + 30αβ) (%)	5.5
aromatics (%)	14	29-5[d]/(29-5[d]+ 30αβ) (%)	14
		30-5[c]/(30-5[c] + 30αβ) (%)	21
GC-FID analysis:		01/(01 + 30αβ) (%)	10
n-alkanes (% of sats)[1]	81	30αβ/Zhopanes [7] (%)	17
Hopane (% of sats)	0.28	∑hopanes/∑steranes 7	22
Pristane/phytane	4.51		
Heptadecane/pristane	1.72	Sterane source ratios:	
CPI (*n*-C_{22} to *n*-C_{32}) [2]	1.12	29DβαR/(29DβαR + 29ααR) (%)	80
MPI-1[3]	0.54	27ββ: 28ββ: 29ββ [8] (%)	21:26:53
R_c (%)[4]	1.31		

[1]Based on resolved components in gas chromatograms.

[2]CPI=0.5[(23+25+27+29+31)/(22+24+26+28+30)+
(23+25+27+29+31)/(24+26+28+30+32)], where numbers represent n-alkane chain lengths.

[3]M ethylphenanthrene index (Radke and Welte, 1983), where MP- 1 = 1.5 (2MP + 3MP) / (P + 1MP + 9MP).

[4]Calculated vitrinite reflectance (Radke and Welte, 1983), where Rc = 0.6 (MPI- 1) + 0.4.
[5]See Table II for identification of components; quantifications based on peak areas of *m/z* 191 response for terpanes and *m/z 217* response for steranes.

[6]20S + 20R isomers.

[7]Sum of hopanes from Ts to 35αβR and sum of steranes from 27DβαS to 29ααR.

[8]Based on *m/z* 218 response for 20S + 20R isomers.
Sats = saturated hydrocarbons.

This inference for the oil from Niger Delta,which lies just offshore, is consistent with theoccurrence of predominantly coaly, organic-richdeposits in the onshore region of Bornu Basin (Olugbemiro et al., 1997; Moumouni et al., 2007; Sinninghe Damste' et al., 2014).
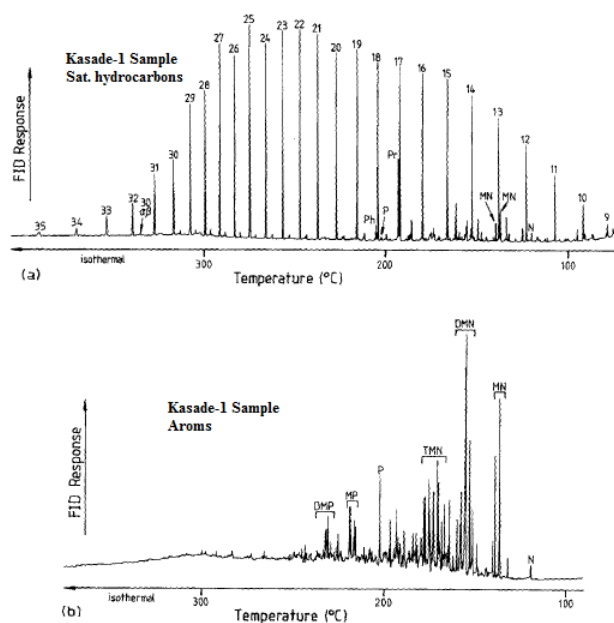

Fig. 3: Gas chromatograms of (a) total hydrocarbon and (b) aromatic hydrocarbon fractions from Kasade-1 sample.

Numbers represent carbon numbers of *n*-alkanes; N/MN/DMN/TMN = naphthalene and its methyl, dimethyl and trimethyl homologues; P/MP/DMP=phenanthrene and its methyl and dimethyl homologues; Pr = pristane; Ph = phytane; $30\alpha\beta$ = 17α (H), 21β(H)-hopane.

The aromatic hydrocarbons of the oil comprise almost entirely alkylated napththalene and phenanthrene species (Fig. 3), with only very minor contributions from sulphur-containing compounds, such as dibenzothiophene, as expected from the low sulphur content of the oil. All the data discussed so far are consistent with the lacustrine depositional environment proposed for Bornu Basin in preliminary geological studies (Olugbemiro et al., 1997; Moumouni et al., 2007).

General biomarker source and depositional environment indications

GC-MS analysis of the branched/cyclic saturates fraction was undertaken to provide additional biomarker information on sources of organic matter and diagenetic conditions. An extended series (to > C_{40}) of head-to-tail (regular) and head-to-head (irregular) acyclic isoprenoids was detected (Fig. 4a), with similar distributions to those reported for offshore Western Mediterranean oils (Albaiges, 1980). The head-to-head series is believed to derive from archaebacterial (possibly thermoacidophilic) cell wall lipids (Albaiges, 1980; Wang and Liu, 2012).

The dominance of C_{29} steranes (Table 1 and Fig. 4b) is consistent with indications from *n*-alkane distributions of a contribution of terrestrial higher plant material to the source of oil Kasade-1(Huang and Meinschein, 1978). A significant contribution from diasteranes was also noted (Fig. 4b), the origins of which are attributable to clay catalyzed rearrangement of sterenes during diagenesis (Ensminger et al., 1978). Aromatic steroids were not detected in the oil, apart, perhaps, from traces of the C_{20} and C_{21} triaromatic components. This absence is unlikely to be due to biodegradation, as aromatic steroids are relatively resistant c.f. steranes and hopanes (Wardroper et al. 1984), or to water washing, as other aromatic components did not show any signs of such effects. It may be due to the preferential formation of diasteranes rather than C-ring monoaromatics during diagenesis (Mackenzie, 1984; Volkman, 2014). A relatively high value of 62% for the $\beta\beta$sterane ratio (Table 1) may also be due to rearrangement reactions at an early stage of diagenesis (Mackenzie, 1984) or, in part, to other factors, such as a contribution from a residual biodegraded oil within the reservoir. While high diasterane concentrations have also been attributed to the effects of migration of oil over large distances (Seifert and Modowan, 1981; Welander and Summons, 2012), such an explanation is thought unlikely here, as petroleum derived from lacustrine sources is often found to be trapped relatively close to

the source rock. The smaller scale of the stratigraphic relationships tends to restrict petroleum migration in lacustrine sequences (Yuretich, 1988; Katz and Liu, 2014).

Terpane distributions, dominated by bacteriohopanes, are shown in Fig. 4c. Series of C_{19}-C_{26} tricyclic diterpanes and various pentacyclic triterpanes were also detected. Among the latter was 18α (H)-oleanane, a terrestrial biomarker usually indicative of a nearshore depositional environment at such relative concentrations (e.g. Ekweozor et al., 1979; Hoffmann et al., 1984; Riva et al., 1986; Mello et al., 1988). Its occurrence seems to be restricted to Tertiary/Late Cretaceous sediments and is probably associated with the evolution of the angiosperms (Philp and Gilbert, 1986; Riva et al., 1988). It is possible, therefore, that oil Kasade-1was sourced in Tertiary sediments.

A relatively high hopane/sterane ratio (Table 1) is indicative of a significant bacterial lipid input, probably resulting from bacterial reworking of terrestrial organic material, which can be associated with lacustrine environments (e.g. Mello et al., 1988; Eickhoff et al., 2014). While an algal contribution to the source organic material cannot be discounted, there was no biomarker evidence for such an input (e.g. no 4-methylsteranes or botryococcanes were detected). The main contributors appear, therefore, to be higher plants and bacteria, which is consistent with carbon isotope data (Table 1).

Identification of pentacyclic triterpane series
In addition to the ubiquitous regular hopanes, a number of other C_{27}-C_{31} pentacyclic triterpanes was detected (27-5 to 31-5, Fig. 4c), the carbon numbers of which were confirmed by GC-MS-SIM analysis of molecular ions. Mass spectra of the four major components, 29- 5[c], 29-5[d], 30-5[a] and 30-5[c], are given in Fig. 5, and are similar to those of the regular hopanes.

The fragment ions up to *m/z* 200, particularly the dominant *m/z* 123 and 191 ions, indicate that all four components share the same AB ring structure and substitution pattern exhibited by many triterpanes, including the hopanes. Higher mass fragment ions suggest that all four compounds possess the hopanoidal pentacyclic ring skeleton. However, the occurrence of significantly more intense molecular ions than in the regular hopanes indicates different substitution patterns in the DE-rings.
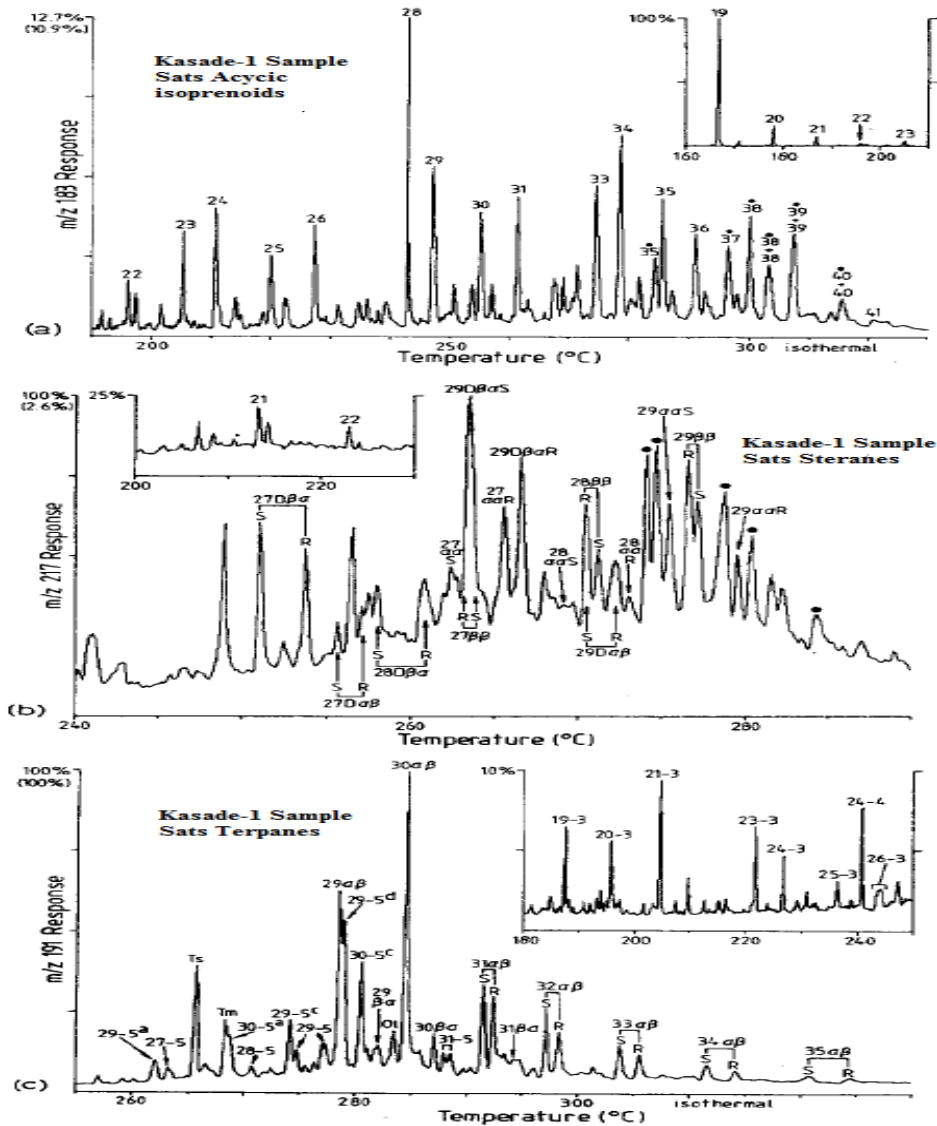
Fig. 4: Single ion chromatograms for the branched/cyclic saturates fraction from oil *303*. (a) Acyclic isoprenoidal hydrocarbon distribution (m/z) 183; numbers indicate carbon number of isoprenoids; components marked with a dot contain head-to-head linkage, others contain head-to-tail linkage). (b) Sterane distributions (m/z 217; components marked with a dot are triterpanes; see Table II for other component identifications). (c) Terpane distributions (m/z 191; see Table 2 for component identifications). Response scaling factors in parentheses are relative to 100% *m/z* 191 response, with equal MS dwell time for each ion.

Table 2: Identification of steroidal and terpenoidal hydrocarbons

TERPANES		STERANES	
$19-3$	C_{19} tricyclic diterpane	21	C_{21} sterane
$20-3$	C_{20} tricyclic diterpane	22	C_{22} sterane
$21-3$	C_{21} tricyclic diterpane	27DβαS/R	20S/R, 13β(H), 17α(H)-diacholestane
$23-3$	C_{23} tricyclic diterpane	27DαβS/R	20S/R,13α(H), 17β(H)-diacholestane
$24-3$	C_{24} tricyclic diterpane	28DβαS/R	20S/R, 13β(H), 17α(H)-diaergostane
$25-3$	C_{25} tricyclic diterpane	29DβαS/R	20S/R, 13β(H), 17α(H)-diastigmastane
$26-3$	C_{26} tricyclic diterpane	29DαβS/R	20S/R, 13α(H), 17β(H)-diastigmastane
$24-4$	C_{24} tetracyclic diterpane	27ααS/R	20S/R, 5α(H), 14α(H), 17α(H)-cholestane
Ts	18α (H),21β(H)-22,29,30-trisnorneohopaneαα	27ββR/S	20S/R, 5α(H), 14β(H), 17β(H)-cholestane
Tm	17α(H),21β(H)-22,29,30-trisnorhopane	28ααS/R	20S/R, 5α(H), 14α(H), 17α(H)-ergostane
$27-5$	C_{27} pentacyclic triterpane	28ββR/S	20S/R,5α (H), 14β(H),17β(H)-erogstane
$28-5$	C_{28} pentacyclic triterpane	29ααS/R	20S/R, 5α(H), 14α (H), 17α(H)-stigmastane
$29-5$	C_{29} pentacyclic triterpane	29ββR/S	20S/R,5α(H), 14β(H), 17β(H)-stigmastane
$30-5$	C_{30} pentacyclic triterpane		
$31-5$	C_{31} pentacyclic triterpane		
$32-5$	C_{32} pentacyclic triterpane		
1.0	18α (H)-oleanane		
29αβ	17α (H) ,21β(H)-30-norhopane		
29βα	17β(H) ,21α (H)-30-normoretane		
30αβ	17α(H) ,21β(H)-hopane		
30βα	17β(H), 21α (H)-moretane		
31αβS/R	22S/R,17α(H),21β(H)-30-homohopane		
31βα	17β(H) ,21α(H)-30-homomoretane		
32αβS/R	22S/R, 17α (H) ,21β(H)-30, 31 -bishomohopane		
33αβS/R	22S/R,17α(H),21β(H)-30,31,32-trishomohopane		
34αβS/R	22S/R,17α(H),21β(H)-30,31,32,33-tetrakishomohopane		
35αβS/R	22S/R, 17α(H),21β(H)-30,31,32,33,34-pentakishomohopane		

The most notable feature of the mass spectrum for 29-5[a] is the greater abundance of the *m/z* 177 ion than recorded for either 29αβ or 29βα.This ion derives from the DE-ring fragment and is stabilized in regular hopanes by the C_{-14} methyl group. The reason for the increased stability of the DE-fragment producing the *m/z* 177 ion relative to that generating the *m/z* 191 ion in 29-5[a] may relate to ring junction configuration or to methyl substitution positions in the DE-rings (e.g., a C_{-13} methyl). It has recently been proposed that 29-5[d] is 18α(H), 21β(H)-30-norneohopane (Philp et al., 1989; Wang and Liu, 2012).

A more detailed analysis of pentacyclic triterpanes involving GC-MS-SIM analysis of molecular ions (Fig. 6) suggested that 29-5[c] and 30-5[c] were members of a previously reported series of apparently hopanoidal alkanes, postulated to be 18 α (H), 21 β(H)-neohopanes (i.e. related to Ts), with C_{27}-C_{35} members and distributions paralleling those of the regular hopanes (Summons et al., 1988; Welander and Summons, 2012).
Based on relative retention times (Table 3), 29-5[c], 30-5[c], 31-5[c] and 31-5[d] in oil Kasade-1appear to be these hopanoids. Hopanoidal structures are supported by the fact that, in common with the regular hopanes, the C_{29}, C_{30} and C_{31} components exhibited enhanced

responses for *m/z* 177, 191 and 205, respectively (Fig. 6), from the DE-ring fragment. This is consistent with members of the series being built from extension of a side-chain attached to the E-ring (as for the regular hopanes). However, the enhanced stability of the molecular ion (Fig. 6) suggests a different substitution pattern in the DE-ring from the regular hopanes. An even greater molecular ion stability is demonstrated by another apparent series of pentacyclic triterpanes: 29-5[b], 30-5[b], 31-5[a], 31-5[b], 32-5[a] and 32-5[b].

Table 3: Hopane retention indices [j] for pentacyclic triterpanes highlighted in Fig. 6

Pentacyclic Triterpane	Hopane Retention Index
29-5 [b]	27.82
29-5 [c]	28.16 (27.96)[2]
29-5 [d]	29.06 (29.06) [2]
30-5 [a]	27.11
30-5 [b]	28.96
30-5 [c]	29.33 (29.26) [2]
30-5[d]	30.23
3 I-5 [a]	29.96
31-5 [b]	30.19
31-5 [c]	30.51 (30.41)[2]
31-5 [d]	30.57 (30.50) [2]
31-5 [e]	31.28
32-5 [a]	30.64
32-5 [b]	31.00

[J] Hopane retention index on methylsilicone stationary phase, calculated from retention times of triterpanes relative to certain regular hopanes with 17α(H), 21,β(H) configuration, which are assigned indices equal to their carbon number: Tm (27.00), *29αβ*(29.00), *30αβ* (30.00), *αβ* S (31.00), *32αβ* S (32.00), *33αβ* S (33.00). A linear scale is applied between these reference compounds.

[2]Values in parentheses correspond to extrapolated values of apparently identical compounds reported in fig. 4 of Summons et al. (1988).

These compounds exhibit the correct retention (Table 3) and abundance characteristics, relative to the regular hopanes detected in oil Kasade-1 (Fig. 6), to be another homologous series of hopanoids. Unfortunately, due to co-elutions and low concentrations, it was not

possible to obtain a mass spectrum of any member of this series, and no members above C_{32} were detected. The C_{29} and C_{31} members appear to give fairly strong *m/z* 177 and *m/z* 205 signals, respectively (Fig. 6), suggesting similar AB-ring substitution patterns to the regular hopanes. It seems unlikely, therefore, that any of these compounds is a 2-methylhopane, although traces of C_{30} and C_{31} 3β-methylhopanes (30-5[d] and 31-5[e], respectively, Fig. 5) were detected, exhibiting characteristically intense *m/z* 205 AB-ring fragment ions (Summons and Jahnke, 1990; Barbanti et al., 2011).

Significance of pentacyclic triterpane series

The pentacyclic triterpanes 29-5[d] and 30-5[c] have been observed in a number of other oils sourced by terrestrial organic matter, often, but not always, accompanied by 18α(H)-oleanane. These include: certain North Slope Alaska crudes (Hughes and Holba, 1988; Eickhoff et al., 2014); oils sourced in the Cretaceous Mowry shale of the Rocky Mountain Overthurst Belt (Seifert and Moldowan, 1981); Greater Ekofisk oils from the North Sea (Hughes et al., 1985); oils apparently sourced by the Upper Jurassic Dingo Claystone formation in the Barrow Sub-basin of Western Australia (Volkman et al., 1983); oils from freshwater lacustrine source rocks in the Shanganning and Chaidamu Basins in China (Philp et al. 1989); and, in particular, certain oils (e.g. Perch and Dolphin) from Late Cretaceous/Tertiary source rocks of the Gippsland Basin in Australia (Philp and Gilbert, 1986).

Oil Kasade-1 shares certain similarities in sources of organic matter and depositional environment with oils from the Gippsland Basin (Philp and Gilbert, 1986; Katz and Liu, 2014). Biomarker features held in common are: the presence of 18α(H)-oleanane, 29-5[d] and 30-5[c]; sterane distributions dominated by C_{29} components with relatively large quantities of diasteranes; high hopane/sterane ratios; the presence of long-chain, head-to-tail, acyclic isoprenoidal alkanes.

However, significant variations exist in that the Gippsland Basin oils contain no tricyclic terpanes or head-to-head, long-chain, acyclic isoprenoids, which probably reflects variation in the types of bacteria in the two basins. While 30-5[c] has been proposed as a terrigenous source indicator, based on evidence from Australian oils in general (Philp and Gilbert, 1986; Volkman 2014), it has not been found in all terrestrially sourced Indonesian oils (Hoffmann et al., 1984), and so it has been suggested that 30-5[c] may be an indicator of a particular plant source or possibly of bacteria that do not give regularhopanes (Philp and Gilbert, 1986; Volkman 2014). In oils sourced from terrestrial organic matter from New Zealand it has been noted (Philp and Gilbert, 1986; Volkman 2014) that 30-5[c] and 18α(H)-oleanane display an inverse relationship in their concentrations: in oils of greater

than Tertiary age the relative abundance of 30-5[c] increases while that of oleanane decreases with increasing age. It has been suggested that this relationship depends on the source material and/or depositional environment (Philp and Gilbert, 1986; Volkman 2014).
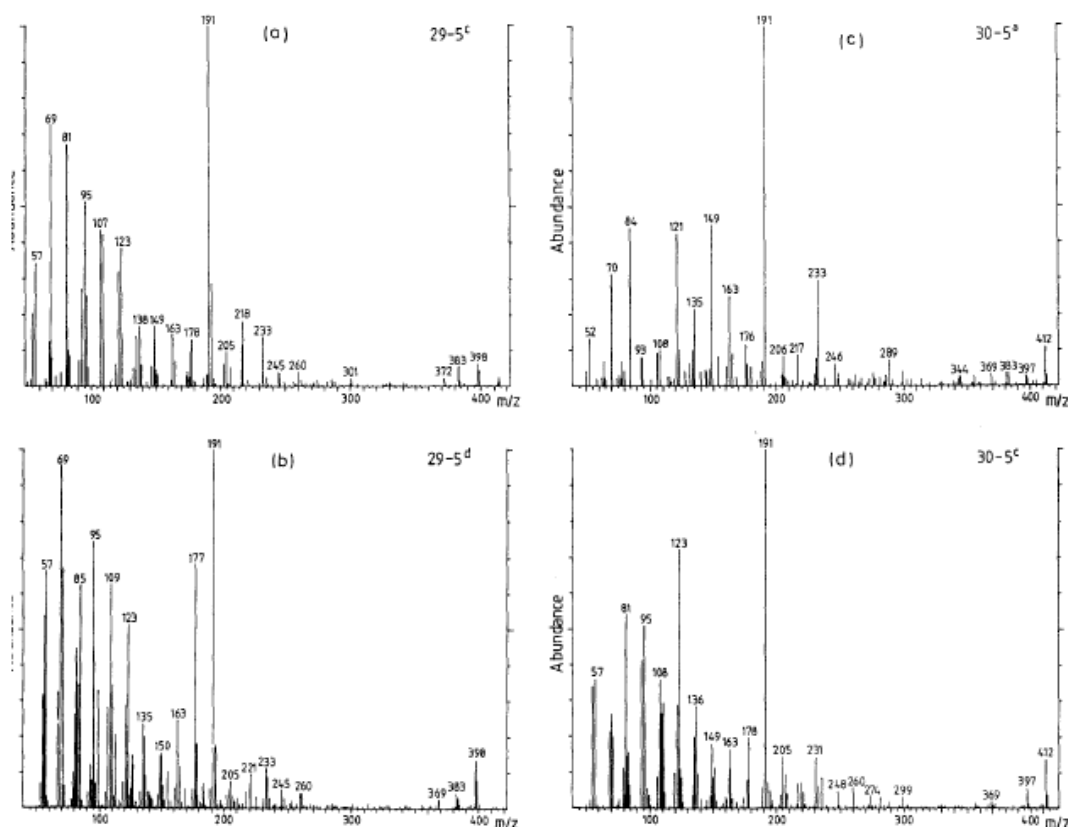

Fig. 5: Mas spectra of the four major, non-regular hopanoidal, pentacyclic treiterpanes; (a) 29-5[c], (b) 29-5[d], (c) 30-5[a], (d) 30-5[c].

After examination of triterpane distributions in coals from certain Nigerian basins, it has further been suggested that 30-5[c] and other terrestrial markers, such as oleanane, in oils from the Anambra Basin may have been picked up during migration of the oil through immature Cretaceous brown coals (Philp and Gilbert, 1986). Such an argument for 18α(H)-oleanane may also apply to oil Kasade-1,as Cretaceous coal deposits have been reported in the adjoining onshore region of the Upper Benue Trough (Olugbemiro et al., 1997; Volkman 2014). If 18α (H)-oleanane is not indigenous to the oil, the age of its source rock need not be confined to the Tertiary/Late Cretaceous.

However, the other pentacyclic triterpanes are probably indigenous to the oil, as they have been detected in another oil and its source rock from Bornu Basin in an area not

associated with coaly strata. This oil, from well Niger Delta in the offshore region (Fig. 1), exhibits higher levels of regular hopanes than oil Kasade-1(Killops et al., 1991; van Winden et al., 2012; Villanueva et al., 2014). As 29-5[d] and 30-5[c] seem to be members of hopanoidal series, the possibility of their being specific plant type markers appears to be ruled out. However, the possibility that they may derive from bacteria that do not give rise to regular hopanes remains.
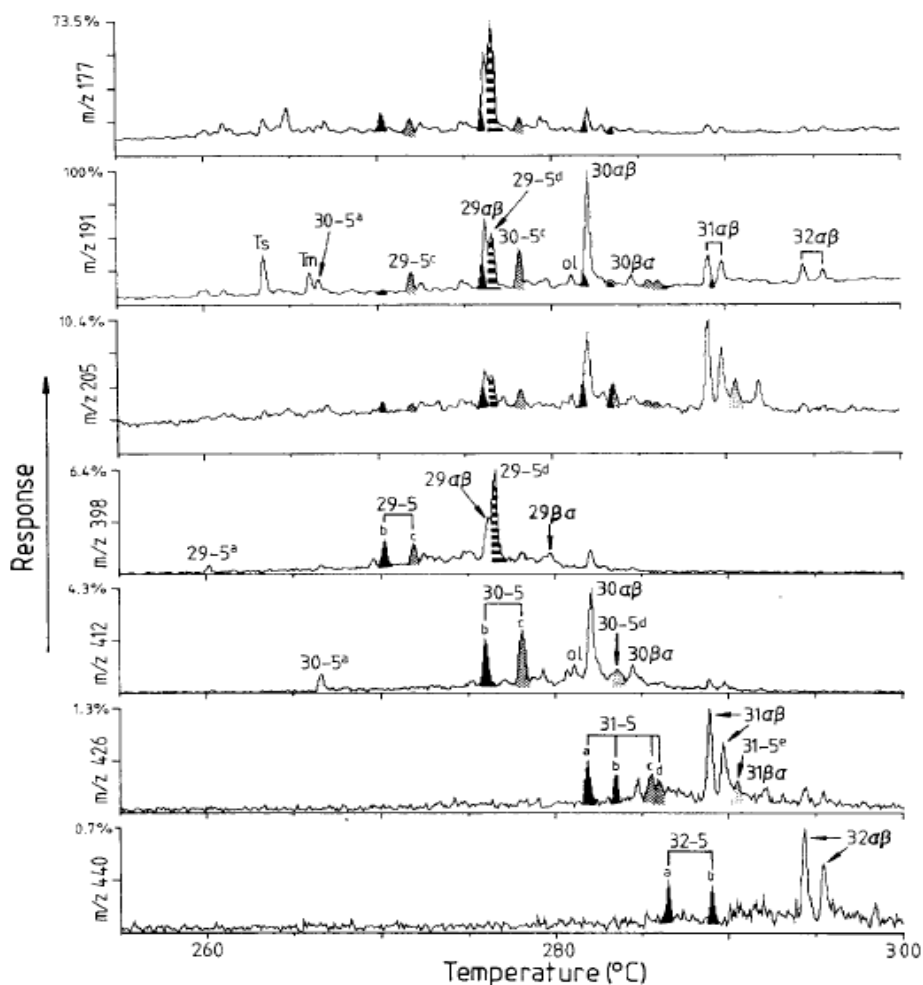

Fig. 6: Series of single ion chromatograms apparently revealing presence of several series of pentacyclic triterpanes in the branched/cyclic saturates fraction from oilKasade-1. See Table 2 for component identifications. Response scaling factors are relative to 100% for *m/z* 191 response, with equal MS dwell time for each ion.

A further alternative is possible, that they are derived from the rearrangement of regular hopanoidal precursors during diagenesis, similar to formation of aromatic secohopanoids (Hussler et al., 1984;Killops, 1991; van Winden et al., 2012). Such a possibility may be reflected in the presence of the relatively large amounts of diasteranes from clay-catalyzed

rearrangements. The two postulated series of hopanoidal alkanes appear to be related to the regular hopanes in exhibiting a dominance of C_{29} and C_{30} members. It is possible, therefore, that the proposed hopanoidal alkane species could derive from the same functionalized hopanoidal precursors that give rise to the regular hopanes. However, such similarity in distributions may alternatively be the result of diagenetic effects on different precursors from different bacteria, as would appear to apply to the 3-methylhopanes *(m/z 205* chromatogram, Fig. 6), which exhibited a related dominance of C_{30} and C_{31} members (Summons and Jahnke, 1990; Villanueva et al., 2014).

In view of the dominance of C_{29} and C_{30} members in the series discussed so far, two further pentacyclic triterpanes, 29-5[a] and 30-5[a] (Fig. 6) may represent another hopanoidal series. If it exists, a C_{30} analogue of 29-5[d] was not detected, but might co-elute with hopane (30αβ).

The above mentioned series of pentacyclic triterpanes, except the 3-methylhopanes, were detected in another oil from the offshore region of Niger Delta Basin (Fig. 1), which exhibited a greater apparent contribution of bacterial lipids (again from bacterial reworking of higher plant material) than oil Kasade-1(Killops et al., 1991; ; Villanueva et al., 2014). However, in the Niger Delta, these pentacyclic triterpane series were at significantly lower levels compared to the regular hopanes than in Kasade-1*,* and the series starting with 29-5[c] was relatively more abundant than the series commencing with 29-5[b]. It follows that the two series are either generated from the same precursors by competing reactions during diagenesis or derive from different precursors. The characteristics of the oils in which these apparently hopanoidal series occur suggest an association with bacterial reworking of higher plant material, possibly under a limited range of environmental conditions.

Conclusion

The oil from well Kasade-1in Bornu Basin appears to be sourced from terrestrial organic material, deposited in a tectonically formed lake and associated with alluvial flood plains and coal-bearing sequences. The higher plant organic matter had undergone some oxidation prior to deposition and was then markedly reworked by bacteria, with bacterial lipids making a major contribution to the oil. There was no direct evidence for significant autochthonous algal contributions. The presence of 18α(H)-oleanane in oil Kasade-1suggests a Tertiary/ Late Cretaceous age for its source rock.

However, the possibility cannot be discounted that this compound was picked up from passage of the oil through Cretaceous brown coals, which would remove the age restriction on the source rock.

Terpane distributions for oil Kasade-1were similar to those observed for certain oils from the Gippsland Basin, Australia (Philp and Gilbert, 1986). The range of C_{27}-C_{32} pentacyclic triterpanes detected in oil Kasade-1may all be bacterial in origin, and possess hopanoidal structures.

The most abundant of these components, 29-5[d] and 30-5[c], have been observed, often accompanied by 18α(H)-oleanane, in other oils derived predominantly from terrestrial organic matter, and so they may be characteristic of certain depositional environments. 30-5[c] appears to be a member of a previously reported series of C_{27}-C_{35} components proposed to be 18α(H)-neohopanes (Summons et al., 1988), the C_{29}-C_{31} members being detected in oil Kasade-1(Fig. 6). A further series of previously unreported pentacyclic triterpanes, with C_{29}-C_{32} members, was detected. This series also appears to comprise hopanoidal alkanes, from consideration of relative retention characteristics and component distributions and abundances. On methylsilicone stationary phase members of this series elute just before the postulated neohopane series. It is possible that these series of pentacyclic triterpanes are indicators of pronounced reworking of higher plant material in a particular depositional environment, and possibly involving particular types of bacteria.

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