PROVENANCE AND DEPOSITIONAL ENVIRONMENT OF ORGANIC MATTER FROM COALS OF THE MAASTRICHTIAN MAMU FORMATION, ANAMBRA BASIN, NIGERIA USING ALIPHATIC BIOMARKERS AS A TOOL.

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Abstract

Maastrichtian coals from Mamu, Anambra Basin, Nigeria, contain well-preserved miospore and megaspore assemblages suggesting a lycopod-dominated forest ecosystem with some ferns, sphenopsids and pteridosperms. Ten outcropped coal samples were collected from two locations (Akwuke and Okaba) in Mamu Formation of Anambra Basin. The samples were subjected GC-MS biomarker analyses. The aliphatic fractions were analyzed by GC–MS using a ThermoFinnigan Trace GC 2000 coupled to a Thermo Finnigan DSQ mass spectrometer. Biomarkers in the aliphatic and polar fractions and distributions in the samples were studied .The low rank of the coals and the well-defined microflora permit assessment of the palaeo-environmental significance of lipid biomarkers during the Early Maastrichtian. Lipid analyses indicate a fully terrestrial depositional environment. Although we also present and discuss a wide diversity of other lipid biomarkers (alkanes, hopanoids, steroids), we focus on the terrestrial derived biomarkers. The abundance of hopanes, homohopanes (C_{31}-C_{35}), benzohopanes and C_{29}steranes and diasteranes in most of the samples indicate terrestrial plant, phytoplankton and cyanobacteria contributions to the organic matter that formed the coal. High (Pr/Ph) ratio (1.73-11.55of individual alkanes of Mamu samples consisted of terrestrial organic matter with marine incursion deposited under oxic/suboxic-oxic in lacustrine-fluvial/deltaic environment.

Keywords: Land plant, biomarkers, terrestrial, terpenoids, Megaspores, Maastrichtian coals, Anambra Basin.

1.0 Introduction

Biomarkers are molecular compounds which can be extracted from crude oils, coals and all kinds of sedimentary rocks (Tissot and Welte, 1984). Biomarkers have numerous biological origins, and their occurrence can be related to a specific source, giving information of the type of fauna/flora present in the environment, or to depositional conditions, such as salinity or temperature

(Peters et al., 2005). For these reasons, biomarkers are regularly used in palaeo-environmental studies (e.g. Olcott, 2007; Eglinton and Eglinton, 2008). Recent applications of biomarkers aim at tracing the evolution of life. In archean rocks, biomarkers give information on the timing and evolution of early forms of life (e.g. Brocks et al., 1999, 2003, 2005; Ventura et al., 2007; Eigenbrode et al., 2008; Waldbauer et al., 2009), while in more recent rocks and sediments, biomarkers help determining taxonomic relationships between taxa (e.g. Arouri et al., 2000; Talyzina et al., 2000). In the last decades, chemotaxonomic applications have been particularly developed for the study of flora associated with amber and coal deposits mostly of Mesozoic to recent age (e.g. Simoneit et al., 1986; Otto et al., 1997, 2002; Bechtel et al., 2005; Stefanova et al., 2005 among others). Chemotaxonomic studies of Palaeozoic land plant based on extractible biomarkers were developed in the 70s (Niklas, 1976a,b; Niklas and Chaloner, 1976; Niklas and Pratt, 1980) but have been relatively limited in more recent years (Schulze and Michaelis, 1990; Fleck et al., 2001; Auras et al., 2006), despite the interest of Palaeozoic plants regarding the evolution of terrestrial life.

The objective of this study is to identify and characterize aliphatic biomarkers for Carboniferous plants preserved in coals and use the resultant data to determine the provenance and depositional environment of the organic matter. Biomarker analyses were performed on ten Maastrichtian coal samples from the Anambra Basin, Nigeria.

2.0 Regional geological setting

The tectonism in Southern Nigeria probably started in Early Cretaceous, with the separation of Africa from South America due to the opening of the Atlantic. This resulted in the development of the Benue Trough which stretched in a NE-SW direction (Fig. 1), resting unconformably upon the Pre-Cambrian basement complex. It extends from the Gulf of Guinea to the Chad Basin and is thought to have been formed by the Y-shaped (RRR) triple junction ridge system that initiated the breaking up and dispersion of the Afro-Brazilian plates in Early Cretaceous (Kogbe, 1989).

After the evolution of the Benue Trough, sediments started depositing in the Trough. Stages of sedimentations in the trough were in three cycles; the Pre-Cenomanian deposit of Asu River Group followed by the Cenomanian-Santonian sedimentation. According to Hogue (1977) the inversion tectonics of the Abakaliki anticlinoria which led to the evolution of both Afikpo Syncline and Anambra basin, represented the third cycle of sedimentation which produced the incipient Nkporo shale, Enugu shale and Owelli sandstone. The Nkporo group is overlain conformably by the Coal Group consisting of the Mamu, Ajali and Nsukka Formations that form the terminal units of the Cretaceous series.
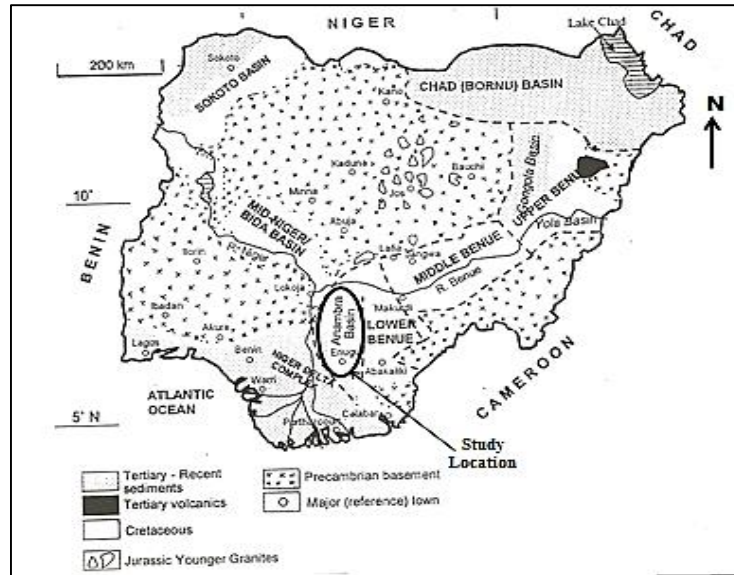
Fig. 1: Geological map of Nigeria showing the study location in the Lower Benue Trough (modified from Obaje et al., 2011).

The Cretaceous series overlying unconformably to the Santonian deformational episode, starts with shales and clays. It continues upward with a succession of silt, sand, gravel, tuff and tuffite levels. The coal deposited right straight on these units. The coal thickness varies between 4 - 13 m and has an average thickness of 8.5 m. Two coal containing levels are present in the area. Two poor quality coal levels composing of 0.30-0.75 m thickcoaly clay and 0.90 m thick clayey coal take place in the alternation of clay and sand 30-35 m above the lower coal seam.

The dip angle of the coaly Cretaceous layers are about 2-5 0C, and almost horizontal (Dagyaran, 1976). The angles eastwardly tend to increase. Enugu Fault, extending along Ekulu River and Milikin Hills, divides the coaly area into two sectors (Figs. 2 and 3).
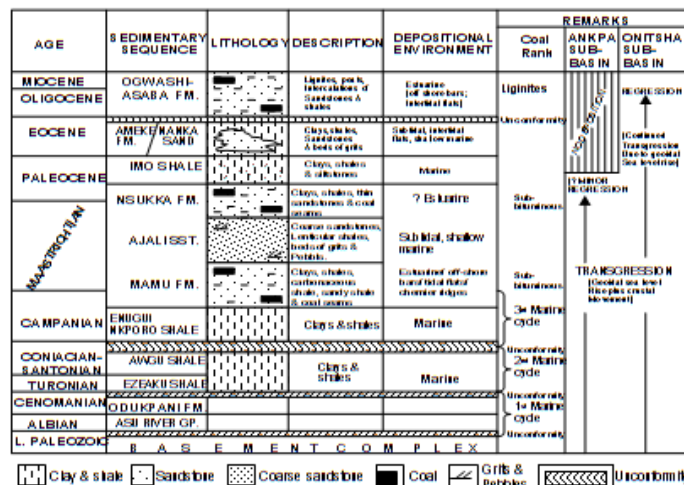

Fig. 2: The stratigraphy of the Anambra Basin southeastern Nigeria (Modified Uzoegbu et al., 2015).

Fig. 3: Field views and mining sites of the studied coals.

3.0 Stratigraphic setting

The sandstones which is about 330 m thick is an extensive stratigraphic unit conformably overlying the Lower Coal Measure (Mamu Formation) and Nkporo Formations that are 400 and 200 m thick, respectively and underlying the Upper Coal Measure (Nsukka Formation) in the Maastrichtian (Reyment, 1965 and Nwajide, 1990) (Fig. 2). The Ajali Formation is typically characterized by white coloured sandstone (Reyment, 1965) while the Mamu Formation is essentially composed of sandy shale and some coal seams; the Nkporo Formation consists mainly of grey - blue mudstone and shale with lenses of sandstone (Obaje, 2009). According to Reyment (1965), the prevailing unit of Ajali Formation consists of thick, friable, poorly sorted sandstone.

4.0 Material and methods

Ten coal samples (Fig. 3) were studied for GC-MS biomarker analysis. The rock fragments were extracted with dichloromethane (DCM) during 24hr in the refrigerator, in order to remove possible contamination on the sample surface. After this first extraction, the rock fragments were crushed to enable extraction of the lipids preserved inside the rock. Approximately 30g of pulverized samples were extracted with a mixture of methanol(MeOH) and dichloromethane (DCM) (1/2, v/v) for 24hr with extensive stirring. This second extract was dried by means of roto evaporation and partly re-solubilized in cyclohexane. The cyclohexane-soluble fraction (maltenes) was further separated by column chromatography.

The apolar fraction was recovered from the maltenes by elution with cyclohexane on an activated silica column. Subsequent elution with a mixture of cyclohexane–DCM (2/1, v/v) recovered the aromatic fraction after which the polar fraction was recovered by elution with a mixture DCM–MeOH (2/1, v/v).

The aliphatic fractions were analyzed by gas chromatography–mass spectrometry (GC–MS) using a ThermoFinnigan Trace GC 2000 coupled to a ThermoFinnigan DSQ mass spectrometer. The column used was a DB5ht (30 m length, 0.25 mm internal diameter, 0.1 μm film thickness). The oven temperature was programmed as follows 100 °C for 1

min, 100 °C–310 °C at a rate of 4 °C/min followed by an isothermal period of 16.5 min at 310 °C.

Helium was used as carrier gas. The mass spectrometer was operated in the EI mode at electron energy of 70 eV. Samples were analyzed in full scan (m/z 50–700; scan rate 1000 amu/s; scan speed 1.49/s, scan time 0.67 s). The organic compounds were identified by comparison of their mass spectra and retention times with available published data.

5.0 Results and discussions

The source, depositional environment and thermal maturity status of the organic matter contained in samples were determined based on the distributions and abundance of aliphatic biomarkers in the coal extracts.

5.1 Distribution of n-Alkane and Isoprenoid in the samples

The *m/z* 85 mass chromatograms showing the distribution of *n*-alkane and isoprenoids in the samples are shown in Figs.4 and 5. Geochemical parameters calculated from the alkane distribution are given in Table 1.
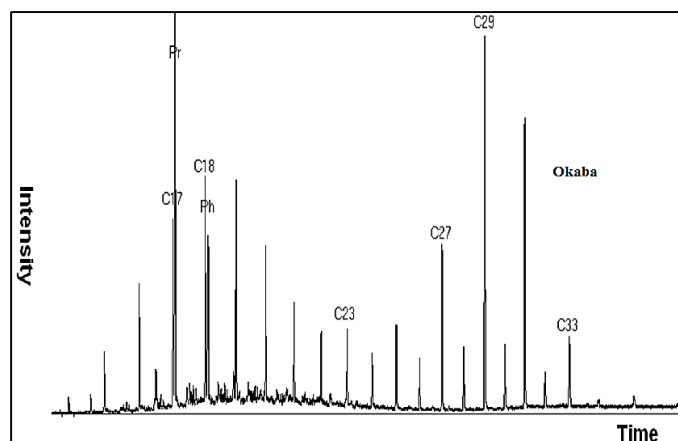

Fig. 4: *m/z* 85 Mass chromatograms of aliphatic fractions of Mamu Formation samples(Okaba) showing the distribution of *n*-Alkanes.
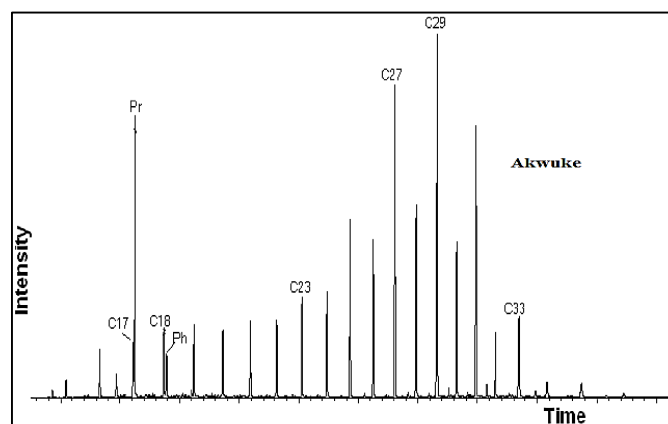

Fig. 5: *m/z* 85 Mass chromatograms of aliphatic fractions of Mamu Formation samples (Akwuke) showing the distribution of *n*-Alkanes.

The *n*-alkanes distribution in Mamu samples range from C_{14}- C_{35}, maximizing at C_{27} or C_{29} (Fig. 4, 5). This pattern indicates organic matter derived mainly from terrestrial organic matter. High proportions of long chain C_{27}-C_{31} members relative to the total *n*-alkanes especially are typical of terrestrial higher plants (Eglinton and Hamilton, 1963; Caldicott and Eglinton, 1973; Tissot and Welte, 1984; Barthlot et al., 1998; Miranda et al., 1999). The Pr/Ph ratios range from 9.33 to 11.55 and 1.73 to 4.08 for Akwuke and Okaba samples respectively (Table 1). All the samples, except some few from Okaba have Pr/Ph ratio greater than 3.0, typical of land plant detritus deposited under aerobic (oxic) condition (Killops and Killops, 2005; Peters et al., 2005; Tuo et al., 2007; Adeosu, 2009).

Table 1: *n*-Alkanes and Isoprenoids Parameters.

Samples N0	Formation	Lithology	Location	Pr/Ph	Pr/nC$_{17}$	Ph/nC$_{18}$	CPI	CPI (1)	OEP (1)	OEP (2)
AKK-1	Mamu	Coal	Akwuke	9.33	1.81	0.23	2.11	1.99	1.22	1.86
AKK-2	"	"	"	10.48	0.50	0.13	2.13	1.87	0.65	1.89
AKK-3	"	"	"	11.55	0.30	0.03	1.97	1.91	0.73	1.93
AKK-4	"	"	"	9.66	0.24	0.06	2.22	1.85	0.86	1.80
AKK-5	"	"	"	9.87	0.68	0.11	2.17	1.96	1.16	1.88
KBA-6	"	"	Okaba	2.11	3.40	1.08	3.76	3.00	1.30	3.08
KBA-7	"	"	"	1.73	2.94	0.72	5.18	5.82	1.29	5.16
KBA-8	"	"	"	3.76	5.42	1.27	7.38	8.72	1.29	7.06
KBA-9	"	"	"	4.08	4.51	0.74	6.51	7.20	1.28	6.28
KBA-10	"	"	"	3.30	2.57	0.70	5.93	6.16	1.38	6.13

Pr- Pristane, Ph- Phytane

CPI = ½[(C_{25} + C_{27} +C_{29} + C_{31} + C_{33}/C_{24} +C_{26}+C_{28}+C_{30}+C_{32}+C_{34}) + (C_{25} + C_{27} +C_{29} + C_{31} + C_{33}/C_{26}+C_{28}+C_{30}+C_{32}+C_{34})], CPI (1) = 2(C_{23}+C_{25}+C_{27}+C_{29})/[C_{22}+2(C_{24}+C_{26}+C_{28}) +C_{30}]

OEP (1) = C_{21}+6C_{23}+C_{25}/ 4(C_{22}+C_{24}), OEP (2) = C_{25}+6C_{27}+C_{29}/ 4(C_{26}+C_{28})
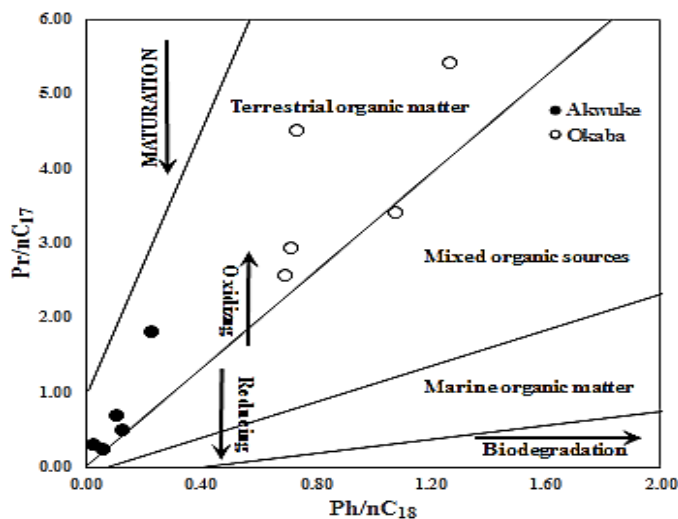

Fig. 6: Plots of Pr/nC$_{17}$ against Ph/nC$_{18}$ of Mamu Formation samples (diagram from Hunt, 1995).

The few samples having low Pr/Ph ratios can be interpreted as being deposited under sub-oxic to oxic settings (Killops and Killops, 2005; Peters et al., 2005; Tuoet al., 2007). The samples plotted within theterrestrial organic matter zone on the plots of Pr/nC$_{17}$ vs. Ph/nC$_{18}$(Hunt, 1995) in Fig. 6.

The Carbon Preference Index (CPI) and Odd-over-even predominance (OEP) values in Akwuke samples range from 1.85 to 2.32 and 0.65 to 2.27 respectively. The value for Okaba samples range from 3.00 to 8.72 and 1.16 to 7.06 respectively.
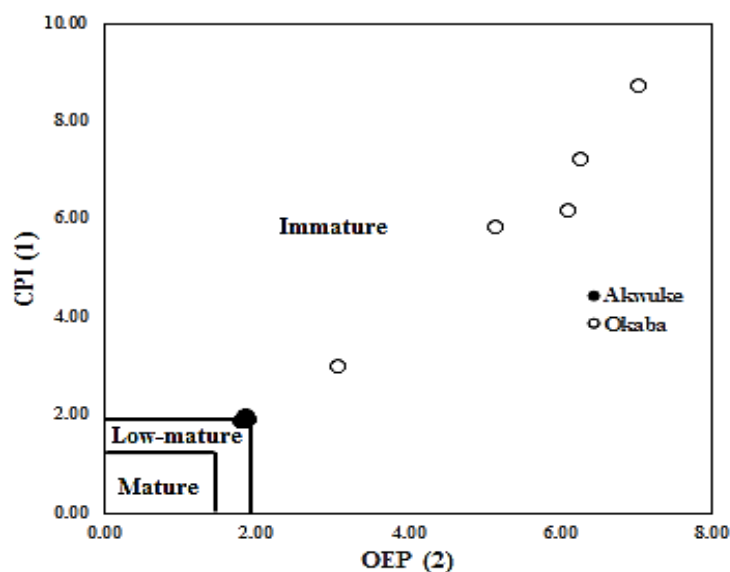

Fig. 7: Plots of CPI against OEP of MamuFormation samples diagram from Tissot and Welte, 1984).

The high CPI (>>1) and OEP values observed are characteristic of low rank coal i.e. subbituminous (Bray and Evan, 1961; Scalan and Smith, 1970; Tissot and Welte, 1984; Bechtel et al., 2004; Sabelet al., 2005; Stefanovaet al., 2005; Adeosu, 2009). The plot of CPI against OEP show that these samples are immature to low mature (Fig. 7).

5.2 Distribution of fatty acids and alkanones

The distributions of fatty acids in the polar fraction have been successfully used to differentiate the biological source of geological materials (Duanet al., 1997). The m/z 58 and m/z 74 mass chromatograms showing the distributions of the saturated n-fatty acids and alkan-2-ones in the coal extracts are shown in Figs. 8 and 9 respectively. Parameters calculated from the fatty acids and alkanones distribution in the coal extracts are listed in Table 2

Mamu samples have saturated n-fatty acids ranging from C$_8$ to C$_{32}$, maximizing at nC$_{16}$ or nC$_{18}$ (Fig. 8 and 9). These distributions reflect organic matter from both marine and terrestrial materials (Volkmanet al., 1998; Adeosu, 2009). However, the dominance of short chain (<C$_{20}$) saturated n-fatty acids maximizing at C$_{16}$ is an indication of substantial contribution of microorganism/algal to the organic matter.

The appreciable quantity of long chain saturated n-fatty acids ($>nC_{22}$) in the samples can be attributed to the contribution of higher plants to the organic matter (Cranwell, 1974). The ATR_{FA} ratios range from 0.85 to 0.96. These values indicate organic matter derived from mixed origin (Wilkes et al., 1999). The carbon preference index (CPI_{LFA}) for the long chain saturated n-fatty acids range between 1.25 and 2.78, indicating a slight even over odd predominance (Table 2). These values indicate low maturity (Wilkes et al., 1999; Adeosu, 2009).
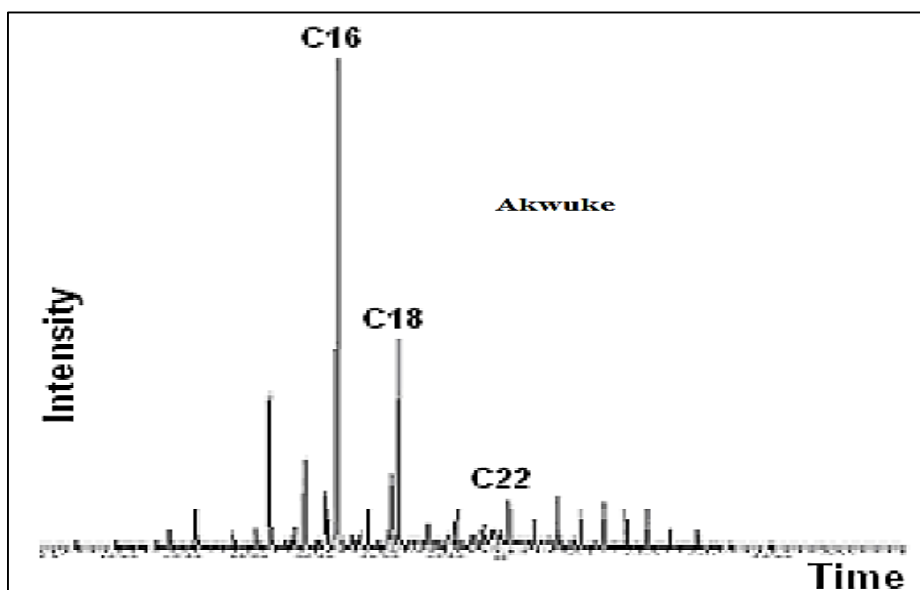

Fig. 8: *m/z* 74 mass chromatogram showing the distribution of *n*-fatty acids in Mamu samples (Akwuke) (Numbers refer to carbon chain lengths of *n*-fatty acids).
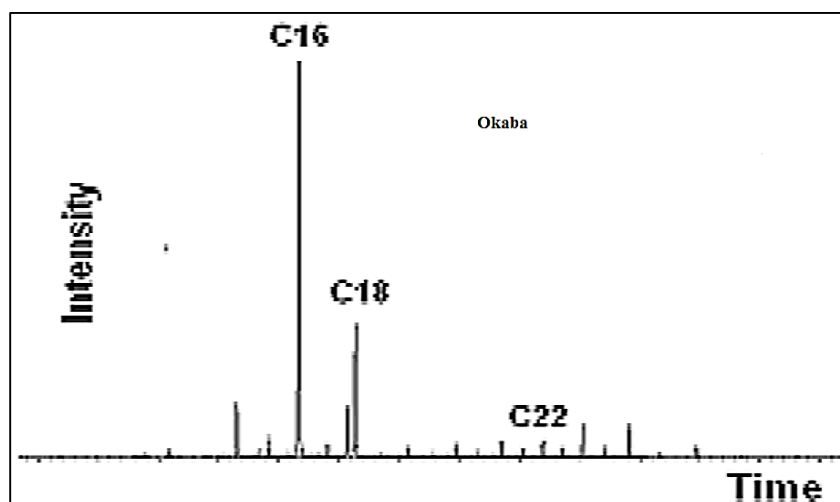

Fig. 9: *m/z* 74 mass chromatogram showing the distribution of *n*-fatty acids in Mamu samples (Okaba) (Numbers refer to carbon chain lengths of *n*-fatty acids).
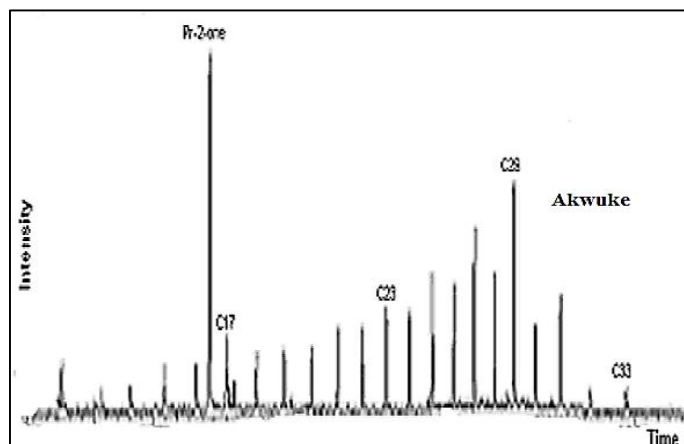
Fig. 10: *m/z* 58 mass chromatograms showing the distributions of alkan-2-ones in Mamu samples (Akwuke) (Numbers refer to carbon chain lengths of alkan-2-ones).
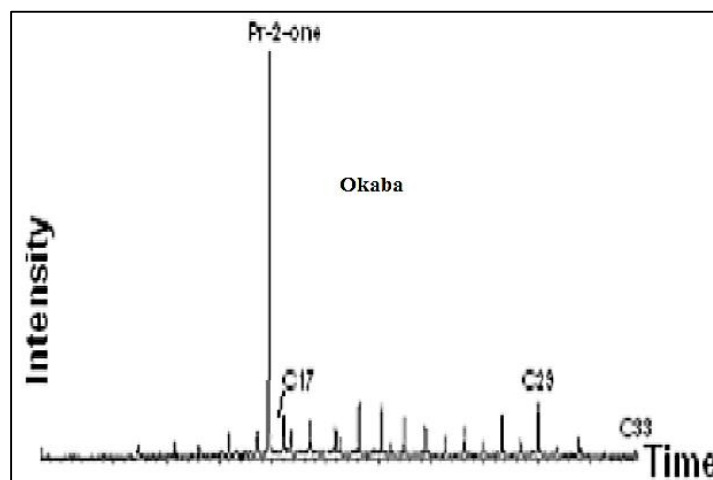

Fig. 11: *m/z* 58 mass chromatograms showing the distributions of alkan-2-ones in Mamu samples (Okaba) (Numbers refer to carbon chain lengths of alkan-2-ones).

Table 2: Parameters calculated from *n*-Fatty acids and alkanones composition of MamuCoal.

Samples N0	Formation	Lithology	Location	ATR_{FA}	CPI_{LFA}	Pr-2-one /C_{17}	CPI (alkanone)
AKK-1	Mamu	Coal	Akwuke	0.95	1.47	4.39	1.27
AKK-2	″	″	″	0.91	1.37	10.54	1.45
AKK-3	″	″	″	0.92	1.61	8.69	1.51
AKK-4	″	″	″	0.92	2.07	12.18	1.69
AKK-5	″	″	″	0.96	1.25	7.45	1.30
KBA-6	″	″	Okaba	0.85	2.78	8.68	2.66
KBA-7	″	″	″	0.93	1.37	7.69	2.25
KBA-8	″	″	″	0.94	1.95	12.69	2.59
KBA-9	″	″	″	0.96	1.44	13.71	2.49
KBA-10	″	″	″	0.91	2.51	21.43	2.10

ATR_{FA} = Short chain/long chain saturated fatty acid

$CPIL_{FA}$= Carbon Preference Index (Longchainfatty acids)

CPI (alkanones)= Carbon Preference Index (alkan-2-ones).

$ATR_{FA} = C_{14} + C_{16} + C_{18} / C_{14} + C_{16} + C_{18} + C_{26} + C_{28} + C_{30}$

$CPIL_{FA}=\frac{1}{2}\{(C_{24}+C_{26}+C_{28}+C_{30}/C_{21}+C_{23}+C_{25}+C_{27})+(C_{24}+C_{26}+C_{28}+C_{30}/C_{23}+C_{25}+C_{27}+C_{29})\}$

$CPI(alkanones)=1/2\{(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/(C_{22}+C_{24}+C_{26}+C_{28}+C_{30}+C_{32})$

$+(C_{25}+C_{27}+C_{29}+C_{31}+C_{33})/ C_{24}+C_{26}+C_{28}+C_{30}+C_{32+34}\}\}$

The *n*-alkan-2-ones range from nC_{12} to nC_{33}, maximizing at nC_{17} or nC_{29} (Fig. 10 and 11). These distributions reflect higher plants and algae inputs to the organic matter (Baiet al.*,* 2006). The CPI values range from 1.27 to 1.69 and 2.10 to 2.66 in Akwuke and Okaba samples respectively (Table 2). These values indicate low maturity status for all the samples (Tuoet al.*,* 2007).

5.3 Distribution of Tricyclic and C_{24} tetracyclic terpanes

The *m/z* 191 showing the distributions of tricyclic and tetracyclic terpanes in the samples are shown in Fig. 12 and 13. Peak identities are listed in Table 3.

Mamu samples are dominated by C_{19}-C_{21}tricyclic terpanes (Table 3). These distributions indicate organic matter derived

Adeosu, 2009).

from terrestrial matter (Ozcelik and Altunsoy, 2005; Adeosu, 2009). The C_{22}/C_{21} tricyclic terpane ratios range from 0.46 to 0.65 and 0.64 to 0.84 in Akwuke and Okaba samples respectively (Table 3). The observed C_{22}/C_{21} tricyclic ratios indicate fluvial/deltaic and lacustrine-fluvial/deltaic depositional environment for Akwuke and Okaba samples respectively (Peters et al.*,*2005). The C_{24}tetra/C_{26}tri(R+S) ratios range between 0.98 and 2.86, probably reflecting terrigenous organic matter input (Philp and Gilbert, 1986). The C_{24}tetra/C_{30}hopane ratios also range from 0.05 to 0.09 and 0.06 to 0.18 in Akwuke and Okaba samples respectively. These values also reflect fluvial/deltaic depositional environment and lacustrine-fluvial/deltaic for Akwuke and Okaba samples respectively (Peters et al.*,*2005;
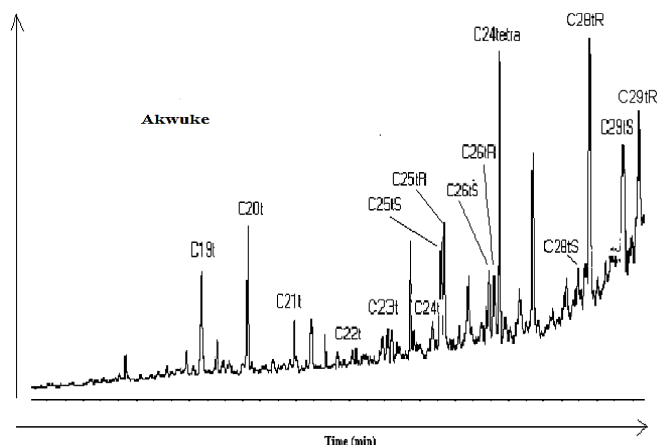

Fig. 12: *m/z* 191 showing the distribution of tricyclic and tetracyclic terpane inMamu Formation samples (Akwuke).
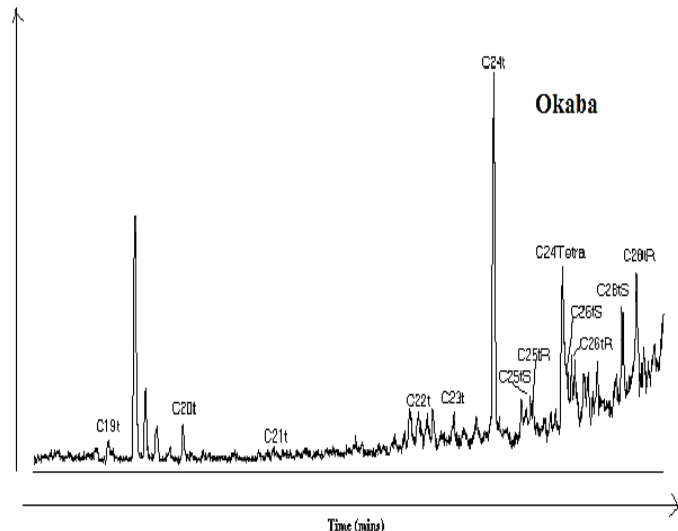
Fig. 13: *m/z* 191 showing the distribution of tricyclic and tetracyclic terpane in Mamu Formation samples (Okaba).

Table 3: Tri- and tetracyclic terpanes source and depositional environment parameters.

Samples N0	Formation	Lithology	Location	C_{24}tetra/ C_{30}hopane	C_{24}tetra/ C_{26}(R+S)tri	C_{22}/C_{21} triterpane	%C_{19}-C_{21} triterpane	%C_{23} triterpane
AKK-1	Mamu	Coal	Akwuke	0.08	2.40	0.65	83.00	17.00
AKK-2	"	"	"	0.09	2.86	0.46	90.00	10.00
AKK-3	"	"	"	0.05	2.11	0.61	72.30	27.70
AKK-4	"	"	"	0.08	2.21	0.64	87.50	12.50
AKK-5	"	"	"	0.09	2.70	0.55	78.50	21.50
KBA-6	"	"	Okaba	0.18	1.66	0.79	73.90	26.10
KBA-7	"	"	"	0.09	2.04	0.66	53.40	46.60
KBA-8	"	"	"	0.06	1.94	0.64	70.40	29.60
KBA-9	"	"	"	0.10	2.53	0.84	81.00	19.00
KBA-10	"	"	"	0.15	2.28	0.72	79.50	20.50

C_{24}tetra/C_{30}hopane = C_{24}tetracyclic terpane/C_{30}hopane

C_{24}tetra/C_{26}(R+S) tri = C_{24}tetracyclic terpane/C_{26}(R+S)tricyclic terpane

5.4 Distribution of Hopanes and homohopanes

The *m/z* 191 mass chromatograms showing the distribution of pentacyclictriterpanes in the samples are shown in Figs. 14 and 15 and the peak identities are given in Table 4.

The C_{27} to C_{35}hopanes are detected in all the Mamu samples but C_{28} was not detected (Fig. 14 and 15). The most prominent hopane in Akwuke samples are $C_{29}\alpha\beta$-norhopane and $C_{30}\alpha\beta$-hopane while $C_{29}\alpha\beta$ norhopane is predominant in Okaba samples (Fig 14 and 15). In the Okaba samples, abundance of $C_{29}\alpha\beta$-hopane in allthe samples reflects major contribution from terrestrial organic matter; however, contribution from prokaryotic organisms is not excluded while abundant $C_{30}\alpha\beta$-hopane with notable

presence of $C_{29}\alpha\beta$ in Akwuke samples reflects significant contribution from prokaryotic organisms as well as vitrinitic (terrestrial) organicmatter. The unusual high abundance of 22R compared to 22S in the C_{31}-17α (H),21β(H) homohopane is evident in all Okaba samples. This is likely due to co-elution of gammacerane (Peter and Moldowan, 1993; Kagya, 1996; Farrimondet al., 1998;Peters et al.,2005; Adeosu, 2009).

Benzohopanes with different distributions were found in Akwuke and Okaba coalsamples (Fig. 14 and 15). There is no previous record of presence of benzohopanes in Mamu coal and coaly organic matter. The C_{32}-C_{35}benzohopaneswere detected in Akwuke samples while C_{32}-C_{33}benzohopanes were detected inOkaba samples. Benzohopanes are thought to be secondary transformation products ofC_{35}bacteriohopanepolyol derivatives (Grice et al., 1998; Peters et al., 2005; Killopsand Killops, 2005; Bechtel et al.,2007a).

Three isomers of oleanenes; olean-18-ene, olean-13 (18)-ene and olean-12-ene were identified in Okaba samples (Fig. 16, 17 and 18). Similar to the benzohopanes,this is the first time oleanene isomers are being identified in Mamu coal and coaly organic matter. These three oleanene isomers are products of late diagenesis from taraxerol and β-amyrin, which are biomarkers for angiosperm (Ten Haven andRullkötter, 1988; Ekweozor and Telnǽs, 1990; Rullkötteret al., 1994; Curiale, 1995). They have also been found useful as indicators of thermal immaturity (Eneogweet al.,2002; Adeosu, 2009;Uzoegbu and Onwualu-John, 2023).

In Akwuke sample, C_{35}/C_{30}hopane ratio range from 0.01 to 0.05 while Okaba samples have values ranging from 0.01 to 0.47. These values indicate fluvial/deltaic and lacustrine-fluvial/deltaic depositional environments for Akwuke and Okabasamples respectively.
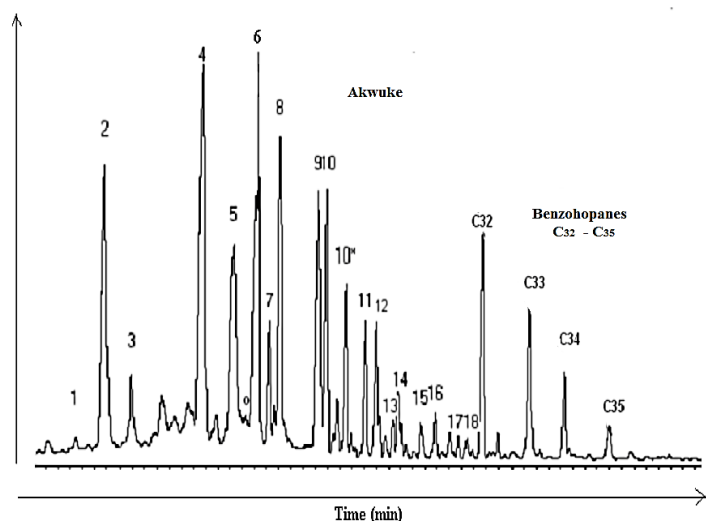

Fig. 14: *m/z* 191 mass chromatogram showing the distribution of hopanes andbenzohopanes in Mamu samples (Akwuke).
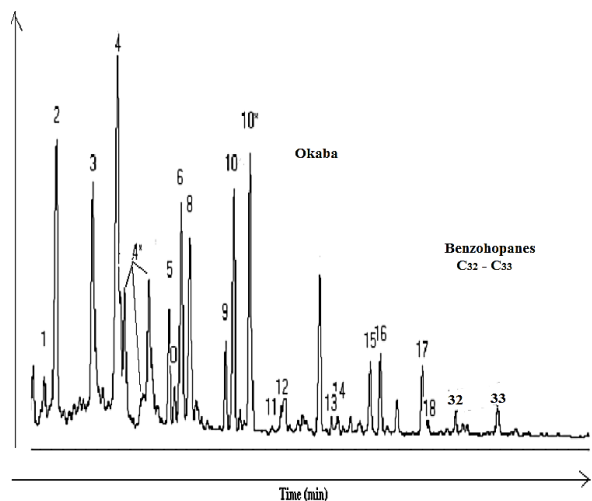
Fig. 15: *m/z* 191 Mass chromatogram showing the distribution of hopanes and benzohopanes in Mamu sample (Okaba).

Table 4: Peak identities on *m/z* 191 mass chromatograms.

Peak	Compound
C19t	C_{19} tricyclic terpane
C20t	C_{20} tricyclic terpane
C21t	C_{21} tricyclic terpane
C22t	C_{22} tricyclic terpane
C23t	C_{23} tricyclic terpane
C24t	C_{24} tricyclic terpane
C25tS	C_{25} 22(S)-tricyclic terpane
C25tR	C_{25} 22(R)-tricyclic terpane
C24tetra	Tetracyclic hopane (secohopane)
C26tS	C_{26} 22(S)-tricyclic terpane
C26tR	C_{26} 22(R)-tricyclic terpane
C28tS	C_{28} 22(S)-tricyclic terpane
C28tR	C_{28} 22(R)-tricyclic terpane
1	C_{27} 18α(H)-22,29,30-trisnorneohopane (Ts)
2	C_{27} 17α(H)-22,29,30-trisnorhopane(Tm)
3	C_{27} 17β(H)-22,29,30-trisnorhopane
4	C_{29} 17α(H), 21β(H)-30-norhopane
4*	Oleanene isomers; olean-18-ene, olean-13 (18)-ene, olean-12-ene

Table 4 (contd.): Peak identities on *m/z* 191 mass chromatograms.

Peak	Compound
5	C_{29} 17β(H), 21α(H)-normoretane
6	C_{30} 17α(H), 21β(H)-hopane
7	C_{30} 17α(H), 21α(H)-30-norhopane
8	C_{30} 17β(H), 21α(H)-moretane
9	C_{31} 17α(H), 21β(H)-30-homohopane (22S)
10	C_{31} 17α(H), 21β(H)-30-homohopane (22R)
10*	C_{30} 17β(H), 21β(H)-hopane
11	C_{32} 17α(H), 21β(H)-30,31-bishomohopane (22S)
12	C_{32} 17α(H), 21β(H)-30,31-bishomohopane (22R)
11*	C_{31} 17β(H), 21β(H)-hopane
13	C_{33} 17α(H), 21β(H)-30,31,32-trishomohopane (22S)
14	C_{33} 17α(H), 21β(H)-30,31,32-trishomohopane (22R)
15	C_{34} 17α(H), 21β(H)-30,31,32,33-tetrakishomohopane (22S)
16	C_{34} 17α(H), 21β(H)-30,31,32,33-tetrakishomohopane (22R)
17	C_{35} 17α(H), 21β(H)-30,31,32,33,34-pentakishomohopane (22S)
18	C_{35} 17α(H), 21β(H)-30,31,32,33,34-pentakishomohopane (22R)
Sp30	18α(H)-28-noroleanane
O	18α(H)-oleanane + 18β(H)-oleanane

Table 5: Source and depositional environment parameters computed from the hopane andsterane distributions in the coals.

Samples N0	Formation	Lithology	Location	%C_{27} sterane	%C_{28} sterane	%C_{29} sterane	%C_{27} diast.	%C_{28} diast.	%C_{29} diast.
AKK-1	Mamu	Coal	Akwuke	24.02	20.18	55.80	28.40	23.37	48.27
AKK-2	″	″	″	11.83	33.64	54.53	23.05	28.61	48.34
AKK-3	″	″	″	10.73	29.71	59.56	25.44	24.33	50.23
AKK-4	″	″	″	16.51	26.46	57.03	20.14	30.31	49.56
AKK-5	″	″	″	12.97	20.08	66.95	17.00	24.06	58.94
KBA-6	″	″	Okaba	20.98	43.20	35.82	13.91	29.66	56.43
KBA-7	″	″	″	19.06	41.28	39.66	11.60	35.63	52.77
KBA-8	″	″	″	10.59	27.73	61.68	21.89	42.34	35.78
KBA-9	″	″	″	11.57	29.61	58.83	26.45	32.19	41.36
KBA-10	″	″	″	17.06	39.20	43.79	32.76	31.00 3	6.24

Table 5Contd: Source and depositional environment parameters computed from the hopane andsterane distributions in the coals.

Samples N0	Formation	Lithology	Location	C_{27}/C_{29} sterane	%Diast./ sterane	Sterane/ hopane	C_{35}/C_{30} hopane	C_{35}/C_{34} $\alpha\beta S$ hopane	Homohopane/ index
AKK-1	Mamu	Coal	Akwuke	0.43	89.00	0.07	0.05	0.23	0.04
AKK-2	"	"	"	0.22	84.51	0.06	0.05	0.25	0.03
AKK-3	"	"	"	0.18	66.56	0.29	0.02	0.32	0.02
AKK-4	"	"	"	0.29	66.30	0.04	0.05	0.29	0.03
AKK-5	"	"	"	0.20	87.23	0.06	0.01	0.28	0.02
KBA-6	"	"	Okaba	0.59	50.32	0.16	0.09	0.62	0.13
KBA-7	"	"	"	0.48	50.69	0.20	0.32	0.81	0.11
KBA-8	"	"	"	0.17	63.72	0.10	0.06	0.76	0.09
KBA-9	"	"	"	0.20	51.76	0.08	0.01	0.59	0.03
KBA-10	"	"	"	0.40	73.84	0.08	0.02	0.92	0.11

Sterane/Hopane=$C_{27}+C_{28}+C_{29}$steranes/$[(C_{29}+C_{30})\alpha\beta$hopane + $(C_{31}+C_{32}+C_{33})\alpha\beta(R+S)$homohopane]

$C_{35}/C_{30} = C_{35}\alpha\beta(R+S)$ homohopane/ $C_{30}\alpha\beta$ hopane + $C_{30}\beta\alpha$ moretane

Homohopane ratio,C_{35}/C_{34} $\alpha\beta S = C_{35}\alpha\beta S/C_{34}\alpha\beta S$ homohopane

Homohopane index = $C_{35}/$ $C_{31}+C_{32}+C_{33}+C_{34}+C_{35})$ $\alpha\beta(R+S)$ homohopane

The homohopane index and homohopane ratio for the samples range from 0.02-0.13 and 0.23-0.92 respectively (Table 5). These values indicate oxic depositional environment for Akwuke samples and suboxic-oxic depositional environments for Okaba samples (Peters and Moldowan, 1991; Hanson et al., 2001; Killops and Killops,2005; Peters et al., 2005; Yangminget al., 2005). There is presence of gammacerane in Okaba samples (Fig. 14 and 15), which indicate water column stratification during organic matter source deposition (Sinninghe Damstéet al., 1995; Yangminget al.,2005).

Table 6: Maturity parameters computed from the hopane and sterane distributions in the coals.

Samples N0	Formation	Lithology	Location	Mor/ Hop	Hop/ Hop+ Mor	Ts/ Ts+Tm	22S/22S+ 22RC_{32} HH	20S/20S + 20R C_{29} steranes	$\alpha\beta\beta/\alpha\beta\beta+$ $\alpha\alpha\alpha$ C_{29} sterane
AKK-1	Mamu	Coal	Akwuke	0.46	0.69	0.04	0.54	0.04	0.25
AKK-2	"	"	"	0.56	0.64	0.03	0.59	0.15	0.19
AKK-3	"	"	"	0.63	0.61	0.04	0.55	0.17	0.20
AKK-4	"	"	"	0.54	0.65	0.03	0.54	0.11	0.24
AKK-5	"	"	"	0.61	0.62	0.02	0.55	0.19	0.16
KBA-6	"	"	Okaba	0.84	0.54	0.13	0.48	0.19	0.30
KBA-7	"	"	"	0.85	0.54	0.16	0.43	0.10	0.33
KBA-8	"	"	"	0.62	0.62	0.24	0.31	0.18	0.21
KBA-9	"	"	"	0.59	0.62	0.11	0.37	0.19	0.50
KBA-10	"	"	"	0.57	0.64	0.14	0.33	0.39	0.56

Mor/Hop = Moretane/Hopane (C_{30})

Hop/Hop + Mor = Hopane/Hopane + Moretane (C_{30})

C_{32}HH = C_{32}homohopane

The Moretane/Hopane, Hopane/Hopane + Moretane, Ts/Ts + Tm, 22S/22S + 22RC$_{32}$homohopane ratios in Akwuke samples range from 0.46 to 0.64; 0.61 to 0.69;0.02 to 0.05; and 0.48 to 0.58 (Table 6) respectively. These values suggest low maturity status(Rullkötteret al., 1985; Kagya, 1996; Peters et al., 2005). The Okaba samples haveMoretane/Hopane, Hopane/Hopane + Moretane, Ts/Ts + Tm, 22S/22S + 22R C$_{32}$homohopane ratios ranging from 0.59-0.93; 0.54-0.64; 0.11-0.24; and 0.16-0.48respectively. These values also indicate that Akwuke samples are thermally immature (Rullköteret al., 1985;Kagya, 1996; Peters et al., 2005).

5.5 Distribution of Steranes
The *m/z* 217 mass chromatograms showing the distribution of steranes and diasteranes in all the samples are shown in Figs. 19 and 20. Peak identities are listed in Table 7.
C29 Diasteranes and steranes are the most abundant steranes in all the samples except few samples from Okaba where C28 predominates. The sterane and diasterane distributions in Okaba samples are increasing in the order of C29>C28>C27.

The predominance of C29 over C27 sterane reflects a greater input of terrestrial relative to marine organic matter (Huang and Meinschein, 1979; Volkman, 1988; Kagya, 1996; Sari and Bahtiyar, 1999; Otto et al., 2005; Peters et al., 2005). The appreciable quantity of C27 and C28 in these samples also reflect contributions from phytoplankton; algae, diatoms, dinoflagellates (Volkman, 1986; Volkmanet al., 1998; Sari and Bahtiyar, 1999; Peters et al., 2005). The ternary plot of C27, C28 and C29 sterane of Mamu samples (Fig. 21) reflects major terrestrial input in Akwuke samples while Okaba samples consist of both terrestrial and marine organic matter (Huang and Meinschein, 1979; Killops and Killops, 1993, 2005; Peters et al., 2005).

The diasterane ternary plot (Fig. 22) shows that most of the Akwuke samples are derived from terrestrial organic matter with few samples having mixed inputs (i.e. terrestrial and marine). Samples from Okaba are majorly derived from mixed origin. There is little variation in sterane and diasterane distribution in Akwuke samples while significant variations are noticed in Okaba samples.
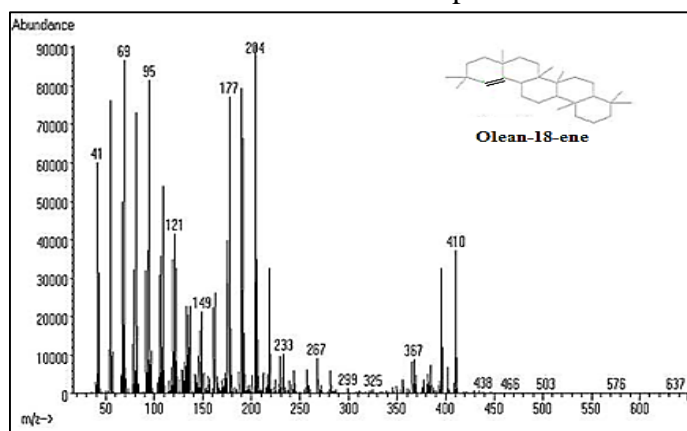

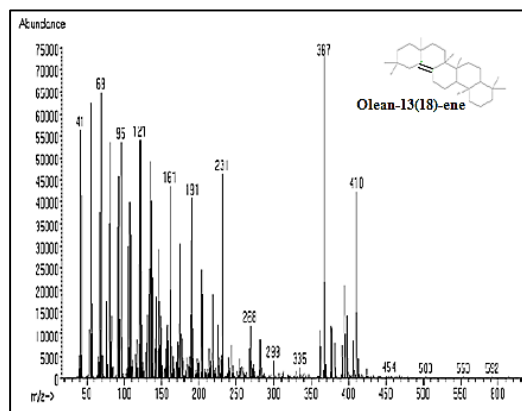Fig. 16: Mass frangmentogram and spectra of Olean-18-ene in Okaba Mine samples (after Adeosu, 2009).

Fig. 17: Mass frangmentogram and spectra of Olean-13(18)-ene in Okaba Mine samples (after Adeosu, 2009).
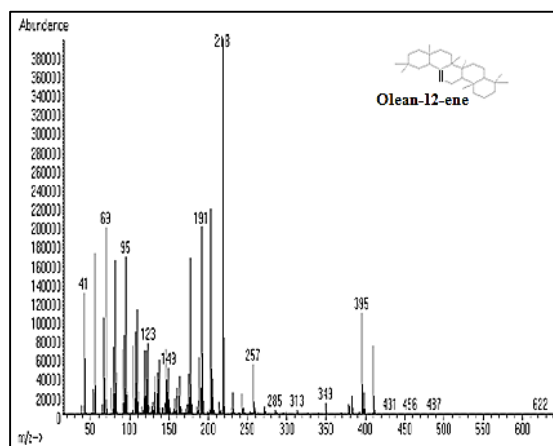

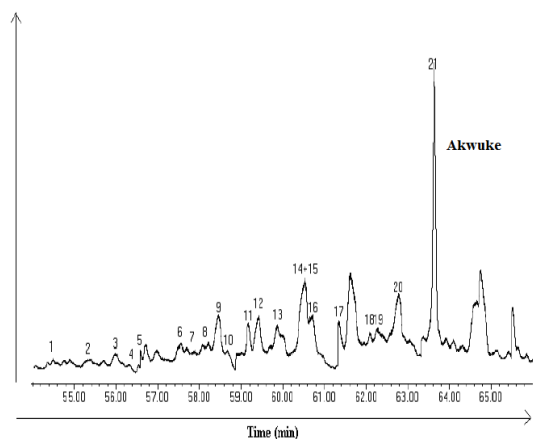Fig. 18: Mass frangmentogram and spectra of Olean-12-ene in Okaba Mine samples (after Adeosu, 2009).

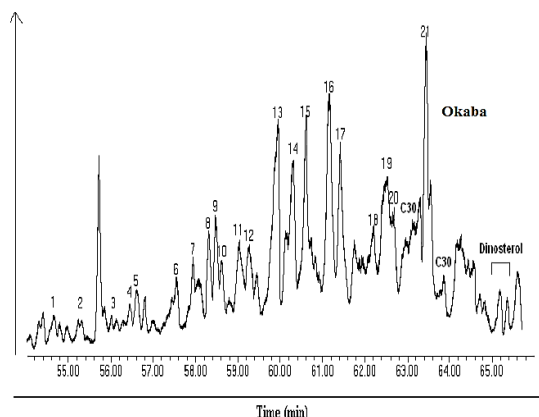Fig. 19: *m/z* 217 mass chromatograms showing the distribution of steranes anddiasteranes in Mamu,Akwuke samples.

Fig. 20: *m/z* 217 mass chromatograms showing the distribution of steranes and diasteranes in Mamu, Okaba samples.

This observation possibly reflects same depositional environments for Akwuke samples (fluvial/deltaic) and lacustrine-fluvial/deltaic depositional environments for Okaba samples. This observation can be supported by the ratio of C27/C29 (Table 7) for the samples. The values range from 0.2 to 0.7 and 0.18 to 0.43 in Okaba and Akwuke samples respectively. The dominance of dinosterol over C30 steranes in Okaba samples reflects typical fresh water lacustrine source rocks (Köhler and Clausing, 2000; Peters et al., 2005).

The 20S/20S+20R and αββ/αββ+ααα C29 ratios range from 0.04 to 0.19 and 0.16 to 0.25 respectively in Akwuke samples while the values range from 0.1 to 0.39 and 0.21 to 0.56 respectively in Okaba samples. The generally low values recorded indicate that the samples are thermally immature. The plot of 22S/22S+22R C32hopanes against C29αββ/αββ+αααsteranes also confirm the thermal immaturity status of Mamu samples (Fig. 23).

6.0 Conclusions
Coal and coaly organic matter samples were collected from coal bearing measures of Lower and Middle Benue Trough, Nigeria. These samples were subjected to Gas Chromatography-Mass Spectrometry. This study was undertaken to re-appraise the hydrocarbon potential of Nigerian coal through source rock evaluation studies, biomarker parameters and carbon isotopic compositions. The distributions of *n*-alkanes and *n*-alkan-2-ones showed that Awgu samples were formed from organic matter derived from both terrestrial and marine organic matter while Mamu samples were derived from terrestrial organic matter.

Table 7: Peak identities on *m/z* 217 mass chromatograms of Mamu coal.

Peak	Compound
1	C_{27} 13β(H), 17α(H)-Diasterane (20S)
2	C_{27} 13β(H), 17α(H)-Diasterane (20R)
3	C_{27} 13α(H), 17β(H)-Diasterane (20S)
4	C_{27} 13α(H), 17β(H)-Diasterane (20R)
5	C_{28} 13β(H), 17α(H)-Diasterane (20S)
6	C_{28} 13β(H), 17α(H)-Diasterane (20R)
7	C_{28} 13α(H), 17β(H)-Diasterane (20S)
8	C_{27} 5α(H), 14α(H), 17α(H)-Sterane (20S) + C_{28} 13α(H), 17β(H)-Diasterane (20S)
9	C_{27} 5α(H), 14β(H), 17β(H)-Sterane (20R) + C_{28} 13β(H), 17α(H)-Diasterane (20S)
10	C_{27} 5α(H), 14β(H), 17β(H)-Sterane (20S) + C_{28} 13β(H), 17α(H)-Diasterane (20R)
11	C_{27} 5α(H), 14α(H), 17α(H)-Sterane (20R)
12	C_{29} 13β(H), 17α(H)-Diasterane (20R)
13	C_{29} 13α(H), 17β(H)-Diasterane (20S)
14	C_{28} 5α(H), 14α(H), 17α(H)-Sterane (20S)
15	C_{28} 5α(H), 14β(H), 17β(H)-Sterane (20R)
16	C_{28} 5α(H), 14β(H), 17β(H)-Sterane (20S)
17	C_{28} 5α(H), 14α(H), 17α(H)-Sterane (20R)
18	C_{29} 5α(H), 14α(H), 17α(H)-Sterane (20S)
19	C_{29} 5α(H), 14β(H), 17β(H)-Sterane (20R)
20	C_{29} 5α(H), 14β(H), 17β(H)-Sterane (20S)
21	C_{29} 5α(H), 14α(H), 17α(H)-Sterane (20R)
C30	C_{30} 5α(H), 14α(H), 17α(H)-Sterane
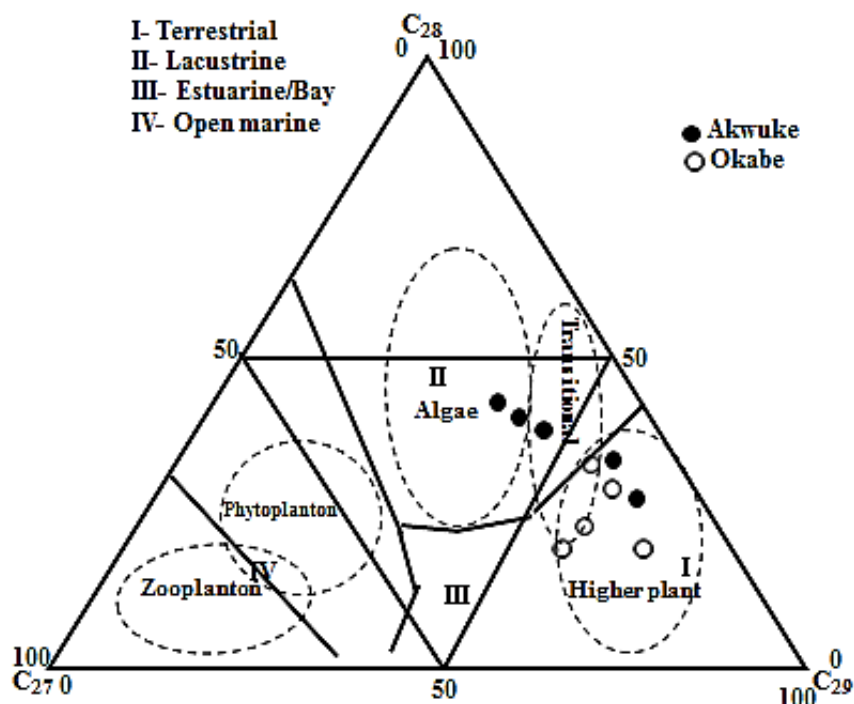
Fig. 21: Ternary plots of C_{27}, C_{28} and C_{29} steranes distributions in Mamu coal (After Huang and Meinschein, 1979).
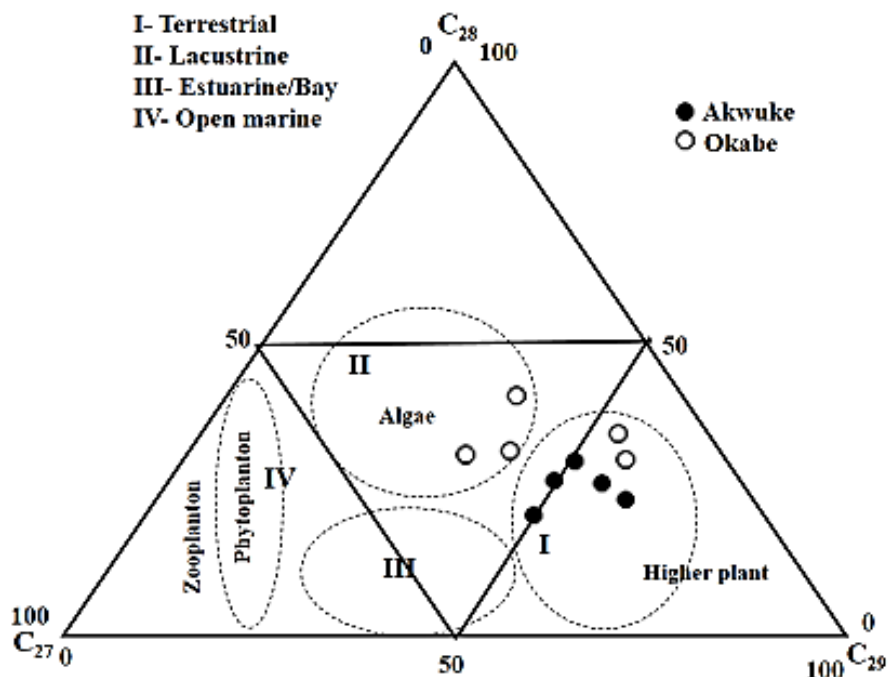
Fig. 22: Ternary plots of C_{27}, C_{28} and C_{29}diasteranes distributions in Mamu coal (After Huang and Meinschein, 1979).
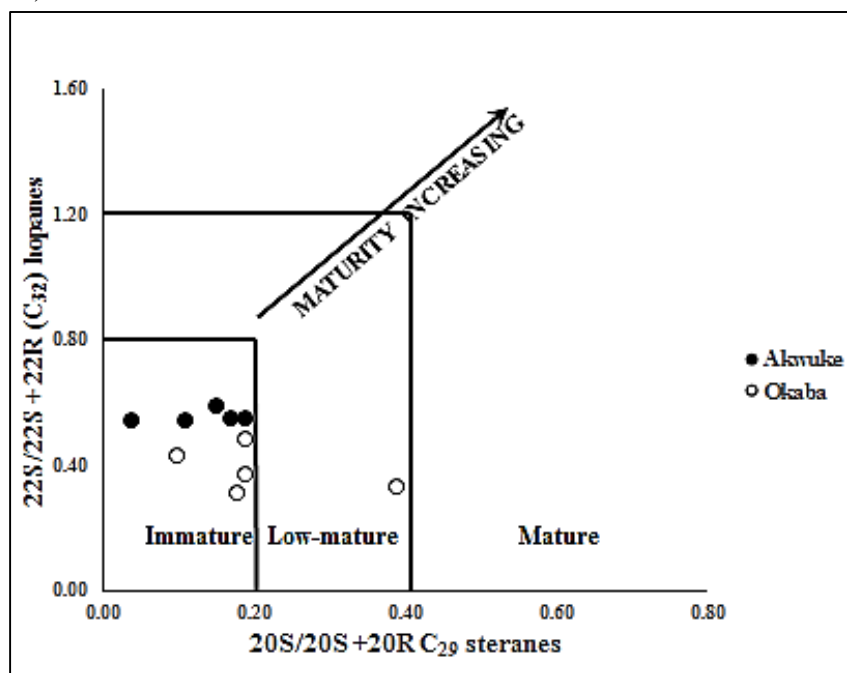

Fig. 23: Plots of 22S/22S+22R C_{32}hopanes against 20S/20S + 20R C_{29}steranes(After Inabaet al.,2001).

The Pr/Phratios of Akwuke samples reflect organic matter deposition under oxic conditions in freshwater-lacustrine and freshwater depositional environment respectively while Pr/Ph ratios of Okaba samples indicate suboxic-oxic conditions during sedimentation in freshwater-lacustrine depositional environments.

The presence of hopane, homohopane (C_{31}-C_{35}) in all the samples showed that bacteriohopanetetrol and other polyfunctional C_{35}hopanoids common in prokaryotic microorganisms have significant contributions to the organic matter that formed the coals. The occurrence of oleanene isomers in Okaba samples favoured terrestrial organic matter deposited in lacustrine-fluvial/deltaic environment. In addition, the detection of gammacerane in Okaba samples represents water stratification during organic matter source deposition. The abundance of C_{29}Steranes and diasteranes in the samples indicate land input to the organic matter that formed the coal.

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