BIOMARKER GEOCHEMICAL EVALUATION OF UPPER CRETACEOUS COAL FROM THE ANAMBRA BASIN, SOUTHEAST NIGERIA: IMPLICATION FOR PETROLEUM GENERATION.

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ABSTRACT

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 (1.73-12.47 indicates Mamu samples consisted of terrestrial organic matter with marine incursion deposited under oxic/suboxic-oxic in lacustrine-fluvial/deltaic environment. The distribution patterns of C_{32}-C_{35} benzohopanes in Mamu samples confirmed the redox condition of organic matter deposition within the Formation. The presence of unsaturated oleanenes in Mamu samples further confirmed their thermal immaturity status. The kerogen types of the samples have capacity to generate both oil and gas. Benzohopanes (C_{32}-C_{35}) and three oleanene isomers; olean-12-ene, olean-13 (18)-ene and olean-18-ene were present in samples collected from Mamu Formation. Coals from Mamu Formation have potential to generate both oil and gas but are presently immature to have formed any significant hydrocarbons.

Keywords: Biomarkers, Organic matter, Coal, Source, Maturity, Depositional Environment, Benue Trough.

INTRODUCTION

The studied area lies between Latitude 5º30´ to 8º00´N and Longitude 6º00´ to 8º30´E (Fig. 1). Coals are remnants of terrestrial higher plants formed under non-marine and paralic conditions (Tissot and Welte, 1984) and found at its site of deposition as a solid and a relatively pure massive organic substance. Many studies have suggested the possibility of non-marine coal sediments having potential capacity to generate petroleum (Katz, 1983; Betrand et al., 1986; Boreham and Powell, 1991; Hunt 1991, 1996; Hutton et al., 1994). Coal, the world's most abundant, accessible and versatile source of fossil energy was brought to the forefront of the global energy scene by the industrial revolution of the 10th century (Balogun et al., 2003). The largest reserves of coal were deposited in the late Carboniferous and Permian with lesser amounts in the Jurassic through the Tertiary (Kotarba et al., 2002).

During the past 20 years, coals and shales containing coaly organic matter (coaly shales) have received increasing attention as commercial quantity of petroleum (oil and gas) have been discovered in many basins around the world containing these type of organic matter (Hendrix et al., 1995; Mario et al., 1997; Petersen et al., 2000; Bechtel et al., 2001; Kotarba et al., 2002; Boreham et al., 2003). Despite the huge reserves of coal in Nigeria, its petroleum potential has not been extensively studied.

Previous studies on geochemistry has indicated that biomarker or geochemical fossils are organic compounds found in geosphere whose structure can be unambiguously linked to their biological origin, despite the possibility of some structural alteration due to diagenetic or other processes. Treibs (1934) was the first to develop the biomarker concept with his pioneering work on identification of porphyrins in crude oils and suggested that these porphyrins may have originated from the chlorophyll of plants. All biomarker molecules have definitive chemical structures, which can be related directly or indirectly through a set of diagenetic alterations to biogenic precursors, and cannot be synthesized by abiogenic processes (Simoneit, 2002). The use of biomarkers as indicators of biogenic, paleoenvironmental, and geochemical processes on Earth has been widely accepted (Mackenzie et al., 1982; Johns, 1986; Simoneit et al., 1986; Brassel, 1992; Imbus and Mckirdy, 1993; Mitterer, 1993; Simoneit, 1998). Biomarkers are widely used in petroleum geochemical studies in source rock evaluation, oil-oil or oil-source rock correlations, basin evaluation and reservoir management (Peters et al., 2005).

n-Alkanes are widely distributed in various plants and other organisms and are probably the most exploited class of biomarkers (Philp, 1985).High proportions of long chain C_{27}-C_{31} members relative to the total *n*-alkanes especially, n-C_{27} and n-C_{29} are typical of terrestrial higher plants, where they occur as main components of plant waxes i.e. leaf curticles, spores, pollens and resins (Bray and Evans 1961; Meinschein, 1961; Kvenvolden, 1962; Eglinton and Hamilton, 1963; Caldicott and Eglinton, 1973; Miranda et al*.,* 1999; Tissot and Welte, 1984; Barthlot et al*.,* 1998). The short chain *n*-alkanes with odd-to-even predominance in the medium molecular weight region (C_{11}-C_{17}) maximizing at n-C_{16} are predominantly found in algae and microorganisms (Clark and Blummer, 1967; Fowler *et al.,* 1986; Miranda *et al.,* 1999; Ficken et al*.,* 2000). The ratio of odd/even carbon numbered *n*-alkanes has been in use over a long period in estimating the thermal maturity of fossil fuels (Bray and Evans; 1961; Philippi, 1965; Scalan and Smith, 1970; Tissot et al*.,* 1977). These ratios can be expressed as Carbon preference index, CPI (Bray and Evans, 1961) and improved Odd-to-even predominance, OEP (Scalan and Smith, 1970). The CPI and OEP values above or below 1.0 indicate low thermal maturity. Values of 1.0 suggest, but do not prove, that an oil or rock extract is thermally mature. The CPI or OEP values below 1.0 are unusual and typify low maturity oils or bitumen from carbonate or hypersaline environments (Peters et al*.,* 2005). Organic matter inputs do affect these ratios and therefore are mostly applied with caution. Some authors such as Bechtel et al. (2003), Hayes et al. (1990), Peters et al. (2005), Tyson (1995), Adam et al. (2006), Grice et al. (1998), Killops and Killops (2005), Matsumoto and Watanuki (1990), Huang et al. (1995), Lockheart et al. (2000), Kogel-Knaber (2002), Yuang and Huang (2005), Tuo and Li (2005), Bai et al. (2006), Gonzalez et al. (2003), Haberer et al. (2006), Stefanova et al. (2002), Otto et al. (2003; 2005), Volkman (2005), Nytoft et al. (2002), Yangming et al. (2005), Jauro et al. (2007), Yessalina et al. (2006) and Galimov (2006) has used biomarkers widely in geochemical studies in petroleum exploration in identifying the source and depositional environment of organic matters. This paper deals with assessing the organic source, depositional environment and maturity of the coal based on the distribution of biomarkers.

REGIONAL STRATIGRAPHIC SETTING
The Benue Trough of Nigeria is a rift basin in central West Africa that extends NNE-SSW for about 800km in length and 150km in width (Fig. 1) (Simpson, 1954; Carter et al., 1963;

Reyment, 1965; Murat, 1972 and Benkhelil, 1989). The trough contains up to 6000m of Cretaceous – Tertiary sediments of which those predating the mid-Santonian were compressionally deformed, faulted, and uplifted in several places (Petters and Ekweozor, 1982; Whiteman, 1982; Zaborski, 1998; and Benkhelil, 1989).

The Benue Trough geographically subdivided into Lower, Middle, and Upper Benue Trough is strictly a sedimentary basin extending from the Gulf of Guinea in the south to the Chad Basin in the north (Fig. 1) (Offodile, 1976; Dike, 1976a,b, 1993, 2002; Adeleye and Fayose,1978; Enu, 1987 and Petters, 1978, 1979b, 1980, 1982, 1991). The origin and tectonic history of the Benue Trough is associated with the break-up of the continents of Africa and South America. This break-up was followed by the drifting apart of these continents, the opening of the South Atlantic, and the growth of the mid-Atlantic ridge (Read and Watson, 1978; Freeth, 1990).

Fig. 1: Map showing the location of studied coals in the Anambra Basin.

Wright (1981) presented a case for regarding the Benue Trough as having been a tensional feature throughout its entire history. His principal supporting evidence being the straight limbs of some folds structures discernible on ERTS (Earth Resources Technology Satellite) imagery. He briefly reviewed and dismissed the case for a seafloor spreading accompanied by subduction for the trough. Jones (1965) and Osazuwa et al. (1981) independently concluded that the Benue Trough is characterized by central gravity "highs" over Amar, Awe, Gboko in the Middle Benue Trough and the Kaltungo area in the Upper Benue Trough. Their results also revealed that the

central gravity "highs" are flanked on both sides by gravity "lows". They interpreted the "lows" as areas of thickest Cretaceous sediments.

The Benue Trough is believed to be an aulacogen (a failed arm of a RRR triple junction) (Benkhelil, 1989). As pointed out by Petters (1982), in the Gulf of Guinea where bifurcating rift system become the site of a triple junction, two of the rifts opened into ocean with marginal basins underlain by half-grabens (e.g. the Dahomey Embayment). Along the third rift system in the Gulf of Guinea triple junction occurred only limited opening (Petters, 1982). This was abandoned as a "failed arm" or juvenile aulacogen which today is the Benue Trough. This trough contains a thick folded sedimentary pile and an aulacogen delta (Niger Delta) at its re-entrant.

Detailed stratigraphic descriptions (Fig. 2) of the sediments in Benue Trough have been presented by Obaje et al. (1999,2004,2006), Obaje and Hamza (2000) and Pearsen and Obaje (2000).

The sedimentary succession in the Lower Benue Trough comprises the basal pre-Abian basement unconformably overlain by the Albian Asu River Group (3000m thick). The Asu River Group is overlain conformably by the Turonian-Early Santonian Cross River Group (2000m) (Petters, 1982; Petters and Ekweozor, 1982). A post-Santonian deltaic and coal measures sequence, about 2000m thick, rest unconformably on the Cross River Group (Fig. 2).

The Asu River Group comprises the oldest marine deposits in the Benue Trough. These are the shales, limestones and sandstone lenses of the Albian Abakaliki Shale, correlating with the Mfamosing Limestone, a lithostratigraphic unit introduced by Petters (1982). The Mfamosing Limestone is a 15m thick limestone sequence exposed along the Oban Massif on the Calabar Flank in the southeastern part of the Benue Trough (Petters, 1982; Ojoh, 1990; Akande et al., 1998; Dike and Onumara, 1999). The fossiliferous Arufu, Uomba, and Gboko Formations in the Middle Benue Trough are the lateral equivalent of the Asu River Group (Petters, 1982).

Overlaying the Asu River Group is transgressive Cenomanian-Santonian lithogenetic unit; the Nkalagu Formation (black shales, limestones and siltstones) and interfingering regressive sandstones of the Agala, Amasiri and Agbani Formations (Petters, 1982). In the Middle Benue Trough, the Awe, Keana, and Makurdi Formations and the marine Ezeaku and Awgu Formations are the lateral equivalents of the Cross River Group (Obaje et al., 1999, 2004, 2006). Late Santonian-Early Campanian folding in the Benue Trough displaced the major depositional axis in the greater parts of the Benue Trough and was quite intense, producing over 100 anticlines and

synclines (Benkhelil, 1989) (Fig. 2). Following the mid-Santonian tectonism (fold phase), depositional axis in the Benue Trough was displaced westward resulting in the subsidence of the Anambra Basin (Akande and Erdtmann, 1998). The Anambra Basin, therefore, is a part of the Lower Benue Trough containing post-deformational sediments of Campano-Maastrichtian to Eocene ages. It is logical to include the Anambra Basin in the Benue Trough, being a related structure that developed after the compressional stage (Akande and Erdtmann, 1998).

In the Lower Benue, post-folding Campano-Maastrictian paralic shales of the Enugu and Nkporo Formations, coal measures of the Mamu and Nsukka Formations and sandstones of the Ajali Formation was deposited (Akande and Erdtmann, 1998).
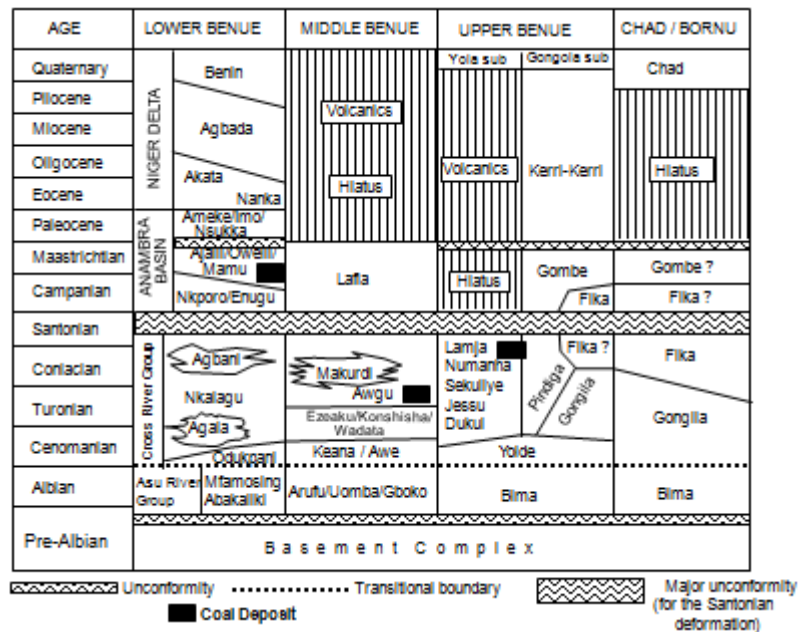

Fig. 2. Stratigraphic successions in the Benue trough and the relationship to the Chad basin and the Niger delta (After Obaje et al., 2004).

MATERIALS METHODS

A total of 12 outcrop coal and carbonaceous coal samples were obtained from the Mamu Formation from the mining pits. Care was taking to avoid weathered portions of the outcrop and to obtain material sufficient for various geochemical analyses. In the laboratory, the samples were reshaped using a rotating steel cutter to eliminate surface that could be affected by

alteration. Chips were cut from the samples and dried in an oven at 105°C for 24 hours. The dried sample was pulverized in a rotating disc mill to yield about 50 g of sample for analytical geochemistry.

The GC-MS analyses of the fractions were performed on a Hewlett-Packard 6890N gas chromatograph interfaced to a Hewlett-Packard 5973N Mass spectrometer. The gas chromatograph was equipped with a DB-5 MS fused silica capillary column (30 m x 0.25 mm) and helium was used as carrier gas with a flow rate of 1ml/min. The Mass spectrometer was operated with electron impact energy of 70 eV and ion source temperature of 230 °C. The GC oven temperature was isothermal for 1min at 80 °C and then programmed from 80 to 280 °C at 3 °C/min and isothermal for 20 min at 280 °C. Individual saturated, aromatic and NSO- compounds were monitored by selected ion monitoring (SIM) at a cycle time of 1s. The GC-MS data were acquired and processed with a Hewlett-Packard Chemstation data system.

RESULTS AND DISCUSSION

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

The m/z 85 mass chromatograms showing the distribution of n-alkane and isoprenoids in the samples are shown in Figs. 3 and 4. Geochemical parameters calculated from the alkane distribution are given in Table 1. The n-alkanes distribution in Mamu samples range from C_{14}-C_{35}, maximizing at C_{27} or C_{29} (Figs. 3, 4). 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; Adedosu, 2009). The Pr/Ph ratios range from 9.33 to 12.47 and 1.73 to 4.08 for Enugu 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; Adedosu, 2009). 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; Tuo et $al.,$ 2007).

The Carbon Preference Index (CPI) and Odd-over-even predominance (OEP) values in Enugu samples range from 1.85 to 2.32 and 0.65 to 2.27 respectively. The CPI for Okaba samples range from 3.00 to 8.72 and 1.16 to 7.06 respectively. 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; Sabel *et al.,* 2005; Stefanova *et al.,* 2005; Adedosu, 2009). The plot of CPI against OEP shows that these samples are immature to low mature (Fig. 5).
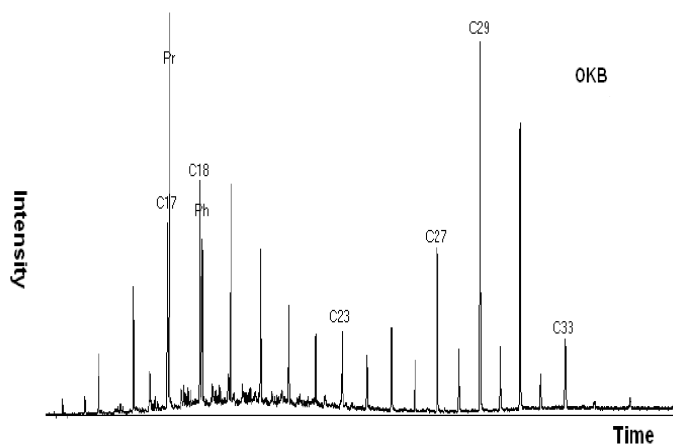

Fig. 3: *m/z* 85 Mass chromatograms of aliphatic fractions of Okaba samples showing the distribution of *n*-Alkanes.
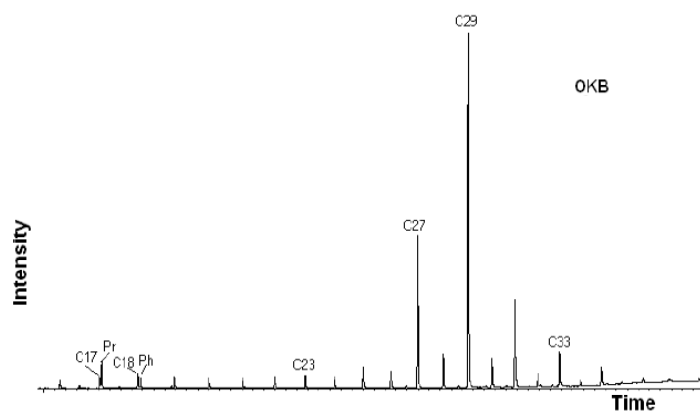

Fig. 3 (contd.): *m/z* 85 Mass chromatograms of aliphatic fractions of Okaba samples showing the distribution of *n*-Alkanes.
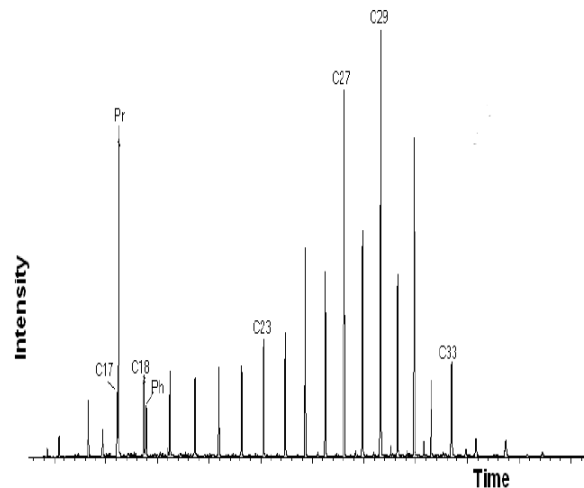
Fig. 4: *m/z* 85 Mass chromatograms of aliphatic fractions of Enugu samples showing the distribution of *n*-Alkanes.
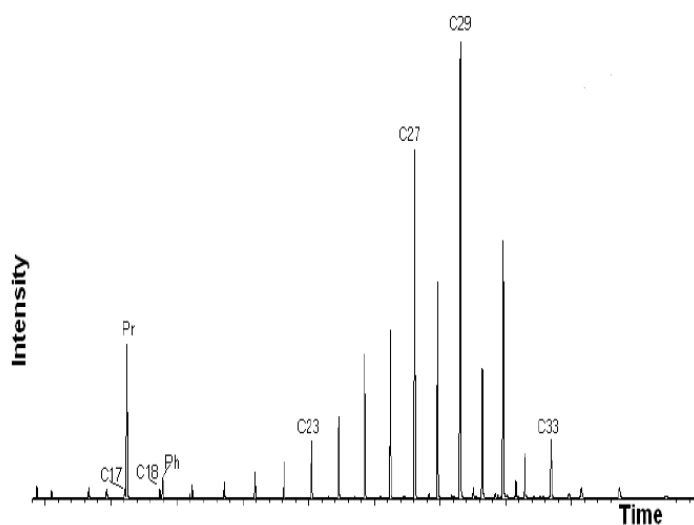

Fig. 4 (contd.): *m/z* 85 Mass chromatograms of aliphatic fractions of Enugu samples showing distribution of *n*-Alkanes.

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 (Duan *et 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. 7, 8 and 9 respectively. Parameters calculated from the fatty acids and alkanones distribution in the coal extracts are listed in Table 2.

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

| Sample Name	Mining Pit	Formation	Lithology	Pr/Ph	Pr/nC$_{17}$	Ph/nC$_{18}$	CPI	OEP
ENUG-1	"	Mamu	Coal	9.33	10.89	0.83	1.99	1.86
ENUG-2	"	"	"	10.48	52.19	2.83	1.87	1.89
ENUG-3	"	"	"	11.55	40.09	2.23	1.91	1.93
ENUG-4	"	"	"	9.66	27.31	3.06	1.85	1.80
ENUG-5	"	"	"	9.87	40.33	1.63	1.96	1.88
ENUG-6	"	"	"	12.47	14.99	1.05	2.12	2.27
OKAB-1	"	"	"	2.11	3.40	1.08	3.00	3.08
OKAB-2	"	"	"	1.73	2.94	0.72	5.82	5.16
OKAB-3	"	"	"	3.76	5.42	1.27	8.72	7.06
OKAB-4	"	"	"	4.08	4.51	0.74	7.20	6.28
OKAB-5	"	"	"	3.30	2.57	0.70	6.16	6.13
OKAB-6	"	"	"	2.11	2.53	0.86	6.48	6.02
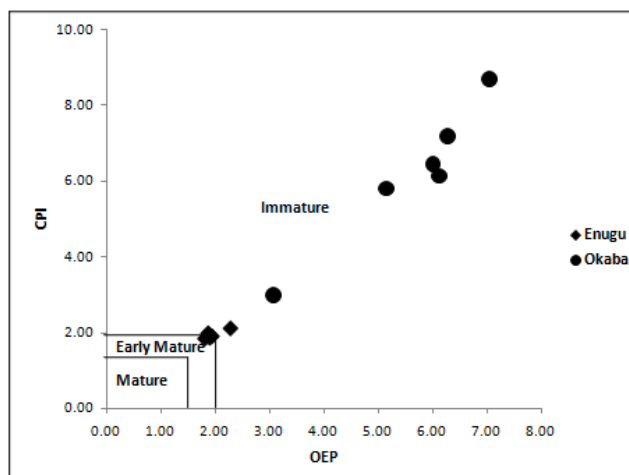
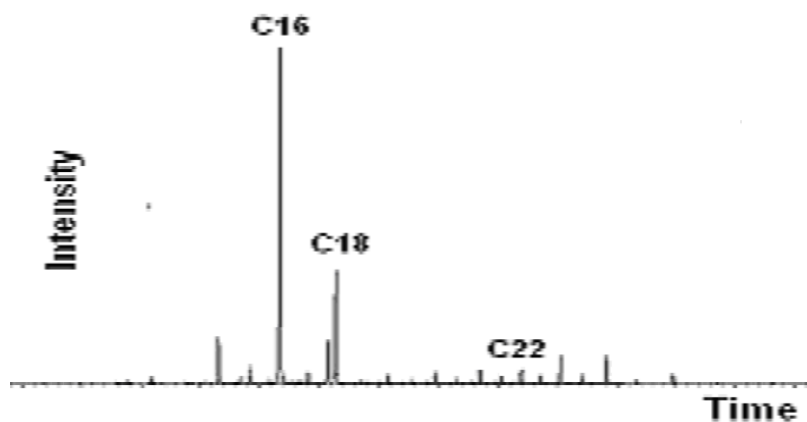Fig. 5: Plots of CPI against OEP of Mamu samples.

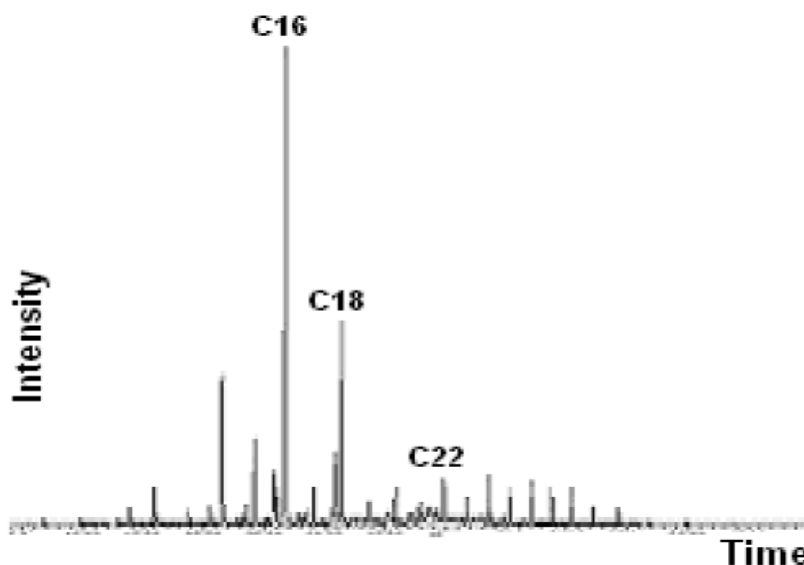Fig. 6: *m/z* 74 mass chromatogram showing the distribution of *n*-fatty acids in Okaba samples.

Fig. 7: *m/z* 74 mass chromatogram showing the distribution of *n*-fatty acids in Enugu samples.

Mamu samples have saturated *n*-fatty acids ranging from C_8 to C_{32}, maximizing at nC_{16} or nC_{18} (Fig. 6). These distributions reflect organic matter from both marine and terrestrial materials (Volkman *et al.,* 1998; Adedosu, 2009). However the dominance of short chain ($<C_{20}$) saturated *n*-fatty acids maximizing at C_{16} is an indication of substantial contribution of micoorganism/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 ATRFA 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 (CPILFA) 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).

The *n*-alkan-2-ones range from nC_{12} to nC_{33}, maximizing at nC_{17} or nC_{29} (Figs. 8 and 9). These distributions reflect higher plants and algae inputs to the organic matter (Bai *et al.,* 2006). The CPI values range from 1.27 to 1.69 and 2.10 to 2.66 in Enugu and Okaba samples respectively (Table 2). These values indicate low maturity status for all the samples (Tuo *et al.,* 2007; Adedosu, 2009).
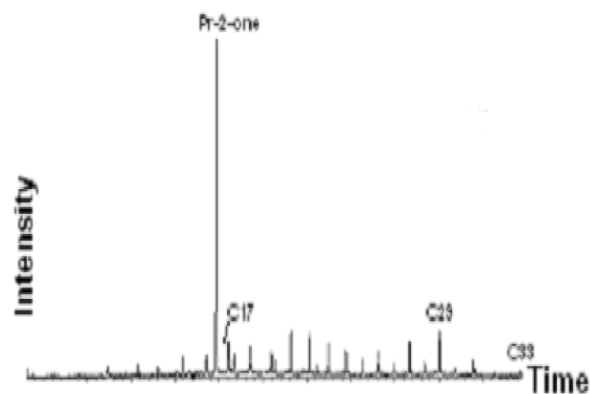
Fig. 8: *m/z* 58 mass chromatograms showing the distributions of alkan-2-ones in Okaba samples.
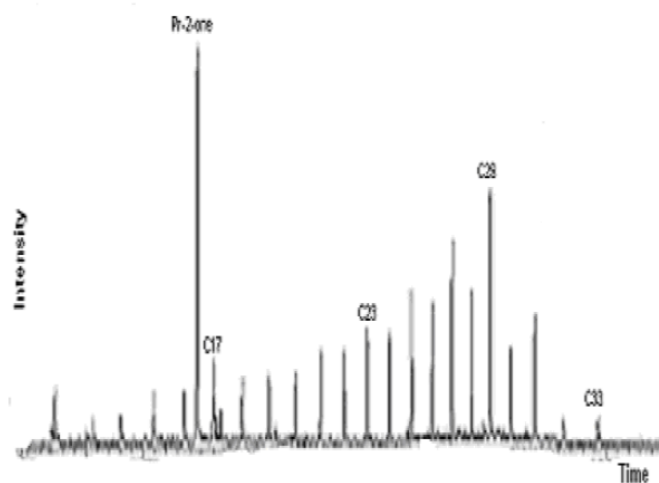

Fig. 9: *m/z* 58 mass chromatograms showing the distributions of alkan-2-ones in Enugu samples.

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

Sample Name	Mining Pit	Formation	Lithology	ATR_{FA}	CPI_{LFA}	Pr-2-ose /C17	CPI (Alkanone)
ENUG-1	"	Mamu	Coal	0.95	1.47	4.39	1.27
ENUG-2	"	"	"	0.91	1.37	10.54	1.45
ENUG-3	"	"	"	0.92	1.61	8.69	1.51
ENUG-4	"	"	"	0.92	2.07	12.18	1.69
ENUG-5	"	"	"	0.96	1.25	7.45	1.30
ENUG-6	"	"	"	0.94	1.61	4.10	1.60
OKAB-1	"	"	"	nd	nd	nd	nd
OKAB-2	"	"	"	0.85	2.78	8.68	2.66
OKAB-3	"	"	"	0.93	1.37	7.69	2.25
OKAB-4	"	"	"	0.94	1.95	12.69	2.59
OKAB-5	"	"	"	0.96	1.44	13.71	2.49
OKAB-6	"	"	"	0.91	2.51	21.43	2.10

Tricyclic and C$_{24}$ tetracyclic terpanes

The *m/z* 191 showing the distributions of tricyclic and tetracyclic terpanes in the samples are shown in Figs. 10 and 11. Mamu samples are dominated by C$_{19}$-C$_{21}$ tricyclic terpanes (Table 3). These distributions indicate organic matter derived from terrestrial matter (Ozcelik and Altunsoy, 2005; Adedosu, 2009).
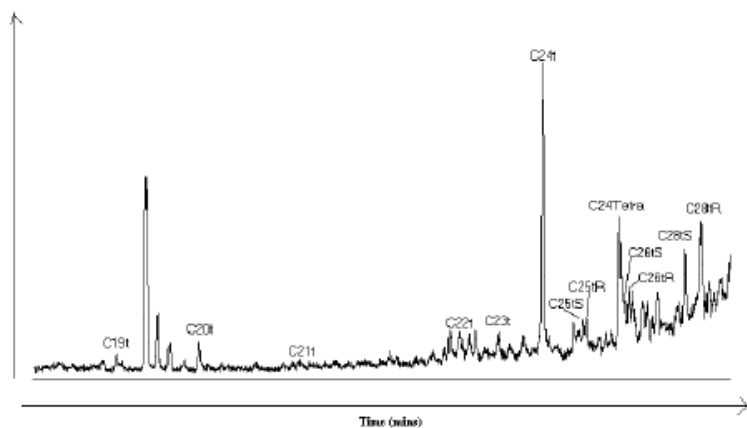

Fig. 10: *m/z* 191 showing the distribution of tricyclic and tetracyclic terpane in Okaba samples.
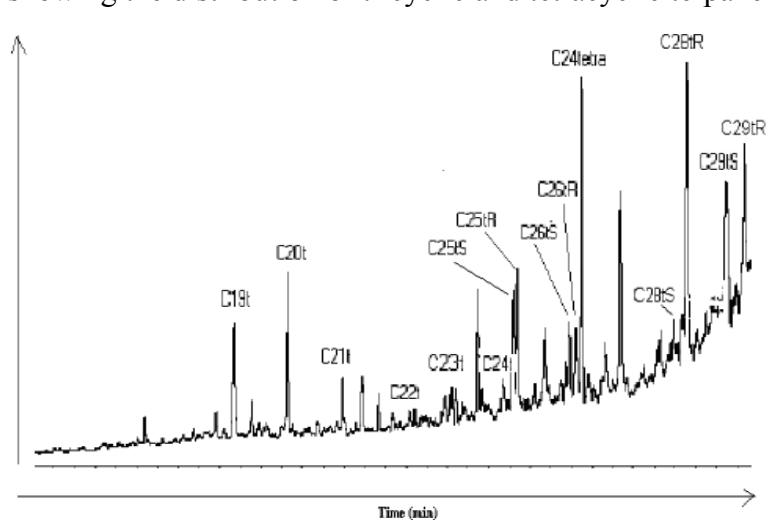

Fig. 11: *m/z* 191 showing the distribution of tricyclic and tetracyclic terpane in Enugu samples.

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

Sample Name	Mining Pit	Formation	Lithology	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
ENUG-1	"	Mamu	Coal	0.08	2.40	0.65	83.00	17.00
ENUG-2	"	"	"	0.09	2.86	0.46	90.00	10.00
ENUG-3	"	"	"	0.05	2.11	0.61	72.30	27.70
ENUG-4	"	"	"	0.08	2.21	0.64	87.50	12.50
ENUG-5	"	"	"	0.09	2.70	0.55	78.50	21.50
ENUG-6	"	"	"	0.06	0.98	0.61	85.80	14.20
OKAB-1	"	"	"	0.18	1.66	0.79	73.90	26.10
OKAB-2	"	"	"	0.09	2.04	0.66	53.40	46.60
OKAB-3	"	"	"	0.08	1.41	nd	nd	nd
OKAB-4	"	"	"	0.06	1.94	0.64	70.40	29.60
OKAB-5	"	"	"	0.10	2.53	0.84	81.00	19.00
OKAB-6	"	"	"	0.15	2.28	0.72	79.50	20.50

The C_{22}/C_{21} tricyclic terpane ratios range from 0.46 to 0.65 and 0.64 to 0.84 in Enugu and Okaba samples respectively (Table 3). The observedC_{22}/C_{21} tricyclic ratios indicate fluvial/deltaic and lacustrine-fluvial/deltaic depositional environment for Enugu and Okaba samples respectively (Peters *et al.,* 2005; Adedosu, 2009).

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 Enugu and Okaba samples respectively. These values also reflect fluvial/deltaic depositional environment and lacustrine-fluvial/deltaic for Enugu and Okaba samples respectively (Peters *et al.,* 2005).

Hopanes and homohopanes

The *m/z* 191 mass chromatograms showing the distribution of pentacyclic triterpanes in the samples are shown in Figs. 12 and 13. The sterane/hopane ratio values range from 0.04-0.51(Table 4).
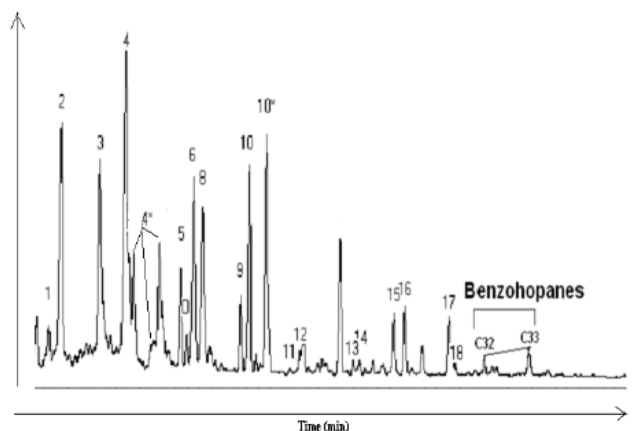
Fig. 12: *m/z* 191 Mass chromatogram showing the distribution of hopanes and benzohopanes in Okaba samples.
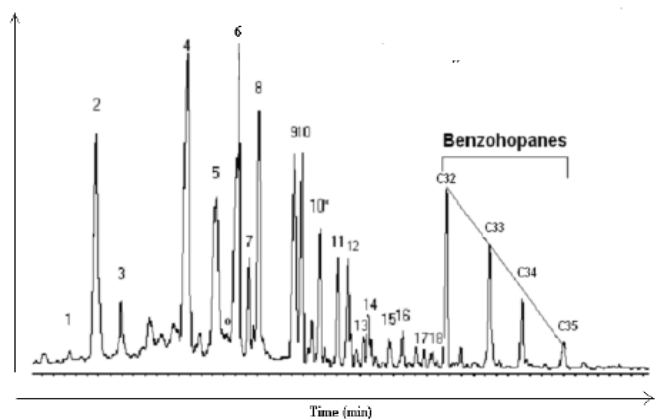

Fig. 13: *m/z* 191 mass chromatogram showing the distribution of hopanes and benzohopanes in Enugu samples.

Table 4: Source and depositional environment parameters computed from the hopane and sterane distributions in the coals.

Sample Name	Mining Pit	Formation	Lithology	$\%C_{27}$ sterane	$\%C_{28}$ sterane	$\%C_{29}$ sterane	$\%C_{27}$ diast.	$\%C_{28}$ diast.	$\%C_{29}$ diast.	C_{27}/C_{29} sterane	%Diast./ sterane	Sterane/ hopane	C_{35}/C_{30} hopane	C_{35}/C_{34} $\alpha\beta S$ hopane	Homohopane/ index
ENUG-1	"	Mamu	Coal	24.02	20.18	55.80	28.40	23.37	48.27	0.43	89.00	0.07	0.05	0.23	0.04
ENUG-2	"	"	"	11.83	33.64	54.53	23.05	28.61	48.34	0.22	84.51	0.06	0.05	0.25	0.03
ENUG-3	"	"	"	10.73	29.71	59.56	25.44	24.33	50.23	0.18	66.56	0.29	0.02	0.32	0.02
ENUG-4	"	"	"	16.51	26.46	57.03	20.14	30.31	49.56	0.29	66.30	0.04	0.05	0.29	0.03
ENUG-5	"	"	"	12.97	20.08	66.95	17.00	24.06	58.94	0.20	87.23	0.06	0.01	0.28	0.02
ENUG-6	"	"	"	20.00	23.38	56.62	17.31	25.94	56.75	0.35	71.37	0.35	0.03	0.59	0.04
OKAB-1	"	"	"	20.98	43.20	35.82	13.91	29.66	56.43	0.59	50.32	0.16	0.09	0.62	0.13
OKAB-2	"	"	"	19.06	41.28	39.66	11.60	35.63	52.77	0.48	50.69	0.20	0.32	0.81	0.11
OKAB-3	"	"	"	10.59	27.73	61.68	21.89	42.34	35.78	0.17	63.72	0.10	0.06	0.76	0.09
OKAB-4	"	"	"	11.57	29.61	58.83	26.45	32.19	41.36	0.20	51.76	0.08	0.01	0.59	0.03
OKAB-5	"	"	"	17.06	39.20	43.79	32.76	31.00	36.24	0.40	73.84	0.08	0.02	0.92	0.11
OKAB-6	"	"	"	10.78	34.31	54.91	19.53	42.62	37.85	0.20	46.77	0.12	0.47	0.85	0.12

Table 5: Maturity parameters computed from the hopane and sterane distributions in the coals.

Sample Name	Mining Pit	Formation	Lithology	Mor/Hop	Hop/Hop+ Mor	Ts/Ts+Tm	22S/22S+22R C_{32} HH	20S/20S+20R C_{29} steranes	$\beta\beta/\beta\beta+\alpha\alpha$ C_{29} sterane
ENUG-1	"	Mamu	Coal	0.46	0.69	0.04	0.54	0.04	0.25
ENUG-2	"	"	"	0.56	0.64	0.03	0.59	0.15	0.19
ENUG-3	"	"	"	0.63	0.61	0.04	0.55	0.17	0.20
ENUG-4	"	"	"	0.54	0.65	0.03	0.54	0.11	0.24
ENUG-5	"	"	"	0.61	0.62	0.02	0.55	0.19	0.16
ENUG-6	"	"	"	0.64	0.61	0.05	0.58	0.19	0.25
OKAB-1	"	"	"	0.84	0.54	0.13	0.48	0.19	0.30
OKAB-2	"	"	"	0.85	0.54	0.16	0.43	0.10	0.33
OKAB-3	"	"	"	0.62	0.62	0.24	0.31	0.18	0.21
OKAB-4	"	"	"	0.59	0.62	0.11	0.37	0.19	0.50
OKAB-5	"	"	"	0.57	0.64	0.14	0.33	0.39	0.56
OKAB-6	"	"	"	0.93	0.52	0.24	0.16	0.22	0.45

The C_{27} to C_{35} hopanes are detected in all the Mamu samples but C_{28} was not detected (Fig. 12 and 13). The most prominent hopane in Enugu samples are $C_{29}\alpha\beta$-norhopane and $C_{30}\alpha\beta$-hopane while $C_{29}\alpha\beta$ norhopane is predominant in Okaba samples (Figs. 12 and 13). In the Okaba samples, abundance of $C_{29}\alpha\beta$-hopane in all the 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 Enugu samples reflects significant contribution from prokaryotic organisms as well as vitrinitic (terrestrial) organic matter. 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; Farrimond *et al.,* 1998; Peters *et al.,* 2005).

Benzohopanes with different distributions were found in Enugu and Okaba coal samples (Figs. 12 and 13). There is no previous record of presence of benzohopanes in Nigerian coal and coaly organic matter. The C_{32}-C_{35} benzohopanes were detected in Enugu samples while C_{32}-C_{33} benzohopanes were detected in Okaba samples. Benzohopanes are thought to be secondary transformation products of C_{35} bacteriohopanepolyol derivatives (Grice *et al.,* 1998; Peters *et al.,* 2005; Killops and Killops, 2005; Bechtel *et al.,* 2007a; Adedosu, 2009).

Three isomers of oleanenes; olean-18-ene, olean-13 (18)-ene and olean-12-ene were identified in Okaba samples (Figs. 14, 15 and 16). Similar to the benzohopanes, this is the first time oleanene isomers are being identified in Nigerian 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 and Rullkötter, 1988; Ekweozor and Telnæs, 1990; Rullkötter *et al.,* 1994; Curiale, 1995). They have also been found useful as indicators of thermal immaturity (Eneogwe *et al.,* 2002).
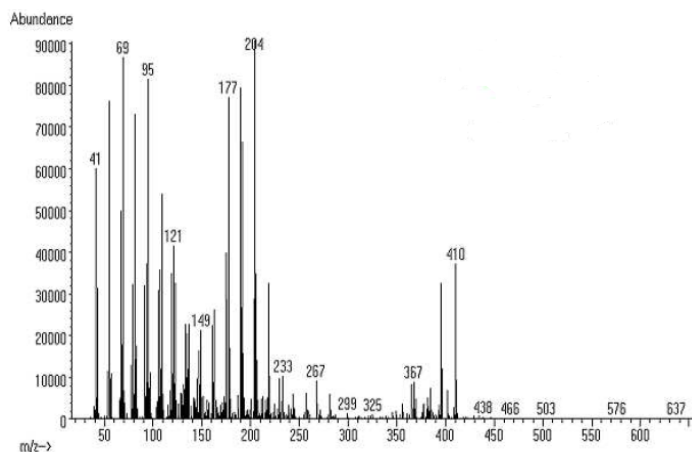

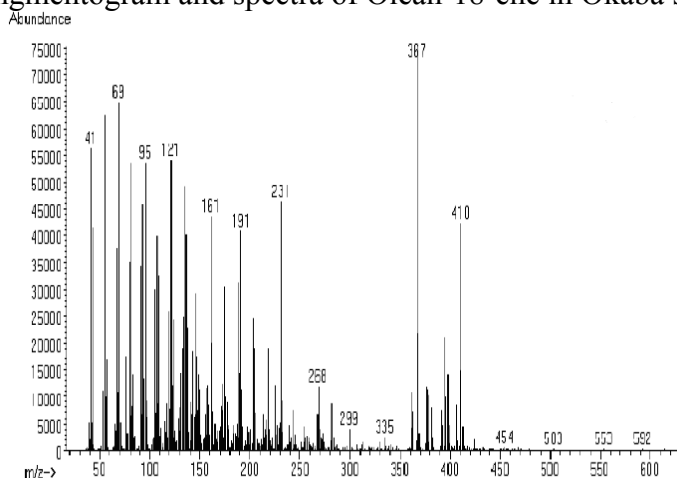Fig. 14: Mass frangmentogram and spectra of Olean-18-ene in Okaba samples.

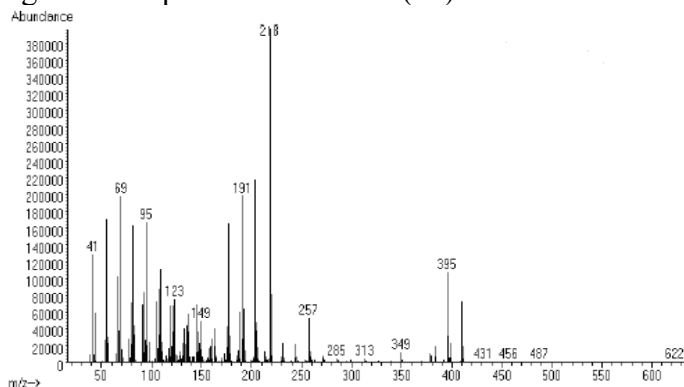Fig. 15: Mass frangmentogram and spectra of Olean-13(18)-ene in Okaba samples.

Fig. 16: Mass frangmentogram and spectra of Olean-12-ene in Okaba samples.

In Enugu 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 Enugu and Okaba samples respectively. The homohopane index and homohopane ratio for the sample ranges from 0.02- 0.13 and 0.23-0.92 respectively (Table 4). These values indicate oxic depositional environment for Enugu samples and suboxic-oxic depositional environments for Okaba samples (Peters and Moldowan, 1991; Killops and Killops, 2005; Peters *et al.,* 2005; Yangming *et al.,* 2005; Adedosu, 2009). There is presence of gammacerane in Okaba samples (Figs. 12 and 13), which indicate water column stratification during organic matter source deposition (Sinninghe Damsté *et al.,* 1995; Yangming *et al.,* 2005). The Moretane/Hopane, Hopane/Hopane + Moretane, Ts/Ts + Tm, 22S/22S + 22R C_{32} homohopane ratios in Enugu 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 5) respectively. These values suggest low maturity status (Rullkötter *et al.,* 1985; Kagya, 1996; Peters *et al.,* 2005). The Okaba samples have Moretane/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 0.16-0.48 respectively. These values also indicate that Enugu samples are thermally immature (Rullköter *et al.,* 1985; Kagya, 1996; Peters *et al.,* 2005).

Steranes

The *m/z* 217 mass chromatograms showing the distribution of steranes and diasteranes in all the samples are shown in Figs. 17 and 18.
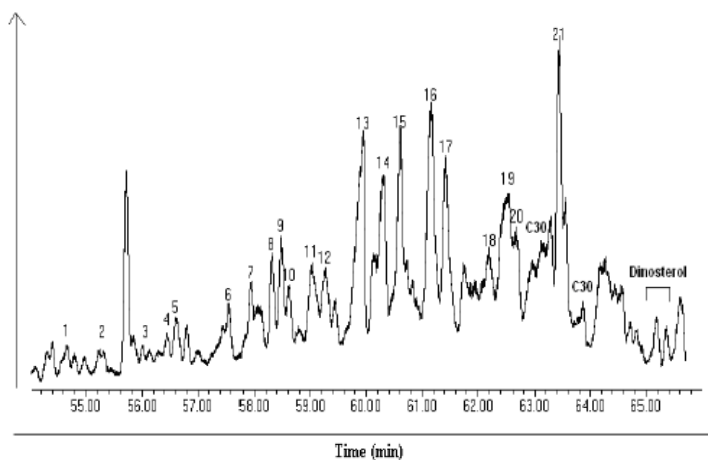

Fig. 17: *m/z* 217 mass chromatograms showing the distribution of steranes and diasteranes in Okaba samples.
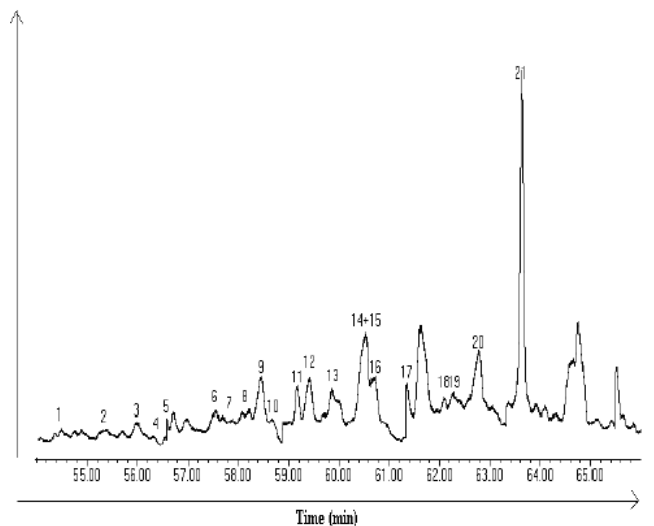
Fig. 18: *m/z* 217 mass chromatograms showing the distribution of steranes and diasteranes in Enugu samples.

C_{29} Diasteranes and steranes are the most abundant steranes in all the samples except few samples from Okaba where C_{28} predominates. The sterane and diasterane distributions in Okaba samples are increasing in the order of $C_{29}>C_{28}>C_{27}$. The predominance of C_{29} over C_{27} 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 C_{27} and C_{28} in these samples also reflects contributions from phytoplankton; algae, diatoms, dinoflagellates (Volkman, 1986; Volkman *et al.,* 1998; Sari and Bahtiyar, 1999; Peters *et al.,* 2005). The ternary plot of C_{27}, C_{28} and C_{29} sterane of Mamu samples (Fig. 19) reflects major terrestrial input in Enugu 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. 20) shows that most of the Enugu 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 (Adedosu, 2009).
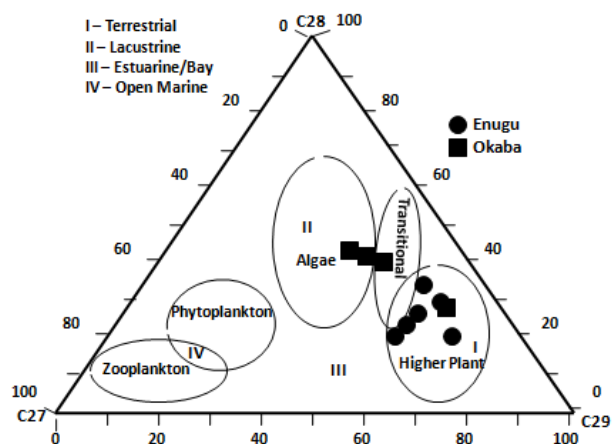
Fig. 19: Ternary plots of C_{27}, C_{28} and C_{29} steranes distributions in Nigerian coal (After Huang and Meinschein, 1979).
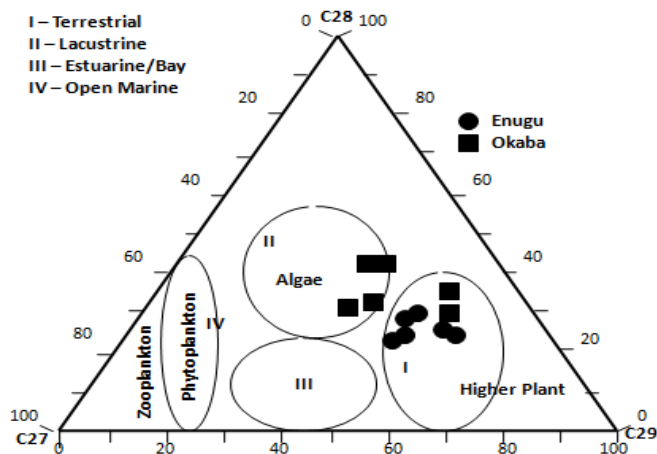

Fig. 20: Ternary plots of C_{27}, C_{28} and C_{29} diasteranes distributions in Nigerian coal (After Huang and Meinschein, 1979).
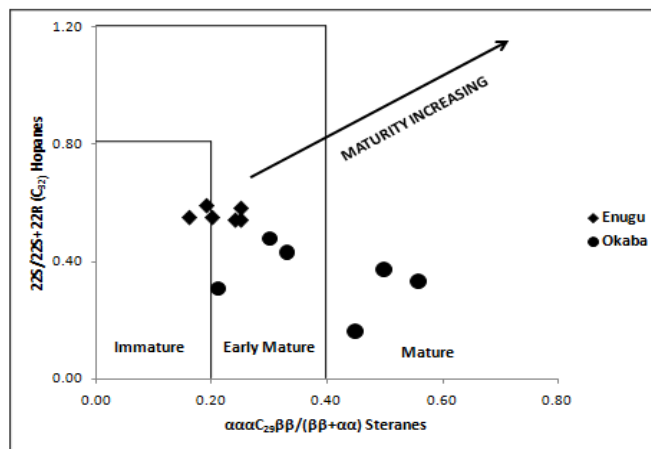

Fig. 21: Plots of 22S/22S+22R C_{32}hopanes against $C_{29}\alpha\beta\beta/\alpha\beta\beta+\alpha\alpha\alpha$ steranes (After Inaba et al., 2001).

There is little variation in sterane and diasterane distribution in Enugu samples while significant variations are noticed in Okaba samples. This observation possibly reflects same depositional environments for Enugu samples (fluvial/deltaic) and lacustrine-fluvial/deltaic depositional environments for Okaba samples. This observation can be supported by the ratio of C_{27}/C_{29} (Table 4) for the samples. The values range from 0.2 to 0.7 and 0.18 to 0.43 in Okaba and Enugu samples respectively. The dominance of dinosterol over C_{30} steranes in Okaba samples reflects typical fresh water lacustrine source rocks (Köhler and Clausing, 2000; Peters *et al.,* 2005; Adedosu, 2009).

The 20S/20S+20R and αββ/αββ+ααα C_{29} ratios range from 0.04 to 0.19 and 0.16 to 0.25 respectively in Enugu 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 (Adedosu, 2009). The plot of 22S/22S+22R C_{32} hopanes against C_{29}αββ/αββ+ααα steranes also confirm the thermal immaturity status of Mamu samples (Fig. 21).

CONCLUSION

The distributions of *n*-alkanes and *n*-alkan-2-ones showed Mamu samples were derived from terrestrial organic matter. The Pr/Ph ratios of samples from Enugu 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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