CARBON ISOTOPE: IMPLICATION ON ORIGIN AND DEPOSITIONAL ENVIRONMENT OF ORGANIC MATTER FROM COALS OF THE MAMU FORMATION, ANAMBRA BASIN SOUTHEAST NIGERIA.

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ABSTRACT

The studied area lies between Latitude 5º30´ to 8º00´N and Longitude 6º00´ to 8º30´E. The sedimentary succession in the Anambra basin, southeast Nigeria is a potential active petroleum system with the generation, migration and accumulation of hydrocarbons in commercial quantities. The Cretaceous sediments in the Anambra Basin (SE Nigeria) consist of a cyclic succession of coals, carbonaceous shales, silty shales and siltstones interpreted as deltaic deposits. This research aims in determining the origin and depositional environment of organic matter from coals of the Mamu Formation in the Anambra Basin. Biomarkers in the aliphatic and polar fractions and aromatic hydrocarbon distributions in the samples were studied using Gas Chromatography- Mass Spectrometry (GC-MS). The Carbon isotope analysis of individual n-alkanes in the aliphatic fraction was performed using Gas Chromatography-Combustion-Isotope Ratio Mass Spectrometer (GC-IRMS). The vitrinite reflectance measurements of the samples were taken using Zeiss standard universal reflected microscope. The $\delta^{13}C$ isotopic values for *n*-alkanes range from –31.7 to –29.2 δ^{13}‰PDB and –30.1 to –28.2 δ^{13}‰PDB in Enugu and Okaba samples respectively. High (Pr/Ph) ratio (1.73-12.47) and isotopic distribution of individual alkanes showed that Mamu coal samples consisted of terrestrial organic matter with marine incursion deposited under oxic/suboxic-oxic in lacustrine-fluvial/deltaic environment.

Keywords: Coal, Organic matter, Biomarker, Carbon Isotope, Origin, Anambra Basin.

INTRODUCTION

The studied area lies between Latitude 5º30′ to 8º00′N and Longitude 6º00′ to 8º30′E (Fig. 1). Chemical methods based on bitumen extracts for assessing the organic matter in source rocks are mainly based on biomarkers. Analysis of biomarkers in source rock extracts gives useful information on sources of organic material.

Stable carbon isotopes have played an important role in many aspects of petroleum geochemistry. Early applications of bulk carbon isotope values included a study by Silverman and Epstein (1958) of a number of Tertiary crude oils from different environment. Marine and non-marine oils have been differentiated on the basis of their carbon isotopic compositions (Revill et al*.,* 1994; Hunt et al*.,* 2002; Meyers, 2003). Other early applications noted a general trend of enrichment of the light 12C isotope with increasing age (Welte et al*.,* 1975; Stahl, 1977), possibly caused by variations in intensity of photosynthesis and changes in the isotopic composition of the atmospheric CO_2. Kvenvolden and Squires (1967) successfully used isotopic age trend to relate and distinguish crude oils on regional basis in West Texas. The $\delta^{13}C$ value may to a certain extent reflect the chemical composition of organic material originating from the same vegetation type (Chabbi et al*.,* 2007). The distribution of ^{13}C among natural products is a sensitive palaeoenvironmental indicator (Hayes et al*.,* 1990) and can provide a great deal of information about ancient biogeochemical processes (Hayes, 1993). Carbon isotopic compositions of low rank coals have been suggested to be useful in reconstruction of changes in the global carbon cycle as well as climatic changes (Lücke et al*.,* 1999; Arens et al*.,* 2000).

Also, it has been shown that *n*-alkane distributions in kerogen using conventional geochemical tools, without detailed stable carbon isotope data can sometimes lead to erroneous interpretations of the precursors contributing to the kerogen even with samples containing abundant biomarkers (Audino et al*.,* 2002). Several studies have utilized the stable carbon isotopic compositions of individual *n*-alkanes to resolve source of *n*-alkanes or *n*-alkanes precursors in ancient sediments (Kennicult and Brooks, 1990; Collister et al*.,* 1994; Boreham et al*.,* 1994, Chabbi et al*.,* 2007).

The distribution pattern of individual *n*-alkane carbon isotopes in different kinds of oil should respond to variations in organic source character (Murray et al*.,* 1994). The shape of *n*-alkane carbon isotopes with a trend towards isotopically lighter values has been suggested for terrestrial organic matter; higher plant origin (Murray et al*.,* 1994; Schouten et al*.,* 2001; Yangming et al*.,* 2005). Marine oil commonly show a flat or positively sloping profile for *n*-alkane isotopes, few

studies have been reported with respect to the sloping profiles of *n*-alkane carbon isotope from saline lake environments (Murray et al*.,* 1994). However, as suggested by Colister et al. (1994), the mixing of materials from multiple sources could complicate *n*-alkane carbon isotope profiles, because *n*-alkanes and their precursors are produced by a broad range of organisms (e.g. algae, bacteria, and terrestrial vascular plants), with some overlap among different classes of organisms. This paper deals with the assessment of the origin of organic matter and depositional environment of coal based on determining the carbon isotopic composition of individual *n*-alkanes in the coal.

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).

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

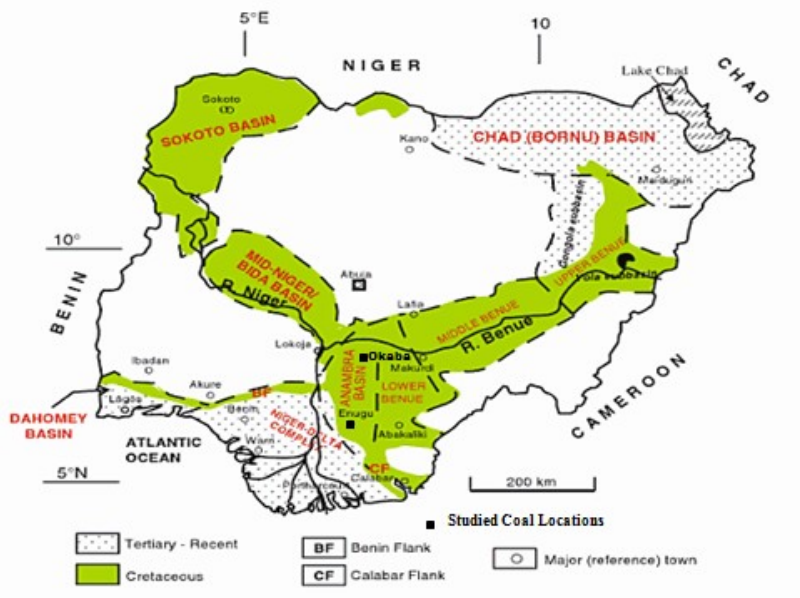

Fig. 1: Map showing the location of studied coals in the Anambra Basin.

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).

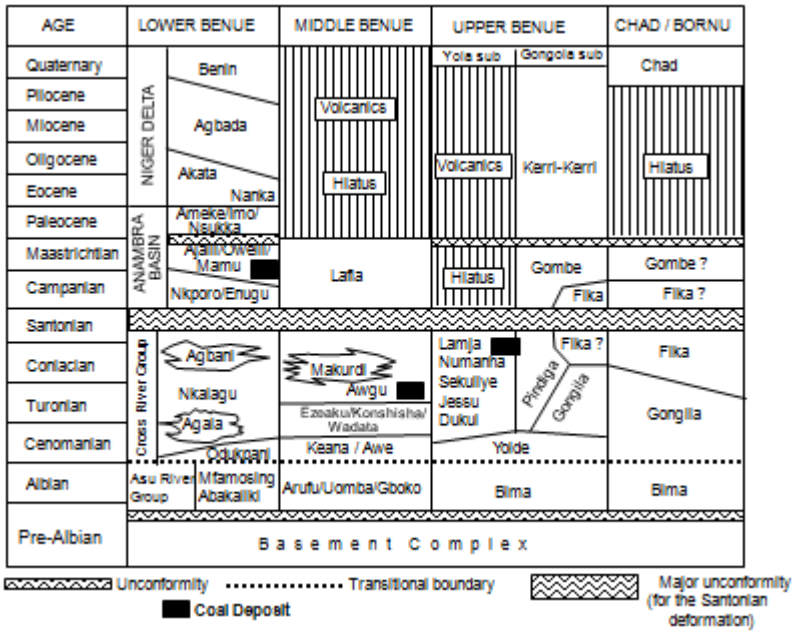

Fig. 2. Stratigraphic successions in the Benue trough and the relationship to the Chad basin and the Niger delta (After Obaje et al., 2004).

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).

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^{o}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 ^{o}C. The GC oven temperature was isothermal for 1min at 80 ^{o}C and then programmed from 80 to 280 ^{o}C at 3 ^{o}C/min and isothermal for 20 min at 280 ^{o}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 δ13C isotopic values for individual *n*-alkanes and whole saturate fractions of the samples are presented in Table 1. The $\delta^{13}C$ isotopic values for *n*-alkanes range from –31.7 to –29.2 δ^{13}‰PDB

and –30.1 to –28.2 δ^{13}‰PDB in Enugu and Okaba samples respectively. This $\delta^{13}C$ isotopic ratio is a typical of organic carbon from a terrestrial source in sediments of Cretaceous age (e.g Hoefs, 1997; Haberer et al., 2006). This The isotopic values are characteristics of plant wax derived *n*-alkanes of C_3-plants (Canuel et al*.,* 1997; Sun et al*.,* 2000; Bi et al*.,* 2005; Tanner et al*.,* 2007; Tuo et al*.,* 2007; Adedosu, 2009). The carbon isotopic compositions of individual alkanes (nC_{15}-nC_{36}) in Enugu and Okaba samples range from –32.19 to –27.15 δ^{13}‰PDB and –32.48 to –27.50 δ^{13}‰PDB respectively. The most depleted values were observed for the long chain alkanes, which are characteristics of plant wax derived *n*-alkanes of C_3-plants (Schouten *et al.,* 2000; Hu *et al.,* 2002).

Most of the coals Pr/Ph ratios > 2, indicating significant terrestrial OM input (Didyk et al., 1978; Powell and Mckirdy, 1993), have $\delta^{13}C$ values between - 26.00‰ to -25.00‰. This was differentiated by Chung et al. (1992) where he classified $\delta^{13}C$ to different environment; > -22.00‰ is classified to marine, -24.00‰ to -23.00‰ to transitional and <-25.00‰ to terrestrial respectively. Notable variation among the $\delta^{13}C$ indicates marine environment.

Table 1: Carbon Isotopic Composition of n-Alkanes in Mamu Samples (δ 13‰PDB).

Sample Name	Mining Pit	Formation	Lithology	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}
ENUG-1	"	Mamu	Coal	nd	-28.80	-28.90	-28.00	-30.00	-32.20	-32.20	-33.10	-33.30	-33.30
ENUG-2	"	"	"	nd	-27.60	-27.40	nd	-30.10	-31.10	-30.10	-31.50	-30.60	-30.50
ENUG-3	"	"	"	nd	nd	-33.90	nd	-33.30	-34.10	-31.20	-29.90	-30.90	-31.00
ENUG-4	"	"	"	nd	-27.90	-26.60	-26.80	-26.30	-28.80	-29.30	-30.60	-29.60	-29.90
ENUG-5	"	"	"	nd	-27.60	-27.50	nd	-28.30	-29.10	-28.90	-29.50	-29.50	-30.40
ENUG-6	"	"	"	nd	-27.60	-27.70	-26.70	-30.80	-30.40	-30.90	-30.70	-33.10	-32.60
Mean				nd	-27.90	-28.70	-27.20	-29.80	-30.90	-30.40	-30.90	-31.10	-31.30
OKAB-1	"	"	"	nd	nd	-27.40	nd	-29.30	-31.30	-30.10	-33.90	-30.80	-31.90
OKAB-2	"	"	"	nd	nd	nd	nd	-29.70	-26.40	-29.00	nd	nd	nd
OKAB-3	"	"	"	-26.20	nd	-28.50	nd	-29.70	nd	nd	nd	nd	nd
OKAB-4	"	"	"	-26.10	-27.20	-29.20	-27.40	-28.30	-28.90	-32.50	-31.20	-29.30	-30.00
OKAB-5	"	"	"	nd	nd	-27.10	-32.10	-28.20	-28.60	-27.10	-32.30	-32.10	-29.90
OKAB-6	"	"	"	nd	nd	-25.30	-26.10	-26.30	-31.00	-32.40	nd	nd	nd
Mean				-26.10	-27.20	-27.50	-28.60	-28.80	-29.10	-30.20	-32.50	-30.70	-30.60

Table 1: Cont'd

C_{24}	C_{25}	C_{26}	C_{27}	C_{28}	C_{29}	C_{30}	C_{31}	C_{32}	C_{33}	C_{34}	C_{35}	C_{36}
-33.00	-31.60	-31.80	-30.80	-31.70	-31.20	-34.20	-30.70	nd	nd	-33.6	nd	nd
-30.10	-31.30	-30.00	-29.20	-30.40	-29.60	-32.10	-30.50	-32.00	-31.90	-29.40	-32.70	-33.10
-31.40	-31.70	-29.80	-29.20	-30.20	-29.10	-31.50	-30.60	-29.70	-29.50	-30.40	-33.00	nd
-30.90	-29.50	-29.20	-28.80	-29.40	-28.80	-29.90	-30.10	-31.00	-28.60	-30.40	-31.40	-29.30
-30.40	-31.00	-29.80	-28.70	-29.40	-28.80	-31.00	-30.00	-30.80	-33.30	-60.90	-31.60	-33.60
-33.60	-32.20	-31.90	-29.60	-30.70	-29.80	-32.30	-30.40	-32.20	-32.80	nd	nd	nd
-31.60	-31.20	-30.40	-29.40	-30.30	-29.50	-31.80	-30.40	-31.10	-31.20	-31.20	-32.20	-32.00
-28.50	-30.10	-29.90	-28.20	-28.20	-30.00	-30.10	-31.10	nd	nd	nd	nd	nd
nd	nd	nd	-31.50	-32.00	-28.50	-28.50	-32.00	-31.10	-31.50	-32.20	-28.70	nd
nd	nd	nd	-28.40	-26.30	-28.20	-26.10	-27.50	-29.70	-31.50	-27.90	nd	nd
-25.50	-31.20	-31.90	-28.80	-30.90	-27.50	-28.60	-32.60	-30.60	-31.10	-32.80	-28.10	-28.70
-32.40	-31.20	-32.10	-29.10	-28.00	-28.10	-27.70	-29.10	-28.60	-28.20	nd	-29.20	nd
nd	nd	nd	-29.40	nd	-30.20	-29.40	-30.20	-30.90	nd	-30.40	nd	nd
-29.80	-30.90	-31.30	-29.20	-29.10	-28.70	-28.40	-30.40	-30.20	-30.60	-30.80	-28.70	-28.70

Significant contribution from marine organic matter (i.e. C_3 algae or cyanobacteria) is reflected in heavier $\delta^{13}C$ isotope values observed in the short chain (nC_{15}-nC_{18}) alkanes in all the samples (Figs. 3 and 4). Both pristane and phytane have essentially the same $\delta^{13}C$ values as the *n*-alkanes, suggesting that they were formed from the same group of organisms (Schwas and Spangenberg, 2007).

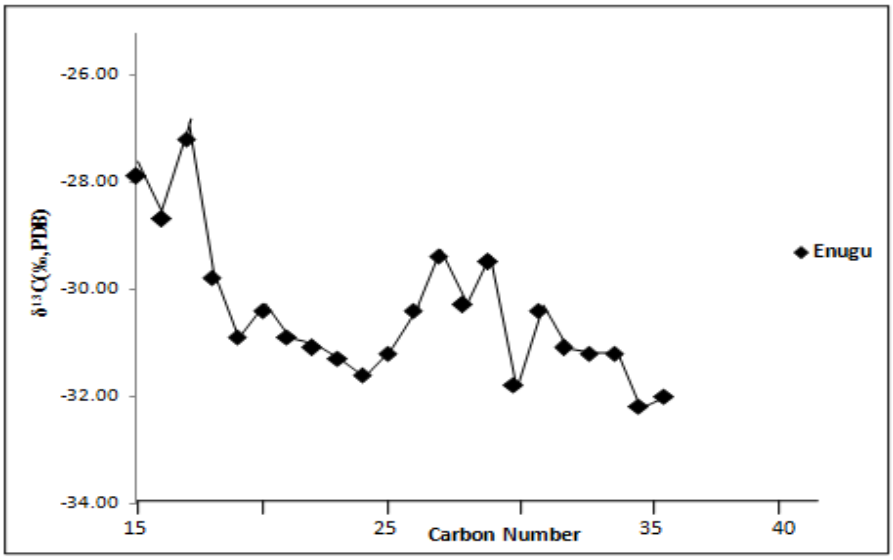

Fig. 3: Carbon isotopic distribution of individual *n*-alkanes in Enugu Samples, (Murray et al., 1994).

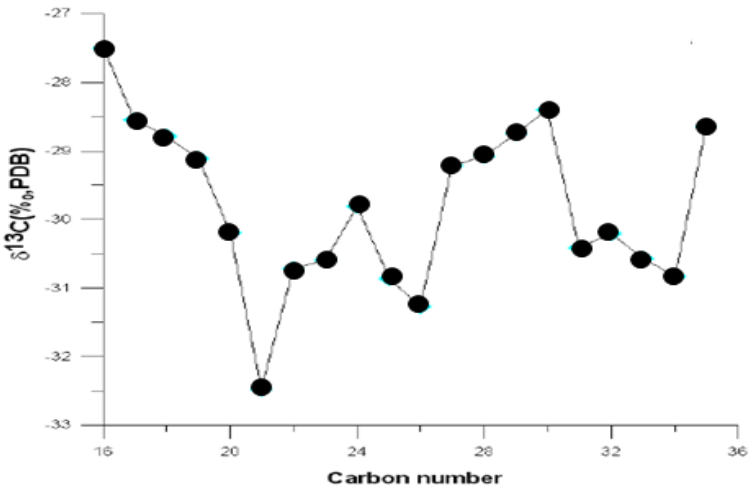

Fig. 4: Carbon isotopic distribution of individual *n*-alkanes in Okaba Samples, (Murray et al*.,* 1994).

However, there is notably flat portion pattern of the *n*-alkane profile between nC_{20}-nC_{25} and nC_{27}-nC_{31} (Figs. 3 and 4) in Enugu and Okaba samples respectively, which is an indication of marine incursion (Murray et al*.,* 1994). These features show that Mamu samples consist of both terrestrial and marine organic matter deposited in fluvial/deltaic (Enugu) or lacustrine-fluvial/deltaic (Okaba) settings.

The tertiary oils from the onshore Gulf of Mexico (Thompson et al., 1990), the Niger Delta (Evamy et al., 1978; Bustin, 1988) and Cretaceous oils from the Scottian Basin, Offshore Canada (Powell, 1982) were classified as terrestrial based on -26.60 and 2.80, -25.60‰ and 3.20 and -25.30‰ and 3.40 respectively.

CONCLUSION

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 and Gas Chromatography-Isotope Ratio- Mass Spectrometry analyses. This study was undertaken to re-appraise the origin and depositional environment of organic matter from Nigerian coal through source rock evaluation studies, biomarker parameters and carbon isotopic compositions. The distribution of carbon isotopic compositions of the individual alkanes in the samples showed that Mamu samples were derived from mixed organic materials (terrestrial and marine) deposited in fluvio-deltaic (Enugu) and lacustrine-fluvial/deltaic settings (Okaba) respectively.

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