

ORGANIC GEOCHEMICAL CHARACTERIZATION AND HYDROCARBON POTENTIAL OF SUBSURFACE SEDIMENTS FROM ANAMBRA BASIN, SOUTHEASTERN NIGERIA

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ABSTRACT

Subsurface samples of Mamu Formation from Ezimo 1235 and Enugu 1327 wells, located within the Anambra Basin were examined for organic geochemical characterization and biomarker content in order to determine the lithofacies association, hydrocarbon potential as well as the palaeodepositional environment. The sediments are made up of siltstone, dark coal, highly fissile shale and mudstone. Selected samples, made up of shale and coal from both wells were subjected to Rock Eval and gas chromatography/mass spectrometry (GC-MS) analyses.

Results of the Total Organic Carbon (TOC) ranges from 5.15 to 69.56wt%, Soluble Organic Matter (SOM) values ranges from 286 to 1700ppm while the Generative Potential (GP) ranges from 10.02 to 311.86kgHC/t. These values suggest that the source rocks are moderately to fairly rich in organic matter. Hydrogen Index (HI) values range from 95-381 mgHC/gTOC and indicate types II and III kerogen. Cross plots of HI against OI signify types II and III kerogen which also indicate oil and gas prone source rocks. Tmax values of 422-437°C and Bitumen Ratio of 6.34 to 101.1 mg ext/gTOC signify low maturation level for the source rock. Ratios of C29 hopane $\beta\alpha/\alpha\beta$, C30 $\beta\alpha/\alpha\beta$, and 22S/22S+22R C32 hopane range from 0.32 to 1.18; 0.21 to 0.57; and 0.13 to 0.52

respectively, and suggest immature organic matter status. Carbon Preference Index (CPI) value ranges from 1.33 to 1.97 suggests immature source rock of terrestrial origin. High values obtained from the C24 tetracyclic/C24 tricyclic terpanes and the C19/C20 tricyclic terpane ratios, (1.52-2.64) and (0.54-1.54) respectively, also portray terrigenous organic matter contribution. The presence of C27 to C29 steranes and diasteranes, signify mixed sources (marine and terrigenous) with prospects to generate both oil and gas; however, the dominance of C29 over C28 and C27 amplify higher contribution of terrigenous materials. The terrigenous input is further amplified by the Pr/Ph ratio ranging from 5.44 to 7.81. Cross plots of Pr/nC17 against Ph/nC18 also denote terrigenous sourced organic matter deposited in oxidizing environment. The high ratio of C30/C29Ts, indicates source rocks deposited under suboxic conditions.

It can be deduced that the sediments are immature, and were deposited in a suboxic, low Eh environment. They are potential source rocks which are moderately to fairly rich in organic input with substantial amount of terrestrial organic matter, having prospects to generate gas at appropriate maturation.

Key Words: Hydrocarbon potential, palaeoenvironment, Anambra basin

INTRODUCTION

The Anambra Basin, with a total sediment thickness of over 6,000m, covers an area of about 40,000 sq.km and presents an ideal geo-kitchen for all manners

of complex chemical reactions that can lead to the formation and occurrence of economically viable hydrocarbon deposits. It is also characterized by enormous lithogenic heterogeneity in both lateral and vertical extensions derived from a range of paleoenvironmental settings ranging from Campanian to Recent (Akaegbobi, 2005)

The initial interest in the search for oil and gas within the Lower Benue Trough (including Anambra Basin)

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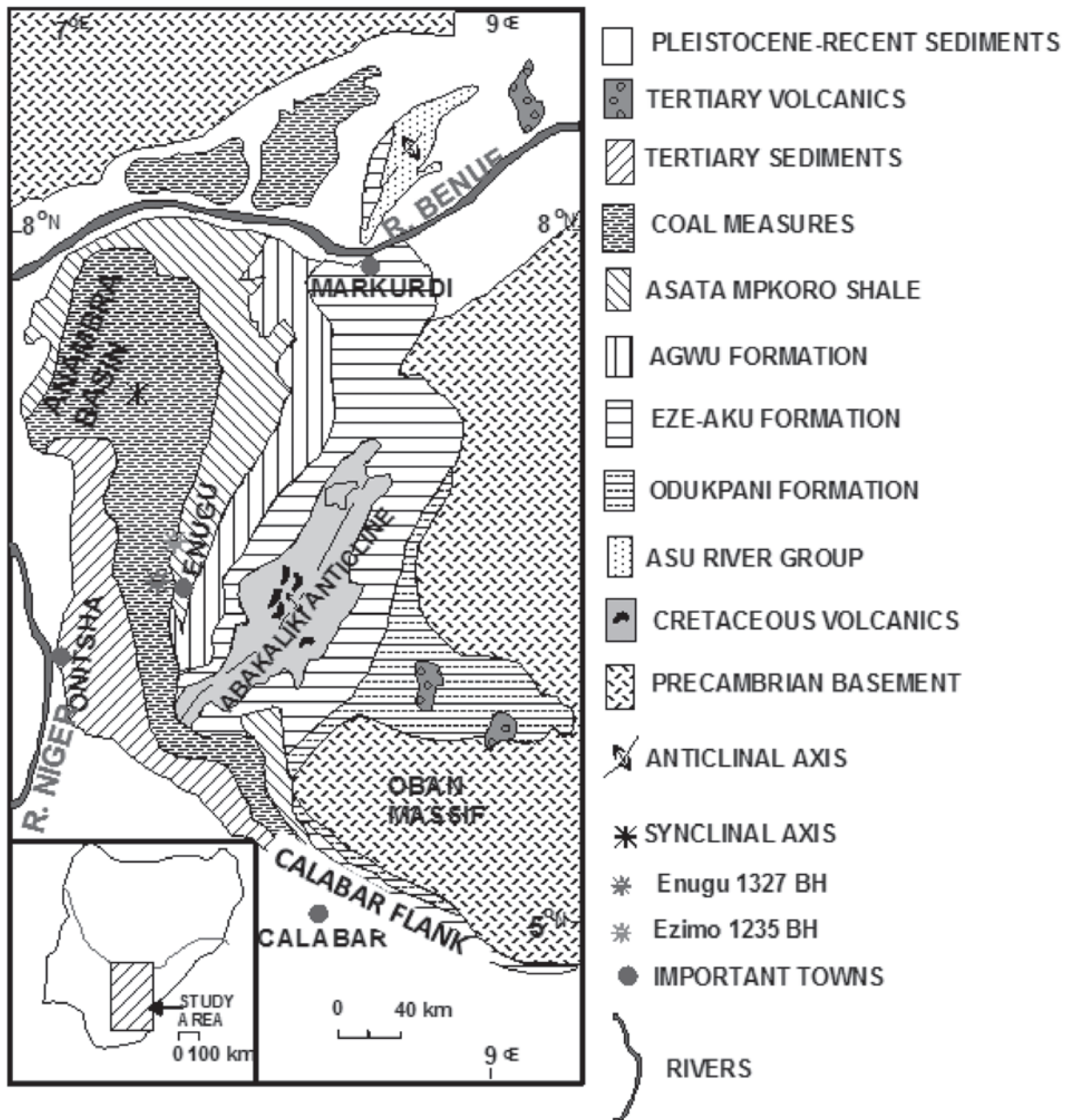


FIGURE 1. Geologic map of the Anambra Basin showing the study area

of Nigeria was aroused by the favourable stratigraphic setting of interbedded shales and sandstones with occasional limestones (Agagu et al., 1985). The exploration for coal and petroleum in the Anambra Basin culminated into commercial production of coal in 1916, while oil exploration was abandoned as the efforts ended in a number of non-commercial discoveries. The search for commercial hydrocarbons in the Anambra Basin in Nigeria has been a concern especially to oil companies and research groups, more so as oil is found in the nearby Niger Delta.

Compared to the Niger delta, petroleum exploration in the Anambra Basin has been on a limited scale, with few wells drilled and two gas discoveries made. In addition, very scanty, old vintage 2-D seismic information have been acquired within the basin, which clearly shows that the Anambra basin is under explored. Based on these facts, the hydrocarbon resources in the Anambra basin, appraised to be about one billion barrels of oil and about 10 trillion cubic feet of gas, could be a gross under estimate (Akaegbobi, 2005). With increasing domestic and global energy demands, the

advent of improved exploration tools, integrated basin analytical tools, the need to circumvent the impending energy crisis, and re-evaluation of data gathered from previous unsuccessful attempts, oil/gas exploration and prospecting activities in Anambra basin has taken a new dimension.

The current study examines two core holes, namely Enugu and Ezimo, drilled within the Anambra basin in order to deduce the different lithofacies, identify the organic source input and thereby evaluate the hydrocarbon potential of the basin by standard organic geochemical and biomarkers studies.

LOCATION OF STUDY AND GEOLOGY

The study was carried out on samples obtained from Ezimo 1235 and Enugu 1327 core holes, located within the Anambra basin in southeastern Nigeria. The Anambra basin lies between latitudes 6°00'N and 6°40'N, and longitudes 7°04'E and 7°13'E (Fig 1). The Anambra Basin is a synclinal structure, consisting more than 6,000m thick of Upper Cretaceous to Recent sediments, representing the third phase of marine sedimentation in the Benue Trough (Akande and Erdtmann, 1998). Following the Mid Santonian tectonism, depositional axis in the Benue Trough was displaced westward resulting in subsidence of the Anambra Basin, thus making the basin an active depocenter.

Geologically, the origin of the Anambra Basin is intimately related to the tectonic and sedimentary cycles responsible for the origin of the adjoining southern Benue Trough during the separation of African from the South American plate in the Mesozoic era (King, 1950; Reyment, 1965; Burke et al. 1972; Benkhelil, 1986). Studies of Murat (1972), Nwachukwu (1972) Hoque and Ezepe (1977) and Ladipo (1986, 1988) among others, have shown that, subsequent to the uplift of the Benue- Abakaliki fold belt during the Santonian, the geological history of the Anambra Basin is linked to the post-Santonian subsidence of the then Anambra platform. This was followed by a series of trans-regression cycles leading to sedimentation of about 6 km thick of Cretaceous and Tertiary sediments (Obaje et al. 2004) within the basin to the west of the Abakaliki uplift during the Campanian— Paleocene. The stratigraphic succession of the Anambra Basin comprises the Campanian to Maastrichtian Enugu/Nkporo/Owelli Formations (lateral equivalents). This is succeeded by the Maastrichtian Mamu and Ajali Formations. The sequence is capped by the Tertiary

Nsukka Formation and Imo Formation. These are presented below:

Enugu-Nkporo Shales Group: These early Campanian units comprised dark grey fissile, soft shale and mudstone with maximum thickness of about 1,000 m and characterized by interbedded sandy units and sulphur coated marl. A shallow marine environment was predicted due to the presence of foraminifera and ammonites (Reyment 1965; Agagu et al. 1985). Akae-gbobi and Schmitt, (1998) evaluated the Campanian—Maastrichtian Nkporo shales as having moderate to super-rich organic matter of types III and some type III/II of immature status sourced mainly from terrestrial higher plants and deposited in cyclic suboxic and anoxic conditions.

Mamu Formation: This is a Late Campanian sedimentary unit, also known as the “Lower Coal Measures” (Simpson, 1954) but later renamed Mamu Formation (Reyment, 1965). It consists mainly of dark blue to grey shales/mudstones units with alternating sandy units and coal seam horizons that form characteristically stripped rock unit. The Mamu Formation was deposited as shallow water of the paralic facies of a deltaic complex (Cratchley and Jones 1965).

Ajali Formation: This is a Maastrichtian sandy unit overlying the Mamu Formation and consists of white, thick friable, poorly sorted, cross-bedded sandstone with thin beds of white mudstone near the base. It is characterized by large scale cross bedding, with dip angle as high as 20°. Studies have suggested that the Ajali Formation is a continental/fluvio-deltaic sequence, characterized by a regressive phase of a short-lived Maastrichtian trans-regression with sediments derived from westerly areas of the Abakaliki anticlinorium and the granitic basement units of Adamawa-Oban massifs to the eastern side of the basin (Benkhelil, 1986; Amajor, 1987; Ladipo, 1986, Tijani et al., 2010). Tijani and Nton (2008) reported on the interplay of hydraulic, textural and geochemical characteristics of the Ajali Formation on groundwater occurrence. They concluded that weathering induced geochemical processes with resultant formation of Fe-Mn-Al-oxyhydroxides and leaching/dissolution mobilization of metals including contaminant trace metals constitute potential aquifer management problems.

Nsukka Formation: This is a Late Maastrichtian unit, lying conformably on the Ajali Formation and consists of alternating succession of sandstone, dark shales and sandy shales with thin coal seams at various horizons. It

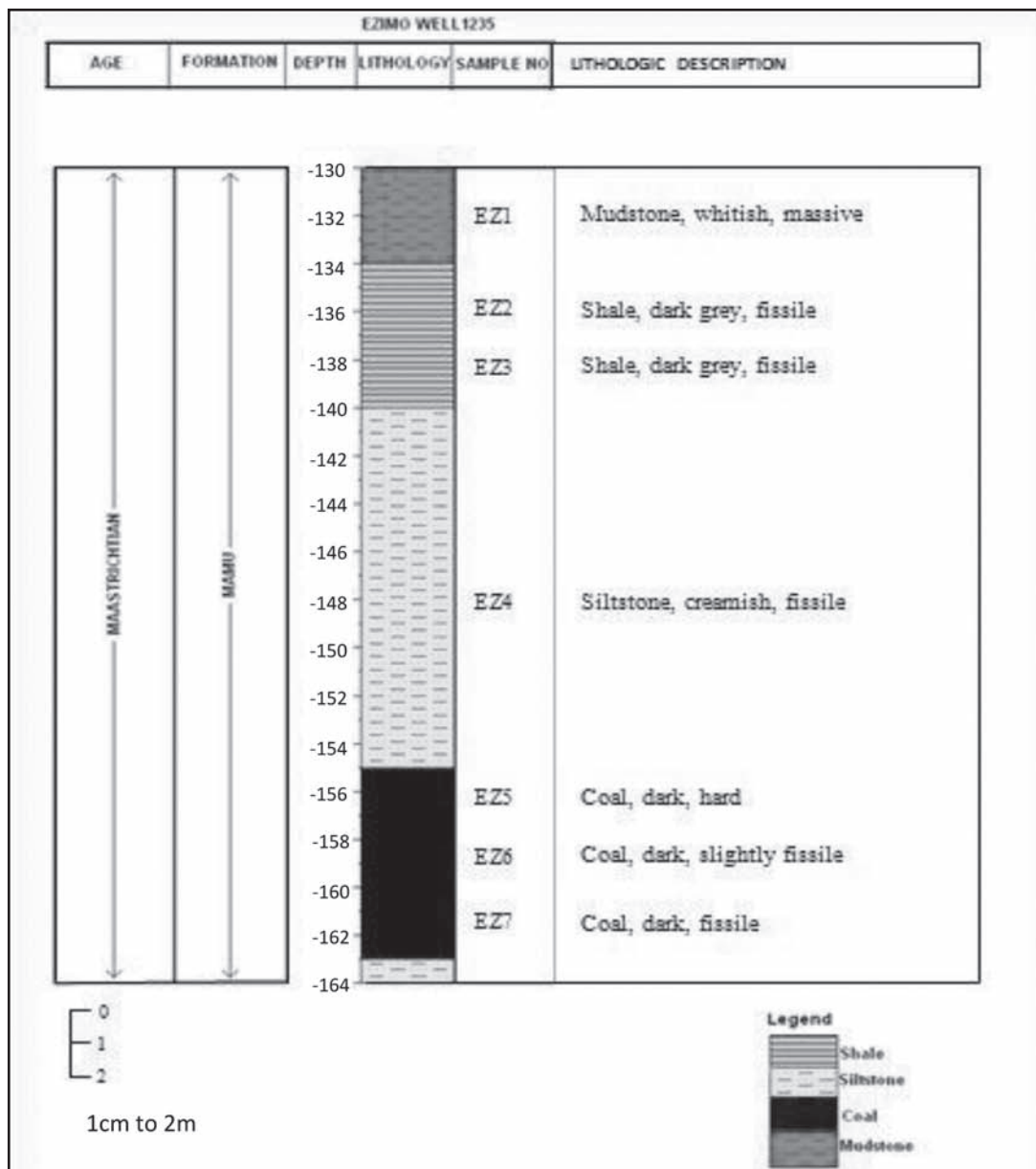


FIGURE 2. Lithologic description of Ezimo 1235 well

has been termed the “Upper Coal Measures”. A strand plain/marsh environment, with occasional fluvial incursions similar to that of the Mamu Formation was inferred for this formation by Agagu et.al, (1985).

Imo Formation: The Imo Formation is Paleocene in age and consists of bluish –grey deep marine shales, up to 500m (Reyment, 1965). Whiteman (1982) described the formation as fine textured, dark grey and bluish grey shale with occasional admixture of ironstone and thin sandstone bands, which occur especially towards the top of the unit. The formation becomes more sandy towards the top, where it consists of alternations of sandstone and shale. The Imo Shale occurs extensively and

at some locations within the basin, it onlaps the Ajali Sandstones. It commonly underlies low, marshy country, except where the sand members (? turbidite sands) occur as highlands (Ladipo et al., 1992). These sands comprise texturally mature quartz arenites, interbedded within deep water marine shales, which suggests that they may represent low stand erosion turbidites on the basin floor or slope edge. Frankly and Cordry (1967) and Short and Stauble (1967) described the Imo Shale as the up-dip equivalent of part of the subsurface Akata Formation in the Niger Delta Basin. The formation marks the climax of the major global early Paleocene transgression (which probably correlated with 64.6my

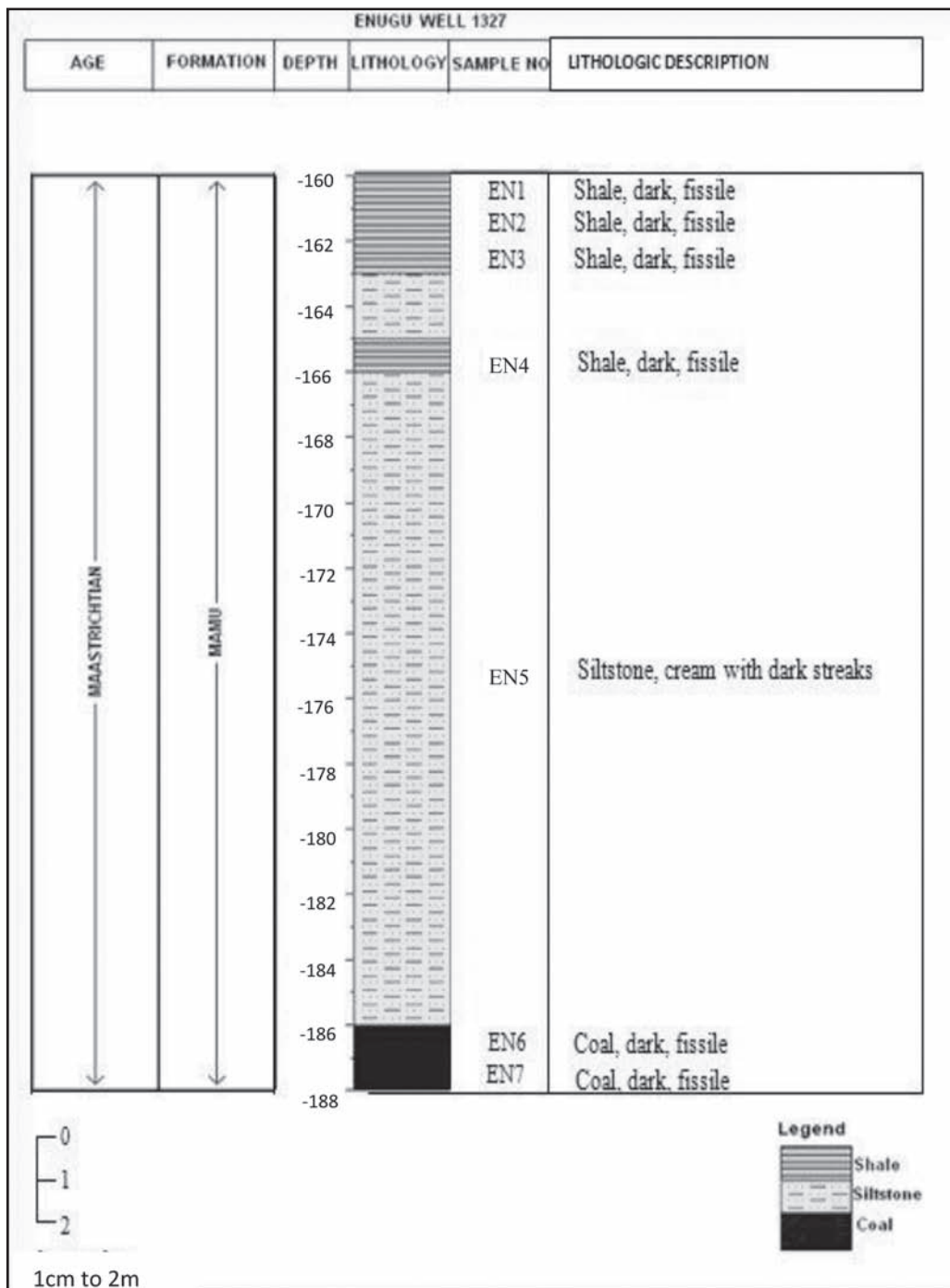


FIGURE 3. Lithologic description of Enugu 1327 well

downlap surface on the Vail et al. cycle). The sedimentary successions indicate a paralic environment.

MATERIALS AND METHODS

Subsurface samples from Ezimo 1235 and Enugu 1327 core holes were obtained from the Nigerian Geological Survey Agency (NGSA), Kaduna for this study. The Ezimo core hole ranges from the interval

130 to 164m (Fig. 2) and made up of a thin sequence of siltstone overlain by a thick coal unit of 8m, middle siltstone (15m), overlain by 6m dark shale and capped by 4m thick of mudstone. The Enugu core hole (Fig. 3) is about 25m and made up of lower coal sequence, middle siltstone of about 20m, successively overlain by shale of 1m thick, overlain by siltstone and capped by 3m of a dark , fissile thick shale.

In this study, fresh shale, coals and mudstones samples were selected for Total Organic Carbon, Rock-Eval pyrolysis determination and Gas Chromatography-Mass Spectrometry analysis for biomarker studies.

Total Organic Carbon (TOC) Determination

100g of twelve (12) pulverized samples to be analysed were placed in four (4) baked metal crucibles. A drop of ethanol was added to each of the samples to prevent rapid reaction when adding other solvents. 37% HCl was added in drops to three of the four crucibles, this removed the carbonates and the water in the rock samples. This continued until effervescence stopped. The crucibles were placed on sand bars and heated for 12 hours to dehydrate the samples. The crucibles and content were then placed in an oven of a calibrated Leco CS 244 analyser and heated for 12 hours. The amount of CO₂ obtained was measured and divided by 3; this gave the average amount organic carbon, while the fourth (4th) crucible content gave the total amount of carbon. The analysis was carried out at Weatherford Geochemical Laboratory Texas, USA.

Rock-Eval Pyrolysis

Based on TOC adequacy, about 100mg of each pulverized sample was weighed into a metal crucible that was previously incinerated at about 550°C under nitrogen atmosphere. This was transferred into desiccators and using helium as carrier gas, to remove oxygen and carbon dioxide. Each sample was pyrolysed at 300°C for 3 to 4mins, followed by programmed pyrolysis at 25 °C/min to 550 °C. Allowing for time to cool the oven, each analysis required about 20 minutes. A flame ionization detector (FID) senses any organic compound generated. The first peak (S1) represents in milligrams the hydrocarbon that can be thermally distilled from one gram of the rock. The second peak (S2), represents hydrocarbon generated by pyrolytic degradation of the kerogen in one gram of rock. The third peak (S3), represents amount of carbon dioxide generated from a gram of rock at temperature programmed up to 390°C and is analyzed by thermal conductivity detection (TCD). The temperature at which maximum amount of S2 hydrocarbons is generated is known as Tmax. The Hydrogen Index (HI) corresponds to the quantity of pyrolysable organic compounds or hydrocarbon (HC) from S2 relative to the total organic carbon (TOC or Corg) in the sample. The oxygen index (OI)

corresponds to the quantity of carbon dioxide from S3 relative to the TOC (i.e. mg CO₂/g Corg). The production index (PI) is defined as the ratio of S1/S1+S2. The analysis was carried out at Weatherford Geochemical Laboratory Texas, USA.

Extraction of Soluble Organic Matter

Arising from TOC adequacy, bitumen extraction was carried out on eight (8) pulverized samples using Methylene Chloride/ Methanol mixture (9:1) as the reagent. The extraction was done using Soxhlet system HT2 unit. The bitumen extracts were dried, weighed and measured in parts per million (ppm). The asphaltenes in the extracts were precipitated by the addition of 10ml of pentane and centrifuged. The solvent left was separated into saturates, aromatic and NSO fractions using liquid chromatography. This analysis was carried out at the Exxon Mobil Geochemical Laboratory Qua Iboe Terminal (QIT), Eket, Nigeria.

Gas Chromatography of whole oil

The Gas Chromatography was taken on whole rock bitumen extract using high resolution capillary columns Hewlett Packard 6890A gas chromatograph, equipped with dual flame ionization detectors (FID). The chromatograph was fitted with Hp-1 capillary column (30mx0.32mm I.Dx0.52microns) using helium as the carrier gas. The column temperature was programmed at 35°C to 300°C/min with a flow rate of 1.1mls/min. The bitumen extract was diluted with drops of carbon disulphide and agitating until sample is dissolved. A limited volume was placed in a labeled auto-sampler vial which was transferred to the auto-sampler tray for the analysis to run. 1.0ul of the diluted extract was rapidly injected into the gas chromatograph in split mode, using a graduated Hp 10ul injection syringe. Chromatographic data were acquired using an HP Vectra XM series 3 computer. Peak integration and associated data processing were accomplished using HP Chemstation software. Peak identification was accomplished by matching chromatographic peaks and profiles using HP Naptha standards.

This analysis was carried out at the Exxon Mobil Geochemical Laboratory Qua Iboe Terminal (QIT), Eket.

Gas Chromatography/Mass spectrometer (GC/MS)

The screened extracts were fractionated by column chromatogram on silica gel. The saturates and aromatic hydrocarbon and polar compound fractions were

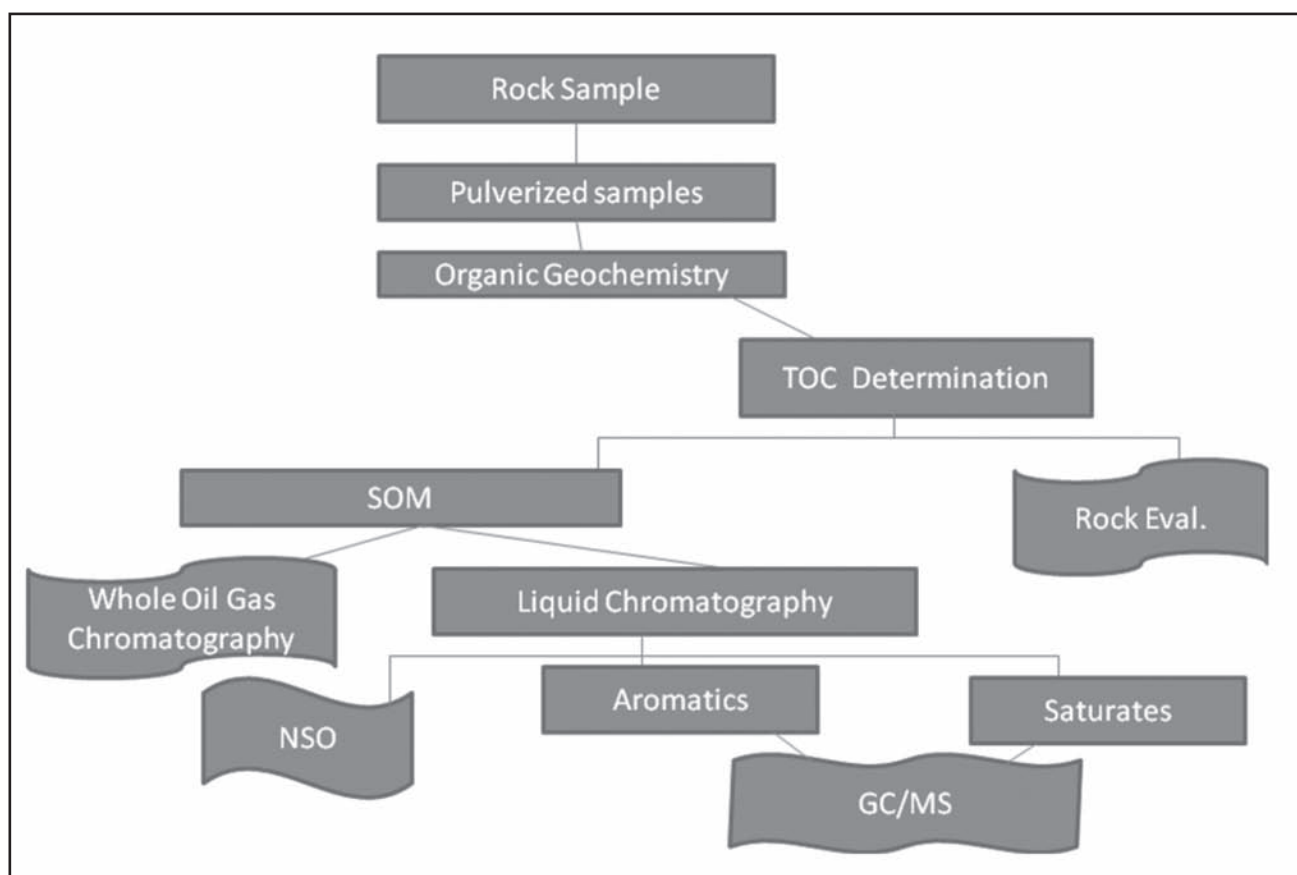


FIGURE 4. Flow chart of the Laboratory Analyses

eluted using 20ml hexane, n-alkanes/dichloromethane (90:10, 25ml) and dichloromethane / methanol (50:50, 30ml) respectively. The saturates and aromatic fractions recovered from the liquid chromatography were analyzed for their biomarkers by Gas Chromatography-Mass Spectrometry (GC-MS) using selected ion monitoring (SIM) mode. Terpanes and steranes were identified using m/z 191 and 217 fragments, respectively. The naphthalene and its derivative were monitored on the m/z 156 and 170; the phenanthrenes were identified with the m/z 219 to 220 while the dibenzothiophene were monitored on m/z 198.

The chromatographic data were acquired using Ms Chemstation software, version G1701BA for Microsoft NT®. This analysis was carried out at the Exxon Mobil Geochemical Laboratory Qua Iboe Terminal (QIT), Eket. The work flow for this study is shown in Fig. 4 and the detailed analytical procedure could be consulted in Awarun (2010).

RESULTS AND DISCUSSION

Organic richness

It is known that adequate amount of organic matter,

measured as percentage total organic carbon (TOC), is a necessary pre-requisite for sediments to generate oil or gas (Cornford, 1986). The results of total organic carbon for the samples are presented in Table 1. The TOC values for the sediments vary from 19.47-67.67 wt.%, (av. 43.76wt%) for Ezimo 1235 well while that for the Enugu 1327 well range from 4.76-69.56wt%, (av.20.64wt%; Table 1). These values indicate that the sediments have above 0.5 wt TOC, the required threshold value for non clastic rocks to generate petroleum (Tissot, and Welte, 1984). Based on Espitalie et al., (1987) and Jarvie (1991), these values indicate high organic richness necessary for hydrocarbon generation from the studied wells.

To further assess the organic richness, the soluble organic carbon (SOM) values for the Ezimo 1235 core hole range from 509 to 1700 ppm (av. 349 ppm) while that of Enugu 1327 core hole range from 390-820 ppm, av. 594 ppm (Table 1). Based on the quality definition concept of Philippi, (1957); Baker (1972), the organic matter is adequate and indicate good hydrocarbon potential for the studied wells.

The Genetic Potential (GP) (S_1+S_2 mg HC/g) is a

TABLE 1. Data of TOC and Rock-eval

SAMPLE ID	TOC wt%	SOM (ppm)	SOM/ TOC mgExt/gTOC	S ₁ mg/g	S ₂ mg/g	S ₃ mg/g	T _{max} (°C)	HI	S2/S3	GP (KgHC/t)	PI
EZ 2	24.10	509	21.12	1.60	77.19	8.04	429	320	9.6	78.79	0.02
EZ 3	19.47	1700	87.3	2.48	48.14	4.78	422	247	10.1	50.62	0.05
EZ 5	40.93	286	6.99	2.90	143.41	12.73	429	350	11.3	146.31	0.02
EZ 6	67.67	429	6.34	4.29	257.55	17.67	437	381	14.6	261.84	0.02
EZ 7	66.62	ND	ND	4.44	190.76	19.04	430	286	10.0	195.20	0.02
EN 1	19.98	ND	ND	1.21	33.88	6.04	428	170	5.6	35.09	0.03
EN 2	5.15	390	75.5	0.43	9.59	1.85	425	186	5.2	10.02	0.04
EN 3	6.36	433	68.1	0.61	11.52	2.10	421	181	5.5	12.13	0.05
EN 5	6.40	647	101.1	1.02	21.73	1.75	430	340	12.4	22.75	0.04
EN 6	69.56	680	9.78	5.12	306.74	1.70	427	95	2.7	311.86	0.04
EN 7	32.25	820	25.4	2.78	80.94	7.42	430	251	10.9	83.72	0.03

Notes:

TOC=weight percent organic carbon in rock

S₁, S₂=mg hydrocarbons per gram of rock

S₃= mg carbon dioxide per gram of rock

Tmax (°C)

ND= Not done

HI=Hydrogen Index= S₂ x 100/TOC

OI=Oxygen Index= S₃ x 100/TOC

GP= Genetic Potential

PI= production index= S₁/ (S₁+ S₂)

measure of hydrocarbon- generating potential and depends on organic matter amount, type and thermal maturity (Espitalie et al, 1977). From the study, the GP ranges from 4.71 -311kgHC/ton. Values for Ezimo 1235 core hole range from 50.62 to 261.84 kg HC/ton (av. of 146.55 kg HC/ton) while that for the Enugu 1327 core holes are from 4.71 to 311.86 kg HC/ton (av. 68.61kg HC/ton). Arising from Tissot and Weltes' (1984) classification, as applied in Dymann et al. (1996), the GP values span from moderate, through good source rock, to excellent source potential.

Organic matter type

The quality of organic matter content of a source rock determines the type of hydrocarbon generated (Tissot et al; 1984). The ratio of S₂ to S₃, obtained from the rock eval can be used to determine the quality of organic matter present in the formation. The S₂/S₃ values for Ezimo 1235 ranges between 9.6-14.6 (av. 11.12), while that of Enugu 1327 core hole is from 2.7- 23.7 (av. of 9.43; Table 1). The average for both wells falls in the gas and gas and oil generated range of Peters, (1986). This implies that the Mamu Formation can generate both gas and oil.

The HI values for Ezimo 1235 well range from 247-381 mgHC/gTOC (av. 317 mgS₂/TOC) and lie in the type II category that generates oil and gas. On the other hand, values from the Enugu 1327 core hole are within the range 95-340 mgS₂/TOC (average of 204 mgHC/gTOC) are indicative of type III kerogen, which has the potential for gas generation. It has been shown that the higher the hydrogen index contents of a sample, the greater the ability to generate oil and gas (Petersen and Nytoft, 2006).

Cross plots of HI against OI (Fig. 5) indicate Type II kerogen for the Ezimo 1235 well, while that of Enugu 1327 lie within Type II and III kerogens. These imply that the Ezimo 1235 well can generate oil while the Enugu 1327 well can generate both oil and gas. Cross plot of Source Rock Potential (S₂) against the TOC (Fig. 6) for both wells indicate types II and II/III for Ezimo 1235 and type III for Enugu 1327 well respectively. It can be interpreted that the kerogen obtained from Ezimo 1235 well is of mixed origin; oil and gas while majority of the samples obtained from Enugu 1327 well is gas prone.

Maturity of organic matter

Thermal maturity describes the extent of heat-driven

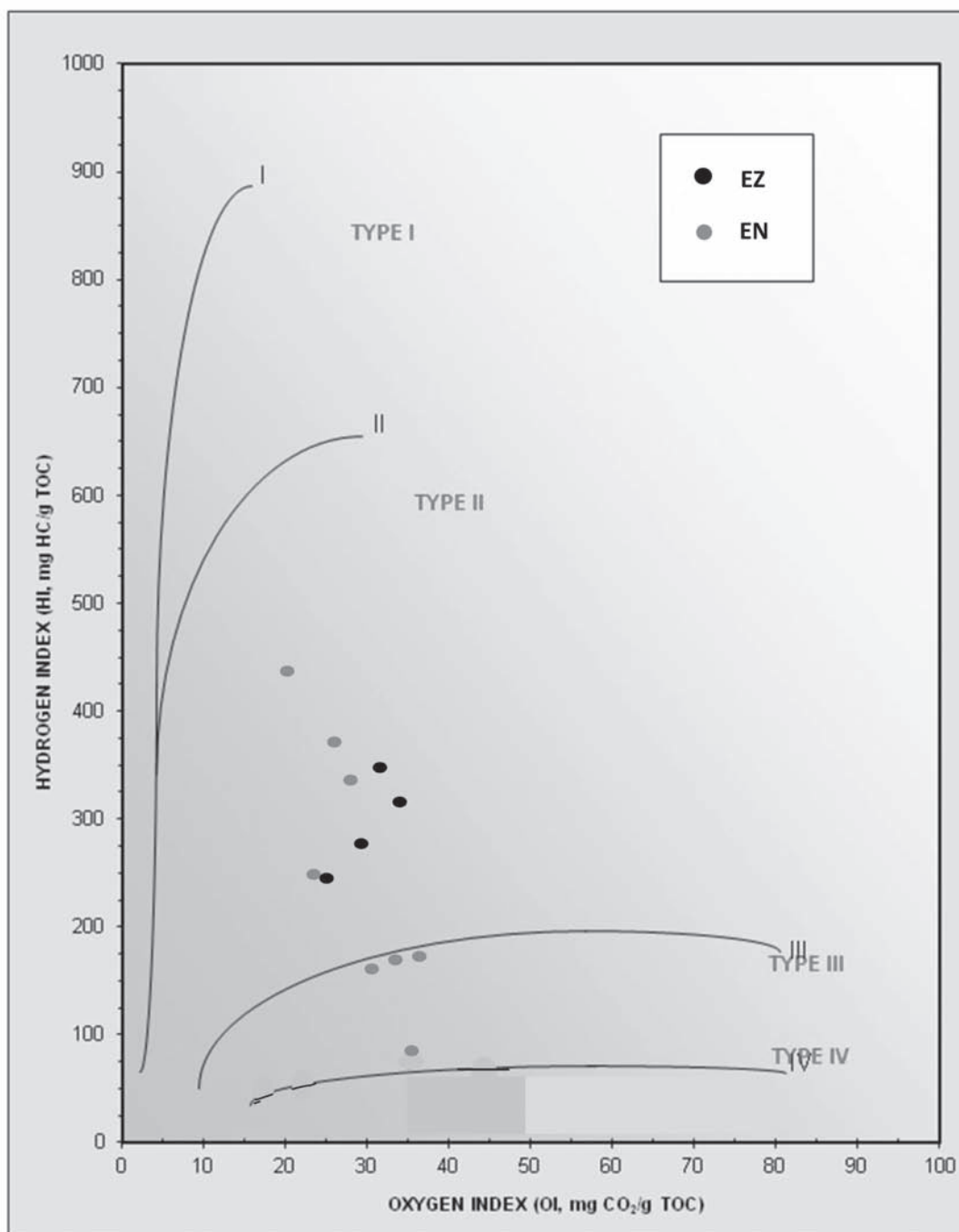


FIGURE 5. Cross plot of Hydrogen Index against Oxygen Index for the studied wells (after Jackson et al. 1985)

reactions which convert sedimentary organic matter into petroleum (Peters and Moldowan, 1993). In general, the extent of maturity depends on the relation of organic matter to the oil generative window. The T_{max} is a thermal stress parameter, dependant primarily on time/temperature conditions and can only be approximately related to the stage of petroleum generation for the rock type. The T_{max} values for the samples range between 421-437°C (Table 1) with an average of 429°C for Ezimo 1235 and 427.14°C for Enugu 1327

well. These indicate that the majority of the sediments are immature to early mature but are generally immature. Cross plots of T_{max} versus hydrogen index (HI) (Fig. 7) shows the samples are also immature and are mainly types III and IV kerogen. This implies mainly terrestrial organic matter input.

The production index (PI), defined as the ratio $S_1/(S_1+S_2)$, can be used to estimate thermal maturity. It is a generation parameter related to how much petroleum has actually been generated from the organic matter

TABLE 2. GC data showing values of n-alkane ratios and their CPI values

Sample ID	Pr/Ph	Pr/nC17	Ph/nC18	CPI
EN2	7.81	2.23	0.31	1.33
EN3	5.88	1.57	0.37	1.46
EN4	6.44	1.56	0.27	1.42
EZ5	5.44	1.26	0.41	1.97
EZ6	5.53	1.73	0.36	1.42

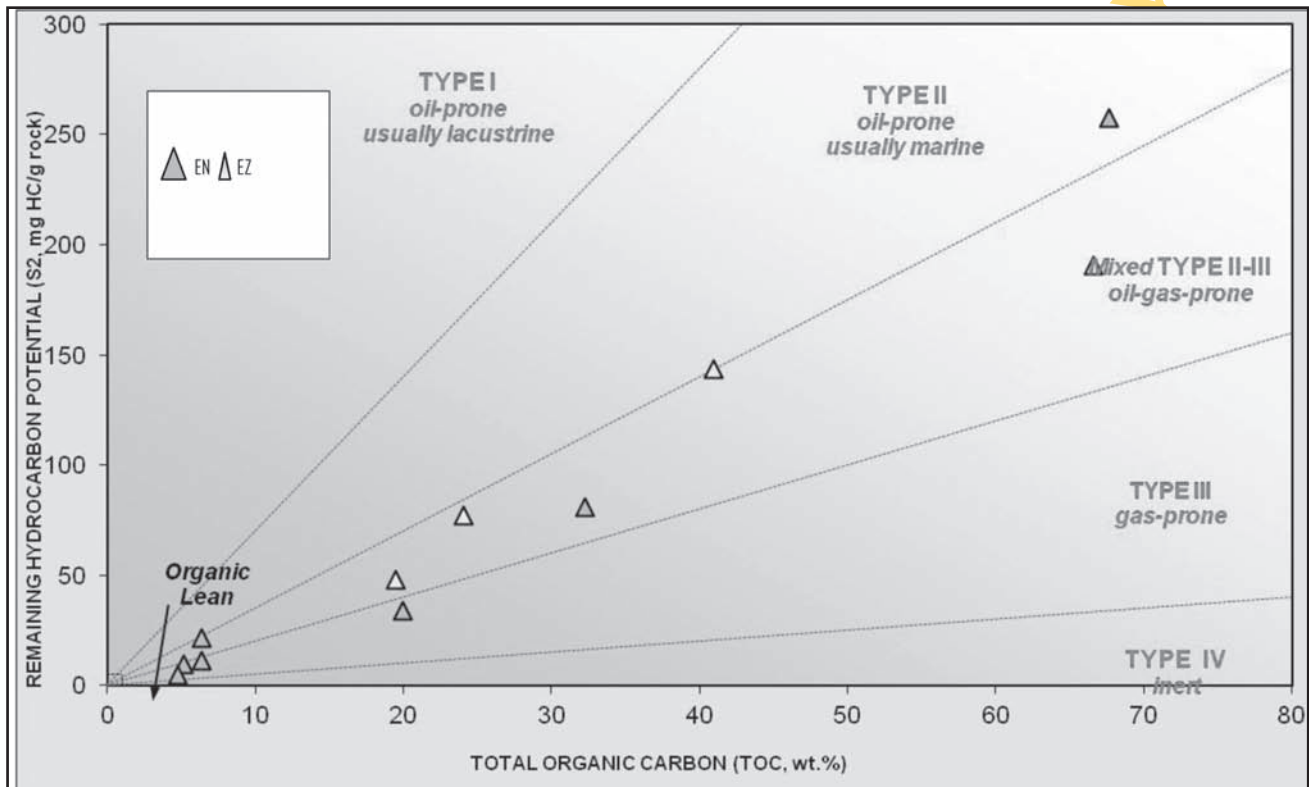


FIGURE 6. Cross plot of S2 against TOC for the studied wells (after Jackson et al 1985)

present in the source rock. According to Peters and Moldowan (1993), Tmax and PI values < 435°C and 0.1%, respectively, indicate immature organic matter. In this study, PI values obtained from both wells range from 0.02-0.05 (Table 1) indicate immature status for the sediments.

The ratio of soluble organic matter to total organic carbon, sometimes called transformation ratio, can be used in determining sediments maturity (Peters and Moldowan, 1993). This ratio varies from near zero in shallow sediments, to about 250mg/g TOC, at the peak of oil generation, and decreases because of conversion of bitumen to gas at greater depths. According to Miles (1989), oil-prone source rocks and gas prone kerogen rarely exceeds 50mg/g TOC at any level of maturity. The ranges of values from 6.34– 101.1 mg extr/gTOC

for both wells (av. 55.9 for Enugu 1327 well and 30.4 for Ezimo 1235 well) portray immaturity. Thus anomalous values (> 50 mg extr/gTOC) shown by few samples are indications of contamination by migrated oil or man-made products.

Plots of SOM/TOC against depth for both wells (Figs. 8a and 8b) show that for example in Ezimo well, SOM/TOC increases correspondingly with depth as the TOC, particularly for the lower coal interval. In the Enugu well, there is a decrease of SOM/TOC with depth, but it is further envisaged that at greater depth, more mature strata may be encountered. It is generally envisaged that at greater depth, more matured strata would be encountered in both wells.

Carbon Preference Index (CPI) is the relative abundance of odd versus even carbon-numbered n-paraffins

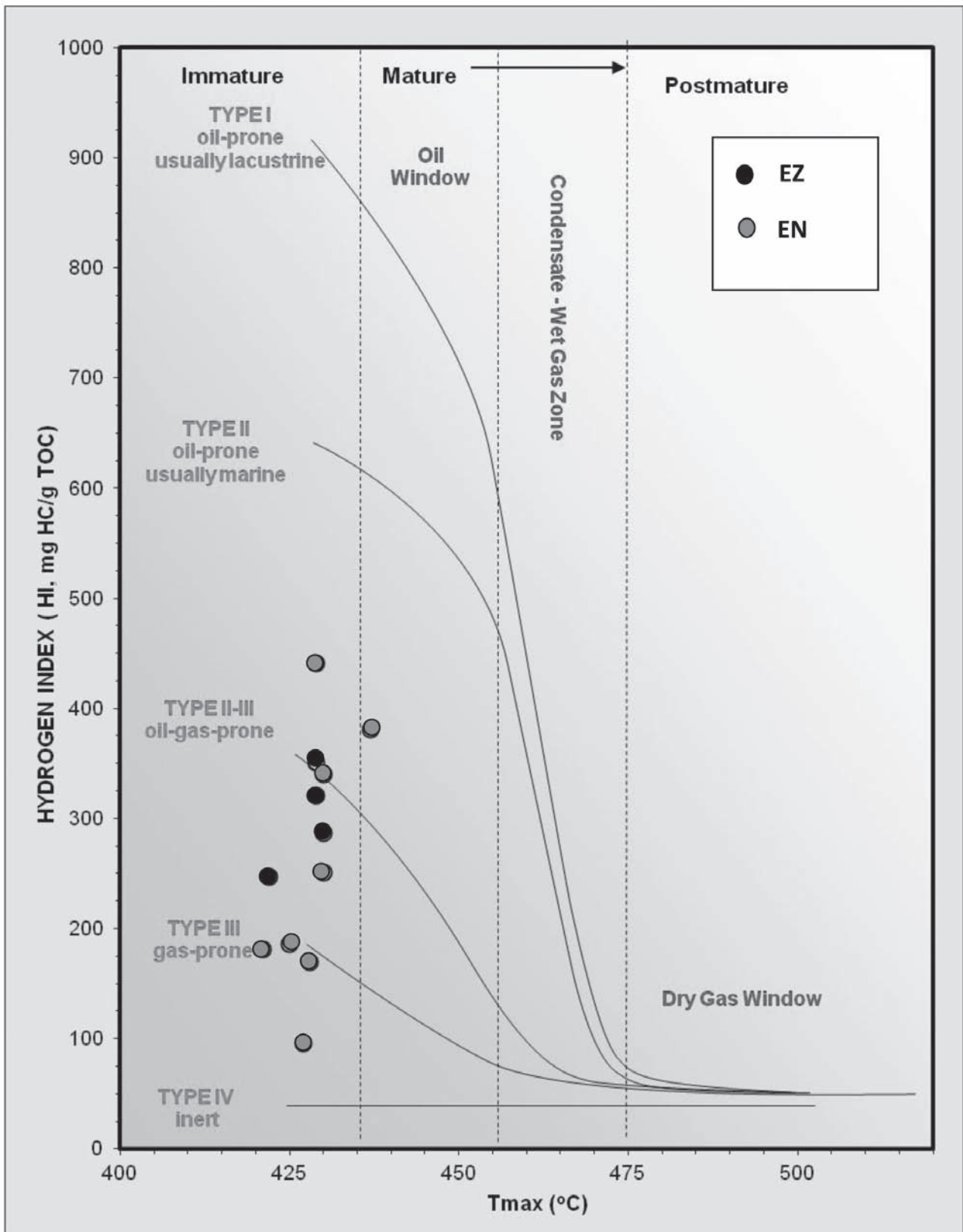


FIGURE 7. Cross plot of HI verses Tmax for the studied wells, (After Jackson et al., 1985)

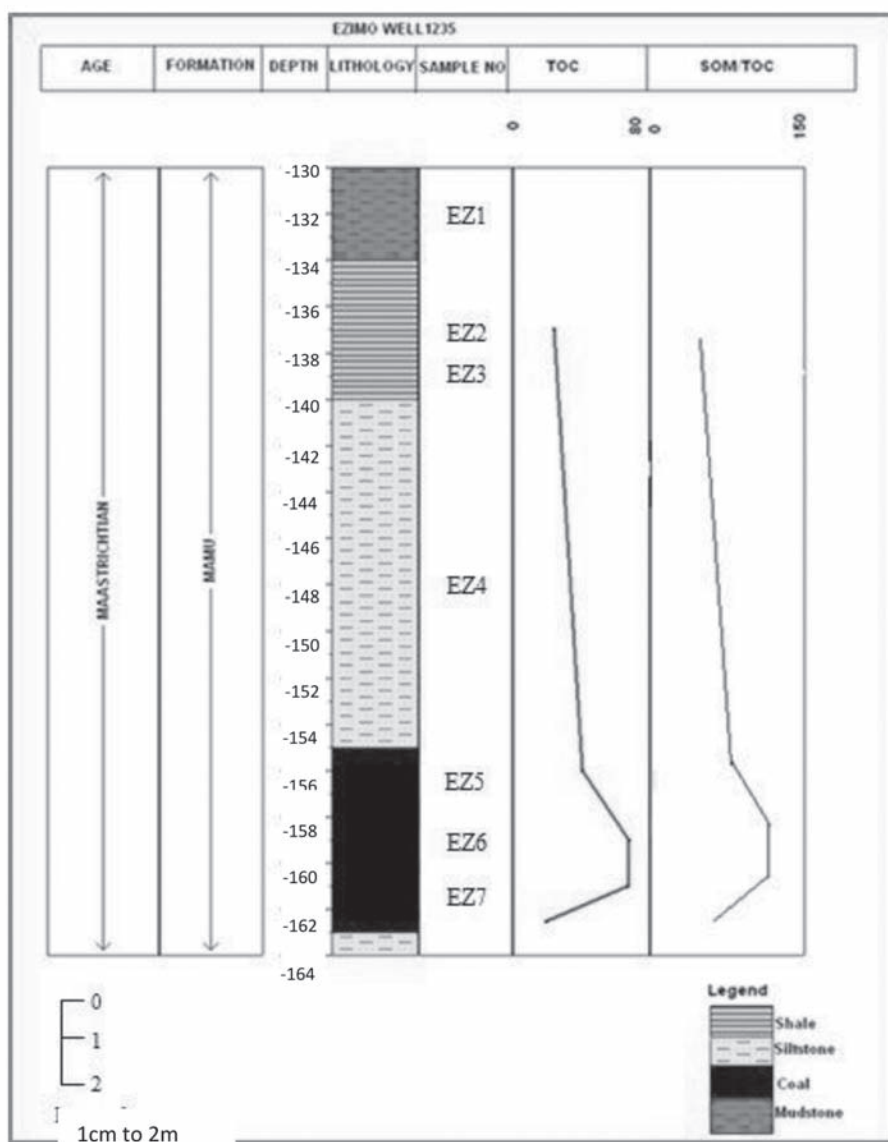


FIGURE 8 (a). Relationship between TOC and SOM/TOC with depth for Ezimo 1235 well

TABLE 3. Result of Saturates biomarker parameters used to describe maturity

Parameters	SAMPLE ID	EN1	EN3	EN5	EN7	EN6	EZ3	EZ5	EZ6
TS/TS+TM		0.039	0.036	0.145	0.023	0.013	0.192	0.076	0.041
C30/C29Ts		1.647	0.104	0.320	0.040	0.842	0.222	0.766	1.010
C29 $\beta\alpha/\alpha\beta$		0.410	0.481	0.316	0.552	0.502	0.825	1.175	0.938
C30 $\beta\alpha/\alpha\beta$		0.427	0.512	0.205	0.570	0.572	0.311	0.405	0.537
C32 22S/22S+22R		0.505	0.497	0.494	0.519	0.515	0.241	0.163	0.132
Homohopane Index		0.019	0.011	0.018	0.015	0.013	0.019	0.013	0.014
C27 Diasteranes/reg steranes		0.712	1.426	0.733	0.369	0.364	0.354	0.777	0.334

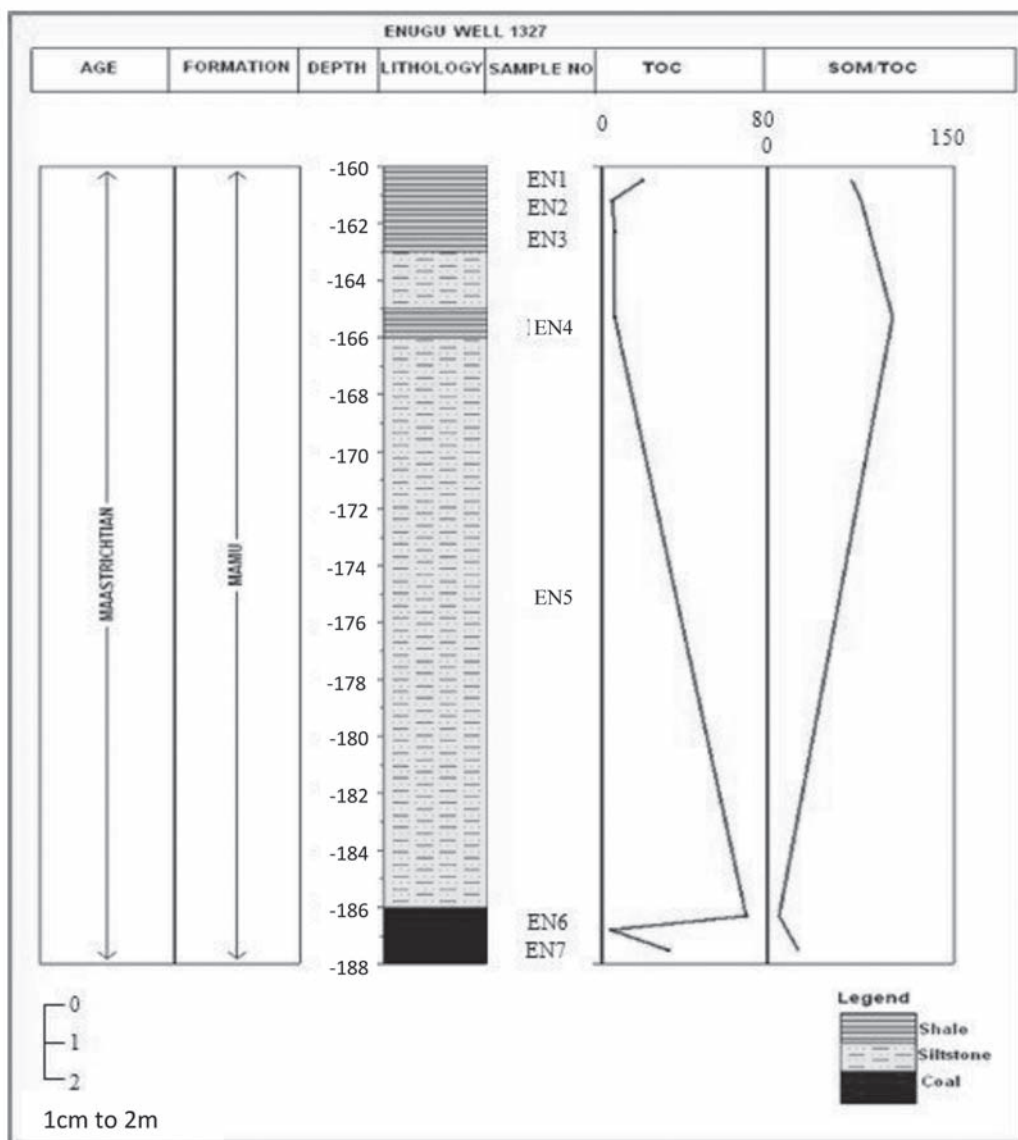


FIGURE 8(b). Relationship between TOC and SOM/TOC with depth for Enugu 1327 well

and can also be used to estimate the thermal maturity of organic matter (Peters and Moldowan, 1993). Hunt (1979) has pointed out that sediments with CPI of 1 at the surface and at all depths indicate marine source, while CPI considerably >1 shows contribution from terrestrial continental plants and also immature. In this study, the CPI values obtained range from 1.33 to 1.97 (Table 2) and are immature sediments from terrestrial precursor. This corroborates the findings of Elueze and Nton (2004) in the eastern Dahomey basin. Maxwell et al., (1971) have shown that strong odd/ even bias of heavy n-alkanes is indicative of sediment immaturity and corroborates the findings in this study. A typical gas chromatogram of one of the samples has hump of unresolved complex mixture (UCM) (Fig 9), which

according to Killops and Al-Juboori (1990) is associated with biodegradation and immaturity of sediments. Such deductions may be applicable to this study.

The composition and distribution of certain diagnostic chemical fossils (biomarkers) can therefore indicate the maximum stress experienced by the rocks or petroleum in which the compounds are found (Ekweozor and Strausz, 1982). Biomarkers are used to describe the maturity of the organic matter present in the source rock depending on its relation to the oil generation window (Peters and Moldowan, 1993). Typical representative gas chromatograms (GC-Ms) of triterpane (m/z 191) and sterane (m/z 217) are shown in Figs 10a and 10b. Arising from the chromatograms, an assessment of the thermal maturity levels were generated

TABLE 4. Source and Environment of deposition parameters computed from the saturate biomarkers distributions in both wells

SAMPLE ID	EN1	EN3	EN4	EN6	EN7	EZ3	EZ5	EZ6
Oleanane/Hopane	0.098	0.039	0.061	0.023	0.049	0.461	0.049	0.019
Tricyclic C19/C20	0.77	0.536	1.018	ND	1.175	1.533	1.048	1.536
Tetracyclic/tricyclic C24	1.526	1.68	1.762	ND	2.051	2.637	1.87	1.732
Homohopane Index	0.019	0.011	0.018	0.013	0.015	0.019	0.013	0.014
Gammacerane/Hopane	0.025	0.029	0.035	0.017	0.022	0.058	0.050	0,32
% C27	13.52	17.73	13.45	3.26	12.39	19.40	19.43	18.33
Sterane % C28	19.12	19.90	15.10	25.83	25.29	22.98	24.11	32.34
% C29	67.36	62.37	71.44	70.90	62.32	57.61	56.45	49.33
C29	0.202	0.172	0.216	0.119	0.209	0,394	0.449	0.263
20S/20S+20R								

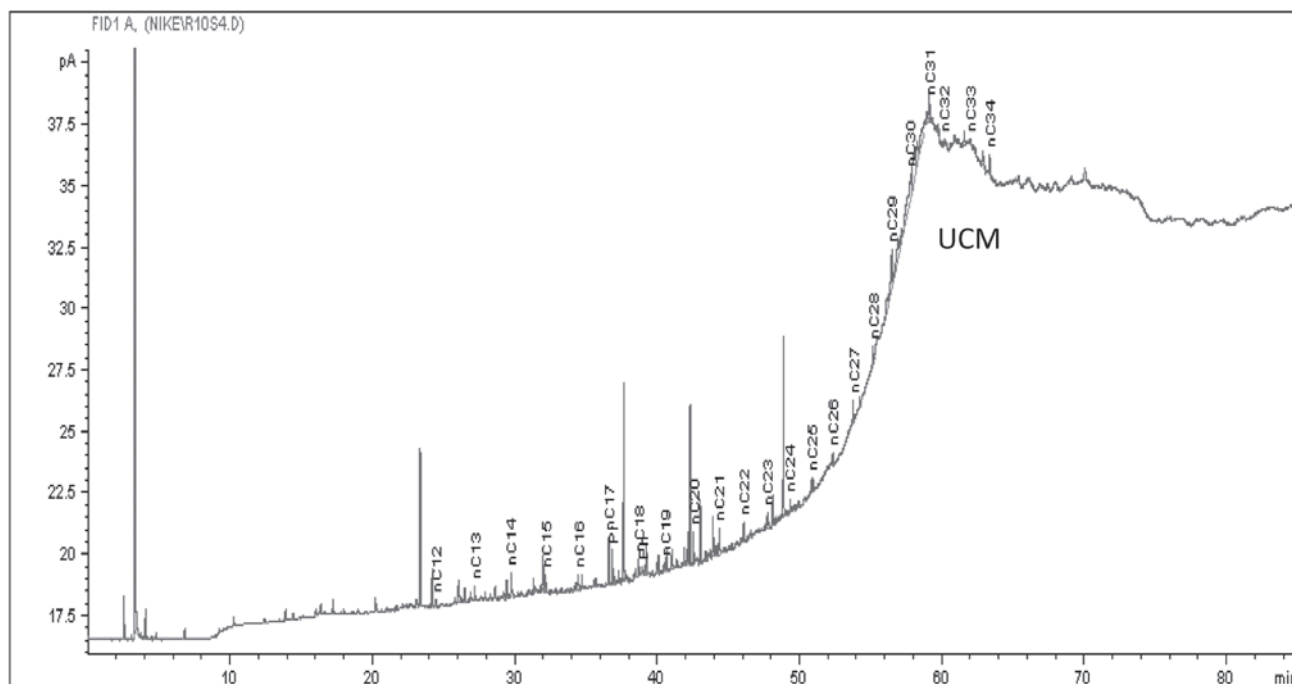


FIGURE 9. Gas chromatogram for EZ 6 showing hump of unresolved complex mixture (UCM)

based on maturity parameters as shown in Tables 3 and 4. Several biomarkers' parameters were used to infer the maturity of the sediments, which include the moretane/hopane ratio i.e. the hopane C_{30} $\beta\alpha/\alpha\beta$ ratio. High values of C_{30} $\beta\alpha/\alpha\beta$ were obtained from both wells, ranging from 0.21-0.57 (Table 3) with an average of 0.44, which is below the 0.5 maturity thresholds; thus

indicating immature source rock as the ratio decreases with increasing maturity (Mackenzie et al., 1980).

The C_{29} hopane $\beta\alpha/\alpha\beta$ is indicative of maturity. For this ratio, the values decrease with increasing maturity, samples with value greater than 0.8 are immature while values less than 0.15 are mature. The samples have high ratio values ranging from 0.32 to 1.18 (av.

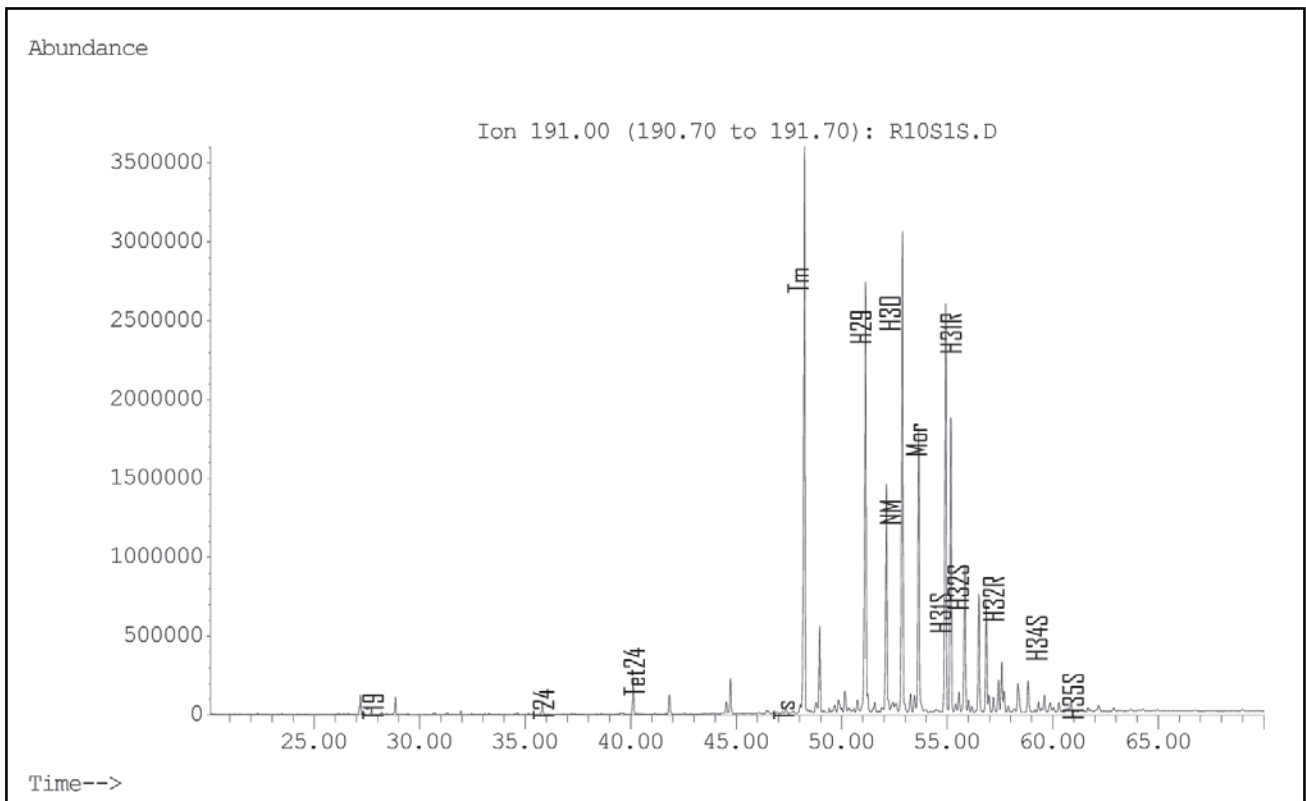


FIGURE 10(a). Partial m/z 191 Mass chromatogram (terpanes) from EN6

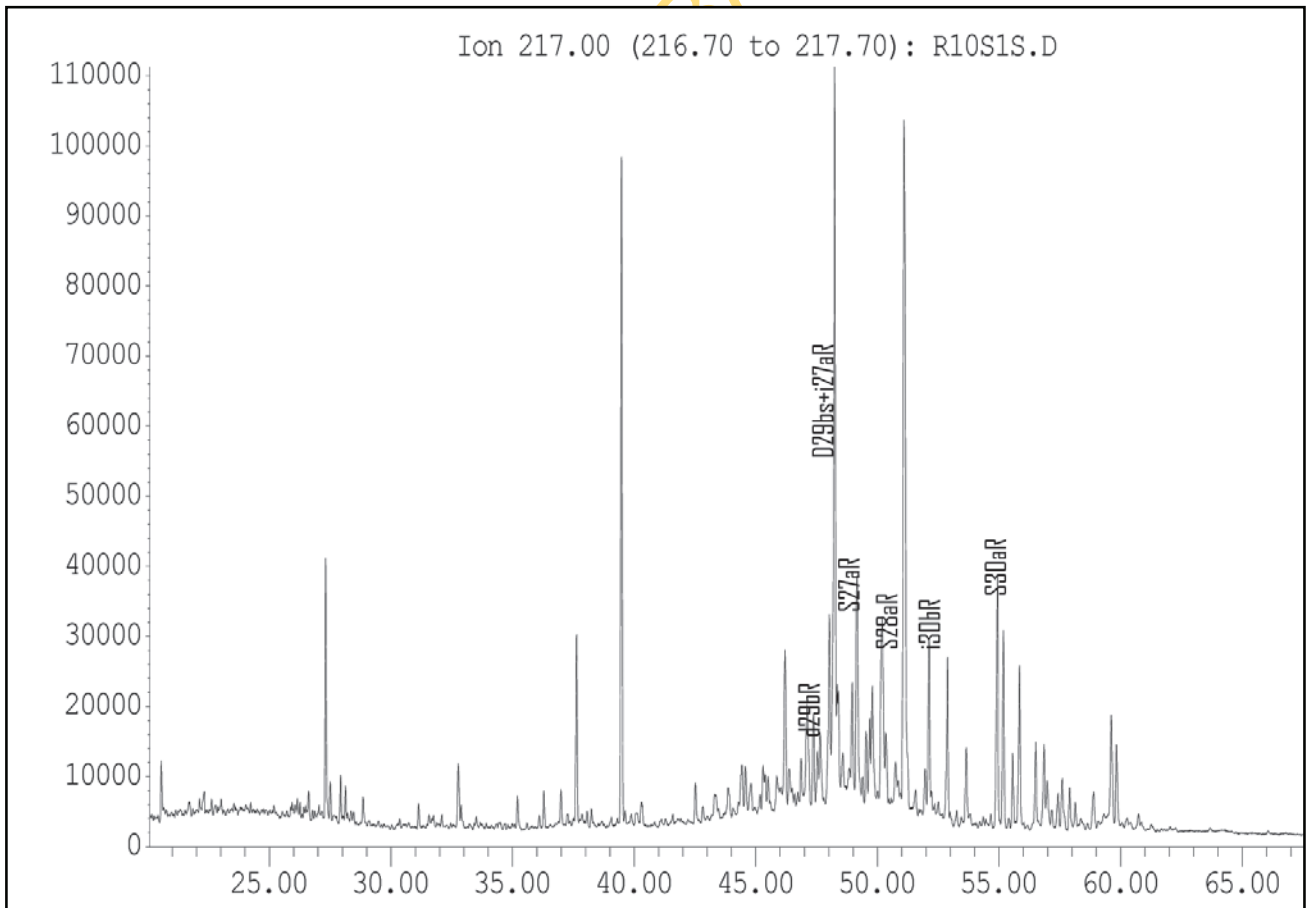


FIGURE 10 (b). Partial m/z 217 Mass chromatogram (steranes and diasteranes) from EN6

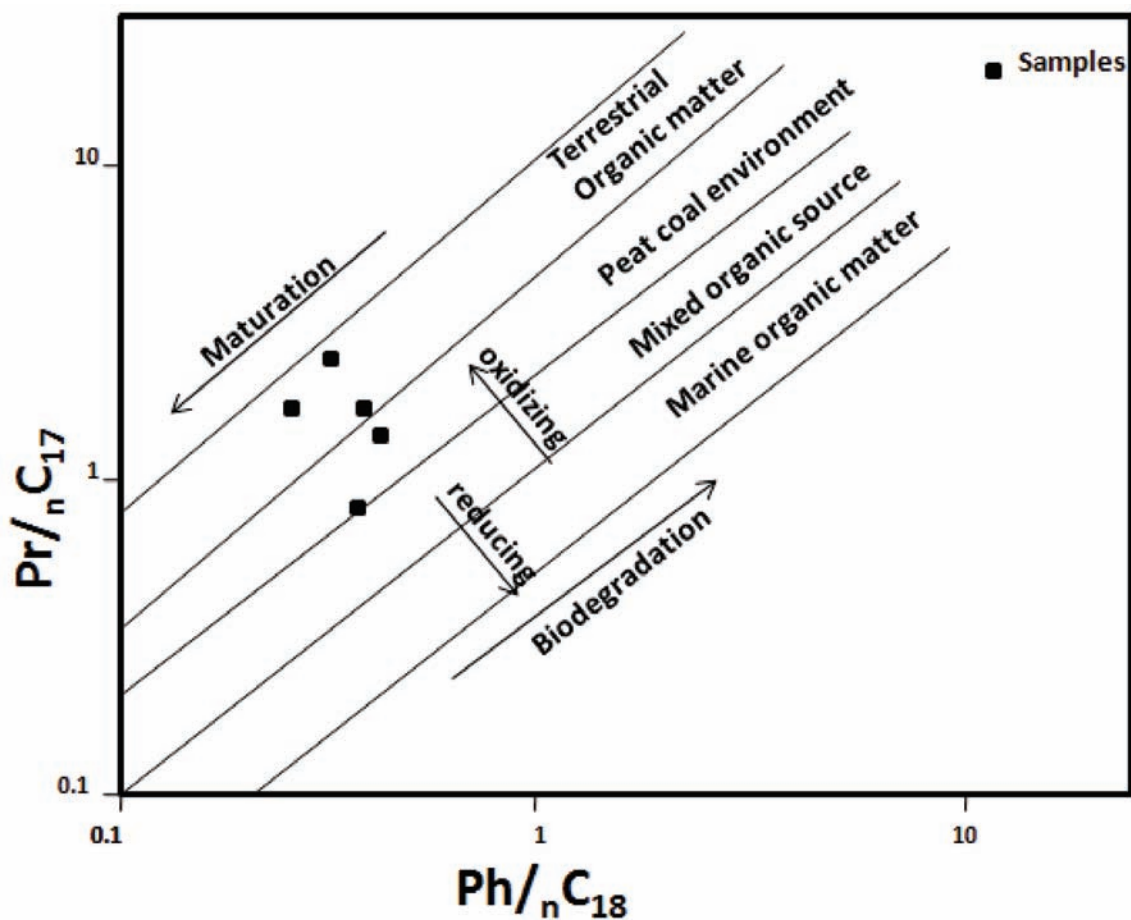


FIGURE 11. Plots of Pristane/nC17 versus Phytane/nC18 (Modified after, Datta et al., 2008).

0.65) this falls in the immature zone. $22S/22S+22R$ C_{32} hopane ratios in the samples range from 0.13 to 0.52 (Table 3). These values indicate that the samples are of very low maturity (Peters and Moldowan, 1993). The values obtained from the TS/TS+TM ratio is low (0.01-0.19) (Table 3) having a high dominance of Tm which is indicative of low maturity.

DEPOSITIONAL ENVIRONMENT

Didyke et al. (1978) have indicated that the pristane/phytane (pr/ph) ratio of sediments can indicate the environment of deposition. According to them, Pr/Ph ratio <1 indicate anoxic deposition while oxic conditions are indicated by ratio >1. The accuracy of these generalization has been challenged often times. Pratt (1984) has therefore suggested that for accurate environmental interpretation, geological data should be incorporated since the ratio decreases with catagenesis. In this study, Pr/Ph ranges from 5.44 to 7.81 (Table 2) and indicate oxidizing environment for the sediments (Lijmbach, 1975), Didyke et al., 1978). The prevalence

of terrestrial organic matter in the sediments (Type III kerogen) favours a continental environment where oxic conditions prevail. In addition, the relative high concentration of higher molecular weight n-alkanes from the gas chromatograms further indicates input from terrestrial plants. Cross plots of isoprenoids/n-alkanes (Fig. 11) reveal that the majority of the sediments is terrestrial organic precursor and was deposited in oxidizing environment.

The presence of *Oleananes*, which are derived from angiosperm, indicate higher plant input, while that of *hopanes* are widely distributed among bacteria found in marine environments (Sonibare and Ekweozor, 2000). These are indicative of organic sourced from both terrigenous and marine organic matter input. High values were obtained from the C_{24} tetracyclic/ C_{24} tricyclic terpanes and the C_{19}/C_{20} tricyclic terpane ratios, (Table 4; 1.53-2.64 and 0.54-1.54) respectively. According to Mello et al. (1988), such high values amplify terrigenous organic matter input. Series of extended hopanes (homohopanes) C_{32} to C_{35} are also

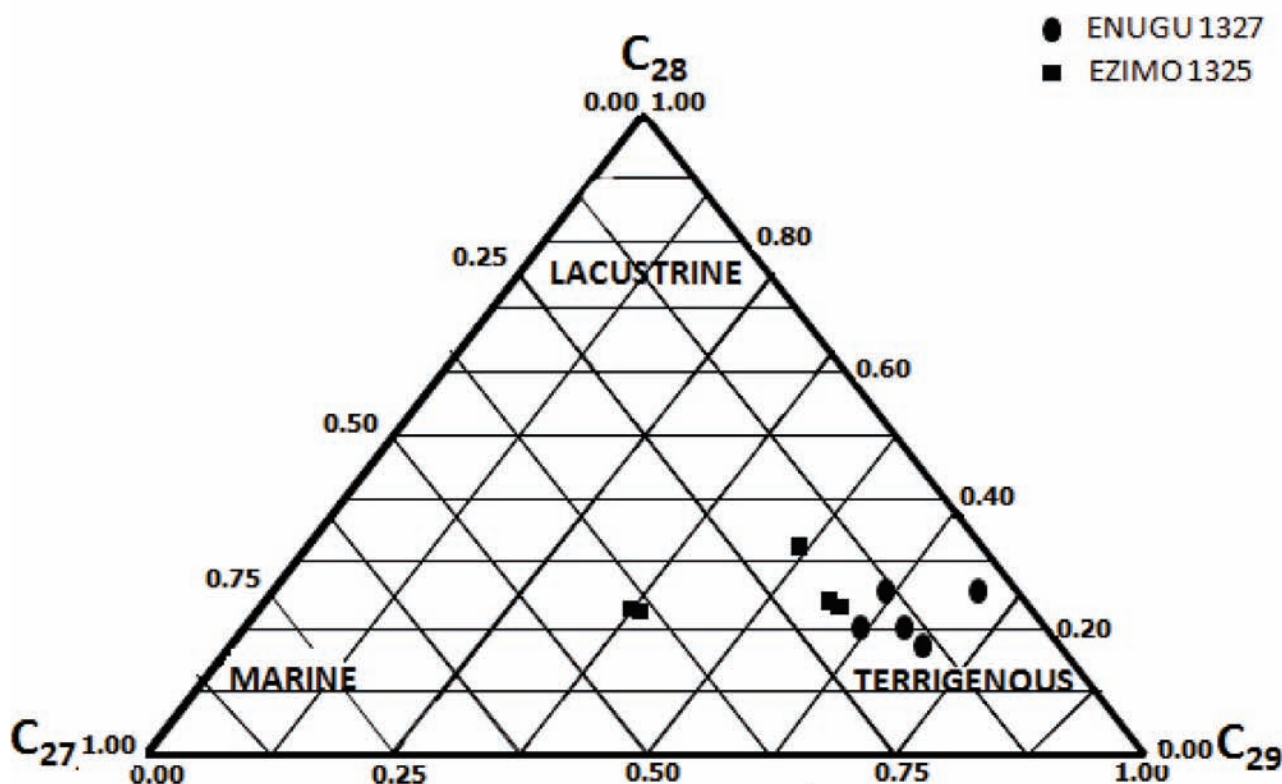


FIGURE 12. Ternary plots of C₂₇, C₂₈, and C₂₉ steranes of associated shales and coals from studied wells (After Huang and Meischein, 1979).

present in appreciable amounts in all the shales and coal samples, although with low amount of C₃₄ and C₃₅ homohopane. Their presence is attributable to suboxic terrigenous environment and corroborates the findings of Peters and Moldowan (1993).

The presence of C₃₀/C₂₉ Ts depends mostly on environment of deposition. As reported by Peters and Moldowan, (1993), source rocks deposited under suboxic conditions show higher ratio than those deposited under anoxic conditions. In this study, the Mamu Formation has high C₃₀/C₂₉ Ts ratio (range, 0.04-1.65; av. 0.62; Table 3), indicating they were deposited under suboxic conditions. The presence of C₂₇ to C₂₉ steranes and diasteranes, indicates that they were derived from mixed sources (marine and terrestrial) with capacity to generate both oil and gas. This is in line with the findings of Czechanska et al. (1988), who have associated the presence C₂₇ and C₂₉ steranes with terrestrial and marine sources respectively. However, the dominance of C₂₉ over C₂₇ and C₂₈ (Table 4) indicates higher contribution of terrestrial materials (Fig. 12).

SUMMARY AND CONCLUSIONS

Subsurface samples from Mamu Formation penetrated by two shallow wells (Enugu and Ezimo) within the Anambra basin, south eastern Nigeria were examined for lithofacies distribution, depositional environment and hydrocarbon prospect based on rock eval pyrolysis and biomarker studies. The lithostratigraphic sequences, penetrated by the wells, consist of shales, siltstones, heteroliths of both lithologies, coals and mudstones. The shales are black and fissile, interlaminated with siltstones. The siltstones are well sorted; medium grained containing planar and wavy laminae, while the coals are fissile.

The source rocks are moderately to fairly rich in organic matter and therefore can be considered as a potential source rock. The organic matter characterization reveals the presence of types II and III kerogen with a preference of type III, which is indicative of a substantial amount of terrigenous organic matter having the potential to generate more gas than oil. Biomarker studies strongly indicate immature status, deposited

in oxidizing environment. The study area is therefore considered to be of good petroleum potential, particularly gaseous hydrocarbon at appropriate maturity. It is envisaged that with greater depth, more matured strata could be encountered.

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