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AN EVALUATION OF THE SOURCE ROCK PROPERTIES OF THE CAMPANO-MAASTRICHTIAN SEDIMENTS IN THE LERU-AGBOGUGU AXIS, ANAMBRA BASIN, SOUTHEASTERN NIGERIA

S. O. Onyekuru, A. I. Opara, E. O. Obiukwu, K. D. Opara, C. J. Iwuagwu

Department of Geology, Federal University of Technology, Owerri

Received June 16, 2019; Accepted September 19, 2019

Abstract

Shale samples from the outcropping profiles of Enugu Shale and Mamu Formation in parts of the southern Anambra Basin, were subjected to geochemical analyses for the evaluation of source rock properties. Nine screened samples were analyzed with the Rock Eval II Plus TOC module to identify type and maturity of organic matter and to detect the petroleum potential of the sediments. Other parameters obtained from the instrument included T_{max}, which is the temperature corresponding to the temperature at which the pyrolytic yield of hydrocarbon (S_2-peak) reaches maximum, production index (PI) and potential yield (PY). Extractible Organic Matter (EOM) was evaluated using Soxhlet Extractor, while biomarker distributions were obtained with the Gas Chromatography (GC). Results revealed that the TOC of the analyzed samples exceeded the threshold value of TOC ≥ 0.5 wt.% requirement for clastics to qualify as source rocks. The cross plots of hydrogen index (HI) against oxygen index (OI) showed that the samples contain type III and mixed type II/III kerogens. The average T_{max} values of 433 and 431°C, respectively recorded for sediments from the Enugu Shale and Mamu Formation, indicate immature to transitionally early mature source rocks. The maceral groups in the analyzed shales are: vitrinites (39 to 59 %), inertnites (11 to 18 %) and the liptinites (9 to 21 %). The vitrinites and inertnites that are more dominant are deficient in hydrogen because of their derivation from the structural parts of plants. The sediments were also deposited in suboxic and low pH paleodepositional environments and therefore, have potentials to generate gas rather than oil given sufficient maturity.

***Keywords**: Biofacies, Maceral, Maturity, Organic, Source Rock.*

1. Introduction

Agbogugu–Leru area, whose underlain geological sediments are being investigated for organic richness and maturity is located in the southern part of the Anambra Basin. The area lies within Longitudes $6^{0}35^{1}$ and $7^{0}45^{1}$ E and Latitudes $5^{0}30^{1}$ and $7^{0}30^{1}$ N, along the Enugu-Port Harcourt expressway (Fig. 1). The Anambra Basin is located south of the regionally extensive northeast-southeast trending Benue Trough. The basin has about 5 km thick of sedimentary packages, comprised of Cretaceous–Tertiary sediments comprising the basal Campanian Nkporo Shale and its lateral equivalent, Enugu Shale, succeeded by the Maastrichtian Mamu Formation and the Ajali Sandstone. The succession in the area is capped by the Tertiary Nsukka Formation [1]. The lithostratigraphic units are characterized by enormous lithologic heterogeneity in both internal and vertical extensions, derived from several paleoenvironmental settings [2]. A comparative assessment of the source rock potential of the accompanying shale sediments is required to understand units that are more likely to form part of the elements of the potential petroleum systems anticipated in the Anambra basin. Recent exploration techniques use modern understanding of organic petrology to identify source rocks, estimate its quality, type and maturation level of the organic matter in the rock. The technique had also fingerprinted identified source rocks in a petroleum system and improved the success rate of petroleum exploration [3].

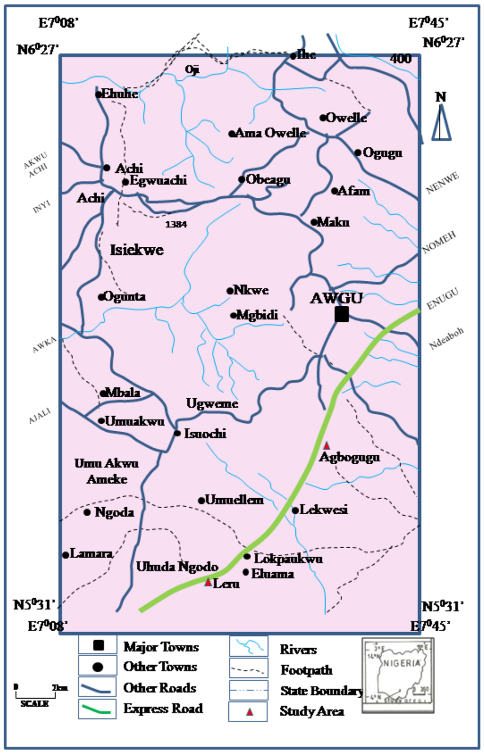

Fig. 1.Map of study area showing sampling l ocations

Evidences of hydrocarbon occurrence abound in the Anambra and adjoining basins. Oil seeps have been known to occur in bituminous shale outcrops of the Ezeaku, Awgu and Nkporo Shales [4]. It has also been recorded that some wells drilled in the basin encountered a number of oil shows [5-6]. It is therefore, probable that potentially profitable deposits that have not been discovered exist in the Anambra basin. Hence, the evaluation of the hydrocarbon potential of sediments in the Anambra Basin remains a subject that deserves consideration and in-depth assessment for possible greater profitability and sustainability.

This study is aimed at identifying pods of active/potential source rocks that may form a part of the elements of the petroleum system in the southern Anambra Basin.

2. Geological setting

The tectonic evolution of southeastern Nigerian sedimentary basins may be traced back to the late Jurassic with the separation of the African and south American plates which left the Benue Trough as a failed arm of an RRR Triple Junction [7-8].

The depositional history of southeastern Nigeria is well documented in literature [5,9-13]. This can briefly be summarized as follows: The first stage of deposition into the then Abakalilki-Benue Trough which is the failed arm of the rift associated with the opening of the south Atlantic was during the Aptian-Santonian [11]. This was marked with the deposition of the Asu River Group, the Ezeaku and Awgu Formations. The second stage of deposition commenced during the Santonian with the tectonic uplift and folding of Albian-Coniacian sediments in the Abakaliki-Benue Trough forming the Abakaliki Anticlinorium. This led to the subsidence of the Anambra Basin and Afikpo Syncline.

Table 1. Stratigraphic successions in the Anambra Basin, Benue Trough and Niger Delta [5]

Age	Basin	Stratigraphic Units						
Oligocene-Recent	Niger Delta	Ogwashi-Asaba Fm			Benin Formation			
Eocene		Ameki/Nanka Fm/Nsugbe Sandstone (Ameki Group)			Agbada Formation			
Thanetian		Imo Formation			Akata Formation			
Danian	Anambra Basin		Nsukka Formation					
Maastrichtian			Ajali Formation					
			Mamu Formation					
Campanian		Nkporo Fm	Nkporo Shale	Enugu Fm	Owelli Ss	Afikpo Ss	Otobi Ss	Lafia Ss
Santonian	Southern Benue Trough	Agwu Formation						

The newly subsided basins now became a major depositional center for sediments derived from the uplifted Albian-Coniancian sediments of the folded Abakaliki Anticlinorium and adjoining areas. During this time, the Nkporo Group (comprising of Nkporo Formation, Enugu Shale, Afikpo and Owelli Sandstone), Mamu Formation, Ajali Sandstone and Nsukka Formation were deposited (Table 1; Fig 2.). The third depositional stage commenced during the Paleocene with the deposition of Imo and Ameki Formations. This period laid the stage for the formation of the present Niger Delta [14].

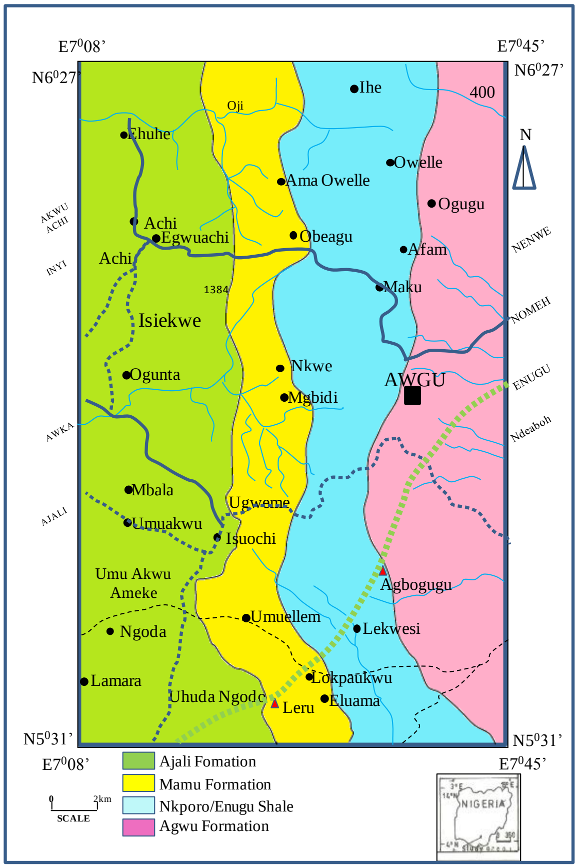

Fig. 2. The geological map of Southern Anambra Basin, showing the study area

3. Materials and methods

Two outcropping sections of Enugu Shale and Mamu Formation exposed at Agbogugu and Leru/Isuochi junction were studied in detail. Bed-by-bed logging and description of the sections noted lithological and structural variations. Sketching of the logged profiles was done to mimic these differences (Figs. 3 and 4). Nine representative shale samples, made up of four from the Enugu Shale and five from Mamu Formation exposures at Agbogugu and Leru/Isuochi junctions, were subjected to organic geochemical analyses:

3.1. Total organic carbon (TOC)

The determination of total organic carbon (TOC) was done with Rock Eval Pyrolysis using the LECO C/S analyzer with a TOC module. The Total Organic Carbon (TOC) was determined on powdered samples that were pretreated with Hydrochloric(HCl) acid to remove carbonates in the sample. 100 mg of pulverized sample was weighed in a special porous crucible and placed in a cold sand bath; the weighed sample was then wetted with few drops of ethanol (to avoid sporadic reactions) and treated with some drops of 10% diluted hydrochloric (HCl) acid until no further reactions occurred. The sample was left in the sand bath for 12 hours at a temperature of 80°C in order to allow excess water to evaporate. Thereafter, the sample was transferred into a laboratory vacuum oven where it was kept for another 12 hours at a temperature of 50°C. One gram of copper chipping was added as catalyst to the oven-dried sample, before the sample was put in the combustion chamber of the LECO Apparatus,where sample was then burnt in the presence of oxygen at a temperature of 1300°C. The evolved gases: Carbon dioxide (CO_2) and sulphuric acid (H_2SO_4) were simultaneously measured quantitatively by infra-red detectors and recorded as percent carbon and sulphur, respectively. This experiment was repeated and TOC values obtained for all the selected samples

3.2. Determination of source rock potential and maturity

The screened samples were also analyzed to determine the hydrocarbon generation potential, kerogen types, maturity and hydrocarbon index (HI) using the Rock-Eval LECO C/S machine outfitted with a TOC module. Other parameters obtained from the analysis include the T_{max}, which is the temperature corresponding to the temperature at which the pyrolytic yield of hydrocarbon (S_2-peak) reaches its maximum, hydrogen index (HI), Oxygen Index (OI), Production Index (PI) and Potential Yield.

3.3. Extraction of extractable organic matter (EOM)

The analyzed sampleswere powdered and EOM were extracted in cellulose thimbles for a period of 36 hours using 100% dichloromethane. The solvent from theresultant solution was removed by means of a rotary evaporator under vacuum whose pressure was not greater than 200 mbar and finally by a flow of nitrogen at a temperature not more than 30^{0}C to yield the Extractible Organic Matter (EOM).The EOM was analyzed bycapillary gas chromatography to produce gas chromatograms from which values of preliminary concentrations of biomarker parameters, including: Pristane/nC17, Phytane/nC18, Pristane/Phytane ratio, etc. were computed from peak heights using equation 1:

$$EOM(ppm) = \frac{Weight of Extract\ (g) x10^6}{Weight of sample\ (g)} \quad \ldots \qquad (1)$$

From the values of the TOC (wt. %) and EOM (ppm), the bitumen ratio was calculated using equation 2:

$$Bitumen\ Ratio\left(mg\frac{ext}{g}TOC\right) = \frac{EOM\ (ppm)}{TOC\ (wt\ \%)\ X\ 10} \qquad (2)$$

3.4. Chromatography (GC)

Gas chromatography was conducted on a Varian 3400 GC fitted with 45m x 0.25mm fused silica column coated with a non-polar stationary phase (DB1). Both the injector and detector temperatures were set at 300°C. The oven-heating program was set at a temperature of 30°C for an initial isothermal period of 2 minutes then increased at the rate of 6to 300°C/min followed by final isothermal period of 13 minutes. The carrier gas, hydrogen, was set at a flow rate of 2mL/min. Collection and processing of GC data was initially done with Atlas software via a chromatographic server. This process produced the respective gas chromatograms as well as the corresponding injection reports containing peak heights and area.

The hydrogen (H_2) carrier gas was calibrated at 2mL/min flow rate. Data acquisition and integration was carried out using the Thermo Scientific™ Atlas Chromatography Data System (CDS) controls chromatography instruments from multiple vendors using the 247 Instrument Controller for data integrity over corporate networks or WANs.

3.5. Organic petrology

Macerals are the remains of various types of plant and animal matter that can be distinguished by their chemistry and by their morphology and reflectance using a petrographic microscope [15].In order to determine the maceral constituents, representative samples collected from the studied sections were crushed to less than2mm and impregnated in epoxy resin, ground and polished for quantitative reflected light microscopy. Microscopic examination was carried outunder X40 oil immersion objective.

4. Results

4.1. Physical properties of the sections

The two well exposed sections of Enugu Shale and Mamu Formation,logged and described at Agbogugu and Leru/Isuochi junctions, respectively, showed a generally increase in sand thicknessup-section, thus displaying a coarsening upwards sequence. Sedimentary structures observed in both sections include planar cross-beds, ripple laminations, bioturbation, parallel laminations and pyritic concretions (Figs.3 and 4).

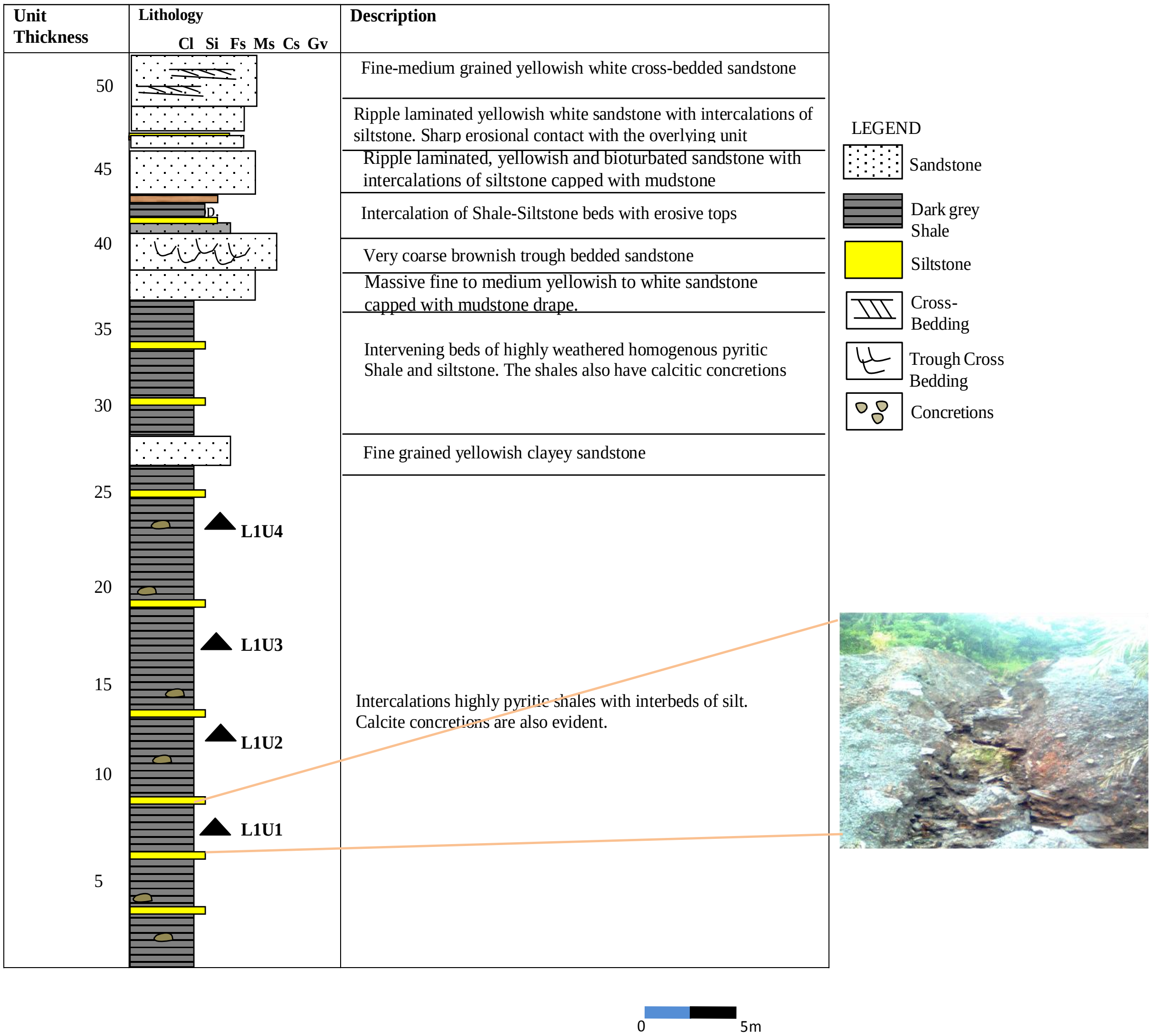

Fig. 3. Lithostratigraphic log of the section exposed at Agbogugu Junction, Ph. /Enugu Expressway

4.2. Organic Geochemistry

Table 2 shows the results of organic geochemical analysis carried out on the nine rock samples. The Total Organic Carbon content (TOC) of the shale samples of Enugu Shale ranges from 0.72 to 4.94 wt. % with an average of 2.2 wt. %. Samples from the Mamu Formation, has TOC values ranging from 0.76 to 2.11 wt. % with an average value of 1.5 wt. %.

4.3. Quantity of organic matter

The results of Extractable Organic Matter (EOM) or Soluble Organic Matter (SOM) content of the Shale samples in the study area reveal that EOM/SOM in the studied shale samples exceeded 500ppm (Table 3). Samples from Enugu Shale have an average value of 683ppm while those of Mamu Formation have an average value of 692ppm.

The plot of TOC (%) against SOM (ppm) shows that most of the Shale samples were clustered within the oil source rock field (Fig. 5).

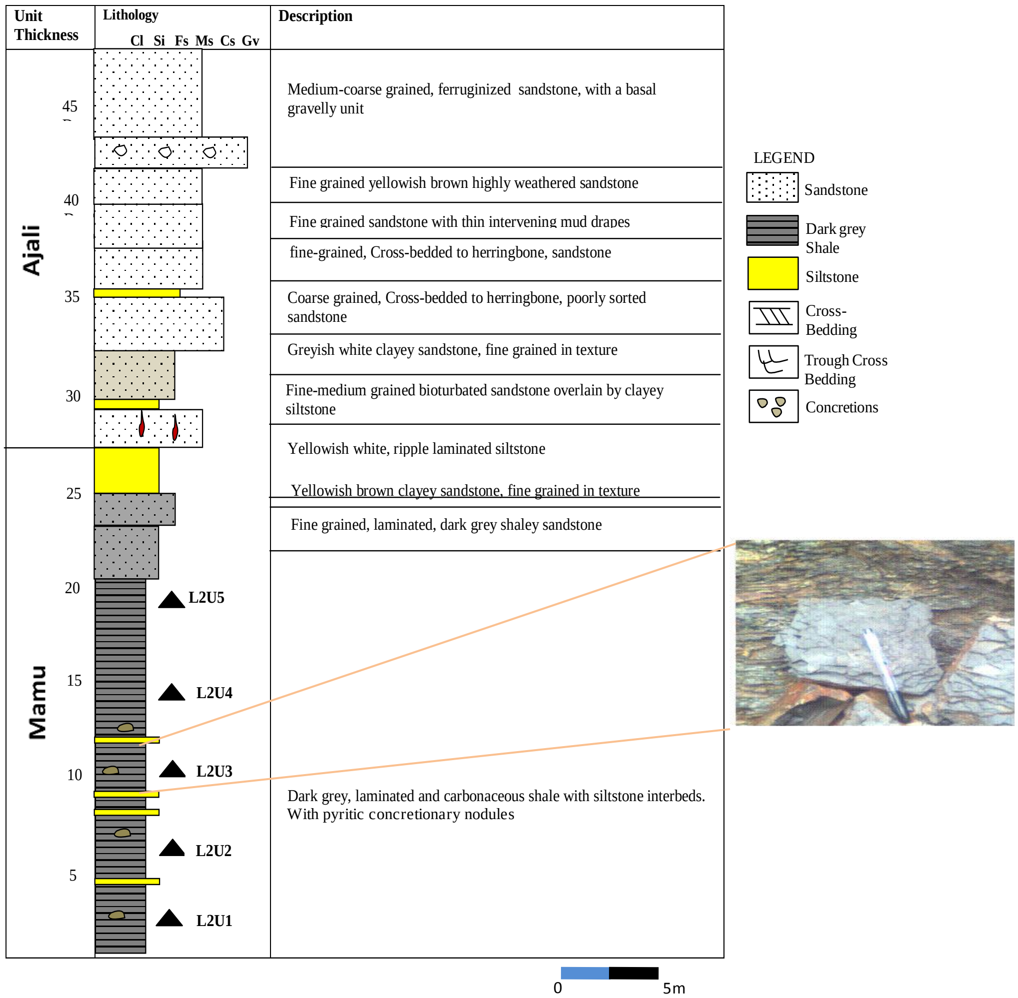

Fig.4. Lithostratigraphic log of section exposed at Leru/Isuochi Junction, Ph./Enugu Expressway

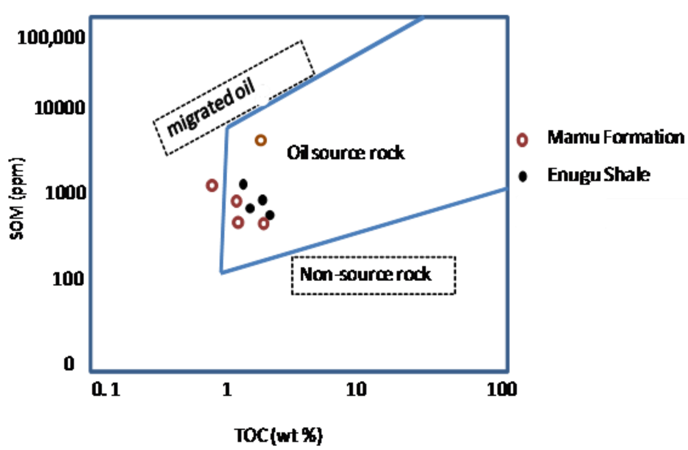

Fig. 5. Plot of SOM (ppm) against TOC (wt. %) (*modified after* [17])

4.4. Quality of organic matter

Results of the geochemical analysisalso showed a Hydrogen Index (HI) value of 43 to 142 mgHC/gTOC for the Enugu Shale with an average value of 95.3mgHC/gTOC (Table 2). Samples from Mamu Formation showed a HI value of 27 – 54mgHC/gTOC with average of 39.4 mgHC/gTOC.

Table 2. Result of maceral analysis and vitrinite reflectance measurement

S/N	ID	Client ID	Sample Type	TOC	S1	S2	S3	(°C)	HI	OI	S2/S3	S1/TOC*100	PI
1	9648	L1U1	Enugu Sh	4.94	0.19	7.00	2.98	437	142	60	2.3	4	0.03
2	9649	L1U2	Enugu Sh	2.46	0.16	1.74	0.82	424	71	33	2.1	7	0.08
3	9650	L1U3	Enugu Sh	0.72	0.04	0.31	0.59	439	43	82	0.5	6	0.11
4	9651	L1U4	Enugu Sh	0.80	0.07	1.00	0.85	435	125	106	1.2	9	0.07
5	9653	L2U1	Mamu Fm	0.76	0.05	0.28	0.65	441	37	86	0.4	7	0.15
6	9654	L2U2	Mamu Fm	1.36	0.04	0.37	1.08	434	27	79	0.3	3	0.10
7	9655	L2U3	Mamu Fm	2.11	0.06	1.14	0.55	429	54	26	2.1	3	0.05

Notes:

"-1" – not measured or invalid value for Tmax
TOC - Total Organic Carbon, wt. %
S1 - volatile hydrocarbon (HC) content, mg HC/ g rock
S2 - remaining HC generative potential, mg HC/ g rock
S3 - carbon dioxide content, mg CO2 / g rock

* - comments regarding contamination
** - low S2, Tmax is unreliable
Meas. %Ro - measured vitrinite reflectance
HI - Hydrogen index = S2 x 100 / TOC, mg HC/ g TOC
OI - Oxygen Index = S3 x 100 / TOC, mg CO2/ g TOC
PI - Production Index = S1 / (S1+S2)

Pyrogram:

f - flat S2 peak
n - normal
ltS2sh - low temperature S2 shoulder
htS2sh - high temperature S2 shoulder
ltS2p - low temperature S2 peak
htS2p - high temperature S2 peak

LECO – TOC on Leco Instrument
RE - Programmed pyrolysis or TOC on Rock-Eval instrument
SRA – Programmed pyrolysis by SRA Instrument
EXT - Extracted Rock
NOPR - Normal Preparation

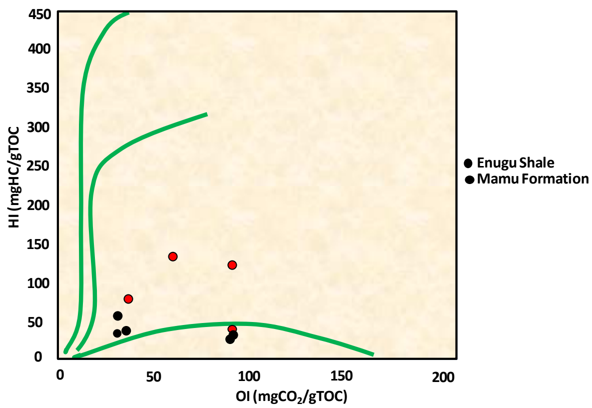

Fig. 6. Plot of hydrogen Index against Oxygen Index [16]

A corresponding Oxygen Index values of 33-106 $mgCO_2$/gTOC was recorded for Enugu Shale with an average of 70.2mg CO_2/gTOC. Mamu Formation on the other hand showed a value of 26-86 mg CO_2/gTOC with average of 49.4 $mgCO_2$/g TOC. A plot of Hydrogen Index (HI) against Oxygen Index (OI) showed that Enugu Shale and Mamu Formation are dominated by Type III kerogen and mixed Type II/III kerogen (Fig. 6). Samples from Mamu Formation were particularly lower in HI (below 60mgHC/gTOC).

4.5. Maceral analysis and thermal maturity parameters

Result of maceral analysis of the shale samples was applied to further assess the quality of the organic matter in the studied samples is shown in Table 3.

Table 3. Extractable organic matter of shale samples in the study area

S/No	Sample No	Formation	Wt. of sample (g)	EOM (ppm)
1	L1U1	Enugu Shale	25	540
2	L1U2	Enugu Shale	25	708
3	L1U3	Enugu Shale	25	564
4	L1U4	Enugu Shale	25	872
5	L2U1	Mamu Formation	25	576
6	L2U2	Mamu Formation	25	572
7	L2U3	Mamu Formation	25	1200
8	L2U4	Mamu Formation	25	568
9	L2U5	Mamu Formation	25	548

The vitrinite maceral group in the analyzed shale samples ranges between 49 to 59%. The inertnites ranged from 11 to 18% while the liptinites range from 9 to 15%. The vitrinite components are mainly desmocollinite, collinite and vitrodetrinite. The inertinite group consists of fusinites and semi fusinites whereas the liptinites components are mainly cutinites and sporinites.

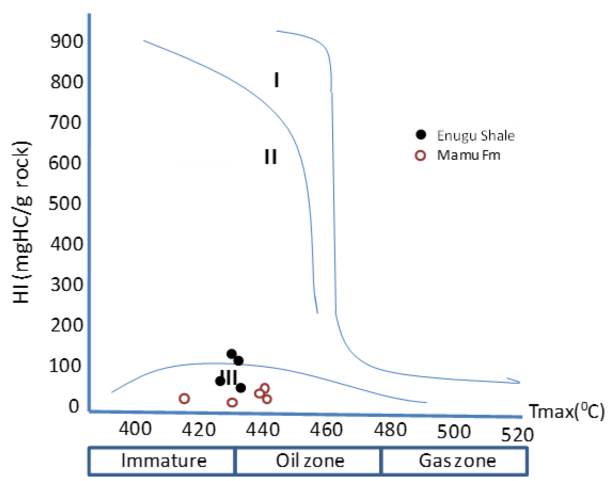

Fig.7. Plot of HI against Tmax showing the thermal maturity and the OM type

In the present study, Tmax ranged from 424°C to 439°C with an average of 433.7°C for sediments in the Enugu Shale and corresponding Hydrogen Index (HI) values ranging from 43 to 142mgHC/gTOC with an average value of 95.3mgHC/gTOC. Mamu Formation sediments on the other hand showed a Tmax value of 417°C to 441°C with an average of 431°C and a corresponding HI value of 26 to 86mgHC/gTOC with average of 39.45mgHC/gTOC (Table 1).

The calculated bitumen ratios for the Enugu Formation ranges from 10 to 109 mgExt/gTOC with an average of 56.7 mgExt/gTOC while that of Mamu Formation ranges from 29.5 to 75.7 mgExt/gTOC with an average of 49.42 mgExt/gTOC. A plot of

HI versus Tmax (Fig. 7) show that the samples plot within the Type III kerogen zone confirming the predominance of Type III organic matter.

The values for the production index (PI) ranges from 0.03 to 0.11 with an average of 0.07 for samples obtained in the Enugu Shale while those from the Mamu Formation ranges from 0.05 to 0.15 with an average of 0.096 (Tables 4). These values thus tell that the organic matter is immature [17]. This is further highlighted by the plot of PI versus Tmax (Fig. 8).

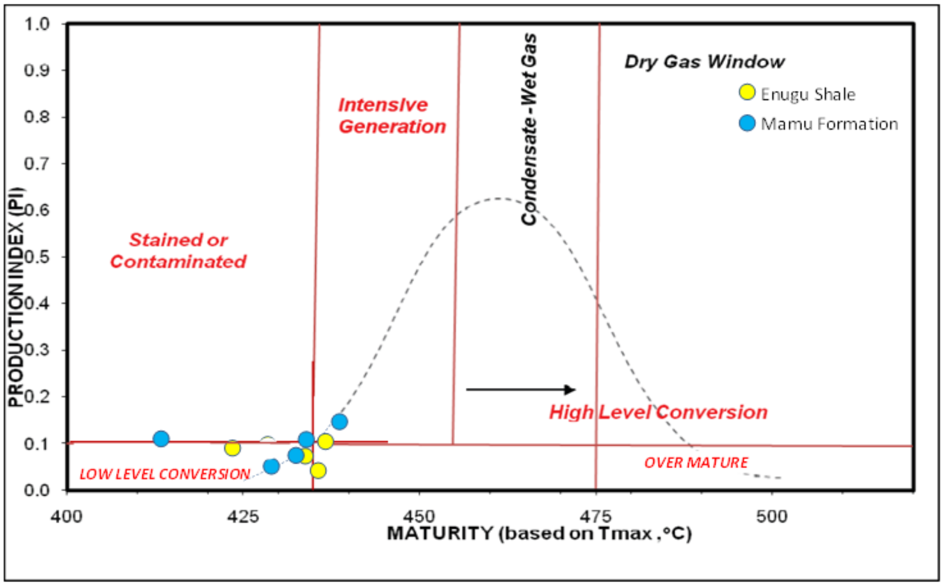

Fig. 8. A plot of Production Index (PI) against Tmax

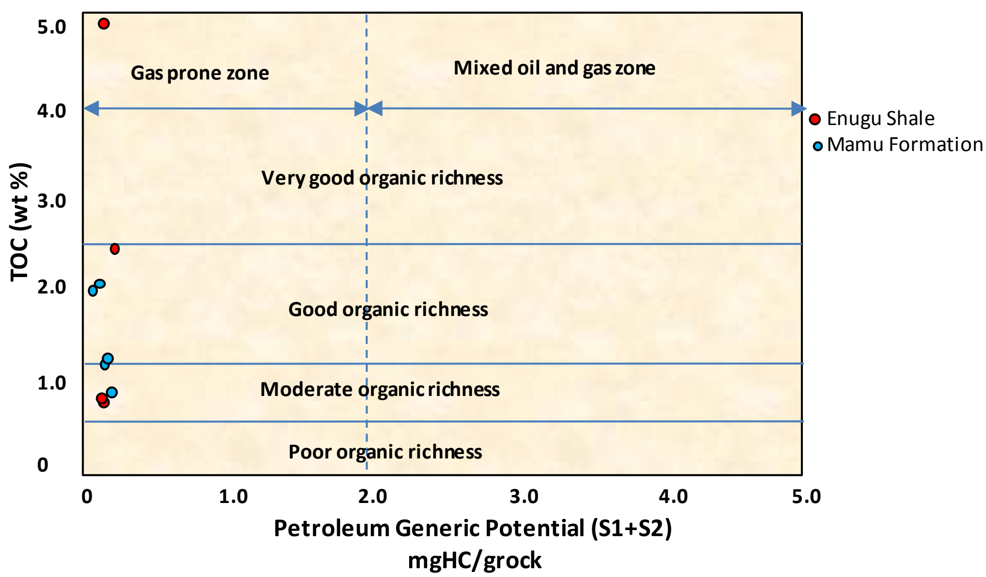

Table 4. Maturity Parameters from Tmax and Production Index

Table 4. Maturity Parameters from Tmax and Production Index.

Formation	Tmax (0C)	PI
Enugu	424 – 439	0.03 - 0.11
Mamu	417 -441	0.05 – 0.15
REMARK	Immature	Immature

4.6. Petroleum generic potential from rock eval pyrolysis

The assessment petroleum generic potential from Rock Eval pyrolysis is based on Tissot and Welte [16] classification as follows: source rocks with Generic Potential (GP) less than 2mgHC/g rock (2000ppm) are suggestive of poor source rock, while rocks with GP of 2 to 6mgHC/g rock (2000 to 6000ppm) implies moderately rich source rock with fair oil potential. Those with GP greater than 6mgHC/g rock (6000ppm) are considered as good or excellent petroleum source rocks [16,19-20]. In the study area, samples from both Enugu Shale and Mamu Formations exhibit average yields (<2mgHC/g rock). This is further ascertained by the plot of Petroleum generic potential against TOC (%) as show below (Fig.9).

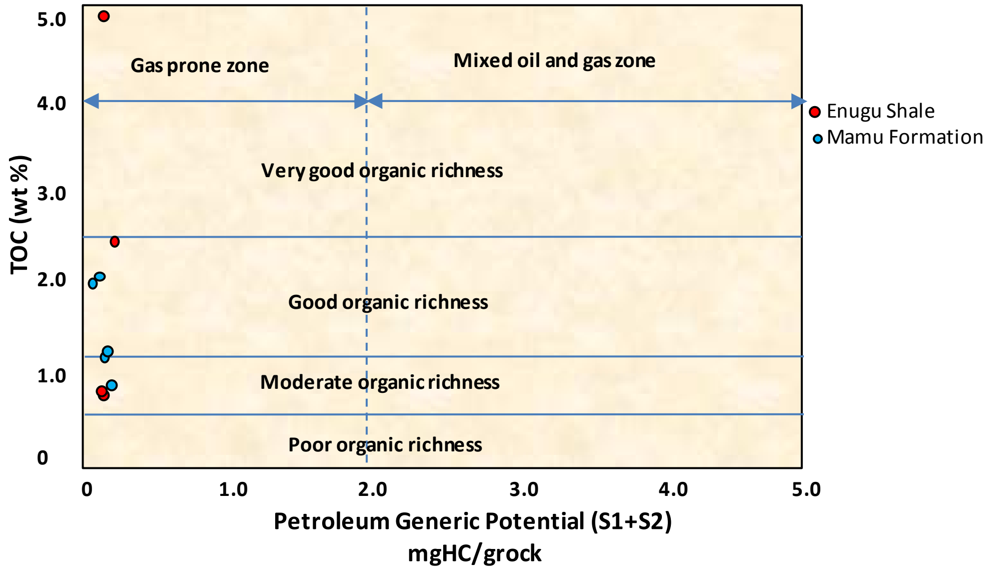

Fig. 9. Plot of TOC against Petroleum generic potential [36]

The plot of hydrocarbon yield or remaining hydrocarbon (S_2) against total organic carbon (Fig.10) classifies effective primary source rocks as those with S_2 greater than 5mgHC/g rock and Effective Non Source (ENS) rocks as those with S_2 less than 1mgHC/g rock.

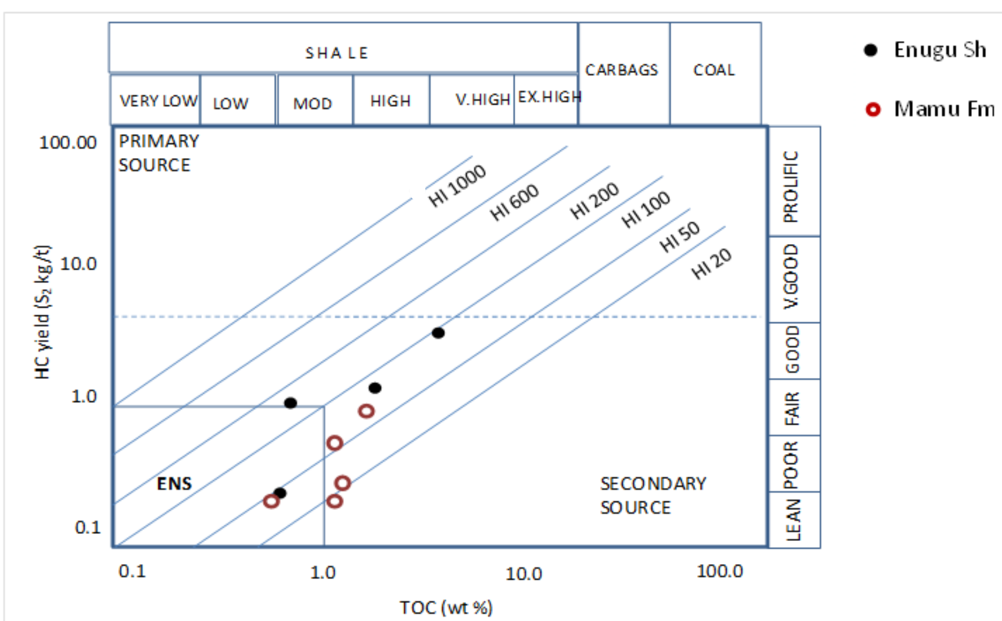

Fig. 10.Plot of hydrocarbon yield against TOC [21]

4.7. Biomarkers

Biomarkers are present in both oil and source rock extracts; they provide a method to relate the two and can be used to interpret the characteristics of the source rocks [22]. In addition, biomarkers can provide information on the organic source materials; environmental condition during its deposition; the thermal maturity experienced by a rock or oil and the degree of biodegradation [23-24].

Murray *et al.* [25] reported that hopane (C_{29}, C_{30}) have microbial origin and some are derived from higher plants and oleananes is from terrestrial plants. Tricyclics are formed by partial aerobic oxidation of bacterial membrane.

The peak identities of both the high molecular and low molecular carbon are shown in Fig. (11a-i).The pristane (nC17), phytane (nC18), CPI and OER values are also shown in Table 5. A plot of Pr/nC_{17} versus Ph/nC_{18} is shown in Fig 12.

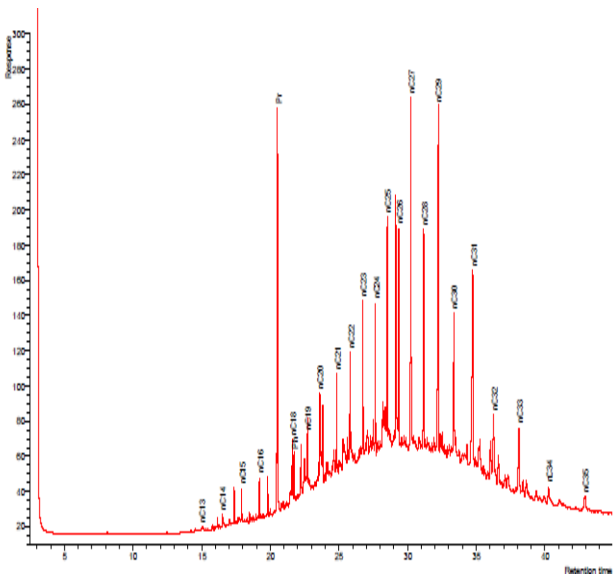

Fig. 11a. Chromatogram of sample L1U1

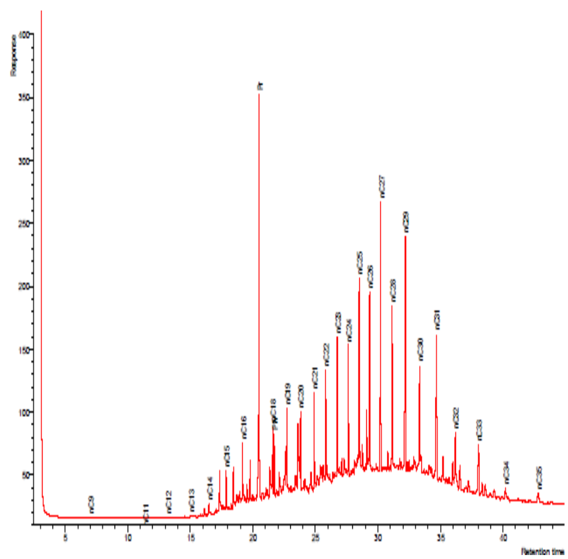

Fig. 11b Chromatogram of sample L1U2

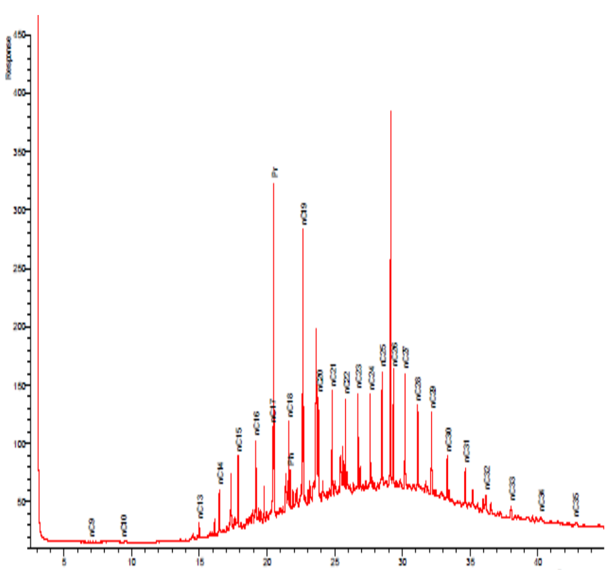

Fig. 11c. Chromatogram of sample L1U3

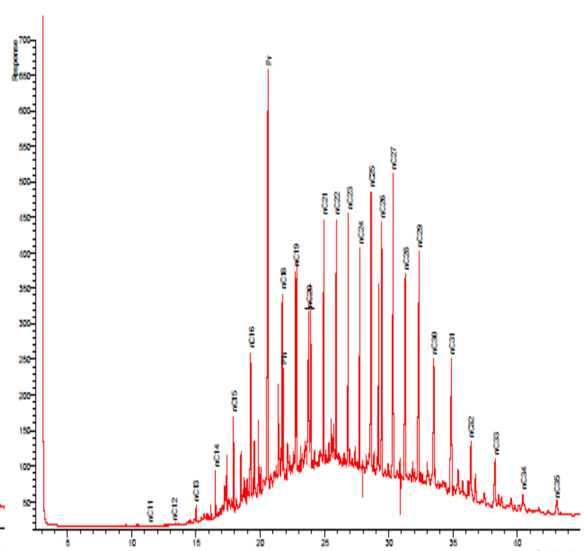

Fig. 11d. Chromatogram of sample L1U4

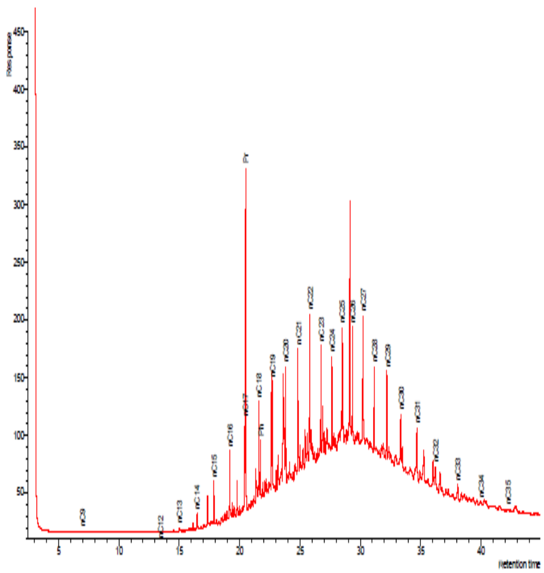

Fig. 11e. Chromatogram of sample L2U1

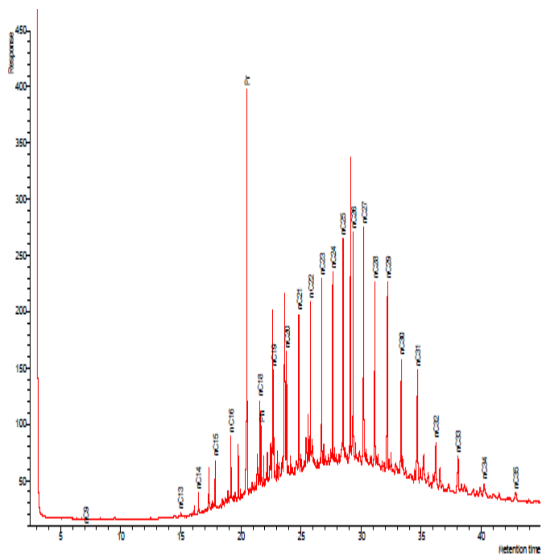

Fig. 11f. Chromatogram of sample L2U2

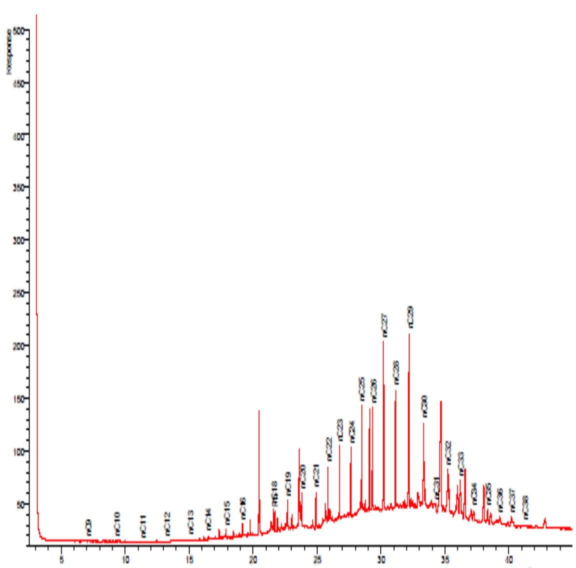

Fig. 11g. Chromatogram of sample L2U3

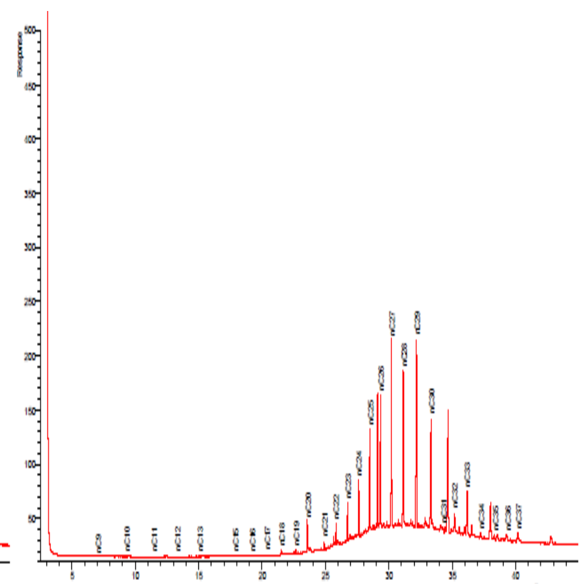

Fig. 11h. Chromatogram of sample L2U4

Table 5. Values of paraffin parameters

Sample No	Pristane/nC17	Phytane/nC18	Pristane/Phytane	OER	CPI
L1U1	9.36	0.83	6.38	0.83	1.73
L1U2	9.55	0.88	6.59	1.62	1.30
L1U3	3.30	0.56	5.63	1.20	1.27
L1U4	NA	0.66	3.03	1.34	1.07
L2U1	3.55	0.65	4.60	1.19	1.06
L2U2	6.94	0.74	5.64	1.22	1.07
L2U3	NA	0.89	NA	1.70	1.14
L2U4	NA	NA	NA	1.40	1.01
L2U5	NA	0.76	6.01	1.43	1.00

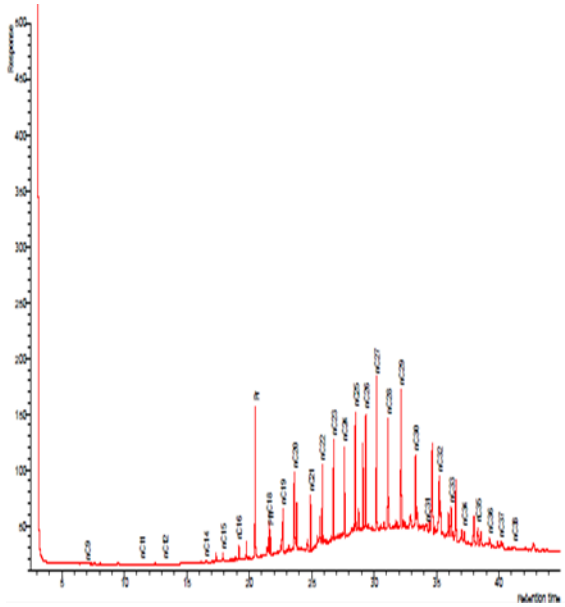

Fig. 11i. Chromatogram of sample L2U5

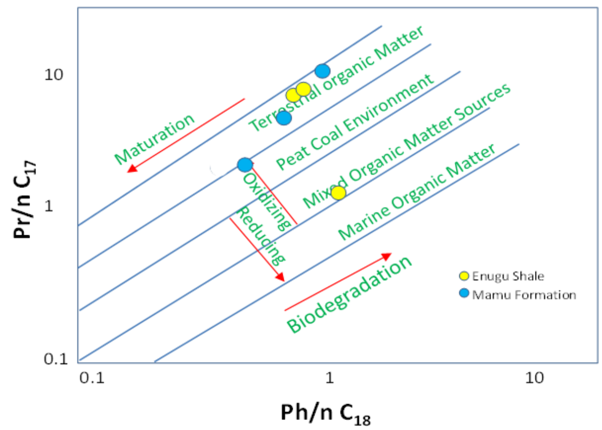

Fig. 12. Plot of Pristane (n17) versus Phytane (n18) (*After Moldowan et al.*, [35]) Carbon Preference Index (CPI) and Odd-Even Carbon Ratio (OER)

4.8. N-Paraffin/Isoprenoid ratios

Pristane/phytane[Pr (n17)/Pr (n18)] ratio of sediments can be used to determine depositional environment [23]. Pr/Ph ratio < 1 indicates anoxic depositional environment, while Pr/Ph > 1 indicates oxic conditions. Pr/Ph < 2 indicates marine sourced organic matter and Pr/Ph > 3 indicates terrigenous organic matter input. Petters and Moldowan [26] stressed that high Pr/Ph (>3) indicates terrigenous input under oxic conditions and low Pr/Ph (<0.8) indicates anoxic hypersaline or carbonate environment.

This is the relative abundance of Odd versus Even carbon numbered N-Paraffins; it can also be used to estimate thermal maturity of organic matter. The CPI values in the studied sediments (Table 5) range from 1.0 to 1.73.

5. Discussion

5.1. Quality, quantity and generic potential of organic facies

Result of the geochemical analysis showed that the mean value of Total Organic Content (TOC%) of the shale samples from Enugu Shale and Mamu Formation exceed the threshold value of 0.5wt% required for a sedimentary rock to be regarded as a petroleum source rock [16,27]. The TOC values suggest that the Shales of the Enugu Shale and Mamu Formations are good to very good sources rocks [28].

The total amount of heavy hydrocarbon (C_{15+}) Extractable Organic Matter (EOM) is the total amount of heavy hydrocarbon and non-hydrocarbon present in a source rock in parts per million (ppm). The total amount of extractable organic matter in a source rock is a direct measure of its oil source possibility, because oil is related to its source. The SOM/EOM of the shale samples of the studied sections exceeds 500ppm. Samples from Enugu Shale has an average value of 671ppm while those of Mamu Formation has an average value of 692ppm. Furthermore, plot of TOC (%) versus SOM (ppm) according to Jovancicevic [17] shows that the sediments can be classified as fair to good source rocks based on the quality definition by Hunt and Meinert [29], and Baker [30].

A plot of Hydrogen Index (HI) against Oxygen Index (OI) showed that Enugu Shale and Mamu Formations are dominated by Type III kerogen and mixed Type II/III kerogen [29].

The Source Potential ($S_1 + S_2$) based on the assessment of Tissot and Welte [16] classification suggest a moderate to good organic richness however with a gas prone tendency as can be shown in the plot of generic potential versus TOC.

Again, the plot of hydrocarbon yield (S_2) against total organic suggest that the two Formations are essentially secondary sources rocks with fair to very good hydrocarbon potential to generate gas and condensate.

Maceral analysis of the shale samples showed a dominance of vitrinite group suggesting derivation from structural part of plants and are deficient in hydrogen. They correspond to type III kerogen [16,31-32]. According to Akande *et al.* [32], the lower Maastrichtian coals of the Mamu Formation are characterized by moderate to high concentration of huminite and some minor amounts of inertinite and liptinite. Akaegbobi and Schmitt [2] supported the earlier reports; that the Nkporo shale is dominated by Type III/II kerogens with dominance of terrestrially derived organic matter in the study area.

5.2. Thermal maturity

Thermal maturity in the studied area has been assessed by the Rock-Eval, Tmax data and by the bitumen ratio. According to Peters [28], variation in kerogen types affect Tmax values. At a thermal maturity that corresponds to a Tmax of 435^{0}C, source rocks with HI greater than 500mg HC/gTOC yield oil while those with HI value ranging from 250 to 500mgHC/gTOC yield oil and some gas. Rocks with HI of 50 to 250mgHC/gTOC produce gas while those with HI less than 50mgHC/gTOC are inert [33].

In the present study, Tmax ranged from 424 to 439^{0}C with an average of 434.1^{0}C for sediments in the Enugu Shale and corresponding Hydrogen Index (HI) values ranging from 43-142 to 54mgHC/gTOC with an average value of 95.3mgHC/gTOC. Mamu Formation sediments on the other hand showed a Tmax value of 417 to 441^{0}C with an average of 431^{0}C and a corresponding HI value of 27 to 54mgHC/gTOC with average of 39.45mgHC/gTOC.

These values suggest that the shales of Mamu and Enugu Formations are immature to transitionally early mature source rocks. The low values of hydrogen index imply that the Enugu Shales and Mamu Formations are dominated by Type III kerogen and mixed Type II/III kerogen of terrestrial origin [28].

The calculated bitumen ratios for the Enugu Formation ranges from 10 to 109 mgExt/gTOC with an average of 56.7 mgExt/gTOC while that of Mamu Formation ranges from 29.5 to 75.7 mgExt/gTOC with an average of 49.42 mgExt/gTOC. From these values, it can be deduced that the shales of Enugu Shales and Mamu Formations are immature source rocks [34].

A plot of HI versus Tmax show that the samples plot within the Type III kerogen zone confirming the predominance of Type III organic matter. The sediments from this plot are immature to transitional in term of their thermal maturity.

5.3. Depositional environment

Pristane/phytane ratio of sediments can be used to determine depositional environment [23]. Pr/Ph ratio < 1 indicates anoxic depositional environment, while Pr/Ph > 1 indicates oxic conditions. Pr/Ph < 2 indicates marine sourced organic matter and Pr/Ph > 3 indicates terrigenous organic matter input. Petters and Moldowan [26] stressed that high Pr/Ph (>3) indicates terrigenous input under oxic conditions and low Pr/Ph (<0.8) indicates anoxic hypersaline or carbonate environment.

From the studied shale samples, Pristine/Phytane ratios are greater than 3. This is typical of sediments deposited in oxidizing, terrestrial or peat environment This is consistent with the geology of the study area as the Enugu Shale and parts of the Mamu Formation are known to be coal bearing [9].High concentration of high molecular weight n-alkanes (C23 to C30) compared to low molecular weight n-alkanes (C15 to C21) (Fig. 11a-i) present indicates organic matter from terrestrial higher plants.

6. Conclusion

A total of nine (9) outcrop samples (shales) were obtained from road cuts sections of Mamu Formation and Enugu Shale along Port Harcourt–Enugu expressway. These samples were subjected to geochemical analyses in order to characterize the source rock potential and investigate the environment of deposition of the sediments.

The following conclusions were made:

- The sediments studied were deposited in a partial/normal marine (under sub-oxic to sub-anoxic water condition)
- The sediments contain about 70% of what it takes to be economic, though largely gas, they present fair prospect in terms of economic viability.

At present level, liquid hydrocarbons have not been generated. The studied areas are therefore considered to be of good petroleum potential particularly gaseous hydrocarbon. With improved 3-D seismic information and more petroleum geological research work in the basin, the hydrocarbon resource of the basin will be enhanced and these will provide information to oil and gas companies operating in the region to optimize the development in exploration and exploitation of petroleum in the basin.

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To whom correspondence should be addressed: Dr. S. O. Onyekuru, Department of Geology, Federal University of Technology, Owerri, E-mail samuel.onyekuru@futo.edu.ng