<https://doi.org/10.36293/sfj.2020.0048>

GEOCHEMICAL CHARACTERIZATION OF ENUGU SHALE, ANAMBRA BASIN NIGERIA: IMPLICATION ON HYDROCARBON POTENTIAL

ADEDOSU, TAOFIK ADEWALE^{1,*}, OGUNGBESAN, GBENGA OLAKUNLE²,
BADMUS, OLADELE SHAKIRU¹, ONYEOCHA JOY¹, ADEYEMI, ADEOLA
KABIRAT¹, POPOOLA, ODUNAYO MARY¹, SUNMONU, OMOTILEWA HAWWAWU¹
AND ADEGBENJO, DAMILOLA CHRISTIANAH¹

¹Pure and Applied Chemistry Department, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

²Department of Earth Sciences, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

Abstract

The need for the diversification of gas sector has intensified search for hydrocarbon in Nigerian Inland Basins such as Anambra Basin. This has necessitated increased effort in the assessment of hydrocarbon generative potential of the source rock facies of the Campano-Maastrichtian Enugu Formation exposed around Enugu, Anambra Basin. The distribution of biomarker and polycyclic aromatic hydrocarbon contents of soluble organic matter (SOM) contained in the samples was studied using Gas chromatography-Mass spectrometry (GC-MS) technique in order to evaluate the hydrocarbon potential of Enugu shale. The n-alkane ranged from nC_{11-35} in most samples maximizing at nC_{18} or nC_{20} that reflected organic matter mainly derived from algae. The Ph/nC_{18} vs. Pr/nC_{17} plot and Pr/Ph (1.11-4.09) ratio showed that the organic matters were mainly Type III kerogen (vitrinite macerals) and were deposited under suboxic - oxic paleoenvironmental conditions. The $C_{31}22R$ -homohopane/ C_{30} -hopane vs. Pr/Ph binary plot, a ternary plot of sterane (C_{27} - C_{29}) and trimethyl-naphthalene ratios suggested organic matters that were deposited in fluvial-deltaic to the estuarine environment. The distribution of methylated naphthalenes is in the order $DMN > TMN > TeMN > MN$ in the samples reflecting organic matter majorly derived from terrigenous material which is in consistent with the ratio of 1-MP/9-MP (0.77-1.03). Various biomarker and polyaromatic hydrocarbon maturity parameters showed that the samples were low mature and increased in maturity with depth was observed. Enugu shale has potential for shale gas but not yet mature to release significant quantities of hydrocarbons at the present total depth.

Keywords: Anambra Basin, biomarker, depositional environment, GC-MS, kerogen.

Corresponding Author Email: taadedosu@lautech.edu.ng; adedosutaofik@gmail.com;

Introduction

Petroleum resources have continuously played a prominent role in the social and economic development of Nigeria since its discovery in 1956. The increasing exploitation of Petroleum without replenishing with new prospecting resources can cause the depletion on the reserves.

Enugu Formation comprising of black shale and mudstone, sandstone-siltstone heterolith, ironstone and laminated sandstone, are vastly deposited in the Cretaceous Anambra basin. Previous studies have focused mainly on the Nkporo and Mamu Formations as the only proven source rock of hydrocarbon in the Anambra Basin. In an attempt to study the hydrocarbon potentials of Enugu Formation, biostratigraphy, organic petrological and palynofacies analysis method have been previously used to assess hydrocarbon generation and characteristics of the potential source rock (Nton and Bankole, 2013, Odunze and Obi, 2013, Abubakar, 2014, Anozie *et al.*, 2014, Chiaghanam *et al.*, 2013, Odundun, 2015, Adiela, 2016). However, the potential of oil and gas in the Enugu shale is yet to be fully understood as there is limited to use geochemical tools e.g. biomarker geochemistry (Chiadikobi and Chiaghanam, 2018) and distribution of Aromatic Hydrocarbons (such as PAHs, alkylated DBTs) to determine the source-rock potential of Enugu formation.

The present study hereby intends to undertake detailed geochemical studies of the shale samples of Campanian-Maastrichtian Enugu Formation in Anambra Basin so as to interpret the organic origin, depositional conditions and thermal maturity of source rock facies.

Geology of Enugu Formation

The Anambra Basin is a roughly triangular shaped depression located in the south-central part of Nigeria (Fig.1). The tectonic evolution and general geology of the basin have recently been summarized in Edegbai *et al.* (2019). The stratigraphic succession of the Cretaceous Anambra Basin comprise (Fig. 2) of the marine

sediments Enugu, Nkporo and Owelli Formations (lateral equivalents) and was succeeded by the marginal marine to marine sediments of Mamu Formation and subtidal to shallow marine Ajali Formations. The succession is capped by the Latest Maastrichtian Nsukka Formation (Nwajide, 2013; Edegbai *et al.*, 2019).

The Enugu Formation is a sub-unit of the basal Nkporo Group in the Cretaceous Anambra Basin. (Odumodu, 2017). The Group comprised of Nkporo, Owelli and Enugu Formations which were deposited in the Late Campanian (Nton and Bankole, 2013). Nkporo Group is conformably overlain by the Early Maastrichtian Mamu Formation (lower coal measure) which consists of shale, siltstone, sandstone and coal seams (Kogbe, 1989). The Maastrichtian Ajali Sandstone conformably overlies the Mamu Formation and consists dominantly of cross-bedded sandstones which are interpreted as sediments of tidal channel/fluvial deposits (Ladipo, 1986). The Late Maastrichtian Nsukka Formation (upper coal measure) conformably succeeded Ajali Sandstone (Obi *et al.*, 2003) and consists of organic-rich mudrocks and shales, sandstones and coal seams (Nwajide, 1990; Obi *et al.*, 2003). The Cretaceous succession of the Anambra Basin was capped by the Tertiary units of the Imo Shale (Paleocene) and Ameki Group (Tijani *et al.*, 2010).

Figure 1: Map of Nigeria showing areas underlain by Basement rocks and locations of sedimentary basins (Modified after Obaje *et al.*, 2004)

Figure 2: Stratigraphy and depositional environments of the rock units in Anambra Basin (adapted from Tijani *et al.*, 2010).

Methodology

Nine (9) Enugu Formation shale were sampled from exposure at Agu-Abor (N6°28'9.1"-N6°28'10.6" and E7°28'16.7" - E7°28'17.3"). The exposure is a road-cut along Onitsha-Enugu highway. Twenty gram (20g) each of the pulverized samples was extracted sequentially using sonicator. The extracts were then fractionated into aliphatic, aromatics and polar fractions following the method described in Adedosu *et al.* (2014). Gas chromatography mass spectrometric (GC-MS) analysis was then performed on both the saturate and aromatics fractions. This analysis was done using a Hewlett-Packard 7890N gas chromatography coupled with a Hewlett-Packard 5973N mass spectrometer. A capillary column made of diphenyl dimethyl polysiloxane fused silica of 30m x 0.25mm diameter and 0.25um phase thickness) was used in the gas chromatograph. The mass spectrometer was operated with electron impact energy of 70eV and ion source temperature of 230°C.

For saturate fraction, the gas chromatographic oven was programmed from 80°C (hold time of 2 min) and increased to 280°C at 3°C/min, held isothermally at 280°C for 20 min. Helium was used as a carrier gas and flow at a rate of 1.5 ml/min. The samples were analyzed in the full scan and SIM mode, and target compounds are *n*-alkanes and isoprenoids (*m/z* - 85), triterpanes (*m/z* - 191), steroids (*m/z* - 217).

For aromatics, the gas chromatographic oven was programmed from 40 °C (hold time of 2 min) and increased to 320 °C at a rate of 4 °C/min, held isothermally at 320 °C for 20 min. Helium was also used as a carrier gas and flow at a rate of 1.0 ml/min. Samples were analyzed in SIM modes and monitored *m/z* 128, 142, 156, 170 and 184 (Naphthalene, methylnaphthalene, dimethylnaphthalene, trimethylnaphthalene and teramethylnaphthalene), *m/z* 178, 192, 206 and 220 (Phenanthrene, methyl-, dimethyl- and trimethyl-phenanthrene) and *m/z* 184 and 198 (dibenzothiophene and methyldibenzothiophene).

The acquired data were processed with an HP chemstation data system. The identification of individual compound was done using their retention times and comparison of ion spectra with previously published works (Adedosu *et al.* 2012, 2014; Chiadikobi and Chiaghanam, 2018).

Results and Discussion

N-Alkanes and Isoprenoids Distribution

The *n*-alkane contents in the samples range from C₁₁ to C₃₅ maximizing at intermediate homologues (i.e. C₁₈, C₂₀) except in EN 2S which carbon maximum at C₁₄ (Fig. 3), suggesting a major contribution of aquatic macrophytes to the organic matter source. This pattern of distribution is similar to those previously reported for the samples of Nkporo and Enugu Formations (Chiadikobi and Chiaghanam, 2018).

The terrigenous versus aquatic ratios (TAR), Paq, Wax, OEP (1) and *n*C₃₁/*n*C₁₉ ratios ranged from 1.06-2.37, 0.43-0.77, 0.57-1.63, 0.61-0.84 and 0.11-0.38 respectively (Table 1). These

values suggest organic matter derived from macrophytes (Ficken *et al.*, 2000). The ternary plots (Pr/Ph vs Pr/ nC_{17} vs Ph/ nC_{18}) and plot of Pr/ nC_{17} vs Ph/ nC_{18} predominantly classified the samples into Type III kerogen (Fig.4a &b) which is capable of producing gas.

The values of Pr/Ph of the samples ranged from 1.11-4.09 (Table 1), which indicated suboxic to oxic condition of deposition in estuarine-fluvio-deltaic settings (Fig. 5a&b). However, this is contrary to the previously reported Pr/Ph ratio of

the Enugu Shale (0.65-0.75; Chiadikobi and Chiaghanam, 2018), which was interpreted as deposition under anoxic condition.

Different maturity parameters calculated from *n*-alkane distribution i.e. CPI, CPI(1), OEP(1), OEP(2) ranged from 1.14-1.38, 0.87-1.20, 0.61-0.84, 1.13-1.34 respectively (Table 1). These values showed immature to low thermal maturity status (Figure 6a&b) (Bray and Evans, 1961; Peter *et al.*, 2005; Adedosu *et al.*, 2012, 2014).

Figure. 3: Ion chromatograms (m/z 85) of the *n*-alkanes and isoprenoids contents in Enugu shale

Table 1: Calculated *n*-Alkanes and isoprenoid ratios for the studied samples of Enugu Shale

Sample	Pr/Ph	Pr/ <i>n</i> C ₁₇	Ph/ <i>n</i> C ₁₈	TAR	Paq	Wax	<i>n</i> C ₃₁ / <i>n</i> C ₁₉	C _{max}	CR	CPI	CPI (1)	OEP (2)	OEP (1)
EN15S	1.78	1.32	0.18	2.37	0.77	0.86	0.11	C ₁₈ , C ₂₀	C ₁₁ - C ₃₅	1.32	1.07	1.26	0.81
EN12S	3.53	3.45	0.18	1.88	0.71	0.57	0.22	C ₁₈	C ₁₁ - C ₃₃	1.38	1.05	1.28	0.70
EN7S	2.06	2.77	0.26	Nd	0.43	Nd	Nd	C ₂₀	C ₁₄ - C ₃₂	1.34	1.20	1.23	0.70
EN6S	1.33	2.19	0.26	1.34	0.81	1.55	0.14	C ₁₈ , C ₂₀	C ₁₃ - C ₃₆	1.14	1.02	1.13	0.84
EN5S	1.55	1.51	0.10	1.89	0.74	0.72	0.15	C ₁₈ , C ₂₀	C ₁₁ - C ₃₅	1.36	0.95	1.34	0.61
EN4S	4.09	5.56	0.40	Nd	0.62	1.63	0.11	C ₂₀	C ₁₄ - C ₃₂	1.34	1.17	1.32	0.71
EN3S	2.50	1.96	0.14	1.45	0.73	0.90	0.21	C ₁₈	C ₁₁ - C ₃₅	1.26	0.99	1.20	0.70
EN2S	1.11	1.58	0.13	1.06	0.71	1.31	0.38	C ₁₄	C ₁₁ - C ₃₅	1.23	1.05	1.16	0.81
EN1S	1.18	2.44	0.19	1.27	0.75	0.91	0.32	C ₁₈ , C ₂₀	C ₁₁ - C ₃₄	1.19	0.87	1.21	0.61

TAR-Terrigenous/Aquatic ratio; OEP-Odd/Even predominance; CPI- Carbon Preference Index; CR-Carbon range; Pr-Pristane; Ph-Phytane; Nd-Not determined; Paq=C₂₃+C₂₅/C₂₃+C₂₅+C₂₉+C₃₁; TAR=C₁₅+C₁₇+C₁₉/C₂₇+C₂₉+C₃₁; Wax=C₂₁-C₃₁/C₁₅-C₂₀; OEP(1)=C₂₁+6C₂₃+C₂₅/4(C₂₂+C₂₄) ; CPI=1/2[(C₂₅+C₂₇+C₂₉+C₃₁+C₃₃)/(C₂₄+C₂₆+C₂₈+C₃₀+C₃₂)+(C₂₅+C₂₇+C₂₉+C₃₁+C₃₃)/(C₂₆+C₂₈+C₃₀+C₃₂+C₃₄)] ; CPI(1)=2(C₂₃+C₂₅+C₂₇+C₂₉)/(C₂₂+2(C₂₄+C₂₆+C₂₈); OEP(2)=C₂₅+6C₂₇+C₂₉/4(C₂₆+C₂₈)

Figure. 4: (a) Ternary plots of *n*-alkanes and isoprenoids, and (b) Kerogen typing of organic matter

Figure. 5a&b: Depositional environment

Figure. 6a&b: Thermal maturity of organic matter

Distribution of Triterpane and Steranes

There was a presence of tricyclic, tetracyclic and pentacyclic terpanes (Fig. 7) that was detected at m/z 191 ion chromatograms in the saturate fraction of the samples. Higher percentages of C_{19} - C_{21} compared to C_{23} tricyclic terpanes suggest a high contribution of terrestrial organic matter (Ozcelik and Altunsoy, 2005). The C_{24} -tetra/ C_{26} .tri(R+S) ratios (0.80-1.67) support terrigenous organic matter type deposited under suboxic to oxic condition in estuarine to fluvio-

deltaic settings (Marynowski *et al.*, 2000; Roushdy *et al.*, 2001; Adegoke *et al.*, 2014). C_{24} tetra/ C_{30} hopane (0.06-0.19) and C_{22} / C_{21} T (0.20-1.00) ratios also reflected organic matter derived from the same source (i.e. terrigenous), which is decreasing with depth. Various depositional environment parameter (i.e. C_{23} T/ C_{24} Te, C_{23} T/ C_{30} H, C_{19} / C_{20} T, C_{20} / C_{23} T, C_{26} (R+S)/ C_{25} T) also supported estuarine-fluvial-deltaic settings (Marynowski *et al.*, 2000; Roushdy *et al.*, 2010; Adegoke *et al.*, 2014).

Figure. 7: Mass chromatogram (m/z 191) of the tri- & tetra-, cyclic terpanes, hopanes and homohopanes contents in the samples

Figure. 8: Plot of $C_{31} 22R-/C_{30}$ -Hopane vs. Pr/Ph showing the depositional environment.

The content of oleanane in the samples also indicate the contribution of terrigenous organic matter with the Oleanane/Oleanane + C_{30} -hopane ratio in the range of 0.16-0.25 (Sinningh-Damsté *et al.*, 1995; Peter *et al.*, 2005) while Gammacerane abundance in the samples indicates hypersaline stratified water column in the environment of deposition (Sinningh-Damsté *et al.*, 1995) and G/C_{30} -hopane ratio (0.05-0.22) supported suboxic to

oxic condition of organic matter deposition. The plots of $C_{31} 22R-/C_{30}$ -hopane vs Pr/Ph (Fig. 8) supported estuarine to fluvio-deltaic depositional environment (Peters *et al.*, 2005). The C_{29}/C_{30} -hopane ratio (0.68-0.98) showed decrease in terrigenous organic matter with increasing depth (Rinna *et al.*, 1996). All biomarker maturity parameters calculated from homohopane distribution depict low thermal maturity status of the samples.

Table 2: Tricyclic terpane ratios

Sample ID	%($C_{19}-C_{21}$)T	% $C_{23}T$	$C_{24}Te/C_{26}T$ (R+S)	$C_{24}Te/C_{30}H$	$C_{22}T/C_{21}T$	$C_{23}T/C_{24}Te$	$C_{23}T/C_{30}H$	$C_{19}/C_{20}T$	$C_{20}T/C_{23}T$	$C_{26}(R+S)/C_{25}T$
EN15S	78.60	21.40	1.17	0.13	1.00	0.86	0.11	0.78	1.50	2.00
EN12S	64.30	35.70	1.25	0.13	0.80	1.00	0.13	1.50	0.40	2.00
EN7S	61.40	38.60	Nd	0.06	0.67	0.62	0.04	0.69	0.55	Nd
EN6S	61.80	38.20	1.00	0.15	0.62	1.44	0.22	0.86	0.54	1.80
EN5S	73.1	26.90	1.67	0.13	0.71	0.70	0.09	1.00	1.00	2.00
EN4S	64.70	35.30	Nd	0.13	0.83	1.5	0.19	1.00	0.50	1.75
EN3S	64.70	35.30	1.60	0.10	0.83	0.75	0.08	1.00	1.00	1.23
EN2S	66.70	33.30	1.50	0.10	1.00	0.67	0.02	3.00	0.25	1.33
EN1S	54.50	45.50	0.80	0.19	0.20	1.25	0.24	1.50	0.40	1.67

Table 3: Hopane and Sterane ratios

Sample	$C_{29}/C_{30}H$	% $C_{27}St$	% C_{28}	% C_{29}	$C_{31}22RHH/C_{30}H$	$G/C_{30}H$	$Ts/Ts+Tm$	$C_{31}H$	$C_{32}HH$	M/H	$C_{29}Ts/C_{29}Ts+C_{29}H$	$O/O+C_{30}H$	$20S/20S+20RSt$	$B\beta/\beta+aa$	$VRcSt$
EN 15S	0.98	31	25	44	0.36	Nd	0.15	0.57	0.40	0.50	Nd	Nd	Nd	0.35	Nd
EN 12S	0.80	30	27	43	0.36	Nd	0.15	0.55	0.43	0.39	0.17	0.25	0.23	0.35	0.50
EN 7S	0.87	33	27	40	0.27	0.22	0.21	0.57	Nd	0.44	0.15	0.18	0.29	0.41	0.56
EN 6S	0.80	36	28	37	0.25	0.05	0.29	0.55	0.52	0.39	0.15	0.20	0.13	0.28	0.42
EN 4S	0.78	36	30	33	0.31	0.22	0.30	0.58	0.38	0.41	0.20	0.18	0.26	0.26	0.53
EN 3S	0.77	36	28	36	0.32	0.05	0.20	0.58	0.43	0.40	0.13	0.17	0.26	0.26	0.52
EN 2S	0.68	34	28	38	0.33	0.07	0.38	0.59	0.52	0.30	0.17	0.25	0.37	0.52	0.65
EN 1S	0.71	29	22	49	0.43	0.19	0.31	Nd	Nd	0.38	0.20	0.16	0.38	0.54	0.66

Figure. 9: Ion chromatogram (m/z 217) depicting the concentrations of steranes and diasteranes in the samples

The higher abundance of C_{29} -sterane over C_{27} -sterane suggested higher input of organic matter derived from terrigenous relative to marine sources (Huang and Meinschein, 1979; Peters *et al.*, 2005). An appreciable quantity of C_{27} -sterane and C_{28} -sterane also suggested contributions from phytoplankton, algae, diatoms, and dinoflagellates (Sari Bahtiyar, 1999; Peters *et al.*, 2005). C_{29} steranes are considered to be terrestrial plant marker, however, can be found in algae species while C_{28} steranes are regarded as both algae and terrestrial higher plant indicators while C_{27} steranes are an indicator of zooplankton sources.

(Peter *et al.*, 2005; Adedosu *et al.*, 2012; Hakim and Abdullahi, 2013).

The $20S/20S+20R$ - and $\beta\beta/\beta\beta+\alpha\alpha$ - C_{29} and VRc ratios range from 0.13-0.38, 0.26-0.54 and 0.42-0.66 respectively. These values showed that the samples have immaturity to low maturity status i.e. early oil window (Peters *et al.*, 2005, Hakim and Abdullahi, 2013, Adedosu *et al.*, 2014). However, an increase in maturity with increasing depth was observed (Fig. 10). The maturity status is similar to the previously interpreted for Enugu Shale (Chiadikobi and Chiaghanam, 2018)

Figure 10: Thermal maturity of Organic matter

Aromatic Hydrocarbon Fractions

The distribution of dimethylnaphthalenes (i.e. 1, 6-, 1, 5- and 1, 2- DMN) in all the samples reflected organic matter derived from terrigenous matter (Achari *et al.*, 1973). The distribution of these methylated naphthalenes (Fig. 11) in the samples reflecting organic matter type with dominance of continental over marine

organic material (Golovko *et al.*, 2014). The trimethylnaphthalene ratios; (1,2,5/1,3,6)-TMN (0.13-0.23) and (2,3,6/2,3,6+1,2,5)-TMN (0.74-0.88) <0.5 and >0.5 respectively represent non-marine depositional environment (Chen Zhilin *et al.*, 1997; Zhang and Paul, 2010). The ratio of 1, 2, 5/1, 2, 4-TMN supported estuarine to fluvio-deltaic depositional environment.

Figure. 11: Mass chromatogram of C_0 - C_4 naphthalenes in the sample

Table 4: Naphthalene and its alkylated derivatives ratios

SID	Location	MNR	ENR	DNR -1	TNR -1	TeM Nr	125/ 124	127/ 137	125/ 136	236/23 6+125
EN15A	N6 ⁰ 28'10.6'' E7 ⁰ 28'16.7''	0.93	4.84	6.15	1.37	0.35	0.47		0.13	0.84
EN12A	N6 ⁰ 28'10.2'' E7 ⁰ 28'16.9''	1.28	3.66	8.29	1.84	0.28	0.39	0.20	0.13	0.87
EN8A	N6 ⁰ 28'10.1'' E7 ⁰ 28'17.4''	0.56	3.50	6.41	1.53	0.56	0.50	0.27	0.14	0.84
EN6A	N6 ⁰ 28'9.8'' E7 ⁰ 28'17.4''	1.71	4.08	7.63	1.12	0.16	0.15	0.46	0.19	0.74
EN3A	N6 ⁰ 28'9.5'' E7 ⁰ 28'17.3''	0.59	2.83	4.80	1.28	0.18	0.28		0.21	0.76
EN2A	N6 ⁰ 28'9.4'' E7 ⁰ 28'17.3''	0.93	3.83	6.33	1.37	0.59	0.50		0.14	0.88
EN1A	N6 ⁰ 28'9.1'' E7 ⁰ 28'17.3''	0.57		1.67	1.04	0.34	0.47		0.23	0.77

MNR= 2MN/1MN

ENR= 2EN/1EN DNR-1= 26-DMN+27-DMN/15-DMN

TNR-1= 236-TMN/146+135-TMN

TeMNR=1,3,6,7-TeMN/(1,3,6,7+1,2,5,6+1,2,3,5-)TeMN

The values of MNR, ENR, DNR-1, TNR-1 and TeMNR range from 0.56-1.71, 2.83-4.84, 1.67-8.29, 1.04-1.84 and 0.16-0.59 respectively, suggesting immature to early oil window.

The distribution of phenanthrene (P) and its methyl derivatives in the aromatic fraction of the samples was shown on mass chromatograms (Fig. 12a). 1-MP/9-MP ratio ranges from 0.77-1.93 which indicated that there were more terrestrial organic matter inputs at the top. The ratio of 1,7DMP/X (Fig. 13a) showed two different classes of organic matter sources i.e.

terrigenous and terrigenous with marine input. This can probably classify its Kerogen into Type III with samples EN2A and EN1A probably Type III/II. The calculated vitrinite reflectance (%Rc), MPR-1, MPI-I, MPI-I*, MPI-2, MPI-3, MPDF, DMPI-1 and DMPI-2 values range from 0.79-1.13, 1.33-2.18, 0.65-1.22, 0.59-1.12, 0.52-1.01, 1.18-1.97, 0.54-0.66, 0.44-0.87, 0.40-0.62 respectively showing that the samples are at the different level of thermal maturity (Fig. 13b).

Figure.12a: Mass chromatogram of C_0 - C_3 phenanthrenes in the sample

Figure.12b: Mass chromatogram of C_0 - C_1 dibenzothiophenes distribution in the sample

Table 5: Phenanthrene, dibenzothiophenes and alkylated derivatives ratios

Sample	1-/9-MP	1,7-DMP/X	MPR-1	%RcMPI	Rm	MP/DMP	MP/TMP	MDR	DBT/P
EN 15A	1.03	1.01	1.57	1.11	1.17	1.46	3.41	2.50	0.12
EN 12A	0.99	1.45	1.49	0.98	1.14	1.39	3.15	2.14	0.08
EN 8A	1.01	0.57	1.70	1.08	1.20	1.45	4.20	2.60	0.11
EN 6A	0.83	1.18	1.33	0.79	1.09	0.70	5.58	2.09	0.05
EN 3A	0.91	1.13	1.35	0.87	1.09	1.67	4.41	2.13	0.06
EN 2A	0.85	0.54	2.18	1.13	1.32	1.69	5.52	2.24	0.14
EN 1A	0.77	0.52	2.05	1.08	1.29	1.58	3.78	2.00	0.09

X= 1,3- + 3,9- + 2,10- + 3,10- DMP; MPR-1= 2-mp/1-mp; %Rc MPI= %Rc, MPI-1= 0.6 (MPI-1) + 0.4; Ro < 1.35%; Rm= 1.1*logMPR+0.95; MDR= 4-MDBT/1-MDBT

Figure.13: (a) Plot of 1,7-DMP/X vs. 1-MP/9-MP for interpreting organic matter kerogen types (b) Binary plot of VRc vs. %RcMPI indicating thermal maturity of organic matter.

Low contents of dibenzothiophene to phenanthrene (Fig. 14a) suggested that the samples of Enugu Shale were deposited in estuarine to fluvial deltaic settings (Hughes *et*

al., 1995). The MDR ratio also showed that maturity is increasing with increase in depth (Fig. 14b).

Figure. 14: (a) Plots of DBT/Phen vs Pristane/Phytane (b) maturity status of organic matter

Conclusions

The *n*-alkane ranged from nC_{11} - nC_{35} in most samples maximizing at intermediate homologue that suggested organic matter mainly derived from algae. The Pr/Ph (1.11-4.09) ratio suggested deposition of the rocks under suboxic to oxic condition. Organic matter contained in the samples were classified as Type III kerogen (dominant) and Type II/III (minor) capable of producing gaseous hydrocarbon with little oil, based on the plot of Ph/nC_{18} vs. Pr/nC_{17} . Different plots (i.e. $C_{31}22R$ -homohopane/ C_{30} -hopane vs Pr/Ph, sterane (C_{27} - C_{29}) and trimethylnaphthalene ratios) derived from biomarkers and aromatics distribution reflected organic matter deposited in fluvio-deltaic to estuarine paleoenvironments. The distribution of methylated naphthalenes is in the order DMN>TMN>TeMN>MN in the samples reflecting organic matter majorly derived from terrigenous material which is consistent with the ratio of 1-MP/9-MP (0.77-1.03). Various biomarker and polyaromatic hydrocarbon maturity proxies suggested immature to early maturity status of the samples. However, an increase in maturity with depth was observed. Enugu shale has potential to generate hydrocarbon but not yet mature to release significant quantities of hydrocarbons at the present total depth. Findings in this study are similar to earlier published works on the Enugu Shale and its lateral equivalent Nkporo Formation.

Acknowledgements

Nigerian Association of Petroleum Explorationists (NAPE) is acknowledged for sponsoring the field trip during the Pre-conference field trip in 2015 that afforded me the opportunity to collect the shale samples.

References

- Abubakar, M.B. (2014). Petroleum Potentials of the Nigerian Benue Trough and Anambra Basin: A Regional Synthesis. *Natural Resources* 5, 25-58
- Achari, R. G., Shaw, G., and Holleyhead, R. (1973). Identification of ionene and other carotenoid degradation products from the pyrolysis of sporopollenins derived from some pollen exines, a spore coal and the green river shale. *Chemical Geology* 12, 229–234.
- Adedosu, T.A., Sonibare, O.O., Jincai Tuo, J. and Ekundayo, O., (2012). Biomarkers, carbon isotopic composition and source rock potentials of Awgu coals, middle Benue trough, Nigeria. *Journal of African Earth Sciences* 66-67, 13–21.
- Adedosu, T.A., T.R. Ajayi, Yongqiang Xiong, Yun Li, Chenchen Fang, Yuan Chen, and A. Akinlua (2014). Geochemical evaluation of Kolmani River-1 well, Gongola Basin, Upper Benue Trough, Nigeria. *Nigerian Association of Petroleum Explorationists* 26 (1), 51-79.
- Adegoke, A.K., Abdullah, W.H., Hakimi, M.H., Sarki Yandoka, B.M., (2014). Geochemical characterization of Fika Formation in the Chad (Bornu) Basin, northeastern Nigeria: implications for depositional environment and tectonic setting. *Applied Geochemistry* 43, 1–12
- Adiela, U. P. (2016). Biostratigraphical and Paleoenvironmental Analysis Enugu Area Anambra Basin Nigeria *International Research Journal of Interdisciplinary & Multidisciplinary Studies (IRJIMS) Volume-II, Issue-II, March 2016, Page No. 58-64.*
- Anozie H.C., Chiaghanam O.I. and Chiadikobi K.C. (2014). Source rock and thermal maturation of campanian Enugu shale in Anambra Basin, south eastern, Nigeria. *International Journal of Geology, Earth & Environmental Sciences* 4 (3), 296-307.
- Bray, E. E. and Evans, E. D., 1961. Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* 22, 2–15.
- Chiadikobu, K.C. and Chiaghanam, O.I., (2018). Biomarkers distribution of the Campano-Maastrichtian Nkporo group of Anambra Basin, Southeastern Nigeria. *Petroleum and Coal* 60 (6), 1161-1175.

- Chiaghanam, O.I., Chiadikobi, K.C., Ikegwuonu, O.N., Omoboriowo, A.O., Onyemesili, O.C., Acra E.J. (2013). Palynofacies and Kerogen Analysis of Upper Cretaceous (Early Campanian To Maastrichtian) Enugu Shale And Mamu Formation In Anambra Basin, South-Eastern, Nigeria. *International Journal of Scientific & Technology Research* 2, 8.
- Edegbai, A.J., Schwark, I. and Oboh-Ikuenobe, F.E., (2019). Campano-Maastrichtian paleoenvironment , paleotectonics and sediment provenance of western Anambra Basin, Nigeria: Multi-proxy evidences from the Mamu Formation. *Journal of African Earth Sciences* 156, 203-239.
- Ficken KJ, Li B, Swain DE, Eglinton G (2000). An n-alkanes proxy for the sedimentary input of submerged/floating fresh water aquatic macrophytes. *Organic Geochemistry* 31(7), 745-749.
- Golovko, A.K., Kontorovich, A.E., Pevneva, G.S., Fursenko, E.A. (2014). Composition and distribution of alkyl naphthalenes in West Siberian oils. *Russian Geology and Geophysics* 55, 737-744.
- Hakimi, M. and Abdullah, W-H., (2013). Organic geochemical characteristics and oil generating potential of the Upper Jurassic Safer shale sediments in the Marib-Shabowah Basin, western Yemen. *Organic Geochemistry* 54, 115–124.
- Huang, W.Y. and Meinschein, W. G., (1979). Sterols as ecological indicators. *Geochimical et Cosmochimica Acta* 43, 739–745.
- Hughes, W.B., Holba, A.G. and Dzhou, L.I.P. (1995). The ratios of dibenzothiophene to phenanthrene and pristine to phytane as indicators of depositional environment and lithology of petroleum source rocks. *Geochemica et Cosmochimica Acta* 59, 3581-3598.
- Kogbe, C. A. (1989): The Cretaceous and Paleocene sediments of southern Nigeria. In: CA. Kogbe. Ed. 2nd ed. Lagos: Elizabeth Publishers; 273–286.
- Ladipo, K. O. (1986): Tidal shelf depositional model for Ajali Sandstone, Anambra Basin, southeastern Nigeria. *Journal of African Earth Sciences* 5 (2), 177–185.
- Nton, M.E. and Shereef A. Bankole (2013). Sedimentological characteristics, provenance and hydrocarbon potential of Post Santonian sediments in Anambra Basin, Southeastern Nigeria. *RMZ – M&G* 60, 47–66.
- Nwajide, C. S. (1990): Cretaceous sedimentation and paleogeography of Central Benue Trough. In: Ofoegbu, C.O. Ed. *The Benue Trough, Structure and Evolution*. International Mongraph Series, Braunschweig; 19–38.
- Nwajide, C.S., (2013). Geology of Nigeria's Sedimentary Basins, CSS Bookshop Ltd., Lagos, 565p.
- Marynowski, L., Narkiewicz, M. and Grelowski, C. (2000). Biomarkers as environmental indicators in a carbonate complex, example from the Middle to Upper Devonian, Holy Cross Mts., Poland. *Sedimentary Geology* 137 (3–4), 187–212.
- Obaje, N.O., H. Wehmer, G. Scheeder, M.B. Abubakar, A. Jauro, (2004). *American Association of Petroleum Geologist Bulletin* 88, 325-353.
- Obi, G. C. and Okogbue C. O. (2003). Sedimentary response to tectonism in the Campanian-Maastrichtian succession, Anambra Basin, southeastern Nigeria. *Journal of African Earth Sciences* 4: 314–323.
- Odumodu, C.F.R., Mode, A.W. (2017) Trace Fossils from the Campanian - Maastrichtian Enugu Formation of the Anambra Basin, South-eastern Nigeria: Implications for Paleoenvironmental Interpretation. *MOJ Ecology & Environmental Science* 2(8): 00055. DOI: 10.15406/moj.2017.02.00055.

- Odundun, O.A. (2015). Use of Geochemical Fossils as Indicators of Thermal Maturation: An Example from the Anambra Basin, Southeastern Nigeria. *Journal of Geochemistry* 2015, 11pp. <http://dx.doi.org/10.1155/2015/809780>.
- Odunze, S.O. and Gordian C. Obi (2013). Sedimentology and sequence stratigraphy of the Nkporo Group (Campanian-Maastrichtian), Anambra Basin, Nigeria. *Journal of Palaeogeography* 2 (2), 192-208.
- Ozcelik, O. and Altunsoy, M. (2005). Organic geochemical characteristics of Miocene bituminous units in the Beypazari Basin, Central Anatolia, Turkey. *Arabian Journal for Science and Engineering* 30(2), 181-194.
- Peters, K.E., C.W. Walters, J.M. Moldowan (2005). *The Biomarker Guide*, Cambridge University Press, Cambridge.
- Rinna, J., J. Rullkötter, and R. Stein (1996). Proceeding of Ocean Drilling Program Scientific Results 151, 407–414.
- Roushdy M I, El-Nady M M, Mostafa Y M, El-Gendy N S, Ali H, (2010). Biomarkers characteristics of crude oils from some oilfields in the Gulf of Suez, Egypt. *Journal of American Science* 6 (11), 911–925.
- Sari, A. and Bahtiyar, I. (1999). Geochemical evaluation of the Besikli oil field, Kahta, Adiyaman, Turkey. *Journal of Marine and Petroleum Geology* 16, 151-164.
- Sinninghe Damsté, J.S., F. Kenig, M.P. Koopmans, J. Köster, S. Schouten, J.M. Hayes, J.W. de Leeuw, (1995). Evidence for gammacerane as indicator of water column stratification. *Geochimica et Cosmochimica Acta* 59, 1895–1900.
- Tijani, M.N., Nton, M.E., Kitagwa, R., (2010). Textural and geochemical characteristics of the Ajali Sandstone, Anambra Basin, SE Nigeria: Implication for its provenance. *Comptes Rendus Geoscience* 342, 136-150.