Geochemical Evaluation of the Lower Senonian Ogugu Shale, Southern Benue Trough, Nigeria: Implication for Source Richness, Quality and Petroleum Potential

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Abstract

The Lower Senonian Ogugu Shale is the topmost layer of the Coniancian-Santonian depositional unit in the Southern Benue Trough. Sediments of this unit have been suggested to have huge potential for hydrocarbon generation. However, detailed geochemical studies on the organic matter source, thermal maturity and the hydrocarbon potential Ogugu Shale are still missing. For the present study, a total of 16 cuttings and 3 core samples of the Ogugu Shale from Amasiodo-1 well were subjected to total organic carbon (TOC), Rock-Eval pyrolysis and gas chromatography mass spectrometry (GC-MS) analyses in order to characterize the organic matter richness, kerogen type and liquid hydrocarbon-generative potential in the samples. The TOC values (0.70 to 1.20 wt. %) and Rock-Eval pyrolysis data S2 (0.26-0.73 mg HC/g rock) as well as its calculated parameters Hydrogen Index (HI; 23-72 mg HC/g rock) and Generative Potential (GP; 0.33-0.84 mg HC/g rock) suggest poor to fair organic rich rock containing dominantly terrestrially derived Type III kerogen. The biomarkers as well as the source-indicating aromatic hydrocarbons in the samples suggest contributions from mixed aquatic and vascular organic matter deposited under oxic-dyoxic conditions of deltaic paleoenvironment. The Rock-Eval pyrolysis Tmax (434-456^0 C) including the derived vitrinite reflectance (Rc; 0.65-1.05%) indicate thermally matured source rocks. The thermal maturity status of Ogugu Shale is further supported by molecular thermal parameters from the saturate and aromatic compounds. This study therefore conclude that that the Senonian Ogugu Shale of the Southern Benue Trough contain thermally matured fair quantity of organic matter with poor hydrocarbon potential.

Keywords: Benue Trough, Kerogen type, Ogugu Shale, Paleoenvironment, Petroleum potential

Introduction

Increasing energy demands with growing population has necessitated continuous hydrocarbon exploration as it remains a major source of energy in Nigeria (Edomah, 2016; Kihonbo *et al.*, 2021). Despite the call for alternative energy sources due to associated problems with fossil fuel (Shaaban and Petinrin, 2014; Ibrahim *et al*., 2021), hydrocarbon exploration has only witnessed slight decline in the developed countries while most developing countries see hydrocarbon exploitation as a major boost to their economic growth (Edomah, 2016). Income from crude oil has been the mainstay of Nigerian economy in the last 5 decades because of her endowed hydrocarbon resources (Oyedepo, 2016). Quite a number of inland sedimentary basins with potentials for hydrocarbon accumulations are known in Nigeria (Obaje *et al.*, 2004). Large hydrocarbon resources have been discovered and exploited from some of these basins while hydrocarbon exploration still continues in others. Benue Trough is one of the basins with good prospect for hydrocarbon resources but very limited hydrocarbons have been reported and this has resulted in several exploration studies by international oil companies and researchers.

The Southern Benue Trough comprising of the Abakaliki folded belt and the Anambra Basin has long been described as a basin with structural elements and stratigraphic succession that favours hydrocarbon formation and accumulation (Whiteman, 1982; Agagu and Adhigije, 1983; Ekweozor and Gormly, 1983). Though, there are only few reports of petroleum accumulations but large gas accumulations and prospects have been reported (Avbovbo and Ayoola, 1981; Unomah and Ekweozor, 1993). Many studies have identified Eze-aku shales, Awgu Shales, Ogugu, Nkporo, Nkalagwu, Mamu, and Imo Formations as source rocks for hydrocarbon generation in the Lower Benue Trough (Akaegbobi and Schmit, 1998; Ehinola *et al.*, 2004; 2005; Ogala, 2011, Nton and Ugochukwu, 2014; Anyiam and Onuoha, 2014; Adeleye *et al.*, 2014; 2016, 2017a, 2017b; Akaegbobi *et al.*, 2017). Awgu Formation consists of three mappable units known as Awgu, Agbani and Ogugu Formations (Agagu *et al.*, 1985). Awgu and Ogugu Formations consist of shally units separated by a sandy unit of Agbani Formation. Geochemical evaluation of Awgu Formation for hydrocarbon generation has been carried out by Ehinola, *et al*. (2004); Adeleye *et al.* (2014); Anyiam *et al.* (2014) among others. However, Ogugu Formation has received very little or no attention with respect to hydrocarbon generation, hence the need for this work. The objectives of this study are to evaluate the organic matter source, richness, and thermal maturity with view of interpreting the petroleum potential and paleoenvironment of the sample of Ogugu Shale encountered in the exploratory well Amansiodo-1.

Materials and Methods
Sampling
In this study, a total of 16 cuttings and 3 core samples of the Late Cretaceous Ogugu Shale from Amansiodo-1 well were obtained from the rock store of the Nigerian Geological Survey Agency. Amansiodo-1 well is one of the exploratory oil wells drilled in the Anambra Basin in the mid-1900s (Whiteman, 1982). It is approximately located on longitude $7^0\ 20^1$ E and latitude $6^0\ 30^1$ N (Figure 1) and reached a total depth of 2291 m in the Late Cretaceous units of Lower Benue Trough. The studied interval (1420-1515 m) composed mainly of bluish grey laminated shales with interbeds of greyish fine grained sandy-shale (Figure 2). The ditch cuttings were sampled at 5 m intervals throughout the studied section while the core samples were obtained at the available depths of 1422 m, 1426 m and 1509 m. The samples were thoroughly washed with distilled water, oven dried at 60 ^{0}C for 2 days and then pulverized to 100 micron mesh size.

TOC and Rock-Eval Pyrolysis
Total organic carbon (TOC) content of all the collected samples was determined using a Elementar Vario EL III elemental analyser (Hanau, Germany). About 20 mg of each sample was first treated with concentrated hydrogen chloride acid to remove the carbonates. The samples were then washed, dried and then analyzed for carbon content.
Pyrolysis was performed on all the samples with a Delsi Rock-Eval Pyrolyzer 6 following procedure outline in Espitalie *et al.* (1986) and Peters (1986). About 100 mg of each sample was first heated to 300^0C (held for 3 min) and then steadily heated to 650 ^{0}C at the rate of 25^0C/min, both in an inert atmosphere. Released hydrocarbons during the pyrolysis were detected and measured by a flame ionization detector (FID). The first peak (S1; mg HC/g TOC) represents the thermally distilled hydrocarbons whereas the second peak (S2; mg HC/g TOC) represents the thermally cracked hydrocarbons. The third peak (S3; mg CO_2/g rock) represents the quantity of carbon dioxide generated during the programmed pyrolysis. The temperature at which the maximum S2 yield is achieved was recorded as Tmax. Other parameters such as hydrogen Index (HI; S2/TOC), Oxygen Index (OI; S3/TOC), Production Index (PI; S1/S1+S2) and Generative Potential (GP; S1+S2) were calculated following Peters (1986). The equivalent vitrinite reflectance (%Rc) was calculated using the formula: $(0.0180 \times T_{max})$ - 7.16 (Jarvie, 1991).
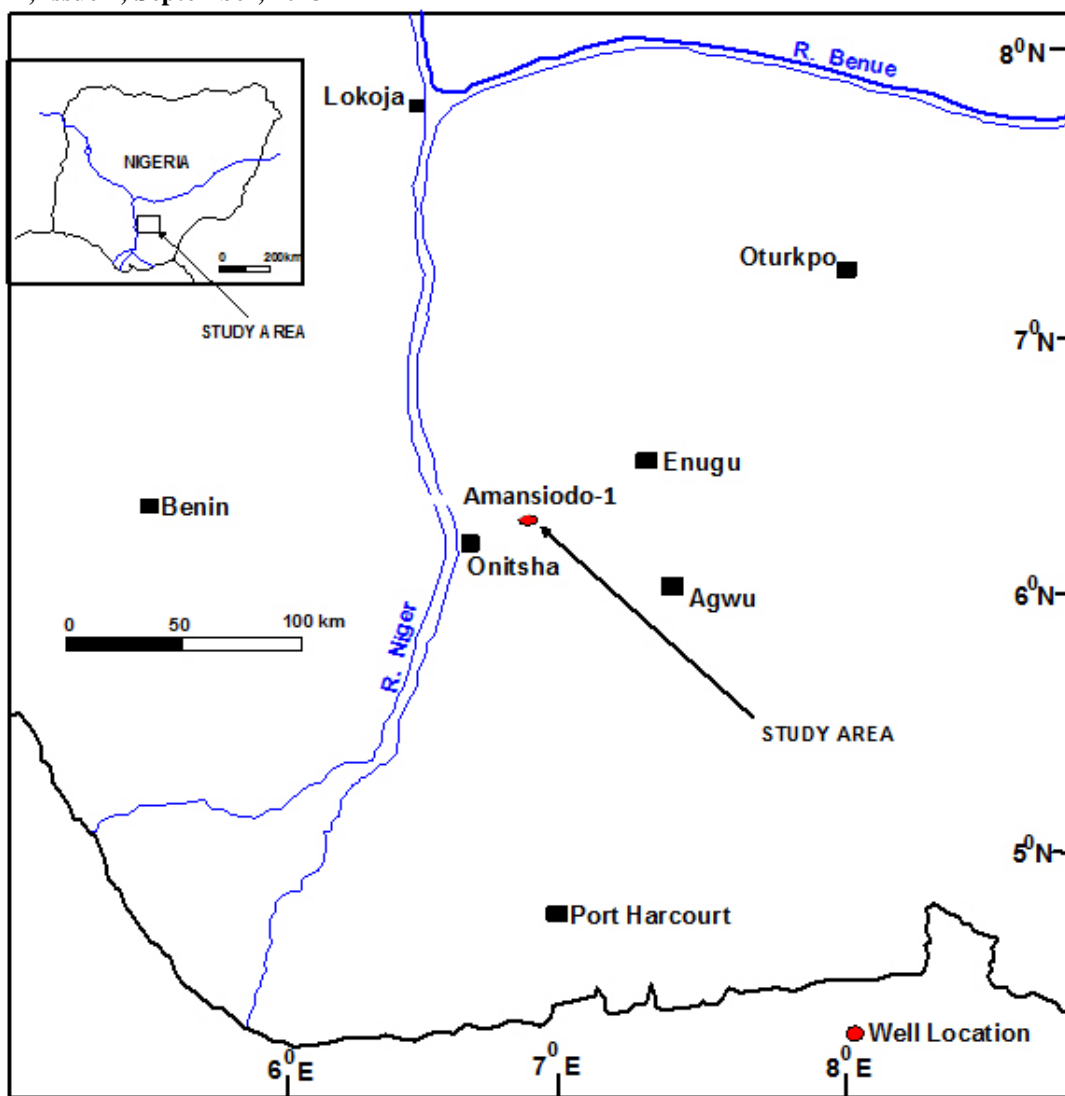
Figure 1: Map of parts of Nigeria showing the location of Amasiodo-1 well

Molecular Organic Geochemistry

The samples preparations, extractions, fractionations and gas chromatography mass spectrometry (GC-MS) analyses were carried out following the outline of Adedosu *et al.* (2010, 2012). About 10 g each of selected 5 samples were ultrasonically treated sequentially with 20 ml of methanol, mixture of methanol and dichloromethane (1:1, v/v) and dichloromethane extracted using methanol and dichloromethane each for 1 hour to extract soluble organic matter in the rock. Afterward each extract was fractionated into aliphatic, aromatic and polar fractions via alumina/silica gel column chromatography using hexane, a mixture of hexane and dichloromethane (4:1, v/v), and a mixture of dichloromethane and methanol (1:1), respectively. The saturate and aromatic fractions were analyzed using an Agilent 7890A/5975 GC-MSD instrument. The gas chromatography was equipped with a HP–5 fused silica capillary column (30 m x 0.25 mm, 0.25μm film thickness) and helium was used as the carrier gas with flow rate of 1 ml/min.

For saturate fractions, oven temperature was programmed from 80 ^{0}C for 2 minutes to 280 ^{0}C at the rate of 3 ^{0}C per minute, followed by an isothermal phase for 20 minutes at 280 ^{0}C. The samples were analyzed in the full scan and selected ion monitoring (SIM) modes respectively. The characteristics ions monitored were *m/z* 85 (*n*-alkanes), *m/z* 191 (triterpanes) and *m/z* 217 (steranes and diasteranes).
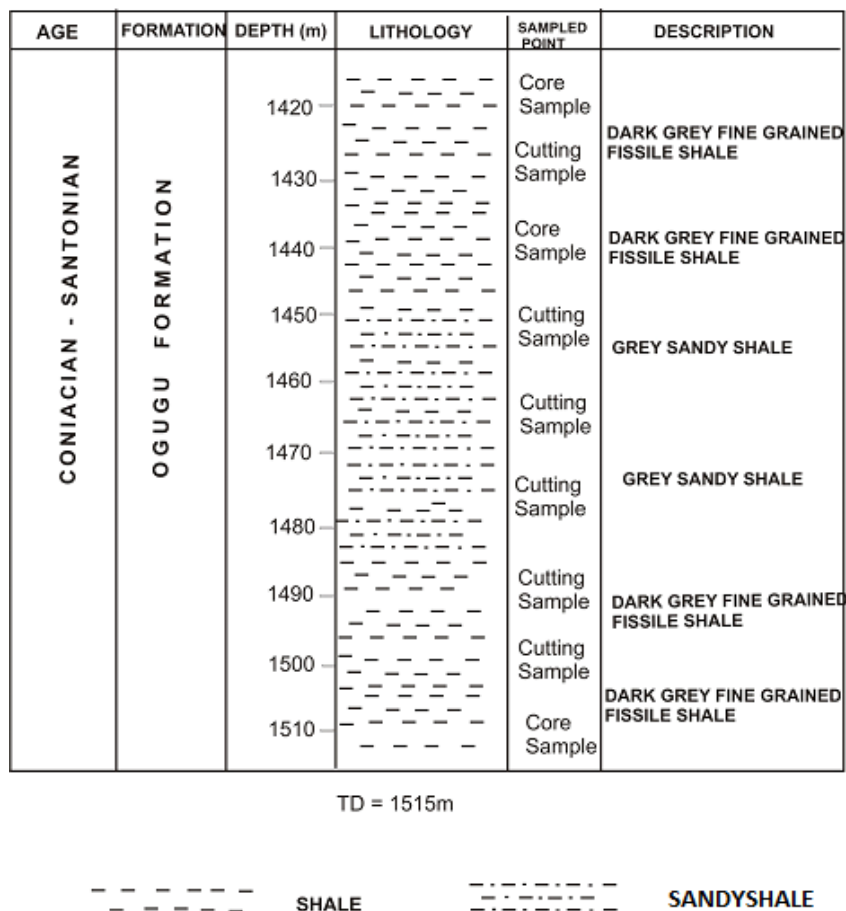
TD = 1515m

Figure 2: Lithological section and description of the studied part of Amansiodo-1 well.

For aromatic fraction, the mass spectrometer was operated with electron energy impact of 70 eV and an ion source temperature of 23^0C. The GC oven temperature was an isothermal of 2 minutes at temperature of 60^0C and then programmed for 60^0C to 290^0C at the rate of 3^0C per minute followed by isothermal phase of 20 minutes at 290^0C. The samples were analyzed in the full scan and SIM modes, respectively. For the SIM mode, the target components were detected using the following ions: naphthalene ($m/z = 128$), methyl- (MN), ethyl- and dimethyl- (EN and DMN), trimethyl- (TMN) and tetramethylnaphthalenes (TeMN) ($m/z = 142+156+170+184$), respectively, biphenyls ($m/z = 168$), phenanthrene (P), anthracene ($m/z = 178$), methyl- (MP), dimethyl- (DMP) and trimethylphenanthrenes (TMP) ($m/z = 192+206+220$), respectively, cadalene ($m/z = 183$), retene & benzonaphthathiophene (BNT) ($m/z = 234$), dibenzofuran ($m/z = 168$), flourene ($m/z = 166$) and methylflourenes ($m/z = 180$), dibenzothiophene ($m/z = 184$), methyl- (MDBT), dimethyl- (DMDBT), and trimethyldibenzothiophenes (TMDBT) at $m/z = 198+212+226$ respectively, fluoranthene, pyrene ($m/z = 202$), benzo(a)anthracene, chrysene ($m/z = 228$), 2-methyl benzo(a)anthracene, 9-methylbenzo(a)anthracene, methylchrysenes ($m/z = 242$), benzo(k+b)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene ($m/z = 252$), and benzo(g,h,i)perylene ($m/z = 276$), Identification was made using relative retention times, mass spectral data and comparison with previous published data (Radke *et al.,* 1982, 2000; Chakhmakhchev *et al.,* 1997; Budzinski *et al.,* 1998; Grice *et al.,* 2007; Asif *et al.,* 2009, 2010, 2011; Adedosu *et al.,* 2012; Li *et al.,* 2012; Fabiánska and Kurkiewicz, 2013).

Results and Discussion
Total organic carbon and Rock-Eval Pyrolysis
The summary of the results for the total organic carbon (TOC) and Rock-Eval pyrolysis analyses including the calculated parameters (HI, OI, GP, PI and R_C) are presented in Table 1. TOC, S1, S2 and S3 values of the shales and sandy shales samples of the Ogugu Shale range from 0.70 to 1.20 wt.%, 0.07 to 0.14 mg HC/g rock, 0.26 to 0.73 mg HC/g rock and 0.29 to 0.61 mg CO_2/g rock, respectively. About 52% of the samples have TOC contents up to 1% while the remaining samples have values less than 1%. The investigated samples of Ogugu Shale as a whole have an average TOC of 1.01 wt.%. The calculated Hydrogen Index (HI), Oxygen Index (OI) and Generative Potential (GP) of the studied samples ranges from 23 to 72 mg HC/g TOC, 19 to 66 mg CO_2/g TOC and 0.33 to 0.84 mg HC/g rock, respectively. Only five samples have HI values up to 50 mg HC/g TOC while other samples have lower HI values. The samples at shallower depth show higher HI values than the samples at deeper depth suggesting variable environmental conditions during the depositional process of the rock unit. The Tmax, calculated vitrinite reflectance (Rc) and Production Index values range from 434 to 456 ^{0}C, 0.65 to 1.05% and 0.11 to 0.33, respectively. Only one sample at the depth 1475-1480 m shows Tmax value lower than 435 ^{0}C. Multivariate correlation analysis of the geochemical data shows negative correlations of depth with S2, HI, and GP values ($r = -0.51$, -0.58 and -0.50, respectively) and weak positive correlation between TOC vs. S2 and S1 vs. S2 ($r = 0.31$ and 0.27, respectively).

Distribution of Aliphatic Compounds
Normal and Acyclic Isoprenoids Alkanes: Partial *m/z* 85 mass chromatograms showing the distribution of *n*-alkanes and acyclic isoprenoids in the studied samples of Ogugu Shale are shown in Figure 3. These compounds dominate the aliphatic fraction of all the shale extracts. Two types of *n*-alkanes distribution can be recognized in investigated samples extracts. The first and dominant is mono-modal with *n*-alkanes distribution maximizing at *n*-C_{20}. The second type is bimodal, with distribution maximizing at *n*-C_{14} and *n*-C_{20}. However, all the samples extracts were characterized with dominance of short-chain compounds (*n*-C_{14} to *n*-C_{21}) over long-chain n-alkanes (*n*-C_{22} to *n*-C_{33}) with the ratio of short-chain to long-chain ranging between 2.25 and 5.10 (C_{21}-/C_{22}+; Table 2). The carbon preference index (CPI) values of the samples also present two scenarios. CPI values in samples B, C and D range from 0.64 to 0.96 (Table 2), reflecting a clear even-over-odd carbon predominance. On the other hand, CPI values near 1.1 in samples A and E reflecting no clear carbon predominance. All the analysed shale extracts contain relatively lower contents of acyclic isoprenoids (pristane and phytane) than *n*-alkanes. Pristane (Pr) is present in lower contents than phytane (Ph) with Pr/Ph ratio ranging from 0.27 to 0.58 (Figure3; Table 2). The lower concentration of acyclic isoprenoids compared to *n*-alkanes is reflected in values of the ratios Pr/*n*-C_{17} and Ph/*n*-C_{18} that range from 0.19-0.27 and 0.04-0.07, respectively (Table 2)

Triterpenoids and Steroids: Partial *m/z* 191 mass chromatograms showing the distributions of triterpenoids revealed the presence of tricyclic, tetracyclic and pentacyclic triterpanes (Figure 4).The tricyclic and tetracyclic triterpanes are observed in lower quantities than pentacyclic triterpanes. Tricyclic terpanes are present as a series of C_{19}-C_{26} cheilantanes with a maximum at C_{23} in all the samples (Figure 4). C_{24}-tetracyclic terpane is also present in all the samples. Important biomarker ratios of the tricyclic and tetracyclic terpanes are presented in Table 2. Pentacyclic triterpanes occur in high abundance in all the extracts, except for sample A in which they occur in poor quantities. These compounds are characterized by the presence of 17α(H)-22,29,30-trisnorhopane (Tm), 18α(H)-22,29,30-trisnorneohopane (Ts), a series of C_{27-31} 17α(H), 21β(H) hopanes (αβ-hopanes), a series of C_{20-31} 17β(H),21α(H) hopanes (βα-moretane) and full range of C_{31}-C_{35} homohopanes (Figure 4). These compounds are mostly dominated C_{30} αβ-hopane followed by C_{29}αβ-norhopane. The homohopanes are dominated by C_{31} homohopane and decreasing

towards the C_{35} homohopane (Figure 4). The Tm dominates over Ts with the Ts/Tm ratio of 0.37-0.60 (Table 2). Oleanane and gammacerane were also observed in low quantities in the samples.

Steranes and diasteranes were identified in the samples of Ogugu Shale by monitoring the *m/z* 217 ion chromatograms (Figure 5). Diasterane (D) contents in the studied samples are lower than sterane (D) with the D/S ratio ranging from 0.27 to 0.53 (Table 2). Diasteranes are present as series of C_{27} to C_{28} βα- and αβ-diasteranes, dominated by C_{27} βα- and C_{28} βα-regular diasteranes. Steranes are dominated by C_{27} 14α(H), 17α(H)-20R regular sterane (C27αα-sterane), although series of C_{27} to C_{29} αα-, αβ-, βα- and ββ-steranes are also identified. The sterane and diasterane contents are dominated with abundance of C_{29}-Sterane (30-40%) and C_{27}-Sterane (37-45) than C_{28}-Sterane (21-28%). The values of the important biomarker ratios C_{29}-sterane ββ/(ββ+αα) and 20S/(20S+20R) range from 0.48-0.56 and 0.40-0.53, respectively (Table 2). Similarly, the calculated vitrinite reflectance (%Rc) based on C_{29}-sterane 20S and 20R ranges from 0.68-0.91 (Table 2).
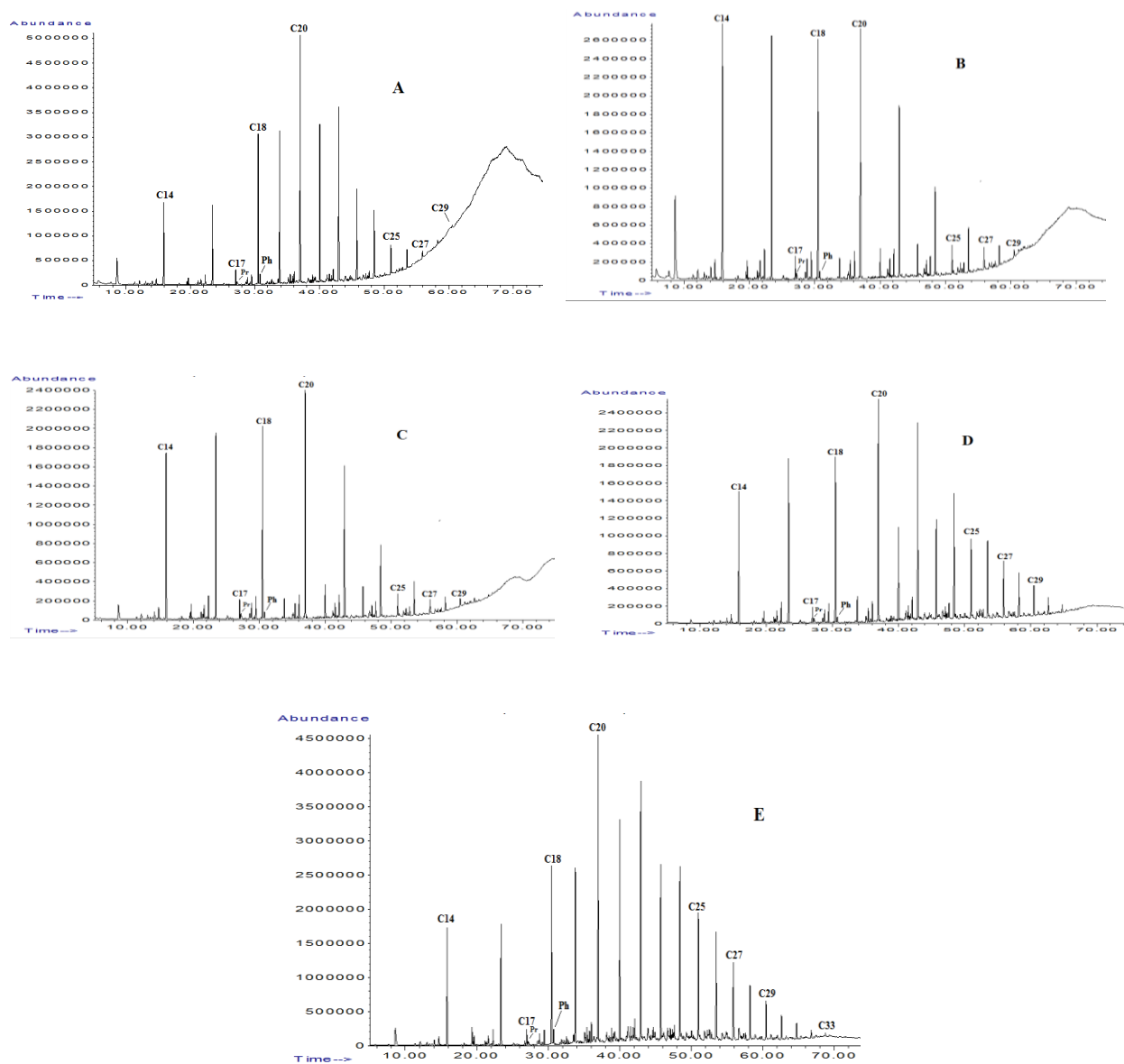

Figure 3: Ion chromatograms (m/z 85) showing *n*-Alkane and isoprenoids distributions in samples of Lower Senonian Ogugu Shale

Table 1: Minimum, maximum and average values of total Organic Carbon (TOC) and Rock-Eval Pyrolysis Results *(N = 19)*

	TOC	S1	S2	S3	HI	OI	Tmax	GP	PI	Rc
Min	0.70	0.07	0.26	0.29	24.00	19.00	434.00	0.33	0.11	0.65
Max	1.60	0.14	0.73	0.61	72.00	66.00	456.00	0.84	0.33	1.05
Average	1.01	0.09	0.45	0.42	45.05	43.74	441.47	0.55	0.18	0.79

N – No of samples; TOC-Total Organic Carbon (wt. %); S1 (mg HC/g Rock); S2 (mg HC/g Rock); S3 (mg CO_2/g Rock); HI-Hydrogen Index (mg HC/g TOC); OI- Oxygen Index (mg CO_2/g TOC); Tmax (^{0}C), GP- Generative Potential (S1+S2; mg HC/g Rock); PI- Production Index (S1/(S1+S2); Rc-calculated vitrinite reflectance (%)

Table 2: *n*-Alkanes, Isoprenoids, Terpanes and Steranes parameters and ratios for analysed samples of Ogugu Shale

| Sample ID	Depth (m)	*n*-Alkanes						Steranes			Regular steranes			Terpanes	
		C_{21}-/C_{22}+	CPI	Pr/Ph	Pr/nC$_{17}$	Pr/nC$_{18}$	D/S	C_{29} 20S/(20S+20R)	C_{29} ββ/(ββ+αα)	%Rc	C_{29}	C_{28}	C_{27}	Ts/Tm	Mor/Hop
A	1422	2.25	1.18	0.28	0.19	0.07	0.38	0.53	0.50	0.91	35.00	21.00	44.00	**0.37**	**0.49**
C	1455-1460	2.51	0.64	0.58	0.22	0.04	0.44	0.42	0.56	0.71	40.00	24.00	37.00	0.56	0.13
D	1470-1475	1.14	0.96	0.56	0.21	0.04	0.30	0.43	0.51	0.72	30.00	28.00	42.00	**0.54**	**0.24**
E	1485-1490	1.09	1.03	0.27	0.27	0.09	0.27	0.43	0.48	0.73	30.00	25.00	45.00	0.60	0.14
B	1509-1512	2.84	0.64	0.54	0.21	0.04	0.53	0.40	0.54	0.68	40.00	23.00	37.00	0.54	0.16
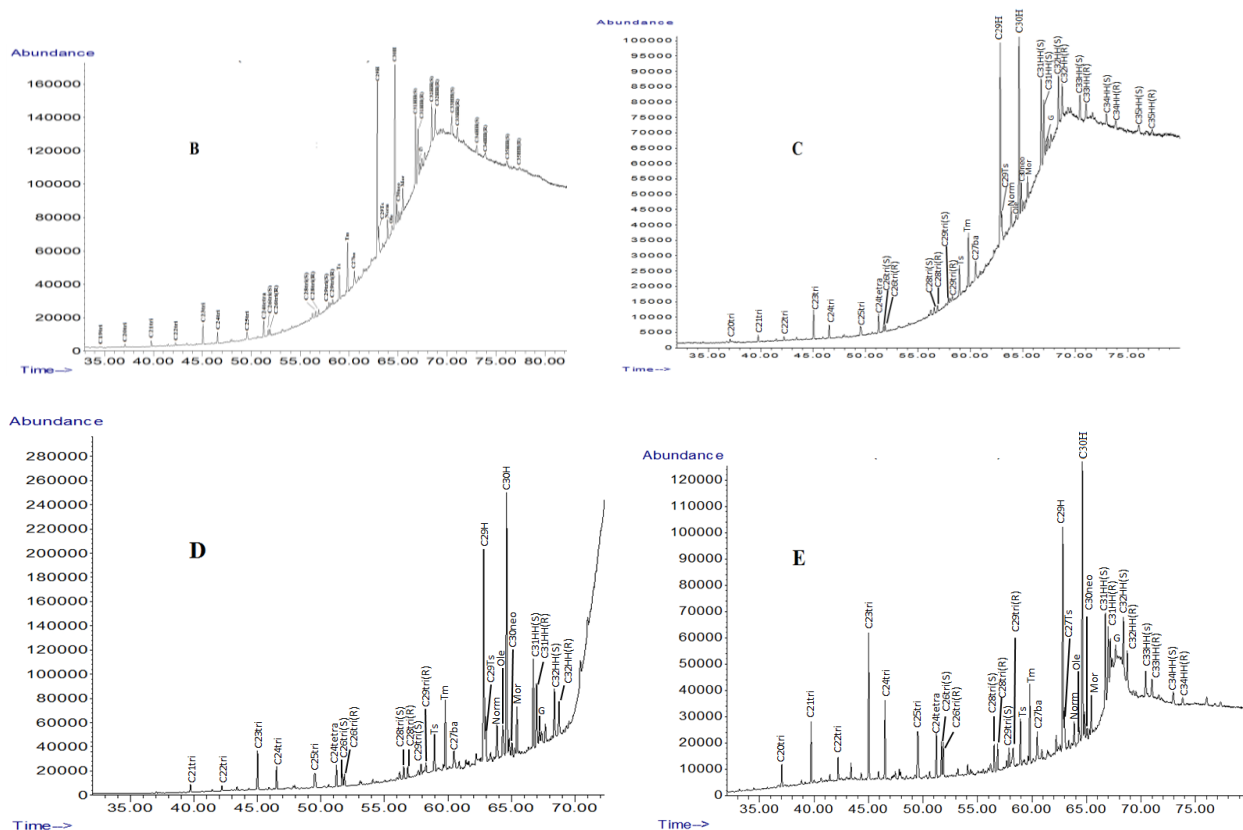
Figure 4: Representative ion chromatograms (*m/z* 191) showing Terpanes and hopanes distributions in samples of Ogugu Shale.
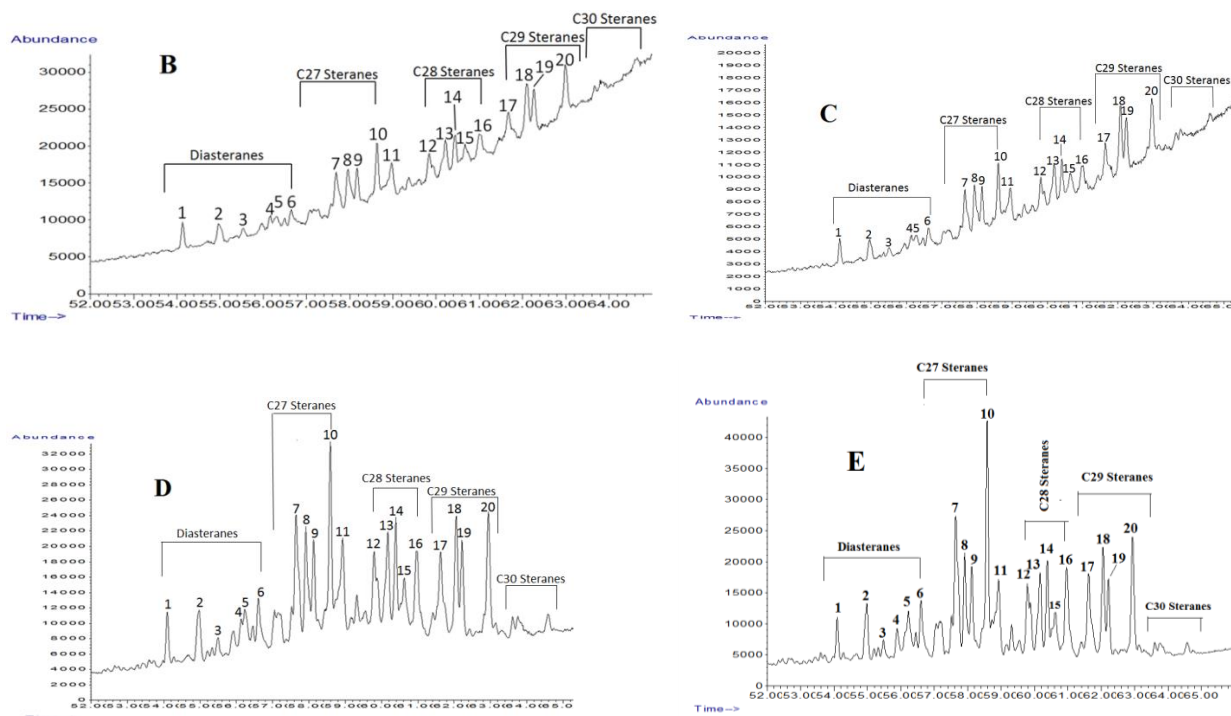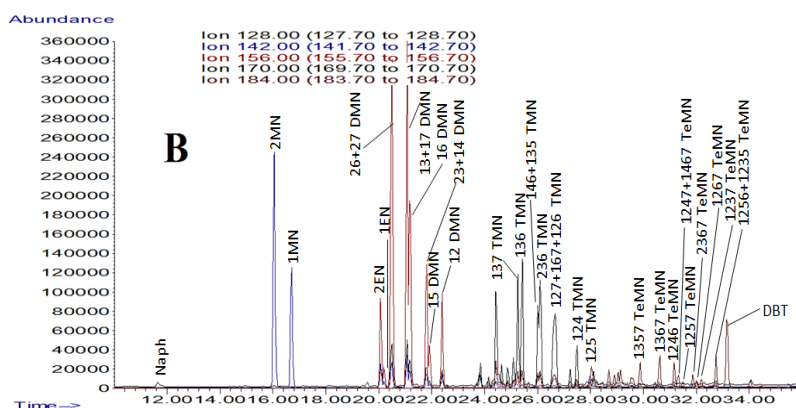

Figure 5: Representative ion chromatograms (*m/z* 217) showing diasteranes and steranes distributions in samples of Ogugu Shale.

Aromatic Compounds

The analysed Ogugu Shale extracts contain high contents of aromatic compounds composed of partially aromatized compounds, unsubstituted polycyclic aromatic hydrocarbons (PAHs) and their methylated derivatives and heterocyclic aromatic compounds.

Alkylnaphthalene, Alkylphenanthrene and Alkylbiphenyl: Contents of alkylnaphthalenes are shown on merged *m/z* 128 + 142 + 156 + 170 + 184 ion chromatograms (Figure 6). Naphthalene occurs in lower concentration than its alkyl derivatives in all the samples. Most analysed samples show trend of increase in concentrations of alkylnaphthalenes with increase in alkyl chain length (Figure 6). This could be attributed to effect of secondary processes such as water washing in these samples. The distributions of methylnaphthalene (MN) and ethylnaphthalene (EN) in the aromatic fraction of the samples of Ogugu Shale show that 2-MN and 2-EN are more abundant than 1-MN and 1-EN, respectively (Figure 6, Table 3). The dimethylnaphthalene (DMN) distribution shows the dominance of 2,6- + 2,7-DMN, 1,3- + 1,7-DMN and 1,6-DMN over 2,3- + 1,4-DMN, 1,5-DMN and 1,2-DMN (Figure 6). The trimethylnaphthalenes (TMN) in the samples are characterized by high abundances of 2,3,6-TMN, 1,3,7-TMN and 1,3,6-TMN, and low abundances of 1,2,4-TMN and 1,2,5-TMN. The tetramethylnaphthalenes (TeMN) are mostly detected in low quantities compared to other alkylnaphthalene and are dominated by 1,3,5,7-, 1,3,6,7- and 1,2,4,6-TeMN. Merged *m/z* 178 + 192 + 206 + 220 mass chromatograms showing the distributions of phenanthrene, methylphenanthrene (MP), ethylphenanthrene (EP), dimethylphenanthrene (DMP) and trimethylphenanthrene in the samples of Ogugu Shale are shown Figure 7. Contrary to naphthalene distribution, phenanthrene shows the higher contents than its alkyl derivatives in the investigated samples. Generally, distributions of alkylphenanthrene decrease with increasing alkyl chain length. This trend suggests that the contents of alkylphenanthrenes in the samples are not influence by secondary processes. The MP isomers show higher abundance in 3-MP and 9-MP than 2-MP and 1-MP, respectively (Figure 7, Table 3). The DMP homologues are typified by higher contents of 1,3- + 3,9- + 2,10- + 3,10-DMP, 2,5- + 2,9- + 1,6-DMP, 3,5- + 2,6-DMP and 1,7-DMP, and low contents of 3,6-DMP, 2,7-DMP, 2,3-DMP, 1,8-DMP, 1,2-DMP and 1,9- + 4,9- + 4,10-DMP. The TMP isomers typically show lower contents compared to other alkyphenanthrenes and are dominated by 1,3,0- + 2,3,6-TMP and 1,3,8-TMP. The distributions alkylbiphenyls in the aromatic extracts of the samples of Ogugu Shale are monitored on *m/z* 168 ion chromatograms (Figure 8). Biphenyl is absent in the all the samples. Methylbiphenyls are relatively abundant in all the samples. 3-Methylbiphenyl occurs in higher concentrations than 4- and 2-methylbiphenyl.
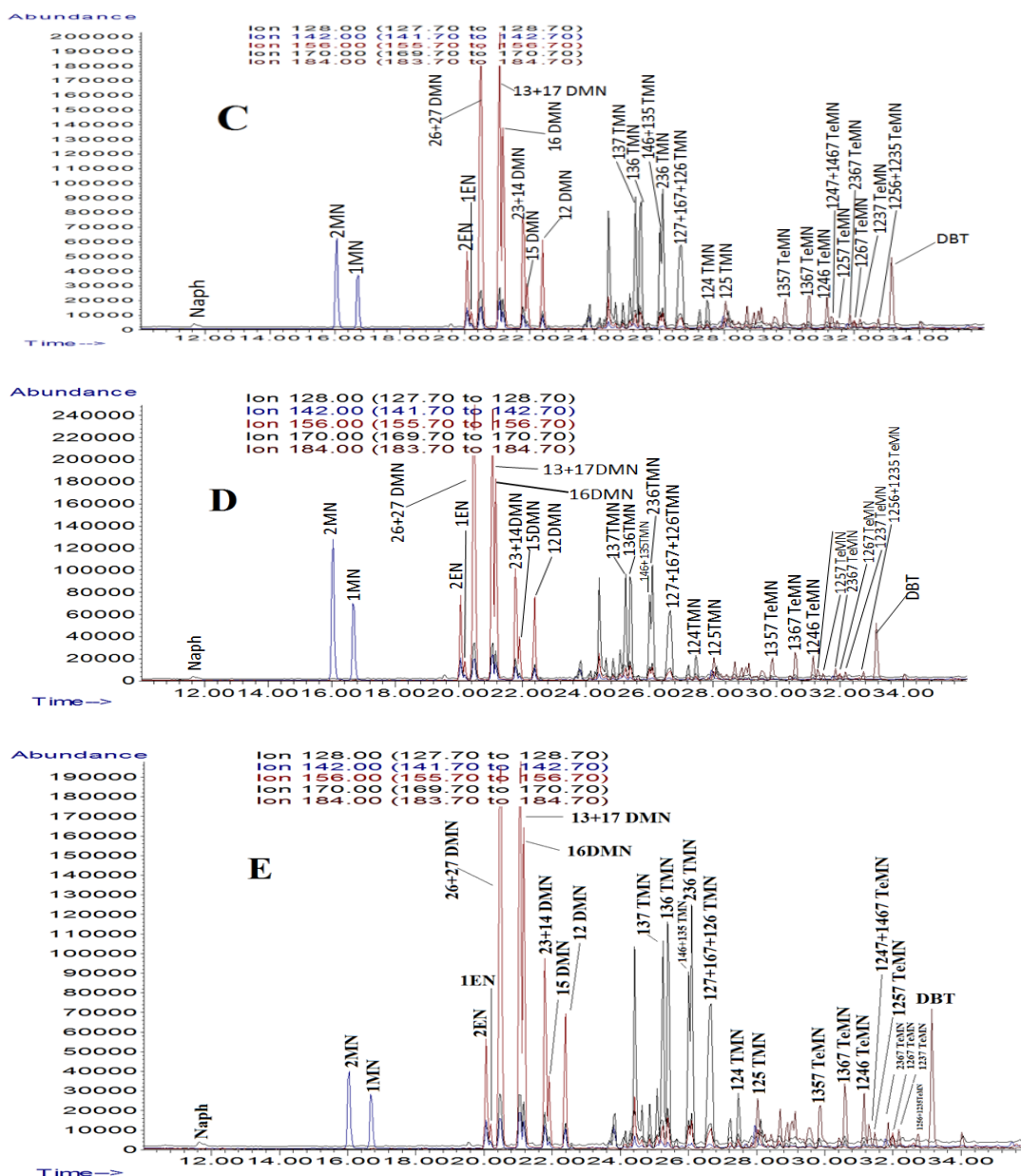
Figure 6: Mass chromatograms of merged *m/z* 128, 142, 158, 170 and 184 showing distribution of Naphthalene and its alkylated derivative in analysed samples of Ogugu Shale (Naph, naphthalene; MN, methylnaphthalene; EN, ethylnaphthalene; DMN, dimethylnaphthalene; TMN, trimethylnaphthalene; TeMN, tetramethylnaphthalene; DBT, dibenzohiophene)

Table 3: Geochemical maturity parameters based on alkylnaphthalene and alklphenanthrene compounds in aromatic fractions of the analysed Ogugu Shales

Sample ID	Depth (m)	Alkylnaphthalene ratios					Alkylphenanthrene ratios					
		MNR[a]	ENR[b]	DNR-1[c]	TNR-1[d]	TeMNr[e]	1MP/9MP	MPR-1[f]	MPI-[g]	MPI-2[h]	MPI-3[i]	%VRcMPI-1
A	1422	2.09	6.14	9.45	1.26	0.78	1.09	1.17	1.05	1.09	1.03	1.03
C	1455-1460	1.59	4.29	7.88	1.56	0.52	0.99	2.30	1.30	1.05	2.22	1.18
D	1470-1475	1.80	5.47	8.12	1.45	0.79	0.96	2.12	1.28	1.04	2.03	1.17
E	1485-1490	1.43	5.59	6.25	1.52	0.80	0.98	1.57	1.20	1.03	1.04	1.12
B	1509-1512	1.87	4.42	9.36	1.28	0.53	0.89	1.33	0.96	0.90	1.17	0.98

[a]Methylnaphthalene ratio = 2-MN/1-MN; *m/z* 142 (Radke *et al.*, 1994)

[b]Ethylnaphthalene ratio = 2-EN/1-EN; *m/z* 142 (Radke *et al.*, 1994)

[c]Dimethylnaphthalene ratio-1 = (2,6-DMN + 2,7-DMN)/1,5-DMN; *m/z* 156 (Radke, 1987)

[d]Trimethylnaphthalene ratio-1 = (2,3,6-TMN)/(1,3,5-TMN + 1,4,6-TMN); *m/z* 170 (Radke *et al.*, 1986).

[e]Tetramethynaphthalene ratio = 1,3,6,7-TeMN/(1,3,6,7-TeMN + 1,2,5,6-TeMN + 1,2,3,5-TeMN); *m/z* 184 (van Aarssen *et al.*, 1999).

[f]Methlphenanthrene ratio-1 = 2-MP/1-MP; *m/z* 192 (Radke *et al.*, 1986).

[g]Methylphenanthrene index-1 = [1.5(2-MP + 3-MP)]/(P + 1-MP + 9-MP); *m/z* 178, 192 (Radke *et al.*, 1986).

[h]Methylphenanthrene index-2 = (3[2-MP])/(P + 1-MP + 9-MP); *m/z* 178, 192 (Radke *et al.*, 1986).

[i]Methylphenanthrene index-3 = (2-MP + 3-MP)/(1-MP + 9-MP); *m/z* 192 (Radke and Welte, 1983)

[l]Calculated Vitrinite reflectance from MPI-1 = 0.6(MPI-1) + 0.4; Ro < 1.35%; *m/z*, 192 (Radke and Welte, 1983)
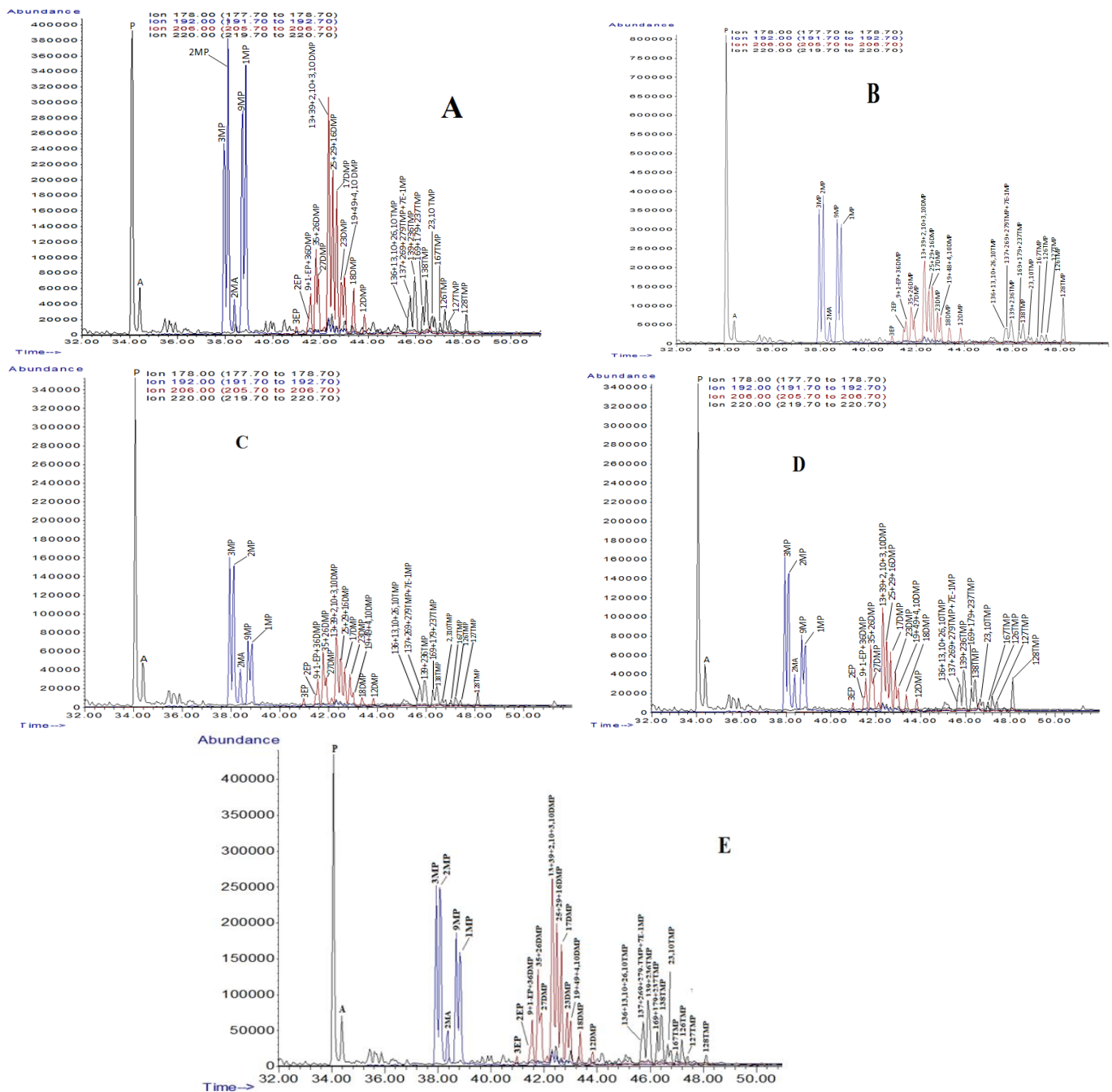
Figure 7: Mass chromatograms of merged ion 178, 192, 206 and 220 showing distributions of anthracene and phenanthrene as well as its alkylated derivative in analysed samples of Ogugu Shale (P, phenanthrene; A, anthracene; MP, methylphenanthrene; EP, ethylphenanthrene; DMP, dimethylphenanthrene; TMP, trimethylphenanthrene)
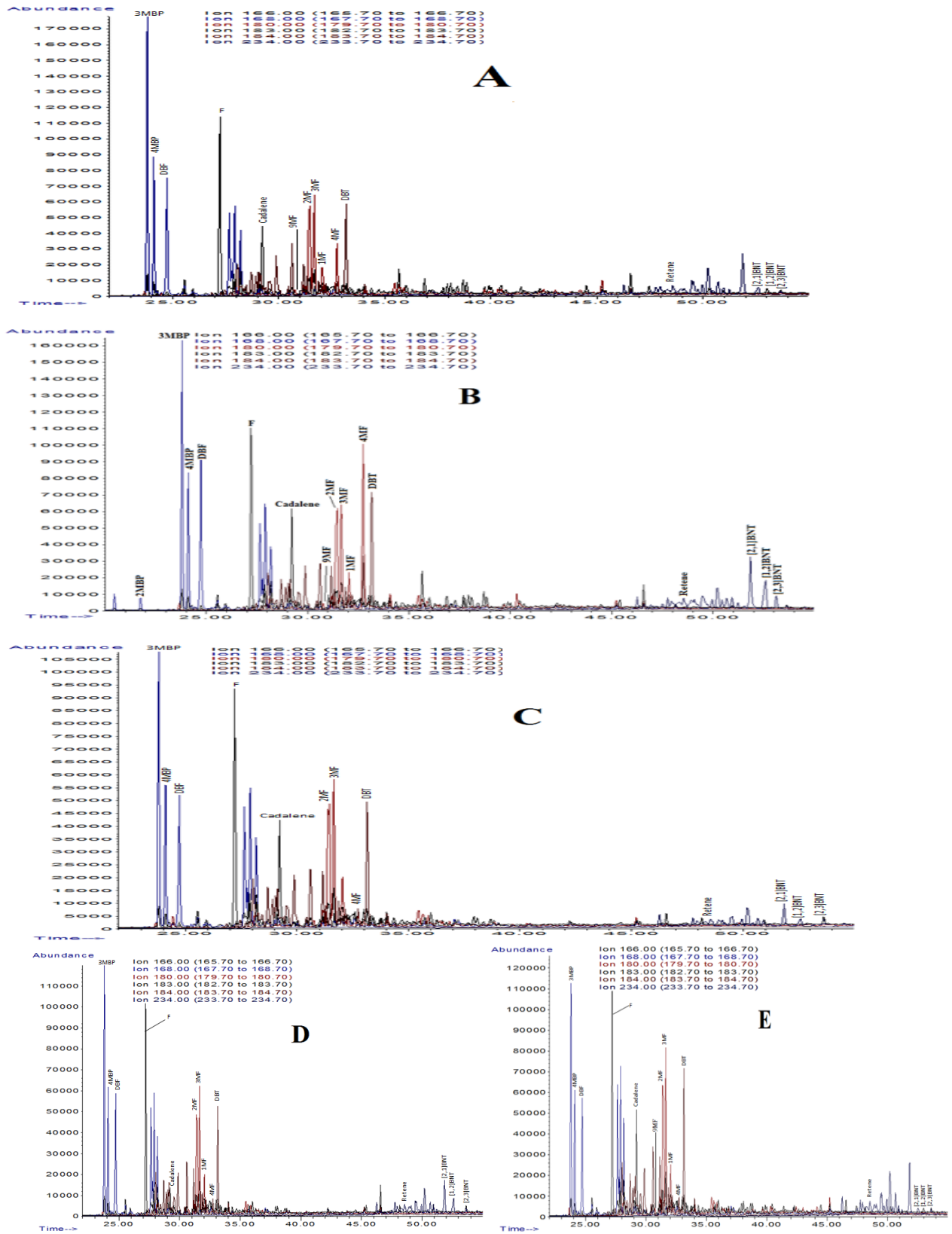
Figure 8: Partial ion chromatograms of *m/z* 166, 168, 180, 183, 184 and 234 showing distributions of methylbiphenyls (MBPs), dibenzofuran (DBF), cadalene, fluorene (F), methylfluorenes (MFs), dibenzothiophene (DBT), retene, benzonaphthiophenes (BNTs) in analysed samples of Ogugu Shale

Polycyclic Aromatic Hydrocarbon (PAH)

The polycyclic aromatic hydrocarbon (PAH) contents of the investigated samples of Ogugu Shale are characterized by the presence of PAH group with 2-5 rings such as phenanthrene, anthracene (m/z-178), fluorene, methylfluorene, cadalene, retene (m/z-166 + 180 + 183 + 234; Figure 8), fluoranthene, pyrene, chrysene, triphenylene, benzoanthracene (m/z-202 + 228; Figure 9), perylene, benzoflouranthene, benzoperylene, benzopyrene, methylchrysene, methylbenzoanthracene (m/z-242 + 252; Figure 10). Benzo(*ghi*)perylene is the only six ring PAH found in all the samples while PAHs with more than six rings are not found in the samples. High contents of phenanthrene, chrysene and pyrene are observed in all the samples. Lower abundance of fluoranthene comparable to pyrene content is observed in all studied samples with the ratio of fluoranthene/pyrene ranging between 0.43 and 0.70. Relatively high abundance of fluorene, anthracene and their methyl derivatives also occur in all the samples. Anthracene and methylanthracene contents are subordinate to phenanthrene and methylphenanthrene, respectively (Figure 7). Similarly, cadalene shows higher content than retene in all the samples (Figure 8) with the ratio of retene/cadalene ranging from 0.05-0.38.

Heterocyclic aromatic compounds

Heterocyclic aromatic compounds, mostly sulphur-containing groups occur in significant concentrations in the studied samples. Dibenzothiophene (DBT) and its alkylated derivatives (methyldibenzothiphene, ethyldibenzothiopene, dimethyldibenthiophene and trimethyldibenzothiophene) are detected on merged m/z 184 + 198 + 212 + 226 mass chromatograms (Figure 11). The distributions of alkyldibenzothiophene are dominated by 4-MDBT, 2- + 3-MDBT, 4,6-DMDBT, 2,6-DMDBT and 2,4,6-TMDBT. The shale extracts also contain low contents of benzonaphthiophene (m/z-234; Figure 8). Higher concentration of dibenzofuran (DBF: an oxygen-containing heterocyclic aromatic compound) than the content of dibenzothiophene (DBT) was observed in most analysed shale extracts (Figure 8).

Thermal maturity

The thermal maturity of the investigated samples of Ogugu Shale based on their Rock Eval Tmax (434-456 ^{0}C) and calculated vitrinite reflectance (Rc: 0.65-1.05%) values, indicate that the study interval is mostly mature. The sample at depth 1475-1480 m with Tmax value lower than 435 ^{0}C is immature. The remaining samples are apparently within the oil window. These suggest an overall thermally mature status for the samples of Ogugu Shale with an average Tmax value of 441 ^{0}C.

The thermal mature nature of the samples of Ogugu Shale is further supported by molecular thermal parameters from the saturate and aromatic fractions of the shale extracts. The CPI values for the investigated samples ranging from 0.64 to 1.18 with average value of 0.89 suggest early thermal maturity (Table 4; Bray and Evans, 1961; Peters and Moldowan, 1993). The low values of moretane/hopane ratio (0.14 to 0.49; Table 4) also support early thermal maturity of the samples of Ogugu Shale (Peters and Moldowan, 1993). Similarly, the values of 22S/(22S+22R) C_{32}-Homohopane, 20S/(20S+20R) C_{29}-Sterane and $\beta\beta/(\beta\beta+\alpha\alpha)$ C_{29}-Sterane ratios (0.50-0.65, 0.40-0.53 and 0.48-0.56 respectively) indicate mature source rocks within the oil window (Figure 11; Seifert and Moldowan, 1980, 1981, 1986; Peters *et al.*, 2005). The aromatic hydrocarbon distributions of phenanthrenes in which the alkylphenanthrene contents decrease with increasing alkyl chains indicate compositions controlled by thermal maturity. Accordingly, the calculated methyphenanthrene indices (MPR-1, MPI-1, MPI-2 and MPI-3) and equivalent reflectance values (% RcMPI-1) are typical of thermally mature samples (Table 3).
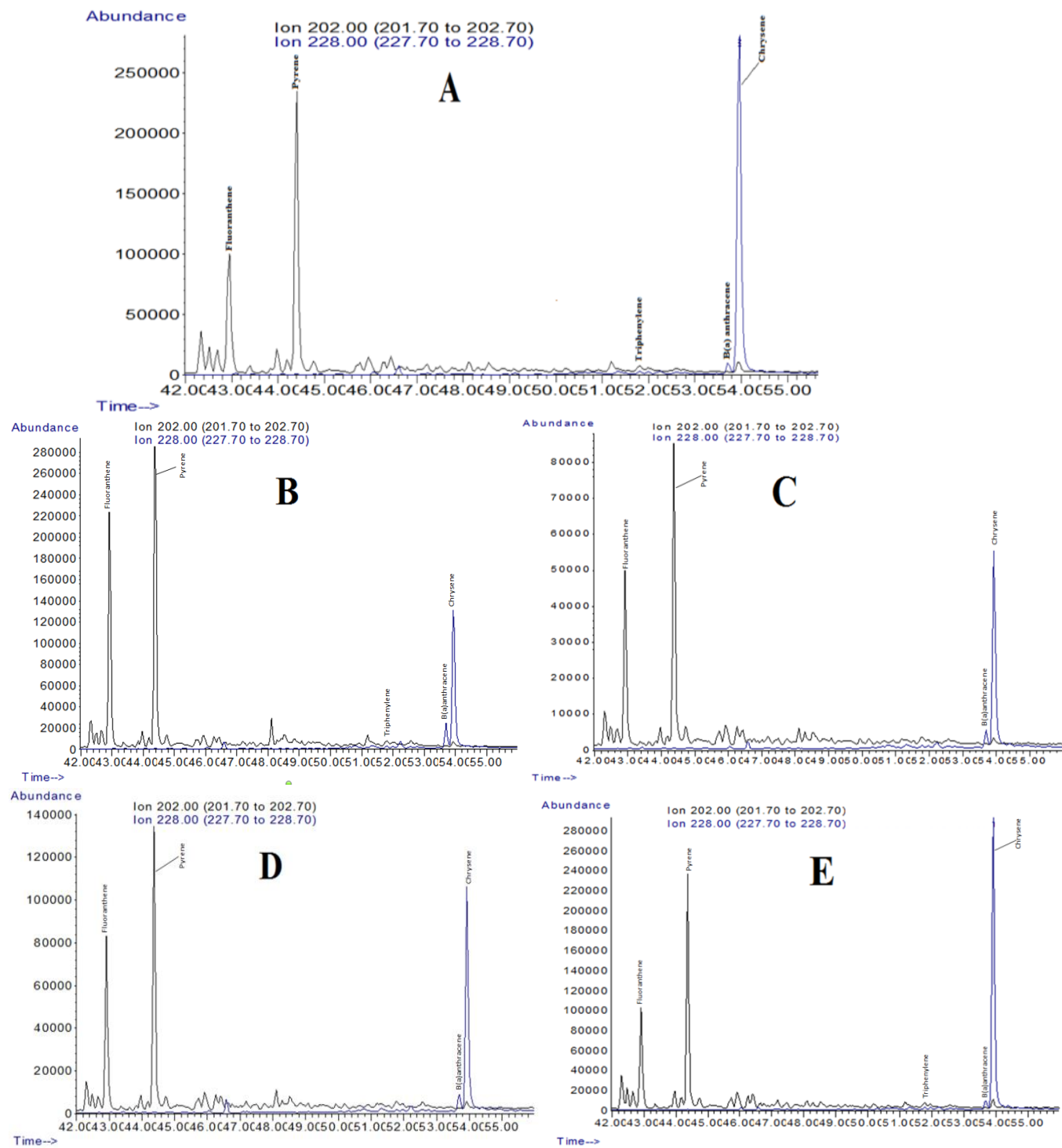
Figure 9: Partial ion chromatograms of m/z 202 + 228 showing distributions of fluoranthene, pyrene, triphenylene, benzo[a]anthracene and chrysene in studied samples of Ogugu Shale.
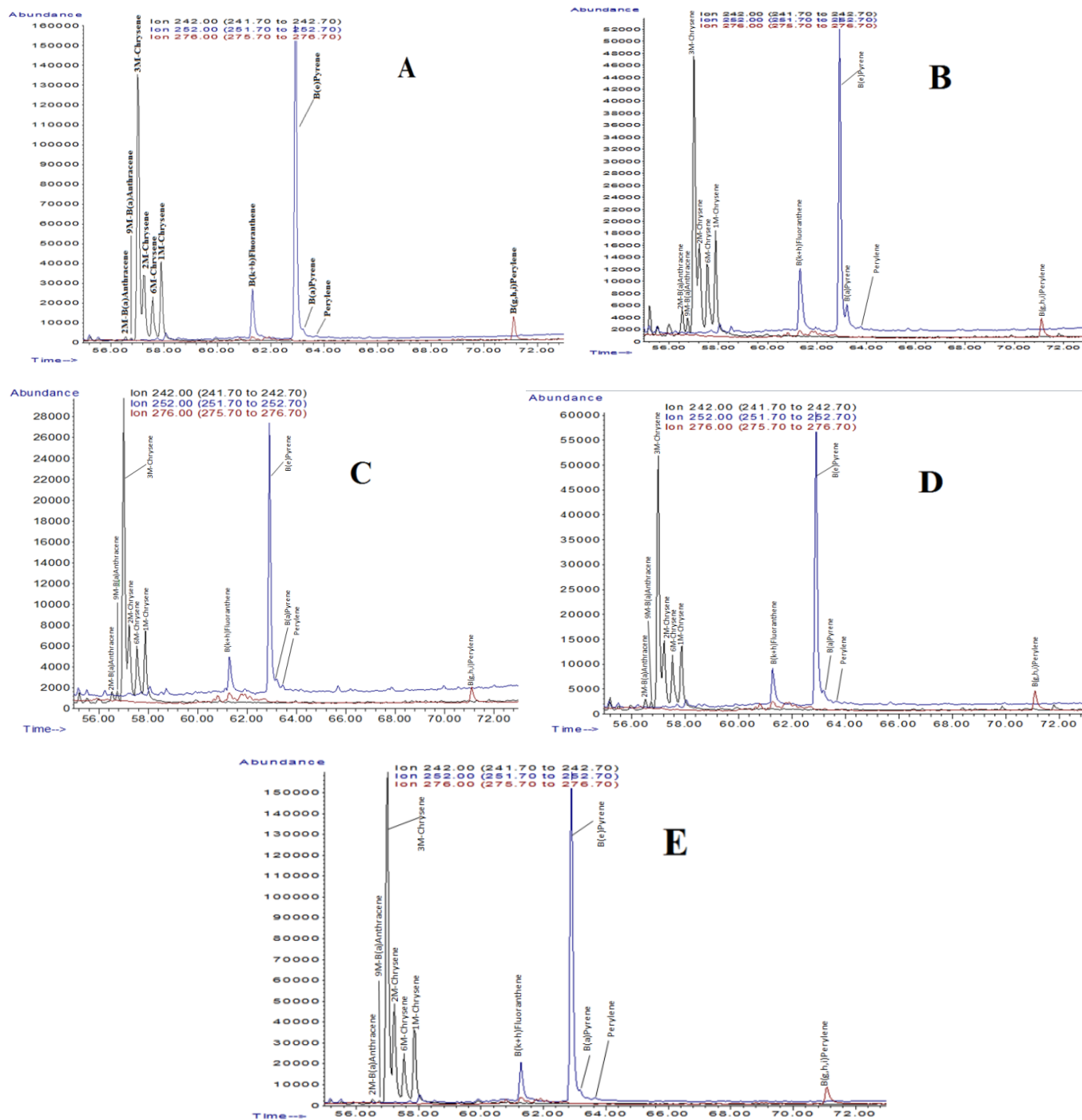
Figure 10: Mass chromatograms of merged ions 242+252+276 showing abundances of benzoanthracenes, methylchrysenes, benzofluoranthene, benzopyrenes, perylene and benzoperylene in studied aromatic extracts of Ogugu Shale
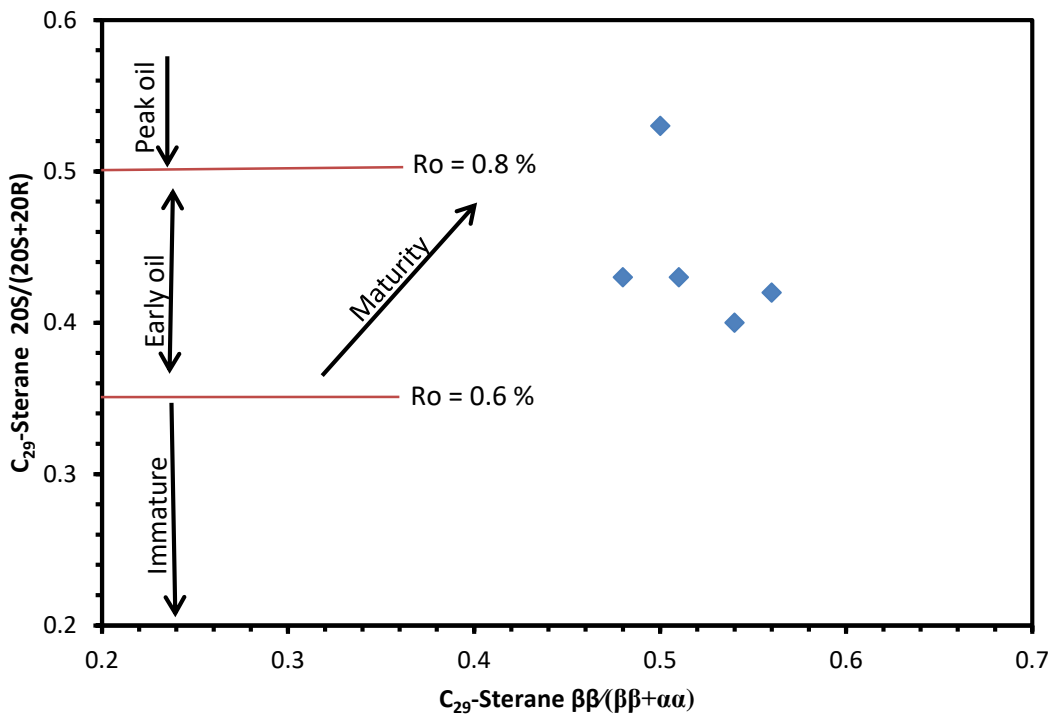
Figure 11: Cross plot of 20S/(20S + 20R)C_{29}-Sterane versus $\beta\beta/(\beta\beta + \alpha\alpha)C_{29}$-Sterane showing range of thermal maturity for the analysed samples of Ogugu Shale. Demarcated boundaries of maturity is after Peters *et al.* (2005)

Organic matter source and Depositional Condition

The low HI values of the investigated samples of Ogugu Shale (23 to 72 mg HC/g TOC) indicate the presence of Type III kerogen (Figure12), suggesting contribution of humic material from terrestrial environment. The dominance of low molecular weight n-alkanes (n-C_{15} to n-C_{21}) suggests a relatively high aquatic organic-matter (algal and bacterial) contribution with a minor content from vascular land plant (Peters and Moldowan, 1993; Adebayo *et al.*, 2018). The predominately aquatic origin organic matter is supported by high abundance of C_{30} hopane over C_{29} norhopane. However, the ratios of Pr/n-C_{17}, Ph/n-C_{18} and Sterane/Hopane (S/H; 0.17-0.82) and the relative distribution of C_{27} (37-45%), C_{29} (30-40%) and C_{28} (21-28) steranes suggest mixed contributions of marine and terrestrial organic inputs typical of deltaic bay or estuarine environments (Figure 13 and 14). The presence of Oleanane, which is a land plant-derived biomarker, also supports important contribution of terrestrial organic matter to the samples (Peters and Moldowan, 1993; Moldwan *et al.*, 1994). The interpretation for mixed organic matter source can also be inferred from aromatic hydrocarbon contents of the investigated samples. The presence of hydrocarbons, 1,2,5,6-tetramethylnaphthalene (1,2,5,6-TeMN), 1-methylphenanthrene (1-MP), pimanthrene (1,7-DMP), cadalene and retene in the samples of Ogugu Shale reflect the terrestrial contribution to the organic matter (Radke *et al.*, 1986; Puttmann and Villar, 1987; van Aarssen *et al.*, 2000; Hautevelle *et al.*, 2006) while the occurrence of 1,3,6,7-TeMN, 9-MP as well as Dibenzothiophene and its methyl derivatives (characteristics of organic matter deposited in anoxic setting which more likely to occur in marine environment) suggest microbial marine organic matter in the samples (Radke and Willsch, 1994; Budzinski *et al.*, 1995; Radke *et al.*, 2000; van Aarssen *et al.*, 2000). The depositional conditions (anoxic versus oxic) can be indicated by the distribution pristine and phytane (Peters *et al.*, 2005). The low Pristaner/Phytance (Pr/Ph) ratio of the investigated samples of Ogugu Shale (0.27-0.58; Table 2) suggest deposition in oxygen-deficient bottom

water (Peters and Moldowan, 1993; Peters *et al.*, 2005). The Pr/Ph ratios of less than 1.0 in the thermally mature rocks like the investigated Ogugu Shale samples are also typical of organic-rich marine sediments (Tissot and Welte, 1984; Peters *et al.*, 2005). However, the low TOC values of the analysed samples, which suggest poor-fair organic rich sediments for Ogugu Shale does not correlate with deposition in anoxic environment. This may be due to the assertion by Peters *et al.* (2005) that Pr/Ph ratio correlate weakly with depositional conditions in thermally mature sediments. Furthermore, the homohopane distributions of C_{31}-C_{35} in terms of homohopane index and C_{35}/C_{34} ratio can be used to evaluate the redox conditions of source rocks (Peters *et al.*, 2005). The low homohopane index (0.03-0.05) and the high concentration of C_{34} homohopane compared to C_{35} homohopane, with relatively low C_{35}/C_{34} ratios suggest oxic condition during deposition of Ogugu Shale. The presence of gammacerane biomarker, although, in low quantity indicates relatively reducing conditions. The depositional conditions of Ogugu Shale can be further investigated using heterocyclic aromatic hydrocarbons (i.e. dibenzothiophene and alkyldibenzothiophenes, dibenzofuran and alkyldibenzofuans, and fluorine and alkylfluorenes). Higher abundances of DBT and its methyl isomers than DBF and F and their methyl isomers are ascribed to anoxic/marine source rocks while vice versa are related to oxic/deltaic depositional settings (Asif and Fazeelat, 2012; Xiangchum *et al.*, 2011; Radke *et al.*, 2000). Relative percentages of DBT, DBF and F in samples of Ogugu Shale show 26-29%, 23-31% and 42-48%, respectively. This point to oxic/deltaic deposition environment for Ogugu Shale samples. The summary of these parameters (TOC, Pr/Ph, Homohopane index, C_{35}/C_{34}, gammacerane and heterocyclic aromatic HC) is that Ogugu Shale was likely deposited in unstable oxic-dyoxic environmental conditions.
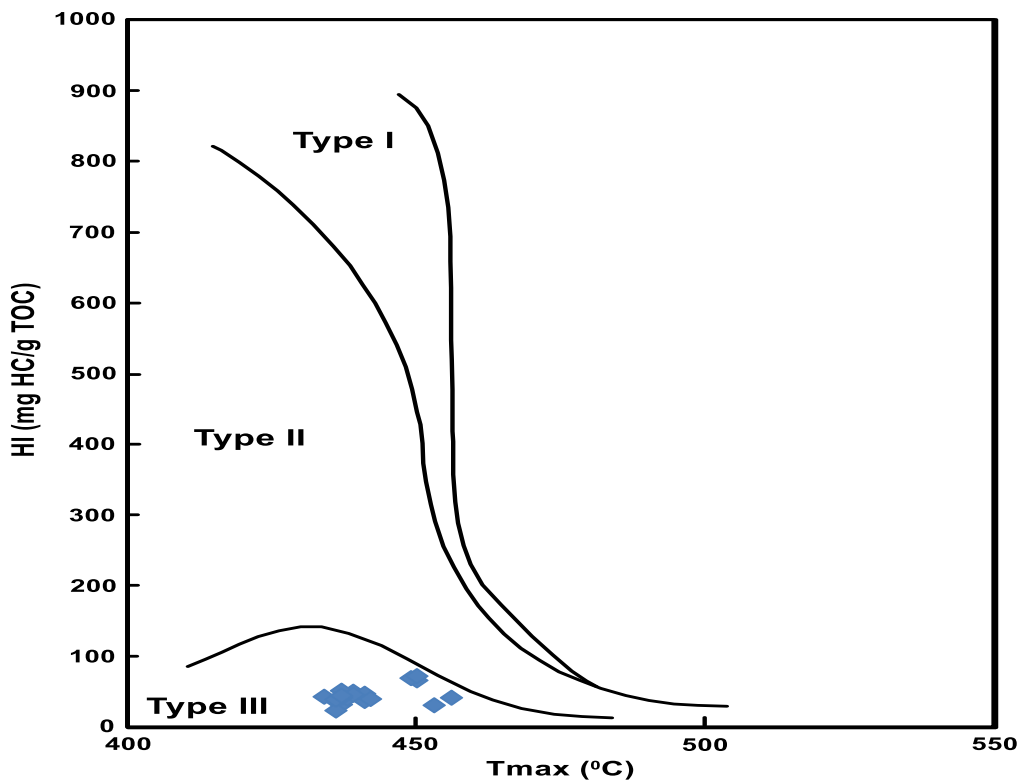

Figure 12: Cross plot of Hydrogen Index (HI) versus Tmax values showing kerogen type of organic matter in analysed samples of Ogugu Shale (after Espitalie *et al.*, 1986)
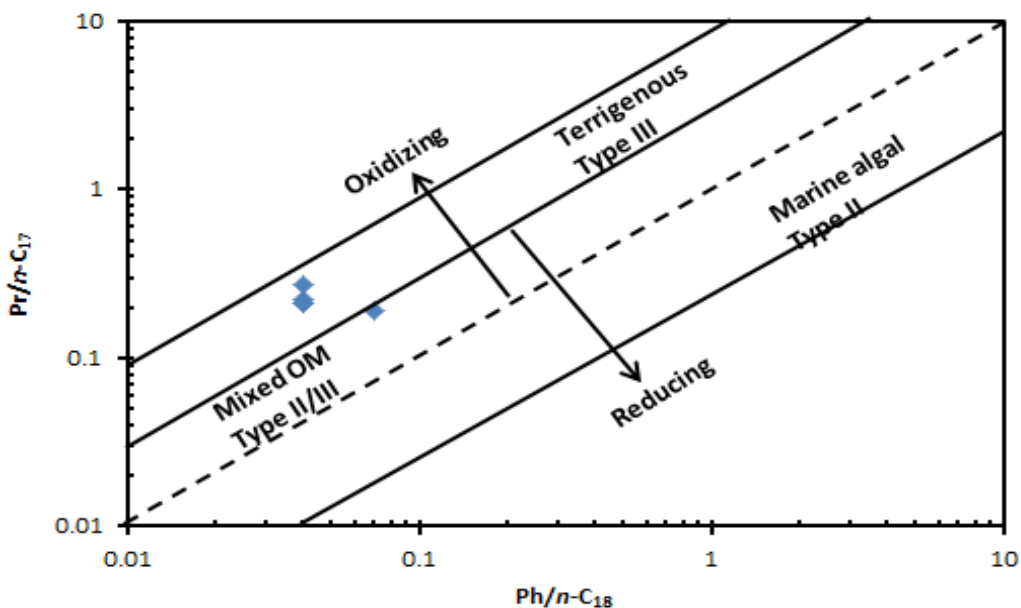
Figure 13: Plot of $Pr/n\text{-}C_{17}$ versus. $Ph/n\text{-}C_{18}$ value for the studied samples of Ogugu Shale interpreting organic matter types (modified after Hunt, 1995)
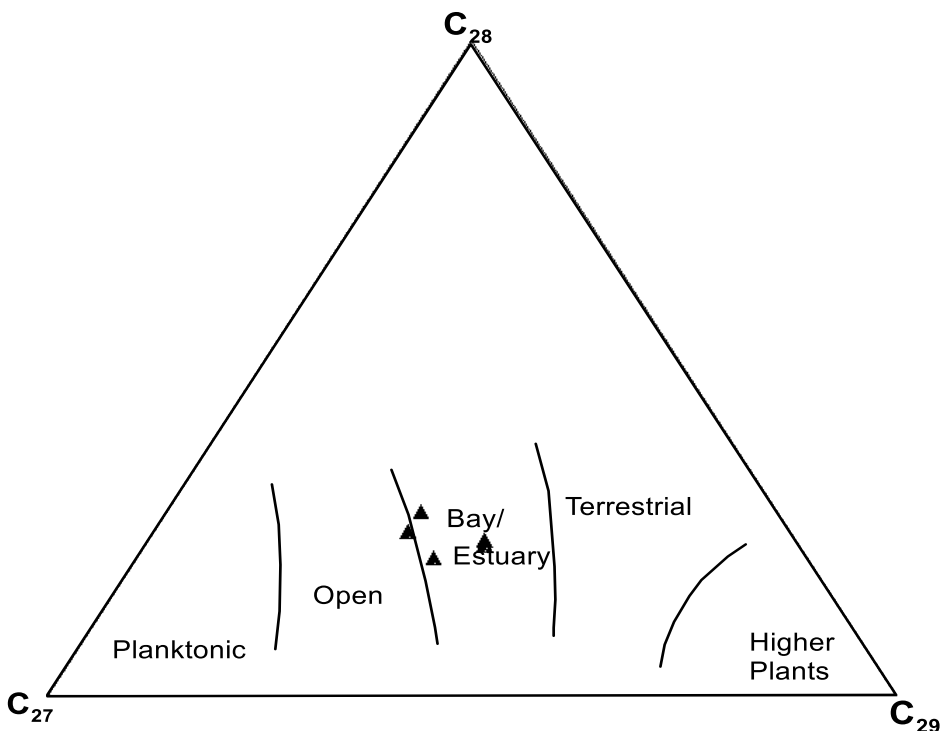

Figure 14: Ternary plot of $C_{28}\text{-}C_{27}\text{-}C_{29}$ steranes for organic matter source and paleoenvironmental interpretation (after Huang and Meinschein, 1979)

Organic richness and petroleum potential

The relative capacity of a source rock to generate petroleum depends on the kerogen's quantity expresses as Total Organic Carbon (TOC), Rock-Eval S_2 and Hydrogen Index (HI). The TOC content of the samples of Ogugu Formation (0.70 – 1.20 wt.%) with an average value of 1.01 wt.% indicating a fair-quality source rock (Peters, 1986). However, the low S_2 (< 2.5 mg HC/g Rock), HI (average < 50 mg HC/g TOC) and GP (S_1+S_2; 0.33 to 0.84 mg HC/g rock) values indicate poor potential source rock containing Type III-IV organic matter, capable of generation little gaseous hydrocarbon at the current thermal maturity level. The biomarker record of the investigated samples of Ogugu Shale have supported deposition in possibly unstable conditions of deltaic/estuarine environment which exhibited a low range of organic matter preservation and thus poor source rock potential.

Conclusion

The investigated sections of the Ogugu Shale penetrated in the Amansiodo-1 well in the Lower Benue Trough are essentially composed of bluish grey laminated shales interbedded with greyish fine grained sandy shale. The TOC and Rock-Eval pyrolysis analyses of Ogugu Shale suggest fair quality source rocks containing Type III organic matter with poor hydrocarbon potential. Source and environmental dependent biomarkers indicate that the organic matter in Ogugu Shale is derived from mixed marine plankton and terrestrial organisms deposited in deltaic environments under oxic-dyoxic conditions. Thermal maturation parameters based on Rock-Eval pyrolysis Tmax as well as molecular saturate and aromatic fraction analyses indicate that Ogugu Shale samples are thermally matured with respect to petroleum generation.

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