



Geochemistry And Depositional Environment Of Organic Matter From Oil Shale, Abakaliki Fold Belt, Southeast Nigeria.

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ABSTRACT

The organic geochemical characteristics and depositional environment of the oil shale deposits in Southeast Nigeria have been examined. Oil shales in all the studied areas are typically characterized by high hydrogen index and low oxygen index values. Abakaliki shales contain dominantly Type I and minor amounts of Type II kerogen. Gas chromatography of Abakaliki oil shales shows C₁₇ and C₁₈ n-alkanes and bimodal distribution dominated by low-number n-alkanes. pristane/phytane (Pr/Ph) ratios of the shales suggests suboxic to anoxic depositional environment Tmax values indicate that oil shales are immature. In addition to gas chromatograms, the biomarker parameters measured using m/z 217 and m/z 191 mass chromatograms indicate that the oil shales contain immature organic matter. Oleanane, a typical biomarker for marine depositional environment, has been determined in all the oil shales. When other biomarker parameters are taken into account, it is apparent that all the shale samples have been deposited in a marine environment. In general, the data obtained by geochemical analyses indicate a marine depositional environment for all of the shale samples in the studied areas.

Keywords: Organic matter, petroleum, oil shale, paleoenvironment, Lokpanta, Abakaliki Anticlinorium, Lower Benue Trough.

INTRODUCTION

The succession of the Cretaceous to recent sediments in the Benue Trough of Nigeria has attracted attention on petroleum prospects. Interest in source rock characterization has increased with the growth in development of unconventional petroleum resources (Katz and Lin, 2014), including lacustrine source rocks, which dominate the petroleum reserves in regions such as China, Indonesia, Brazil and Nigeria (Katz and Lin, 2014; Osuji, 2015; Okon and Olagunju, 2017; Omorie, 2017). An oil shale deposit, possibly of high economic value and corresponding to the Turonian Ezeaku shale (lower Nkalagu formation) of the lower Benue Trough, was found in a 1.5 x 1.0 km belt in Lokpanta near Okigwe in Imo State, Nigeria (Ekweozor and Unoma, 1990; Ehinola et al., 2005). With the discovery of the Mid-Cretaceous oil shale deposits in the Lower Benue Trough and Abakaliki Anticlinorium, the reserves of shale oil in Nigeria provide a substantial potential energy outlook for the country. Through the chemical processes of extraction, isolation, and characterization, the kerogen of the oil shales has been shown to be of Type I – II (Oil-Prone), and of intermediate thermal maturity status. Further appraisal of the economic potential of the fossil fuel deposits by pyrolysis (modified Fischer Assay), indicated an average oil-yield of more than 42 liters tonne⁻¹, which is the lower acceptable threshold for economic exploitation (Ekweozor and Unomah, 1990; Ehinola et al., 2005; Grow, 1980).

With a reserve-to-production ratio of 42 years for crude oil, Nigeria has a significant oil shale potential (Osuji, 2015). The most important oil shale deposits are located in Lokpanta (Okigwe) and Abakaliki anticlinorium (Fig. 1). The deposits are characterized by the following values for oil shale sequence thickness (m) and reserves (million tonnes): at an average of 2.2 million barrels of oil per day, Nigeria has a reserve-to-production ratio of 42 years for oil and 152 years for gas (Osuji, 2012) respectively. These oil shale deposits have been studied by numerous researchers. Geologic, geochemical and economic investigations of these fields have been conducted (Şener et al., 1994; 1994; Gülbay and Korkmaz, 2008; Fu et al., 2009; Zeng et al., 2011).

Geological and economic features of oil shale fields have been studied separately. The objectives of this study is to characterize organic geochemical (organic material content, maturity, type and biomarker distribution) of oil shale deposits, determine its depositional environments and hydrocarbon potentials.

Regional Geological Setting

The Abakaliki anticlinorium, which is one of the depocenters in the lower Benue Trough, contains approximately 3600 m thick sediments. The studied mid-Cretaceous Lokpanta oil shale is located within the area of latitudes 5°24'17" to 6°30'35"N and longitudes 7°00'18" to 8°05'53"E (Fig. 1). The tectonism in Southern Nigeria probably started in Early Cretaceous, with the separation of Africa from South America due to the opening of the Atlantic. This resulted in the development of the Benue Trough which stretched in a NE-SW direction (Fig. 1), resting unconformably upon the Pre-Cambrian basement complex.

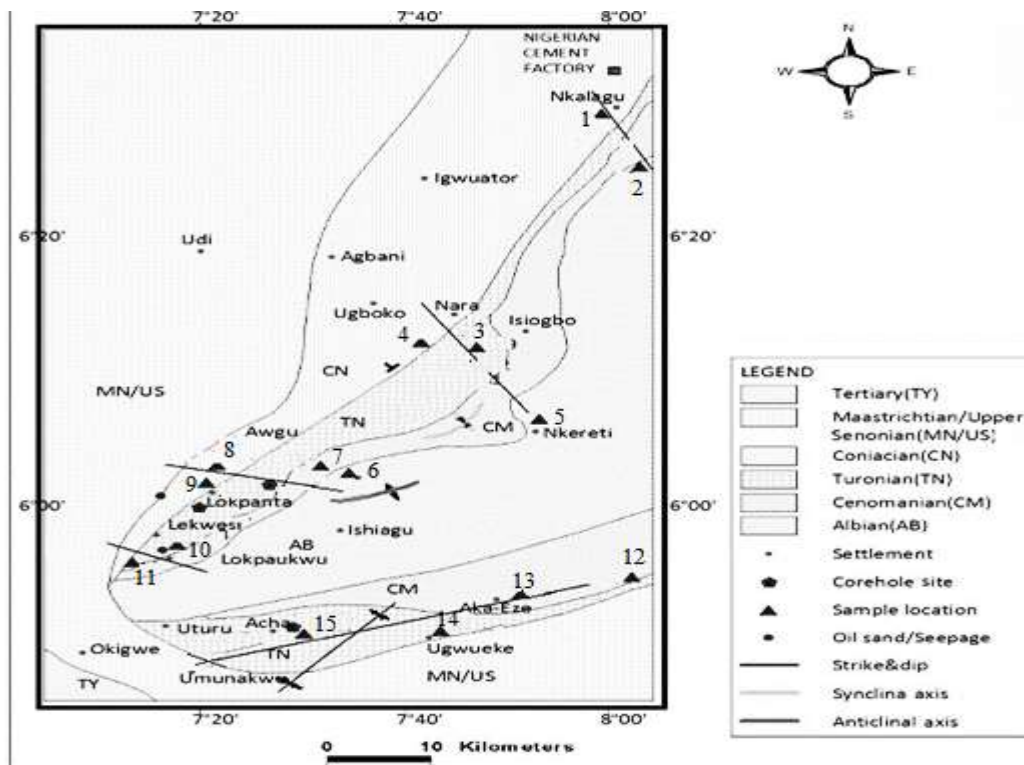


Fig. 1. Geological map of the lower Benue Trough, SE Nigeria (Modified from Ehinola, 2002).

It extends from the Gulf of Guinea to the Chad Basin and is thought to have been formed by the Y-shaped (RRR) triple junction ridge system that initiated the breaking up and dispersion of the Afro-Brazilian plates in Early Cretaceous (Kogbe, 1989). After the evolution of the Benue Trough, sediments started depositing in the Trough. Stages of sedimentations in the trough were in three cycles; the Pre-Cenomanian deposit of Asu River Group followed by the Cenomanian-Santonian sedimentation.

According to Hogue (1977) the inversion tectonics of the Abakaliki anticlinoria which led to the evolution of both Afikpo Syncline and Anambra basin, represented the third cycle of sedimentation which produced the incipient Nkporo shale, Enugu shale and Owelli sandstone. The Nkporo group is overlain conformably by the Coal Group consisting of the Mamu, Ajali and Nsukka Formations that form the terminal units of the Cretaceous series.

AGE	SEDIMENTARY SEQUENCE	LITHOLOGY	DESCRIPTION	DEPOSITIONAL ENVIRONMENT	REMARKS		
					Coal Rank	ANKPA SUB-BASIN	ONITSHA SUB-BASIN
MIocene OLIGOCENE	OGWASHI-ASABA FM.		Lignites, peels, intercalations of Sandstones & shales	Estuarine (off shore bars, intertidal flats)	Lignite		REGRESSION (Continued transgression Due to postglacial Sea level rise)
EOCENE	AMEKE/NANKA FM. SAND		Clays, shales, Sandstone & beds of grits	Sub tidal, intertidal flats, shallow marine	Unconformity		
PALEOCENE	IMO SHALE		Clays, shales & siltstones	Marine		(? MINOR REGRESSION	TRANSGRESSION (Global sea level Rise plus crustal Movement)
MAASTRICHTIAN	NSUKKA FM.		Clays, shales, thin sandstones & coal seams	Estuarine	Sub-bituminous	↑	
	AJALI SST.		Coarse sandstones, Lenticular shales, beds of grits & pebbles.	Subtidal, shallow marine			
	MAMU FM.		Clays, shales, carbonaceous shale, sandy shale & coal seams	Estuarine/ off-shore bars/ tidal flats/ chenier ridges	Sub-bituminous		
CAMPANIAN	ENUGU/ NKPORO SHALE		Clays & shales	Marine	3 rd Marine cycle	Unconformity	2 nd Marine cycle
CONIACIAN-SANTONIAN	AWGU SHALE		Clays & shales	Marine			
TURONIAN	EZEAKU SHALE					Unconformity	1 st Marine cycle
CENOMANIAN	ODUKPANI FM.					Unconformity	
ALBIAN	ASU RIVER GP.					Unconformity	
L. PALEOZOIC	B A S E M E N T C O M P L E X						

Fig. 2: The stratigraphy of the Anambra Basin southeastern Nigeria (Modified Uzoegbu et al., 2015).

Stratigraphic Setting

The sandstones which is about 330 m thick is an extensive stratigraphic unit conformably overlying the Lower Coal Measure (Mamu Formation) and Nkporo Formations that are 400 and 200 m thick, respectively and underlying the Upper Coal Measure (Nsukka Formation) in the Maastrichtian (Reyment, 1965; Nwajide, 1990) (Fig. 2). The Ajali Formation is typically characterized by white coloured sandstone (Reyment, 1965) while the Mamu Formation is essentially composed of sandy shale and some coal seams; the Nkporo Formation consists mainly of grey - blue mudstone and shale with lenses of sandstone (Obaje, 2009). According to Reyment (1965), the prevailing unit of Ajali Formation consists of thick, friable, poorly sorted sandstone.

MATERIALS AND METHODS

Sampling

Ehinola et al. (2005) examined the geologic mapping and Rock Eval characteristics of 17 samples of the Lokpanta oil shale recovered from drilling/coring. The studied drill-core samples are taken from sites located near the towns of Lokpanta, Onoli-Awgu and Acha (Fig. 1). A total of 15 samples were collected from the section.

Twelve of them were collected from oil shale seams with a vertical sampling interval of 1 m on average, and the other three samples were collected from micritic limestone layers. The present-day burial depth of the samples is about 50 cm.

The samples for geochemical analysis and Rock-Eval pyrolysis were all crushed and ground to 120 mesh. Total organic carbon (TOC) and Rock- Eval pyrolysis were determined using a TOC module-equipped

Rock-Eval VI type instrument. About 100 mg of sample was heated from ambient temperature up to 600 °C in a helium atmosphere (Fu et al., 2009). Analyzed samples were extracted with chloroform in a Soxhlet apparatus for 72 h. Extracts were separated into saturated hydrocarbons, aromatic hydrocarbons and polar NSO fractions by column chromatography using a silica gel-alumina column after the precipitation of asphaltenes (Fu et al., 2009).

Table 1: Peak definitions of steranes of m/z 217 mass chromatograms of the Abakaliki oil shale.

Peak No	Compound
1	C ₂₇ 13β(H),17α(H)-Diasterane (20S)
2	C ₂₇ 13β(H),17α(H)-Diasterane (20R)
3	C ₂₇ 13α(H),17β (H)-Diasterane (20S)
4	C ₂₇ 13α(H),17β (H)-Diasterane (20R)
5	C ₂₈ 13β(H),17α(H)-Diasterane (20S)
6	C ₂₈ 13β(H),17α(H)-Diasterane (20R)
7	C ₂₈ 13α(H),17β (H)-Diasterane (20S)
8	C ₂₇ 5α(H),14α(H),17α(H)- Sterane (20S)+ C ₂₈ 13α(H),17β (H)-Diasterane (20S)
9	C ₂₇ 5α(H),14 β(H),17β(H)- Sterane (20R)+ C ₂₉ 13β (H),17α(H)-Diasterane (20S)
10	C ₂₇ 5α(H),14 β(H),17β(H)- Sterane (20S)+ C ₂₈ 13α(H),17β(H)-Diasterane (20R)
11	C ₂₇ 5α(H),14α(H),17α(H)- Sterane (20R)
12	C ₂₉ 13β(H),17α(H)-Diasterane (20R)
13	C ₂₉ 13α(H),17β (H)-Diasterane (20S)
14	C ₂₈ 5α(H),14α(H),17α(H)- Sterane (20S)
15	C ₂₈ 5α(H),14β(H),17β(H)-Sterane (20R)+ C ₂₉
16	C ₂₈ 5α(H),14 β(H),17β(H)- Sterane (20S)
17	C ₂₈ 5α(H),14α(H),17α(H)- Sterane (20R)
18	C ₂₉ 5α(H),14α(H),17α(H)- Sterane (20S)
19	C ₂₉ 5α(H),14 β(H),17β(H)- Sterane (20R)
20	C ₂₉ 5α(H),14 β(H),17β(H)- Sterane (20S)
21	C ₂₉ 5α(H),14α(H),17α(H)- Sterane (20R)
22	C ₃₀ 5α(H),14α(H),17α(H)- Sterane (20S)

Table 2: Peak definitions of triterpanes of m/z 191 mass chromatograms of the Abakaliki oil shale.

Peak No	Compound
1	C ₁₉ Tricyclic Terpane
2	C ₂₀ Tricyclic Terpane
3	C ₂₁ Tricyclic Terpane
4	C ₂₂ Tricyclic Terpane
5	C ₂₃ Tricyclic Terpane (18,19-Bisnor-13β(H),14α(H) Cheilanthaneane)
6	C ₂₄ Tricyclic Terpane
7	C ₂₅ (22S+22R) Tricyclic Terpane
8	Tetracyclic Hopane (Secohopane)
9	C ₂₆ 22(S) Tricyclic Terpane
10	C ₂₆ 22(R) Tricyclic Terpane
11	C ₂₈ Tricyclic Terpane
12	C ₂₉ Tricyclic Terpane
13	C ₂₇ 18α(H)-22,29,30-Trisnorneohopane (Ts)
14	C ₂₇ 17α(H)-22,29,30-Trisnorhopane (Tm)
16	C ₃₀ Tricyclic Terpane
18	C ₂₉ 17α(H),21β(H)-30-Norhopane
19	C ₂₉ Ts (18α(H)-30-Norneohopane
21	C ₂₉ 17β(H),21α(H)-30-Normoretane
22	Oleanane
23	C ₃₀ 17α(H),21β(H)- Hopane
24	C ₃₀ 17β(H),21α(H)-Moretane
25	C ₃₁ 17α(H),21β(H)-30-Homohopane (22S)
26	C ₃₁ 17α(H),21β(H)-30-Homohopane (22R)
27	Gammacerane
28	Homomoretane
29	C ₃₂ 17α(H),21β(H)-30,31-Bishomohopane (22S)
30	C ₃₂ 17α(H),21β(H)-30,31-Bishomohopane (22R)
31	C ₃₃ 17α(H),21β(H)-30,31,32-Trishomohopane (22S)
32	C ₃₃ 17α(H),21β(H)-30,31,32-Trishomohopane (22R)
33	C ₃₄ 17α(H),21β(H)-30,31,32,33-Tetrakishomohopane (22S)
34	C ₃₄ 17α(H),21β(H)-30,31,32,33-Tetrakishomohopane (22R)
35	C ₃₅ 17α(H),21β(H)-30,31,32,33,34-Pentakishomohopane (22S)
36	C ₃₅ 17α(H),21β(H)-30,31,32,33,34-Pentakishomohopane (22R)

Saturated fractions were analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). An aliquot of each saturated fraction was separated into *n*-alkanes and branched/cyclic alkanes by urea adduction.

The GC-MS analysis was performed using a Finnigan Voyager gas chromatography/mass spectrometer. This instrument was equipped with a DB5-MS fused silica capillary column of 30-m length, 0.25-μm film thickness and 0.32-mm inner diameter. Helium was used as the carrier gas. For routine GC analysis, the oven was isothermally held for 1 min at 35 °C, programmed from 35 to 120 °C at 10 °C/min, then from 120 to 300 °C at 3 °C/min, with a final holding time of 30 min (Xiong and Geng, 2000; Qian et al., 2008). The MS was operated with an ionization energy of 70 eV and a source temperature of 200 °C (Xiong and Geng, 2000; Fu et al., 2009; Fu et al., 2010).

For the analysis of biomarkers, metastable ion transition for sterans (m/z 217) and triterpanes (m/z 191) was recorded at a dwell time of 25 ms per ion and a cycle time of 1 s. Compounds were identified through retention time. Triterpane and sterane distributions were quantified by measuring peak heights in the m/z 191 and m/z 217 chromatograms for saturated hydrocarbons, respectively. The peaks recorded in chromatograms are defined in Tables 1 and 2.

RESULTS AND DISCUSSION

Total organic carbon (TOC) and Rock-Eval pyrolysis

The total organic carbon (TOC) average value of the Abakaliki oil shale samples 7.05wt.%, (Table 3). The TOC values of the Abakaliki oil shale samples show a large variation. On the other hand, the samples from the other areas show a more or less homogenous TOC distribution.

Hydrogen index (HI) value obtained from Rock-Eval analysis are exceptionally high, but oxygen index (OI) values are low as it is expected in oil shale samples. The average HI value of Abakaliki oil shales is 740mg HC/g TOC, and their average OI value is 36.33mg CO₂/g TOC.

S₁, S₂ and S₃ values are also measured by using a Rock-Eval analyzer. The ratio of S₂/S₃ gives an idea about the kerogen type (Gülbay and Korkmaz, 2008; Uzoegbu and Onwualu-John, 2023). Potential yield (PY) (S₁+S₂) values are the reflection of hydrocarbon potential of a rock sample, and finally production index (PI) [S₁/(S₁+S₂)] ratio is used for maturity evaluation. In the studied samples, generally, S₂/S₃ ratios and PY values are relatively high and PI are low (Table 3).

The Tmax values, which are measured by the Rock-Eval analyzer and show the maturity level of the organic matter are, on average of 433.02 °C for the Abakaliki oil shale samples (Uzoegbu and Onwualu-John, 2023).

Table 3: Results of Rock-Eval/TOC analyses Abakaliki oil shale samples.

Sample No.	Lithology	TOC (wt.%)	S ₁ (mgHC/g rock)	S ₂ (mgHC/g rock)	S ₃ (mgCO ₂ /g rock)	Kerogen Type S ₂ /S ₃	(PY) (S ₁ +S ₂) (mgHC/g rock)	(PI) S ₁ /(S ₁ +S ₂)	Tmax (°C)	(HI) S ₂ /TOC (mgHC/g TOC)	(OI) S ₃ /TOC (mgCO ₂ /g TOC)	Residual Carbon
OSH-1	Oil Shale	3.02	1.43	19.51	1.96	9.95	20.94	0.07	430.00	646.00	64.00	1.28
OSH-2	"	5.85	1.89	45.54	21.18	20.89	47.43	0.04	436.00	778.00	37.00	1.90
OSH-3	"	11.64	2.60	87.37	4.37	19.99	89.97	0.03	433.00	750.00	37.00	4.15
OSH-4	"	10.61	3.32	70.57	4.55	15.51	73.89	0.04	433.00	807.00	26.00	10.46
OSH-5	"	28.14	15.73	194.93	8.15	23.92	210.66	0.07	424.00	692.00	28.00	10.59
OSH-6	"	2.04	0.94	12.54	0.93	13.48	13.48	0.07	427.00	614.00	45.00	0.92
OSH-7	"	2.53	0.23	18.66	0.87	21.45	18.89	0.01	442.00	737.00	34.00	0.96
OSH-8	"	8.26	1.06	62.96	1.49	42.26	64.02	0.02	441.00	762.00	18.00	2.93
OSH-9	"	6.48	2.27	58.88	1.12	52.57	61.15	0.04	440.00	908.00	17.00	1.39
OSH-10	"	3.84	0.46	13.64	1.34	10.18	14.10	0.03	427.00	355.00	34.00	2.67
OSH-11	"	5.36	2.80	50.52	1.81	27.91	53.32	0.05	437.00	942.00	33.00	0.92
OSH-12	"	3.21	0.63	23.46	1.60	14.66	24.09	0.03	432.00	730.00	49.00	1.21
OSH-13	"	2.54	0.77	20.36	0.77	26.44	21.13	0.04	428.00	801.00	30.00	0.78
OSH-14	"	2.06	0.53	14.00	1.38	10.14	14.53	0.04	426.00	679.00	66.00	0.85
OSH-15	"	10.16	3.56	92.04	2.82	32.64	95.60	0.04	442.00	905.00	27.00	2.20
Average		7.05	2.55	52.33	3.62	22.80	54.88	0.041	433.20	740.40	36.33	2.88

Composition

The extraction analysis is performed on 12 samples selected from different areas. Total bitumen amounts are divided according to TOC values which indicate expulsion efficiency, and maturity of the samples is generally low (varies from 0.024 to 0.073). Only the value from the OSH-11 oil shale sample (0.116) is relatively high compared to the other samples (Gülbay and Korkmaz, 2008; Uzoegbu and Onwualu-John, 2023).

n-Alkanes and isoprenoids

Only C₁₇ and C₁₈ *n*-alkanes are recorded in the gas chromatograms of the Abakaliki oil shale samples (Fig. 3). Isoprenoids are dominant in the gas chromatograms. High peak intensity is observed in the biomarker region.

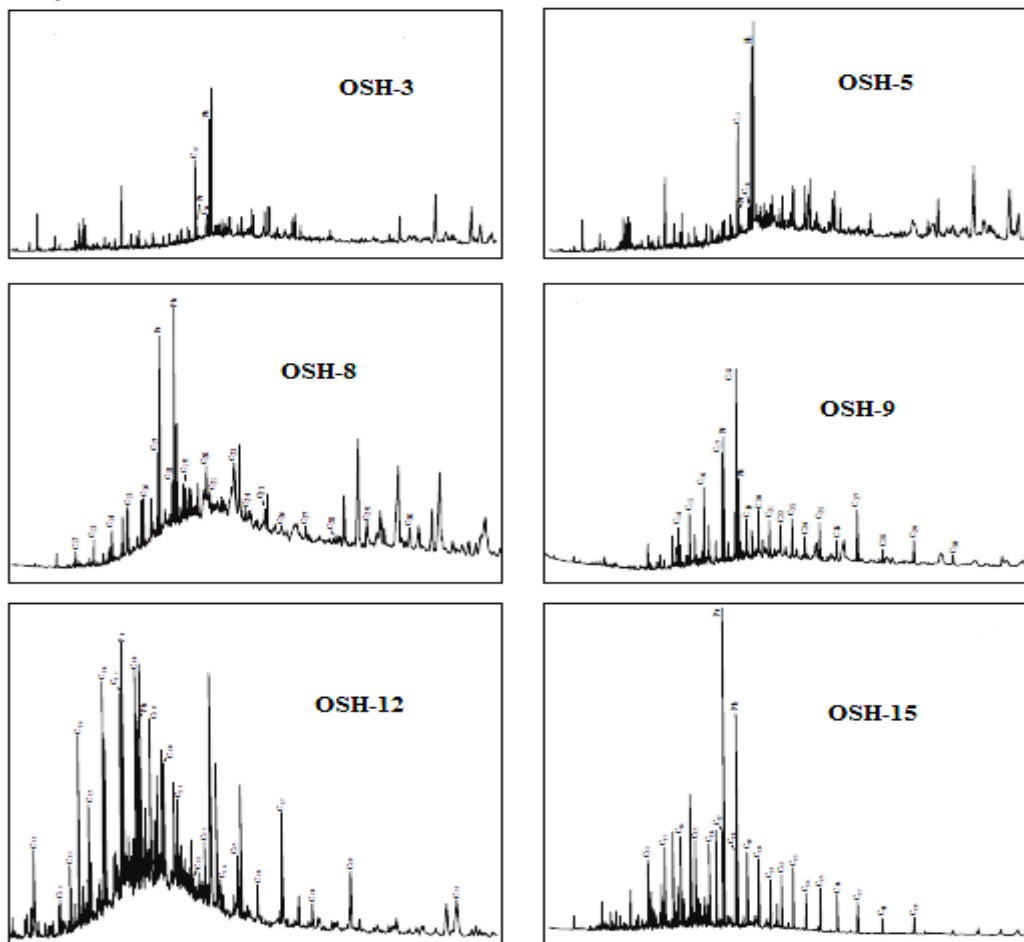


Fig. 3: Gas chromatograms of the Abakaliki oil shale samples.

A bimodal distribution, where the *n*-alkanes with low carbon number are dominant, is generally observed in the gas chromatograms of the extracts obtained from the oil shale samples (Fig. 3). Gas chromatograms of the oil shale extracts show a bimodal distribution where C₁₈ and C₂₃ are the center, the maximum peak belonging to C₁₈ *n*-alkane. C₁₇ is the maximum *n*-alkane peak in the gas chromatograms from the oil shales, and a bimodal distribution with C₁₇ and C₂₃ in the center is observed (Uzoegbu and Onwealu-John, 2023). The *n*-alkanes are the dominant peaks in the gas chromatograms from the oil shale samples, and isoprenoids are widely observed (Fig. 3). The *n*-alkanes are the dominant peaks in the gas chromatograms from the oil shale samples (Fig. 3).

The Carbon Preference Index (CPI) values are calculated in C₂₄-C₃₄ $\{[(C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{26} + C_{28} + C_{30} + C_{32} + C_{34}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33}) / (C_{24} + C_{26} + C_{28} + C_{30} + C_{32})] / 2\}$ and C₂₂-C₃₀ $\{2(C_{23} + C_{25} + C_{27} + C_{29}) / [C_{22} + 2(C_{24} + C_{26} + C_{28}) + C_{30}]\}$ (Peters and Moldowan, 1993) ranges from the gas chromatograms of the oil shale samples and these CPI values are 1.36, 1.31; 1.76, 1.68; 2.29, 1.48 and 3.60, 1.55, respectively. CPI values are evidently higher than 1.0 for all oil shale samples, which means that the odd number *n*-alkanes are dominant (Seifert and Moldowan, 1978; 1980; Gülbay and Korkmaz, 2008; Uzoegbu and Onwualu-John, 2023).

The pristane/phytane (Pr/Ph) ratios calculated for the oil shale samples are 0.14; 0.17; 1.47; 0.93; 1.54 and 1.52, respectively.

Biomarkers

The m/z 217 and m/z 191 mass chromatograms showing the sterane and triterpane distributions in the oil shale samples from different areas are presented in Figs. 4 and 5; the peaks recorded in chromatograms are defined in Tables 1 and 2.

Many biomarker parameters, which are used to find different characteristics of the organic matter, are obtained by using the sterane and triterpane distributions (Table 4). In general, when the sterane distributions belonging to different areas are studied, it is observed that C_{29} is the dominant sterane in the OSH-3 and OSH-5 oil shales. As for the OSH-7 and OSH-8 oil shales, C_{27} is observed as a dominant sterane, but C_{29} sterane shows values close to C_{27} . Considering that C_{27} steranes are recorded together with diasteranes in m/z 217 mass chromatograms, it can be concluded that C_{29} sterane is probably a little bit more dominant in these OSH-3 and OSH-5 oil shales. Traces of C_{30} sterane are recorded only for the OSH-10 oil shales (Fig. 4), as for the m/z 217 mass chromatograms from the other shales, C_{30} sterane is not recorded (Gülbay and Korkmaz, 2008; Zeng et al., 2011; Uzoegbu and Onwualu-John, 2023). While the isosteranes are dominant in comparison to the normal and rearranged steranes in the Abakaliki oil shales, very high ratios of the normal steranes and rather low ratios of the rearranged steranes characterize the Abakaliki oil shales. The diasterane/sterane ratios are generally very low (Table 4). Diasteranes are widely observed only in the Abakaliki oil shales.

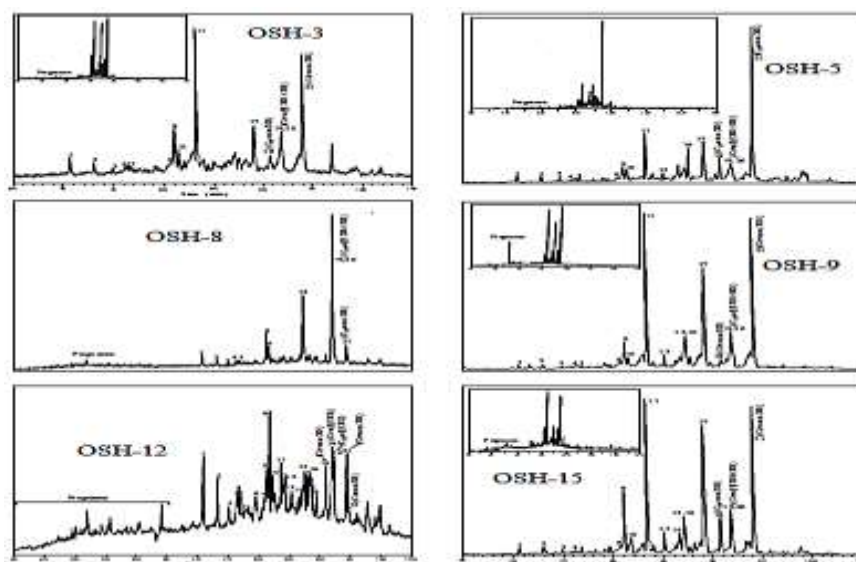


Fig. 4: The m/z 217 mass chromatograms of the Abakaliki oil shales (for peak definition see Table 1).

The m/z 191 mass chromatograms of oil shales from all areas show low concentrations of tricyclic terpane. T_m (C_{27} $17\alpha(H)$ -22,29,30-trisnorhopane) is more dominant than T_s (C_{27} $18\alpha(H)$ -22,29,30-trisnorneophane) in all oil shale samples. The OSH-10 oil shale sample contains more C_{29} norhopane than C_{30} hopane, and C_{30} hopane is more dominant in the samples of the other two locations. Low amounts of the oleanane are recorded in the oil shales with high ratios of gammacerane detected in the samples (Fig. 5). In general, a homohopane distribution where C_{31} is dominant is observed in all oil shale samples (except OSH-15 where C_{32} dominates) (Fig. 6). Homohopane distribution typical of OSH-3, OSH-8 and OSH-12 oil shales decreases smoothly towards higher numbers. C_{35} homohopane indexes and C_{35}/C_{34} homohopane ratio for the oil shale samples are 15 and 0.91, (Gülbay and Korkmaz, 2008; Uzoegbu and Onwualu-John, 2023) respectively.

Table 4: Biomarker parameters calculated from m/z 217 and m/z 191 mass chromatograms

PARAMETERS	RESULTS
$C_{35}/(C_{31}-C_{35})$ Homohopane Index	15%
C_{35}/C_{34} Homohopane Ratio	0.91
C_{25}/C_{26} Tricyclic Terpane Ratio	0.82
Gammaceran Index [Gammacerane/ C_{30} Hopane]	0.48
Oleanane Index [(Oleanane/ C_{30} Hopane)x100]	14%
C_{29}/C_{30} Hopane Ratio	0.34
C_{27}, C_{28}, C_{29} (Sterane Percent)	37, 28, 35%
Normal-sterane, Isosterane, Rearranged-sterane	44, 43, 13%
Diasterane/Sterane Ratio	8.50
Sterane/Hopane Ratio 20S/(20S+20R)	2.49
Sterane Ratio (C_{29}) $\beta\beta/(\beta\beta+\alpha\alpha)$	0.19
Sterane Ratio (C_{29}) 22S/(22S+22R)	0.19
Homohopane Ratio (C_{31})	0.36
Ts/(Ts+Tm)	0.21
Moretane/Hopane Ratio	0.22

Type of organic matter

The type of organic matter in a rock sample can be determined by using the results of pyrolysis, GC and GC/MS. Kerogen types of the oil shale samples are determined by using S_2 -TOC (Langford and Blanc-Valleron, 1990), HI-Tmax (Mukhopadhyay et al., 1995) and HI-OI (Espitalie et al., 1977; Gülbay and Korkmaz, 2008; Uzoegbu and Onwualu-John, 2023) kerogen classification diagrams (Figs. 7 and 8).

In the S_2 -TOC diagram, the Abakaliki oil shale samples are plotted in the Type I-II area (Fig. 7). In the HI-Tmax and HI-OI diagrams, the samples taken from all the locations generally in the Type I area, and only one sample from each of the locations in the Type II area (Fig. 8). Accordingly, it is found that the oil shales generally contain Type I kerogen, only in some samples of oil shales contain very low ratios of Type II kerogen. Type I kerogen characteristics of all the oil shales imply that they dominantly contain algal (lacustrine) organic matter. The presence of small amounts of Type II kerogen in the Abakaliki oil shales is probably caused by spores and pollen of land plants and their leaf and stem cuticles.

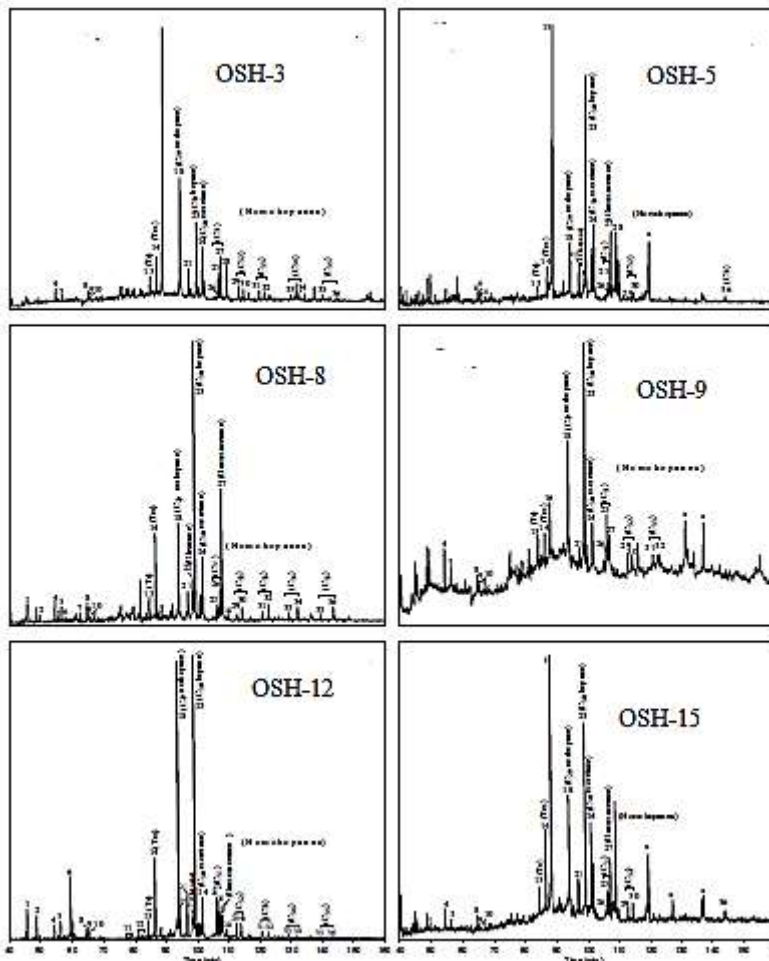


Fig. 5: The m/z 191 mass chromatograms of the Abakaliki oil shales (for peak definition see Table 2).

Bimodal distribution where the low number *n*-alkanes are dominant is observed in the gas chromatograms of the Abakaliki oil shale samples. Such a distribution shows the addition of very little amounts of terrestrial organic matter with algal dominance (Tissot and Welte, 1984; Waples, 1985). Furthermore, the oleanane recorded in m/z 191 mass chromatograms indicates contribution of organic matter from angiosperms of Cretaceous and younger higher plants (Ekweozor and Udo, 1988; Riva et al., 1988; Waples and Machihara, 1991; Peters et al., 2004; Hunt, 1995). Oleanane is detected in the Abakaliki oil shales (Fig. 5) and the oleanane indices calculated are 14% respectively. These values show that, according to Hunt's (1995) classification, the Abakaliki oil shales contain a little input of terrestrial organic matter. The fact that the oleanane is not recorded in the m/z 191 mass chromatograms of the other shale samples does not indicate that there is no terrestrial input (Liu et al., 2009; Fu et al., 2010; Uzoegbu and Onwualu-John, 2023). The sterane/hopane ratio gives an idea about the organic matter input. Steranes originate mainly from algae and higher plants, and hopanes originate from the cell material of bacteria (Peters et al., 2004). The sterane/hopane ratio calculated for the Abakaliki oil shales is 2.49. This value shows the presence of algal organic matter and dominance of the sterane for the other locations of oil shale samples. Abundance of hopane in the oil shale samples shows the dominance of bacterial organic matter compared to its content of the other oil shales. In general, Type I kerogen characteristic of these oil shales, bimodal *n*-alkane distribution where the low carbon number alkanes are more abundant, and the other biomarker data indicate the dominance of algal organic matter and low inputs of bacterial and terrestrial organic matter.

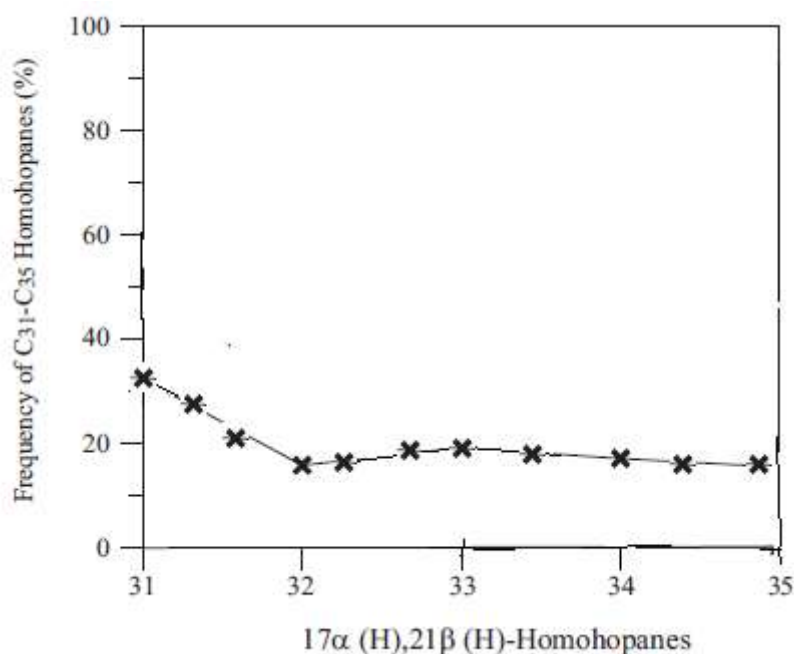


Fig. 6: C₃₁-C₃₅ homohopane distributions (%) for the Abakaliki oil shale samples.

Maturity of organic matter

The maturity of the organic matter is determined by the creation process of hydrocarbon compounds through undergoing physical and chemical changes by different agents like heat, pressure, burial and time after deposition in a sedimentary basin (Tissot and Welte, 1984). Thermal history of the organic matter changes many of its physical and chemical characteristics, and the maturity of the organic matter can be measured by making use of these characteristics. In this work, the maturity of the kerogen is interpreted by using the results of pyrolysis, GC and GC/MS analysis (Seifert and Moldowan, 1978; 1980).

It is found that the Tmax value measured during the pyrolysis and the calculated PI values are closely related to thermal history of the organic matter (Tissot and Welte, 1984; Waples, 1985). The average Tmax values calculated for the Abakaliki oil shales is 433.20 °C. This value show that the oil shales, except some are characterized by low Tmax values and show immature characteristics. The average Tmax value of 433.20 °C characterizing the Abakaliki oil shales generally reflects the character of early maturity, and it corresponds to the maturity at the entrance into oil generation window (Gülbay and Korkmaz, 2008; Peters and Moldowan, 1993; Uzoegbu and Onwualu-John, 2023).

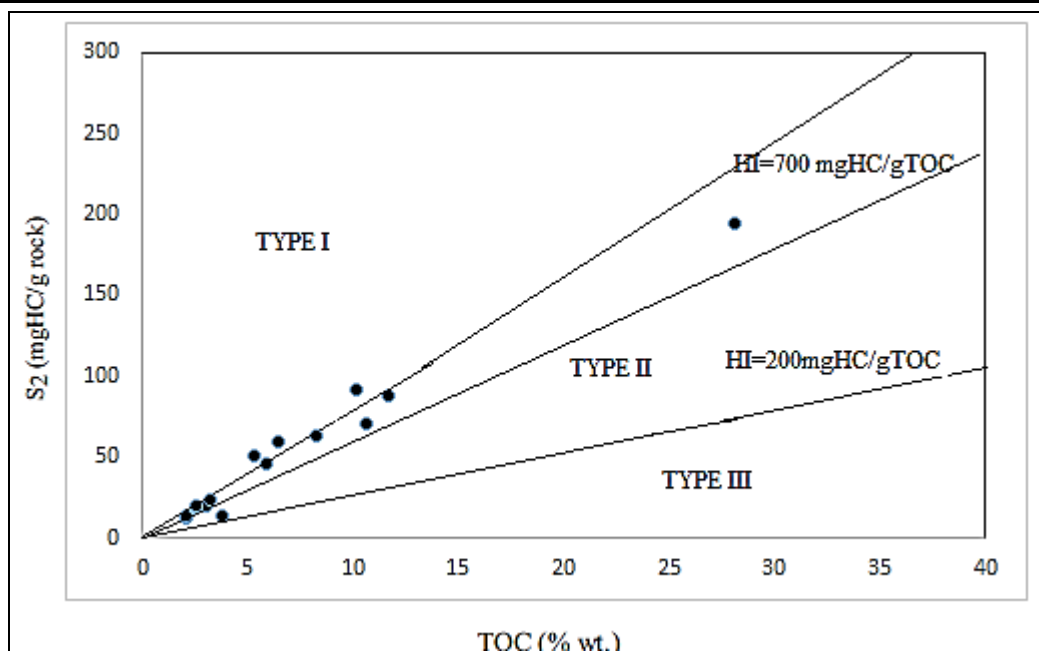


Fig. 7: Distribution of the oil shale samples in S_2 vs total organic carbon (TOC) diagram.

However, considering that these oil shales contain Type I kerogen, it becomes clear that this T_{max} value is not sufficient for oil generation (Tissot and Welte, 1984), and it reflects immaturity. The PI values of all oil shales are quite low (Table 3), corresponding to the immature character in the maturity classification made by the Production Index (Merrill, 1991; Fu et al., 2010). Average value of the bitumen/TOC ratio, calculated for the Abakaliki oil shales, 0.041, also reflect their immaturity. Isoprenoids dominate in the gas chromatograms and they are also widespread in the Abakaliki oil shales (Fig. 3). High concentrations observed in the biomarker region of the gas chromatograms of the Abakaliki oil shales (Fig. 3) show also low maturity. Furthermore, CPI values which are evidently higher than 1.0 for the Abakaliki oil shales result from their low maturity degree (Hunt, 1995; Peters and Moldowan, 1993; Zeng et al., 2011).

The $20S/(20S+20R)$ sterane ratio increases with increasing maturity degree (Waples, 1991; Peters and Moldowan, 1993; Mackenzie et al., 1980; Spiro, 1984; Seifert and Moldowan, 1981; 1986). This ratio could not be determined for the Abakaliki oil shale samples, due to quite low values that have not reached equilibrium value yet (Table 4). Another maturity parameter calculated using the sterane data is the $\beta\beta/(\beta\beta+\alpha\alpha)$ ratio, and this ratio increases with increasing maturity (Waples, 1995; Waples and Machihara, 1991; Mackenzie et al., 1980; Spiro, 1984; Uzoegbu and Onwualu-John, 2023). This ratio is very low values therefore characterize the organic matter in the area as calculated (Table 4). The transformation has not reached the equilibrium in the area. These two ratios calculated for steranes also reflect immaturity of all oil shales.

The $22S/(22S+22R)$ homohopane ratio increases with maturity (Waples and Machihara, 1991; Hunt, 1995). The equilibrium value for the homohopane ratio is measured to be 0.57-0.62 (Seifert and Moldowan, 1986; Uzoegbu and Onwualu-John, 2023). This ratio, which has not reached the equilibrium value for all the samples, reflects the immature characteristics of Turkish oil shales (Gülbay and Korkmaz, 2008).

The $T_s/(T_s+T_m)$ ratio also increases in proportion with maturity (Hunt, 1995; Seifert and Moldowan, 1978), but the moretane/hopane ratio decreases (Kvenvolden and Simoneit, 1990; Grantham, 1986). In general, all the oil shale samples are immature enough, according to their low $T_s/(T_s+T_m)$ ratio and the moretane/hopane ratio exceeding 0.15 (Waples and Machihara, 1991; Uzoegbu and Onwualu-John, 2023). The maturity data obtained indicate that all the oil shales are immature.

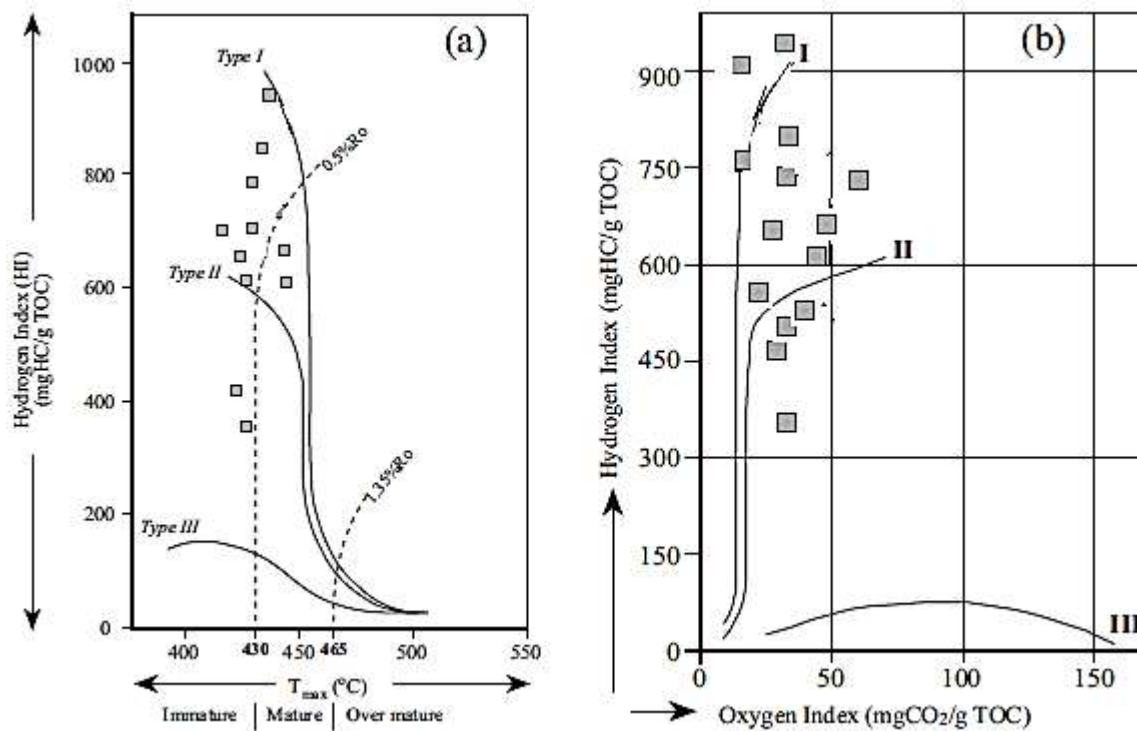


Fig. 8: Distribution of the oil shale samples in HI vs Tmax (a) and HI vs OI (b) diagrams.

Depositional environment

Depositional environments of oil shales are interpreted by using the data of the organic geochemical analyses. Biomarkers provide information about the type of the environment where the organic matter deposits, the conditions existing in the depositional environment during the deposition and the lithology of the rock in which the organic matter is present. The $17\alpha(H)$ -homohopane distributions change extensively from sample to sample and provide information about the paleoenvironment (Waples and Machihara 1991; Wang and Philp, 1997; Gülbay and Korkmaz, 2008; Seifert and Moldowan, 1978; 1980). A homohopane distribution with the dominance of low-number homologues is observed in the m/z 191 mass chromatograms of the oil shale samples (Fig. 4, 6), and homohopane index is very low for all the oil shale samples (Table 4). Such a homohopane distribution with low C_{35} homohopane index values generally corresponds to a suboxic depositional environment (Hunt, 1995). Furthermore, the homohopane distributions, which have a regular decrease in the peak height from C_{31} to C_{35} , especially in the Abakaliki oil shales, indicate clastic facieses (Waples and Machihara 1991). The Pr/Ph ratio reflects the redox potential of the depositional environment (Peters and Moldowan, 1993; Didyk et al., 1978; Uzoegbu and Onwualu-John, 2023). The Pr/Ph ratio calculated for the Abakaliki oil shales is 0.93. It is evident that some oil shales having a Pr/Ph ratio lower than 1.0 have been deposited in an anoxic environment. The homohopane and Pr/Ph data evaluated together indicate that the Abakaliki oil shales are the products of a suboxic depositional environment.

The C_{29}/C_{30} hopane ratio is used to distinguish the carbonate and clastic lithology (Waples and Machihara 1991; Riva et al., 1989; Uzoegbu and Onwualu-John, 2023). The ratios measured for the Abakaliki oil shales is 0.34 and this value indicate clastic rocks. The C_{29}/C_{30} ratio higher than 1.0 characterizing oil shales shows that they contain much carbonate components; this conclusion concurs with the fact that the some oil shale samples contain actually marl as has been indicated in literature many times.

Gammacerane, which is a typical biomarker for the lake and sea sediments of high salinity (Waples and Machihara, 1991; Hunt, 1995; Peters and Moldowan, 1991; Connan, 1993), is recorded in in medium to higher abundances for the Abakaliki oil shales. The gammacerane index characterizing these shales is

0.48. Furthermore, the pregnanes that are another indicator of salinity are present in low to medium amounts Abakaliki oil shales, and in abundance in some samples of the oil shales (Fig. 3). The presence of both gammacerane and pregnane shows that all the oil shales have been deposited in a saline environment (Gülbay and Korkmaz, 2008; Uzoegbu and Onwualu-John, 2023).

The C_{25}/C_{26} tricyclic terpane ratio is used to distinguish the marine and non-marine environments (Burwood et al., 1992; Hanson, 1999; Hanson, 2000). The values higher than 1.0 indicate a marine environment, whereas the low values a non-marine environment.

This ratio calculated for the Abakaliki oil shale sample is 0.82. The ratio lower than 1.0 calculated for the Abakaliki oil shales and the existence of C_{26} tricyclic terpane without recording C_{25} tricyclic terpane for the other areas indicate that all the oil shales are the products of a non-marine depositional environment. Based on the data about lithology and fossils of the oil shales in the former studies performed in these area (Ehinola, 2010), it was suggested that they have been deposited in a lacustrine environment (Talu, 1967; Yanilmaz et al., 1980; Taka and Şener, 1988; Şener and Şengüler, 1992; Özçelik, 2002; Şengüler et al., 1982; Şener and Şengüler, 1997; Gülbay and Korkmaz, 2008). The biomarker and the other data obtained in this study also indicate a lacustrine depositional environment.

Potential of hydrocarbon generation

The potential yield (PY) parameter calculated by adding S_1 and S_2 values gives an idea about the hydrocarbon generation potential of a rock (Tissot, B. P., Welte, 1984; Uzoegbu and Onwualu-John, 2023). PY values of the Abakaliki oil shale samples range between 13.48 to 210.66 mgHC/g rock, respectively, and the average value is 54.88 mgHC/g rock. In general, the oil shales of all the areas are characterized by a rather high PY values. However, some oil shales show rather high values in comparison with the others. The high PY values indicate that hydrocarbon generation potential of the oil shales is rather high.

The average hydrogen index (HI) value of the Abakaliki oil shale samples is 740.40 mgHC/gTOC. Such high HI values show that (Type I kerogen) oil shales have a potential to generate oil (Merrill, 1991; Mann et al., 1998; Gülbay and Korkmaz, 2008; Uzoegbu and Onwualu-John, 2023). Furthermore, S_2/S_3 rate is found to be rather high for all the samples, and this rate higher than 5 also indicates that these oil shales can generate oil ((Merrill, 1991). Therefore, the formation of crude oil was not possible due to immature nature of the oil shales, although hydrocarbon potential of the oil shales of all the locations is high.

CONCLUSIONS

The average TOC values of the Abakaliki oil shales are determined to be 7.05. This TOC value show that organic matter content of the oil shales is very high. HI-OI, HI-Tmax and S_2 -TOC kerogen type classification diagrams indicate that the Abakaliki oil shales contain Type I kerogen dominantly and Type II kerogen in small quantities. These kerogen types indicate the dominance of algal (lacustrine) organic matter. Gas chromatograms of the Abakaliki oil shales all show bimodal distributions. The dominance of low carbon-number n -alkanes indicates that these oil shales consist mainly of algal and less of terrestrial organic matter. The oleanane index for the Abakaliki oil shales also indicates that there is very little input of terrestrial organic matter.

The PY value of 54.88 mgHC/g rock calculated, concluded that the oil shales are the source rocks with high hydrocarbon potential. High HI values and high S_2/S_3 ratios of oil shale samples from all fields show that oil shales have a potential to generate oil.

The Tmax values of pyrolysis of the Abakaliki oil shales is 433.20 °C. According to this value, all the oil shales are immature. In addition to gas chromatograms, m/z 217 and m/z 191 mass chromatograms also indicate that these oil shales are immature. Therefore, their alteration to form crude oil was not possible due to immature nature, although the oil shales of all the locations are characterized by high hydrocarbon potential.

The Pr/Ph ratios of the Abakaliki oil shales have been deposited in an anoxic and the Abakaliki oil shales in a suboxic environment. Gammacerane was recorded in medium to higher abundances for the Abakaliki

oil shales. According to the gammacerane presence and other parameters, all the oil shales may be considered to have been deposited in a saline environment.

The C₂₅/C₂₆ tricyclic terpane ratio lower than 1.0 calculated for the Abakaliki oil shales and the existence of C₂₆ tricyclic terpane without recording C₂₅ tricyclic terpane for the other areas indicate that all the oil shales are the products of a non-marine depositional environment. Based on the data about lithology and fossils of the oil shales in the former studies performed in these area, it can be said that they have deposited in a lacustrine environment. The biomarker and the other data obtained in this study also indicate a lacustrine depositional environment.

Based on the whole geochemical data mentioned indicates that the oil shales studied from Abakaliki anticlinorium were deposited in a similar depositional environment and conditions as that of the organic matter from the Niger Delta area.

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