

Comparative Analysis of Hydrocarbon Generation in the Nigerian Frontier Basins: Insights from Late Cretaceous Hydrocarbon Source Rocks and Confined Pyrolysis Experiments

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ABSTRACT

Increasing interest in oil and gas exploration in the Nigerian inland frontier basin has necessitated re-evaluating the once-neglected Late Cretaceous Hydrocarbon Source Rocks from the basins. In this study, hydrocarbon generation characteristics of representative Cretaceous outcrop source rocks and geochemical properties of their generated products are investigated using a confined gold tube pyrolysis experiment. Conventional geochemical analyses (TOC and Rock-eval) reveal that the source rocks are rich in organic matter and in the immature hydrocarbon generation stage. The gold tube experiment at six (6) different temperature stages (300°C to 500°C) indicates that the source rocks produced oil and gas in different proportions, and the pyrolysis products contained a certain amount of C₆₊ liquid hydrocarbons. Observed peak oil yields of the Bida, Dahomey, and Anambra shales were 5.80, 24.09, and 6.63 mg/gTOC, respectively. The gas yields of the source rocks drastically increased with rising heating temperatures (maturity). After exceeding 450°C (about EasyRo of 2.0%), methane and ethane gases were the dominant components in the pyrolyzates, which means that oil in the products gradually cracked into gas during the high-temperature stages. Maximum gas-to-oil ratio (GOR) of the shales ranges from 2.52 to 5.50. The $\delta^{13}\text{C}$ of C₁, C₂ and C₃ from the pyrolyzates are similar to those generated from the Niger Delta and this could be a result of marine connections among the basins. This study is valuable for further exploration in the Nigerian Frontier Basins, reducing over-dependence on the Niger Delta Basin for hydrocarbon exploration.

Keywords: Gold tube pyrolysis; hydrocarbon; source rocks; Frontier Basins; Anambra basin.

1.0 Introduction

The global perspective on the future of hydrocarbon exploration in an energy transition era especially in China, the USA, and Nigerian inland basins depends on integrating and exploring modern techniques in the search for hydrocarbon and comparing notes across regions. This has taken many dimensions in recent times. For instance, Ayinla^{1,2} and Liang³ used integrated

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¹ Ayinla, H. A., Abdullah, W. H., Makeen, Y. M., Abubakar, M. B., Jauro, A., Yandoka, B. M. S., & Abidin, N. S. Z. (2017a). Petrographic and geochemical characterization of the Upper Cretaceous coal and mudstones of Gombe Formation, Gongola sub-basin, northern Benue trough Nigeria: Implication for organic matter preservation, paleodepositional environment and tectonic settings. *International Journal of Coal Geology*, 180, 67-82.

² Ayinla, H. A., Abdullah, W. H., Makeen, Y. M., Abubakar, M. B., Jauro, A., Yandoka, B. M. S., & Abidin, N. S. Z. (2017b). Source rock characteristics, depositional setting and hydrocarbon generation potential of Cretaceous coals and organic rich mudstones from Gombe Formation, Gongola Sub-basin, Northern Benue Trough, NE Nigeria. *International Journal of Coal Geology*, 173, 212-226.

approaches involving organic geochemistry and organic petrography in source rock evaluation of the Inland basin in Gongola Sub-basin and of Oil Sands from the Middle Jurassic Yan'an Formation in the Southern Ordos Basin, China, respectively. Just as Aigbadon⁴ used the Palynology and geochemical method in the Anambra and Bida basins. Nigeria is rich in gas (about 75% volume) compared to oil (about 25%) and there is potential in the inland basins. These include Chad Basin, Gongola Basin (Northern Benue Trough) where Kolmani River wells were built based on Shell data, and Middle Benue Trough with Ebenyi-A well in Nasarawa State still comatose. Anambra Basin is operated by Orient Petroleum Ltd and Dahomey Basin where Yinka Folawiyon Petroleum is making headway. It has to be noted that the Bida and Sokoto basins are still awaiting serious commitment and deploying advanced technologies following Ebenyi-A well in Nasarawa State. Although Obaje⁵ emphasized that there are many challenges faced by the Nigeria National Oil Industry Management (NNPCL/NUPRC/NMDPRA), they are surmountable even in the Bida, Anambra and Dahomey basins.

Previous research in these areas is most often limited to a particular basin without a comparative analysis of hydrocarbon generation in Nigerian Frontier basins. A typical example is the work of Nton⁶ who used Rock-Eval pyrolysis and biomarker geochemistry to assess organic matter characteristics of subsurface samples from EE-1 well, offshore Eastern Dahomey Basin and suggests the potential to generate hydrocarbon at relevant thermal maturity. Similarly, Aigbadon and Igbinigie used Paleocene ostracods of the Eastern Dahomey basin to suggest a potential for hydrocarbon exploration in the area. Aigbadon⁴ carried out hydrocarbon prospectivity of the southern Bida and northern Anambra basins, Nigeria using palynological and geochemical studies and suggest fair potential for Type II/III kerogen within the area. Apart from the fact the Gold tube experiment was not conducted in the study Dahomey basin samples were not considered.

The present study employed an integrated approach in the comparative analysis of hydrocarbon generation in Nigerian Frontier basins with insights from Late Cretaceous hydrocarbon source rocks and confined gold tube pyrolysis experiments. This is aimed at evaluating and comparing the oil and gas generation potential across the three (3) inland basins (Dahomey, Anambra and Bida basins) to better understand the variations or similarities among the basins.

2.0 Geologic setting

Bida Basin (Fig. 1) is one of Nigeria's inland basins that lies at latitudes 8°00'N and 10°30'N and longitudes 4°30'E and 7°00'E in central Nigeria, trending NW and SE. It forms the NW extension of the Anambra Basin. The basin has about 4700m of sedimentary fill (using magnetic data).

³ Liang, Y., Makeen, Y.M., Abdullah, W.H., Hao, G., Tong, L., Lawal, M., Zhao, R., & Ayinla, H.A. (2019). Geochemical Characteristics of Oil from Oligocene Lower Ganchaigou Formation Oil Sand in Northern Qaidam Basin, China. *Natural Resources Research*. Published by Official Journal of the International Association for Mathematical Geosciences, available online at DOI: 10.1007/s11053-019-09466-9

⁴ Aigbadon, G. O., Christopher, S. D., Akudo, E. O., & Akakuru, O. C. (2022). Sedimentary facies and textural characteristics of Cretaceous sandstones in the southern Bida Basin, Nigeria: implication for reservoir potential and depositional environment. *Energy Geoscience*, 3(3), 323-341.

⁵ Obaje, N.G., (2024). Developing Critical Mineral and Energy Resources in a Data-Driven Global and Digital Economy, 1st annual internal conference and exhibitions, confluence Geoconference, 2024.

⁶ Nton, M.E., Emordi, E.E., and Ayodele, I. (2022). Hydrocarbon Potential and Biomarker Studies of EE-1 Well, Offshore Eastern Dahomey Basin, SW Nigeria. *Materials and Geoenvironment*, 69 (1), 33-46.

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Owing to limited subsurface data, the basin is the least explored. The origin of the Bida Basin has been a subject of controversy. It is believed to be linked to Benue Trough's syntectonic development during the Cretaceous that led to the opening of the Gulf of Guinea and the South Atlantic Ocean⁷. The stratigraphic succession in the Southern Bida Basin comprised of Campanian Lokoja Formation and Maastrichtian Patti and Agbaja formations⁸ (Fig. 2).

The Anambra Basin (Fig. 1) is located in a complex tectonic feature that was originally

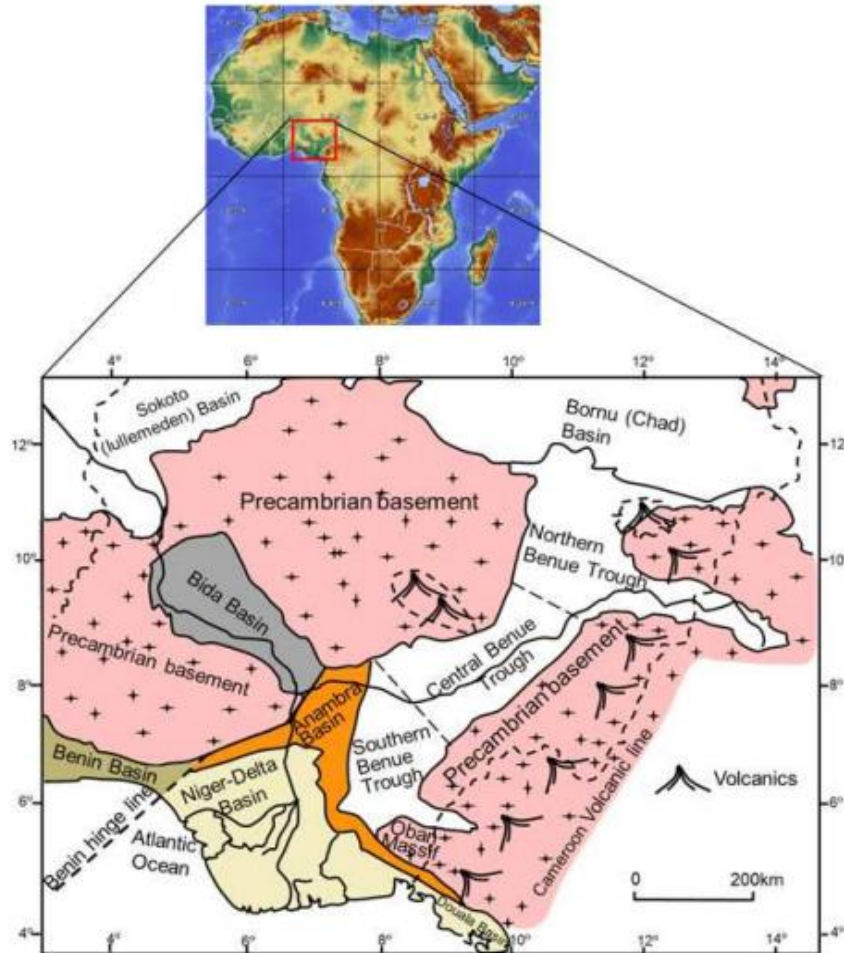


Figure 1. Map of Nigeria showing the studied basins
(Adapted from ⁹)

⁷ Obaje, N.G., Wehner, H., Scheeder, G., Abubakar, M.B., and Jauro, A. (2004). Hydrocarbon prospectivity of Nigeria's inland basins: From the viewpoint of organic geochemistry and organic petrology. *AAPG Bulletin*, Vol, 88, no3, pp. 325-353.

⁸ According to Akande, S. O., Ojo, O. J., Erdtmann, B. D., & Hetenyi, M. (2005). Paleoenvironments, organic petrology and Rock-Eval studies on source rock facies of the Lower Maastrichtian Patti Formation, southern Bida Basin, Nigeria. *Journal of African Earth Sciences*, 41(5), 394-406.

⁹ Edegbai, A.J., Schwark, L., Oboh-Ikuenobe, F.E. A review of the latest Cenomanian to Maastrichtian geological evolution of Nigeria and its stratigraphic and paleogeographic implications. *J. Afr. Earth Sci.* 2019a, 150, 823-837.

formed through the separation of the South American Plate from the West African and Central African Plates during the Cretaceous. This basin is the folded arm of a very complex rift system and it represents the north-western element of the Lower Benue Trough of Nigeria. The Anambra Basin extends and disappears beneath the Tertiary and Quaternary sediments of the famous Niger Delta. It is a nearly triangular-shaped depression, and it covers about 3000 km² with about 6000m thick Cretaceous and Tertiary sediments.¹⁰ Evolution of Lower Cretaceous-Neogene aged sediments in the Anambra Basin was reported to have been controlled by five main transgressive cycles and these transgressive cycles started in the Lower Cretaceous when the sea found its way into the Benue Trough. The oldest Nkporo Formation in this basin lies unconformably on the basement rocks and most commonly basal conglomerate with subrounded to rounded quartz pebbles lie directly on the basement rocks (Fig. 2). The overlying Mamu Formation comprises dominantly of argillaceous sediments including claystone, coal, siltstones, and shales (Fig. 5). It is believed that Anambra Basin harbours one of the largest deposits of lignite and sub-bituminous coal in Nigeria and in some places during the fieldwork, coal mining activities were ongoing (Fig. 5).

The Dahomey Basin (Fig. 1) is a combination of inland, coastal, and offshore basin that extends from southeastern Ghana through Togo and the Republic of Benin towards southwestern Nigeria. It is separated from the Niger Delta by a subsurface basement high that is referred to as the Okitipupa Ridge. Although its offshore extent is poorly defined in general, sediment deposition follows an east-west trend. In Nigeria, the basin stretches from Ondo state through Ogun and to some parts of Lagos state. The stratigraphic succession in the area ranging from the Cretaceous Abeokuta Group to the Quaternary Benin Formation as shown in Fig. 2.

3.0 Methods of study

In this research work, the methods employed were fieldwork (for sample collection) and laboratory analyses. Fieldwork was carried out to collect fresh and unweathered representative Cretaceous outcrop shales of the Anambra, Bida and Dahomey basins. The source rock samples were subjected to laboratory analyses to determine and compare their hydrocarbon generation characteristics. This involves the determination of organic matter richness (quantity), organic matter quality (Kerogen Type) and thermal maturity of the samples. In addition, molecular and isotopic compositions of the light hydrocarbons generated through simulation experiments were determined.

¹⁰ Ekine, A. S., & Onuoha, K. M. (2008). Burial history analysis and subsidence in the Anambra. *Nigerian Journal of Physics*, 20(1), 145-154.

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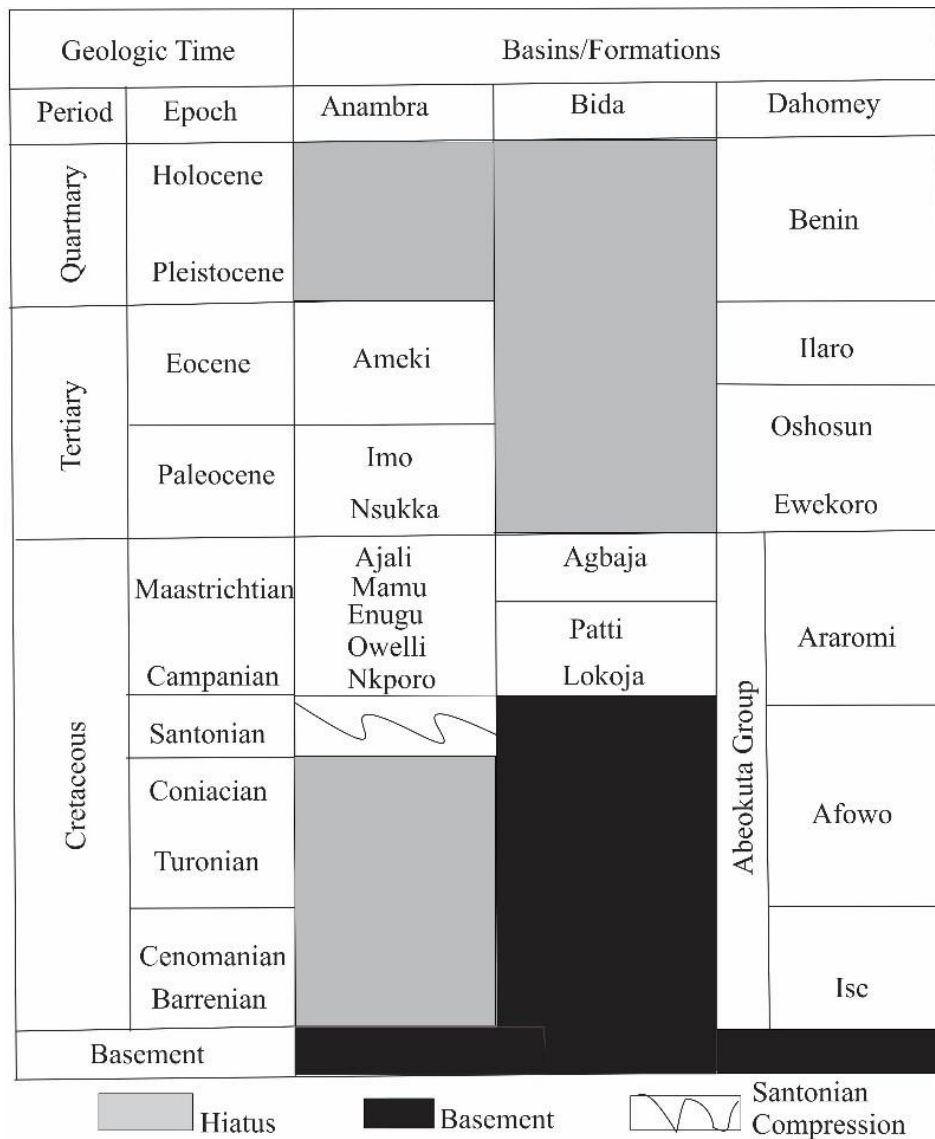


Figure 2. The stratigraphic succession of the Bida, Anambra and Dahomey Basins.

Field Observations

To collect fresh outcrop samples, exposed sections of road cuts, outcrops and river channels were mapped and systematically logged. Fresh and unweathered source rock samples of Cretaceous age were collected from locations of interest in parts of the Anambra, Bida, and Dahomey basins. The exposed sections were studied by making necessary observations and accurate measurements. Fresh samples were collected in polythene bags and labelled appropriately. In addition, sections were thoroughly examined for any significant sedimentological structures and microfossil assemblages (photographs were taken where necessary) that could also help in interpretation. The various locations visited are described below:

Bida Basin

For this current research work, exposed, mapped, and logged sections are along Lokoja - Abaji road, Ahoko and Ogongoro village, Lokoja-Okene road, Felele, Agbaja Plateau/Hill, Mount-Patti, and Idu village, all in Kogi State, Nigeria. The mapped/logged sections belong to the Patti Formation and the exposed sections were targeted because potential source rocks in this basin are believed to be exposed along this axis based on previous literature. Lithological facies identified include shales which are greyish, dark greyish-black in colour, claystones and ironstones (concretionary and banded). The shales were found dominantly as roadside exposure and a few were found at an abandoned mining site at Ahoko village. Dark-greyish claystone occurred as roadside exposure with some also occurring along stream channels (see Fig 3d). Ahoko shales show upward variation in terms of composition with the shales becoming enriched in likely any of the sulphur minerals up the section (Fig. 3d). These shales also form the basal bed at an abandoned mining site at Ahoko village (Fig. 4). Concretionary ironstones are interbedded with the basal claystone beds, especially at the road cut exposure along the Lokoja-Abaji road (Fig. 3d). Up the section, the concretionary ironstones are completely absent while, the banded forms become so prominent (Figs. 4). At the basal part of roadside exposure at Ahoko, some of the ironstones were stained by whitish substance (sulphate minerals?) (See the basal bed in Fig. 4). In addition, some claystone and shale beds were also fractured (Fig. 3). At an existing mining site close to Ahoko village (N 08° 19' 32.1"; E 006° 52' 49.9"), greyish-dark claystone make up the basal beds and these claystone beds were overlaid by ferruginized siltstones beds. Up the section, there are alternating beddings of ferruginized mudstones and bands of ironstones. Previously, coal within the Patti Formation was only reported at Idu village in Kogi State of Nigeria but, during this fieldwork, a new coal deposit within the Patti Formation was discovered at Ogongoro village, also in Kogi State. The coal deposit is majorly occurring along the river bank channel and has not been reported in any existing literature in the past.

Anambra Basin

Coal samples of the Mamu Formation (Cretaceous age) were collected from existing mining sites (Fig. 5d). In addition to the coal, shales were also collected from different locations (Fig. 5c). Dominantly, in the outcrops, shales and coals within the Anambra Basin overlies conglomeratic sandstones which are basically of rounded-sub-rounded pebbles (Fig. 5b).

Dahomey Basin

For this research work, exposed sedimentary sections were mapped at Onikitinbi Village, Ogun State, Ilubinrin and Idobilayo villages in Ondo State, Nigeria. These sections are exposed on the Eastern axis of Dahomey Basin and they belong to the Ise and Afowo formations. The oldest units encountered during the fieldwork include basal conglomerate, claystone and mudstones which are lying directly on the basement complex rocks (Figs 6 a & b). These litho facies are members of the Ise Formation. Rock fragments from the underlying basement were observed and were identified as schist. In the basal conglomerate, there are dominantly pebbles and sandstones. The pebbles which are dominantly made up of quartz are subangular-subrounded (Fig. 6a) indicating proximity to their source area. The sandstone units are light-reddish in colour and are medium to fine-grained. They are well sorted and are friable. The absence of feldspar

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Figure 3. Contact between Basement rock and conglomeratic sandstone of the Lokoja Formation at Lokoja-Okene road, (b) greyish claystone exposed at Idu village, (c) Laminated shale exposed at Agbaja Hill, (d) Exposed greyish shale at Idu village (All photos taken from the southern axis of the Bida Basin)

Depth (m)	Lithology	Sample Number	Description	Formation	Age
20	[Dotted pattern]	AQ-B10	Light-grey Claystone with interbedding ironstones	Patti Formation	Upper-Cretaceous
		AQ-B9			
15	[Dotted pattern]	AQ-B8	Concretionary iron stone		
		AQ-B7			
		AQ-B6			
10	[Dotted pattern]	AQ-B5	Light-grey Claystone with interbedding ironstones		
		AQ-B4			
		AQ-B3			
5	[Horizontal lines]	AQ-B2	Dark-grey Shale		
		AQ-B1	Light-grey Claystone		

Figure 4. Lithostratigraphic section exposed at abandoned mining site, Ahoko village, Bida Basin, Nigeria (08° 18' 14.9", E 006° 51' 26.8")

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Figure 5. (a) Basement rock in Anambra Basin, (b) Basal conglomerate with rounded-subrounded pebbles (c) Exposed section of Mamu shale at Ojodu village (d) An existing coal mining site at Iteke village, Kogi State

in the sandstones suggests possible chemical weathering which might have weathered out all the feldspars and deposited them elsewhere as clay.

At Onikitinbi village, the mapped section comprises a basal 2.5m thick greyish-black coaly shale with very viscous black bitumen (Fig. 6d). This basal bed is overlain by 0.6m thick tar sand. At the time of the visit to this location, it was observed that bitumen was seeping out from the tar sand. The uppermost unit of this mapped section comprises 1.5m thick, well-sorted, fine to medium-grained, reddish sandstones. In addition, a shallow well was recently drilled at this same location by the University of Cape Town, South Africa in collaboration with the Ogun State Government of Nigeria and from the cuttings on the ground, greyish-black shales enriched in bitumen are the likely underlying rocks in this well (Fig. 6d). The lithostratigraphic log of the mapped section is shown in Figure 7.

Samples and experimental methods

Six (6) representative outcrop shale samples were collected from Anambra (AN-1, AN-2), Bida (BD-1, BD-2) and Dahomey (DAH-1, DAH-2) basins. The source rock samples were first

analysed for their organic richness, quality and thermal maturity using total organic carbon (TOC), Rock-Eval pyrolysis and vitrinite reflectance. In addition to these, a hydrocarbon generation simulation experiment through a confined gold tube was carried out. All the experiments in this present work as outlined below were carried out at the China University of Petroleum, Beijing laboratories.



Figure 6: (a) Subangular-subrounded pebbles from the basal conglomerate and micas from the rock fragments, (b) An exposure of Ise Formation along Lagos-Abeokuta Road. (c) First bitumen drilled well at Agbabu village, Ondo State (d) Exposed section of Lower Cretaceous greyish shale at Onikitinbi village, Ogun State.

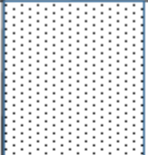


Thickness (m)	Lithology	Description	Formation	Age
4		Fine-medium grained, friable and well sorted sandstone	Afovo	Cenomanian - Turonian
		Bituminous tar sand,		
2		Dark-grayish, poorly laminated coaly shale		

Figure 7: Lithological section of exposed rocks at Onikitinbi, Ogun State, Nigeria

Total organic carbon (TOC)

As a measure of the quantity of organic matter in the potential source rocks, total organic carbon (TOC) determination analysis was conducted on the representative samples. The samples were first crushed to < 0.2 mm (80 mesh) in diameter. About 100 mg was weighed and placed in crucibles. The samples were then diluted with hydrochloric acid (1.5 mol/L) to remove inorganic carbon compounds completely. Deionized water was used to flush through the samples to remove any possible contaminants for 48 hours. Clean samples were put crucible and oven-dried at 80°C. The TOC (wt %), of each sample was measured using the LECO CS-400 machine and their values (both TOC and TS) were recorded accordingly.

Rock-Eval pyrolysis

The six representative samples were subjected to a Rock-Eval pyrolysis experiment using the HAWK pyrolysis machine. The weight of samples used ranges from 30 - 60mg depending on the source rock's TOC. The Hawk machine has some advantages over the common Rock-Eval II/III machine in the sense that about 120 samples can be loaded at a time and the results will be made available without it being attended to. In addition, Rock-Eval parameters such as production index, hydrogen and oxygen indices are automatically calculated by the Hawk whereas in the case of the Rock-Eval II/III machine, this is manually calculated. Rock-Eval pyrolysis is a widely used and highly regarded tool that is used by petroleum geochemists for source rock geochemical profiling. The data obtained from this experiment provides tools to identify organic matter type and to evaluate their petroleum (oil and gas) potential, generation, and thermal maturity (^{11, 12, 13, 14, 15}).

¹¹ Hunt, J. M., (1996). Petroleum Geochemistry and Geology. W. H. Freeman, New York, 699p.

Organic petrography

Polished whole rock blocks were prepared from the six source rock samples. The samples were first cut perpendicular to bedding planes, epoxy resin and hardener were added, and they were allowed to firm for 3 days. Each source rock block was polished on a Buehler automatic grinding and polishing machine (EcoMet 250 with AutoMet 250) to have a smooth surface. The polishing was done using a set of polishing clothes (600, 400 and 300 grits), and alumina powder was added to achieve the desired roughness and a relief-free surface. Macerals in each sample were identified with the aid of a LEICA DM4-M microscope under reflected and fluorescent lights at the Organic Petrology Laboratory, China University of Petroleum, Beijing. In addition, reflectance measurement was carried out on the polished block samples. Overall, an average of about 50 - 100 reflectance measurements on vitrinite/huminite macerals were made using high magnification (400×), under oil immersion. The reflectance values obtained were recorded as mean random reflectance (Ro).

Confined gold tube pyrolysis

The hydrocarbon generation simulation experiment was carried out in sealed gold tubes (24 mm x 4.2 mm x 2.2 mm i.d.) by following the procedures of Hill et al.¹⁶ Distilled water was added to the samples in the ratio of 1:1, as this would promote thermal cracking which will lead to hydrocarbon generation, and it will also inhibit carbon-carbon bond cross-linkage which can result in pyrobitumen formation¹⁷. Before the samples were loaded into the gold tubes, one end of each gold tube was sealed and welded using an argon arc welding device. Weighed samples (100-400mg and 30-150mg for shale and coal respectively) were placed in the welded tubes. After loading the samples, the gold tubes were flushed with argon to remove air bubbles and the other open end was crimped and welded. To avoid loss of volatile compounds, the first sealed end of the gold tubes was submerged in water during welding of the second end. The experiment was performed at temperatures between 300°C and 500°C at a heating rate of 2°C/hr. The experimental temperatures were controlled using pairs of thermocouples which were attached to the outer wall of each autoclave. Constant confining pressure was also maintained at approximately 50 MPa using a water pump to prevent the rupturing of gold tubes at elevated temperatures. All the gold tubes were weighed before and after the samples were loaded. At the end of the experiment, the gold tubes were re-weighed to assess the integrity of the experiment. The procedures employed in the hydrocarbon generation simulation experiment in the present study are shown in Figure 8.

Huss, E. B., & Burnham, A. K. (1982). Gas evolution during pyrolysis of various Colorado oil shales. *Fuel*, 61(12), 1188-1196.

¹² Waples D.W., Ramly M., and Leslie W., (1995). Implications of vitrinite reflectance suppression for the tectonic and thermal history of the Malay Basin. *Bul Geo Soc Mal.*, 37:26-28.

¹³ Peters, K.E., (1986). Guidelines for evaluating petroleum source rocks using programmed pyrolysis. *AAPG Bull.* 70, 318-329.

¹⁴ Espitalie, J., Deroo, G., Marquis, F., (1985). La pyrolyse rock-eval et ses applications. Partie 1. *Revue de l'Institut Francais du Petrole*, 40 (5), pp. 563-579.

¹⁵ Tissot, B. P., Welte, D. H., (1978). Sedimentary processes and the accumulation of organic matter. *Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration*, 55-62.

¹⁶ Hill, R. J., Y. C. Tang, P. D. Jenden, and I. R. Kaplan, 1996. The influence of pressure on oil pyrolysis: *Energy and Fuels*, v. 10, p. 873-882.

¹⁷ Winters J.C., Williams J.A., and Lewan M.D., 1983. A laboratory study of petroleum generation by hydrous pyrolysis. In *Advances in organic geochemistry 1981* (Edited by Bjoroy M. et al.), pp. 525-533. Wiley, Chichester.

Gas analysis of C₁-C₅

After completing the pyrolysis experiment, each gold tube was cleaned with dichloromethane to remove any contaminants and the gas components in each tube were analysed. The gold tube was placed in a vacuum collector which was equipped with a toepler pump, calibrated burette and also connected to an HP 5890 II gas chromatograph. The gold tube was then pierced with a steel needle and the generated gases were released into the vacuum collector. After allowing the gas to come into a balance between the gold tube and the vacuum collector for about 30 seconds, the gas was channelled into a gas chromatograph with the aid of a control valve. Gaseous hydrocarbons (C₁-C₅) and non-hydrocarbon gas (CO₂) were quantified and identified using external standards. Each gas was identified using an Agilent 8890 gas chromatography (GC) machine. The GC machine was fitted with eight columns (two capillary columns and six packed columns) and three detectors (one FID and two TCD), these allow simultaneous measurement of hydrocarbon and non-hydrocarbon gases. Helium was used as a carrier gas. The GC oven was initially held at 70°C for 5 min, and it was later heated to 130°C at 15°C/min. The oven was further heated to 180°C at 25°C/min and held for 4 minutes.

Quantification of C₆-C₁₄ by GC

Upon completion of gas analysis, each punctured gold tube was cut open with clippers and soaked in pentane solution in a small, labelled bottle. An internal standard solution of D₃₄C₁₆ (0.5mg/ml) was added to each bottle and they were allowed to stay for 48 hours to concentrate the remnant samples. Thereafter, the pentane solution was then decanted and the C₆-C₁₄ components of each sample were analysed using a Trace 1300 Gas Chromatography machine.

Stable carbon isotope of gaseous products

The carbon isotopes of C₁-C₃ gases were measured using a VG Isochrom II mass spectrometer which was interfaced to an HP 5890 GC system. The machine was fitted with a Poraplot Q-column (30mm x 0.32 mm), and helium was used as the carrier gas. The oven temperature was set to 20°C/min from an initial temperature of 50 and held for 4 minutes, the final temperature set for the machine was 190 °C (held for 5 min). The stable carbon isotopes of C₁, C₂ and C₃ were obtained and were recorded in δ notation relative to PDB standard.

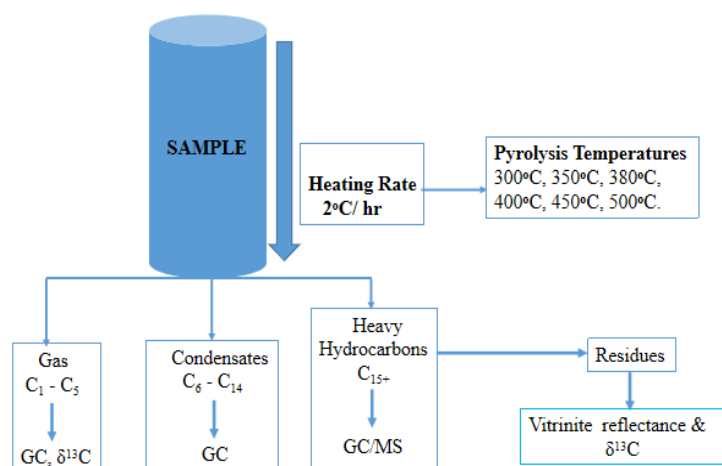


Figure 8. Experimental procedures adopted in the gold-tube simulation experiment.

4 Results

4.1 TOC and Rock-Eval pyrolysis

Total organic carbon (TOC) and Rock-Eval pyrolysis results are presented in Table 1. Shales from the Dahomey Basin have the highest TOC values (10.51 and 11.34 wt %), while the lowest value was obtained in Bida shales (4.98 and 5.67 wt %). The highest HI values were obtained in the Dahomey shales (202 and 273 mgHC/gTOC), whereas the lowest values of HI (108 and 122 mgHC/gTOC) were obtained in the Anambra shales. All the analyzed samples were in the immature stage of hydrocarbon generation based on the Tmax (< 435 °C) and vitrinite reflectance (< 0.5 %) values (Table 1).

Table 1: Total organic carbon and Rock-pyrolysis results for analyzed samples

Samples	Lithology	S1	S2	S3	S2/S3	S1+S2	TOC	Tmax	HI	OI	TS (%)	V.R%
Anambra-1	Shale	0.28	8.57	1.27	6.75	8.85	7.93	417	108	16	3.70	0.27
Anambra-2	Shale	0.31	8.53	1.15	7.41	7.88	6.97	419	122	17	3.61	0.30
Bida -1	Shale	0.30	7.57	2.12	3.57	7.87	5.67	427	133	37	0.13	0.34
Bida -2	Shale	0.28	7.41	1.98	3.74	7.69	4.98	431	149	40	0.17	0.36
Dahomey-1	Shale	3.81	28.73	6.06	4.74	32.54	10.51	428	273	57	0.40	0.34
Dahomey -2	Shale	2.16	22.98	6.12	3.75	25.14	11.34	426	202	54	1.01	0.27

4.1.1 Organic richness and petroleum generative potentials

To predict the potential of source rocks to generate hydrocarbon, its organic richness, hydrocarbon proneness, and the type of organic matter must be known.^{18, 19} These parameters are critical to making decisions when assessing exploration risks in sedimentary basins. Previous authors^{20, 21, 22, 23}, believed that before a rock can be considered as a potential source for hydrocarbons, it must have sufficient organic matters and hydrogen indices, which can be identified using petroleum geochemical techniques such as total organic carbon (TOC), and

¹⁸ Peters, K.E. and Cassa, M.R., (1994). Applied source rock geochemistry. In: Magoon, L.B., Dow, G.W. (Eds.). The Petroleum System-From Source to Trap. AAPG Mem. 60pp. 93- 120.

¹⁹ Tissot, B. P., & Welte, D. H. (1984). Kerogen: composition and classification. Petroleum formation and occurrence, 131-159

²⁰ Asiwaju, L., Mustapha, K. A., Abdullah, W. H., Ayinla, H. A., & Abd Aziz, A. (2023). Organic matter input, paleovegetation and paleoclimate of Upper Cretaceous lignite from Maiganga coalfield, Upper Benue Trough, Nigeria: Insights from biomarkers and stable isotopes. Journal of African Earth Sciences, 205, 105010.

²¹ Peters, K.E. and Moldowan, J.M., (1993). The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice-Hall, Inc., Englewood Cliffs, New Jersey (363pp.)

²² Brooks, P. W., Fowler, M. G. and Macqueen, R. W., (1988). Biological marker and conventional organic geochemistry of oil sands/heavy oils, Western Canada Basin. Organic Geochemistry, 12, 519-538.

²³ Burtner, R. L. and Warner, M. A., (1984). Hydrocarbon generation in Lower Cretaceous Mowry and Skull Creek Shales of the Northern Rocky Mountain area. In: Hydrocarbon Source Rocks of the Greater Rocky Mountain Region (J. Woodward, F. F. Meissner and J. L. Clayton, eds.), Rocky Mountain Association of Geologists, Denver, CO, pp. 449-467.

Rock-Eval pyrolysis. Guidelines which are often used to describe potential hydrocarbon source rocks are presented in Table 2.

Generally, source rocks can be classified as poor, fair, good, very good, and excellent depending on their organic carbon richness.^{18, 13} In the present research work, values of TOC obtained for the studied shales classified them as excellent source rocks. Furthermore, values of pyrolysis S2 for shales from the Dahomey Basin (Table 1), classified them as very good source rocks, while the shales from both Anambra and Bida basins are classified as good source rocks (Fig. 9).

The generative potential (GP), of source rock is related to its carbon content,^{24, 25} and this is dependent on the original TOC and HI capacities of its kerogen.²⁶ Source rocks with a GP < 2 are considered to have poor potential, values between 2 and 5, have fair potentials, and those with GP between 5 to 10 and above 10 are considered to have good and very good generative potentials, respectively.¹¹ The GP values of the studied source rock samples (Table 1) indicate very good generative potentials in the Dahomey shales, while the Anambra and Bida shales have good potentials to generate hydrocarbon.

4.1.2 Kerogen/organic matter type

There are several ways through which organic matter type in hydrocarbon source rocks can be classified. In the past, several attempts have been made to classify organic matter types based on their precursors. Kerogen is a complex mixture of different organic particles and in most cases, they are a mixture of two basic categories of organic matter that are analogous to vitrinite and liptinite maceral groups of coal.²⁷

Demaison et al^{28, 29} used kerogen elemental compositions to classify kerogens into Type I (very oil-prone), Type II (oil-prone), Type III (gas-prone) and Type IV (inert) kerogens which contain very little hydrogen. A Type II-S; a sulfur-enriched form of type II kerogen was also proposed³⁰. However, in most source rock studies, hydrogen index (HI) has been used as an effective parameter to figure out the type of kerogen and the nature of hydrocarbon products from source rocks¹⁸. Thus, based on HI obtained in the studied source rocks in this study, shales from the Anambra and Bida Basins are dominantly classified as Type III. However, in the Dahomey Basin shales, the HI values show types II/III kerogen. In addition, organic matter types and the nature of hydrocarbon that can be produced from source rocks can also be figured out using the

²⁴ Bordenave, M.L., Espitalié, L., Leplat, P., Oudin, J.L., Vandenbroucke, M., (1993). Screening techniques for source rock evaluation. In: Bordenave, M.L. (Ed.), Applied Petroleum Geochemistry Paris: Editions Technip, pp. 217-278.

²⁵ Jarvie, D. M. (1991). Total organic carbon (TOC) analysis: Chapter 11: Geochemical methods and exploration.

²⁶ Peters, W., Miller, J. B., Whitaker, J., Denning, A. S., Hirsch, A., Krol, M. C., ... & Tans, P. P. (2005). An ensemble data assimilation system to estimate CO₂ surface fluxes from atmospheric trace gas observations. Journal of Geophysical Research: Atmospheres, 110(D24).

²⁷ Stach, E., (1975) Coal Petrology. Gebruder Borntraeger, Berlin, 428 pp.

²⁸ Demaison, G.J., Hoick, A.J.J., Jones, R.W., Moore, G.T., (1983). Predictive source bed stratigraphy; a guide to regional petroleum occurrence. In: Proceedings of the 11th World Petroleum Congress, vol. 2. John Wiley & Sons, Ltd., London, p. 17.

²⁹ Tissot, B., Durand, B., Espitalie, J., & Combaz, A. (1974). Influence of nature and diagenesis of organic matter in formation of petroleum. AAPG bulletin, 58(3), 499-506.

³⁰ Orr, W.L., (1986). Kerogen/asphaltene/sulfur relationships in sulfur-rich Monterey oil. Org. Geochem. 10, 499-516

graphical cross-plots of HI-Tmax^{31, 14, 32}. The HI-Tmax cross plot is preferred by some petroleum geochemists because it serves as an indicator of both kerogen type and thermal maturity. As shown in Figures 10 and 11, shales from the Dahomey Basin are type II/III, while those from the Anambra and Bida basins are type III.

4.1.3 Thermal maturity of the studied source rocks

Thermal maturity is an extremely important feature that is related to the generation of oil and gas, as organic matters have to reach a certain level of maturation before it starts to thermally degrade and begins to be converted into liquid or gaseous hydrocarbons. It is good to state that the threshold for oil generation in source rocks varies depending on the kerogen type. For example, a Type II-S kerogen which is enriched in sulfur generates oil at a lower temperature than a typical Type II which is not enriched in sulfur. Information such as this is critical in any hydrocarbon exploration study and modeling in sedimentary basins.³⁰ By adopting the classical interpretation of Tmax values^{13, 33} in addition to vitrinite reflectance values, all the studied source rocks in the three basins are in the immature stage of hydrocarbon generation. This is supported by the cross plot of HI vs Tmax (Fig. 11).

4.2 Hydrocarbon and non-hydrocarbon gas yields

4.2.1 C₁₋₅ and CO₂ gas generation

C₁₋₅ gas yields from the pyrolysed samples are presented in Table 2 and are pictorially shown in Fig. 12 (a-c). From the results, the C₁ yield increases with pyrolysis temperature and reaches its maximum at the final temperature (500°C) in all the samples. At 500 °C, out of all the shales, Dahomey shale generates the highest quantity of C₁ with a maximum of 29.62mg/gTOC. This is followed by Anambra shale (13.06mg/gTOC), and the least, 11.21mg/gTOC was generated by Bida shale. Maximum C₁ yields in the studied samples follow this trend: Dahomey shale>Anambra shale>Bida shale.³⁴ reported demethylation of solid residue or cracking of C₆₊ extracts as the main cause of the late generation of methane (C₁) at high temperatures. Overall,

³¹ Dahl B, Bojesen-Koefoed J, Holm A, Justwan H, Rasmussen E., (2004). A new approach to interpreting Rock-Eval S2 and TOC data for kerogen quality assessment. *Org Geochem*, 35:1461-1477.

³² Katz B.J., and Elrod L.W., (1983). Organic geochemistry of DSDP site 467, Offshore California, middle Miocene to lower Pliocene strata. *Geochim Cosmochim Acta*, 47:389-396 [171]

³³ Teichmüller, M., Durand, B., (1983). Fluorescence microscopical rank studies on liptinites and vitrinites in peat and coals, and comparison with results of the Rock-Eval pyrolysis. *Int. J. Coal Geol.* 2, 197-230

³⁴ Behar, F., Kressman, S., Rudkiewicz, J.L., Vandenbrouke, M., 1992. Experimental simulation in a confined system and kinetic modeling of kerogen and oil cracking. *Org. Geochem.* 19, 173-189.

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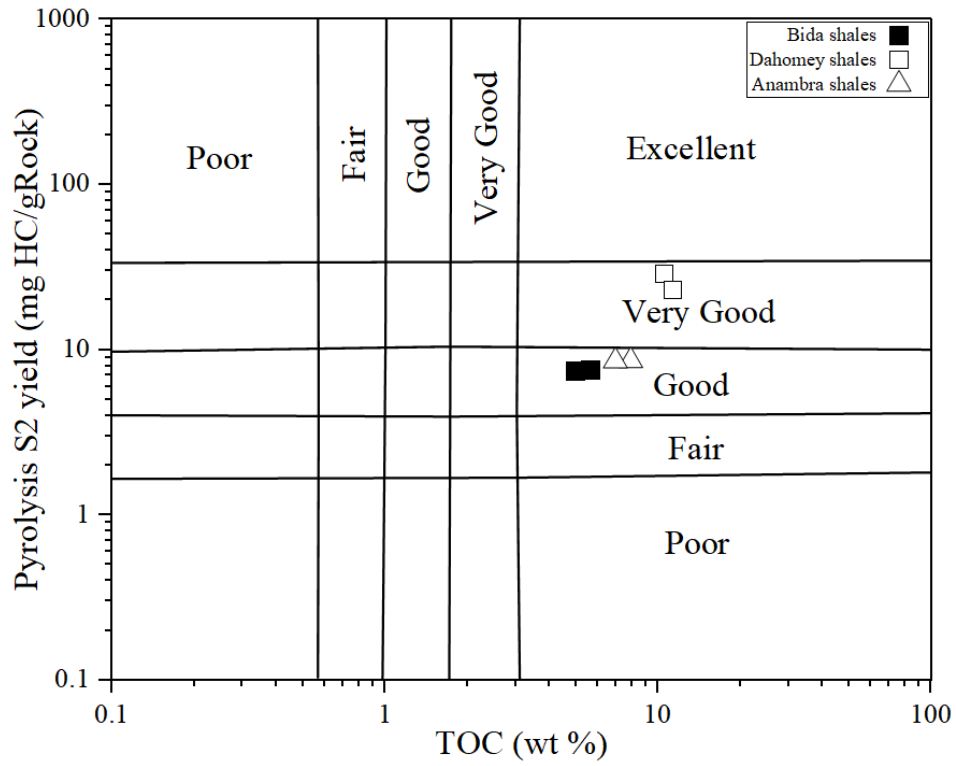


Figure 9: The plot of pyrolysis S2 and TOC

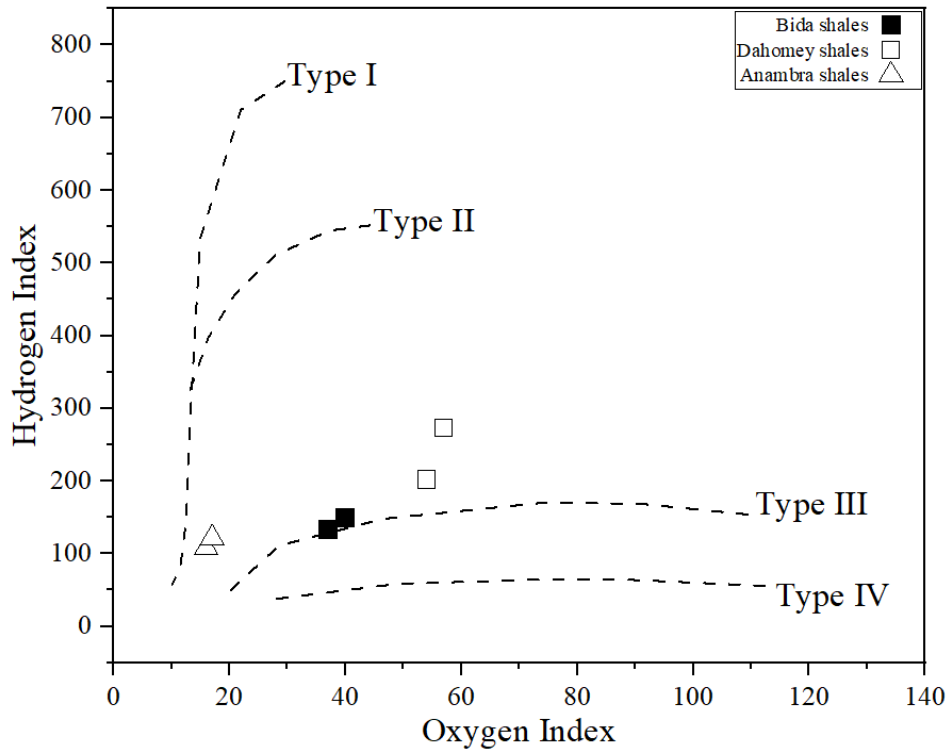


Figure 10: The plot of oxygen index against hydrogen index showing the types of organic matter in the studied source rock samples from the three basins.

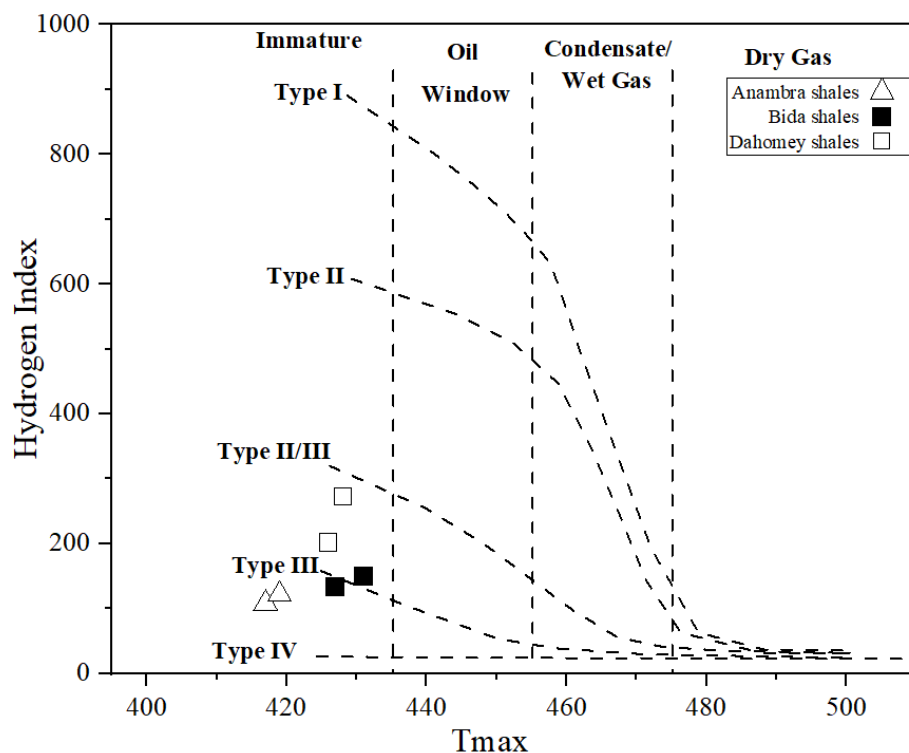


Figure 11: The plot of Tmax against hydrogen index depicting the kerogen type and the level of thermal maturity attained by the studied source rock samples

variations in maximum C_1 yields in the present study could be attributed partly to differences in the TOC of the samples (Table 1). Furthermore, maximum C_2 yield was also generated at the final pyrolysis temperature of 500°C in all the samples. The C_2 maximum yield follows this trend: Dahomey shale > Bida shale > Anambra shale. For the other hydrocarbon gases, (i.e., C_3 , C_4 and C_5), maximum C_3 , C_4 and C_5 yields were generated at 450°C, 400°C and 380°C respectively, in the Bida shale. As for the Dahomey shale, the highest was generated at 450°C (C_3 -8.77mg/gTOC), and 400°C (C_4 -2.69mg/gTOC, C_5 -1.29mg/gTOC). However, in the Anambra shale, maximum C_3 , C_4 and C_5 were also generated at 400°C, 380°C and 350°C, respectively (Table 2, Fig. 12, a-c). Notably, the decline in C_{1-5} gases as observed in this study first began in C_5 , through C_4 , C_3 and the last in C_2 , this is consistent with the earlier results of Lorant et al³⁵. In addition, the decline in C_{2-5} gases with increasing pyrolysis temperature is attributed to secondary cracking³⁵.

The yields of CO_2 in the pyrolysates follow a similar trend to C_1 gas; the yields increase with rising pyrolysis temperature, and this is similar to the result of Burnham et al³⁶. The CO_2 yields

³⁵ Lorant, F., Prinzhofer, A., Behar, F., & Huc, A. Y. (1998). Carbon isotopic and molecular constraints on the formation and the expulsion of thermogenic hydrocarbon gases. *Chemical geology*, 147(3-4), 249-264.

³⁶ Burnham, A. K., Braun, R. L., & Samoun, A. M. (1988). Further comparison of methods for measuring kerogen pyrolysis rates and fitting kinetic parameters. *Organic geochemistry*, 13(4-6), 839-845.

follow this trend; Dahomey>Anambra>Bida. Earlier authors³⁷ believed that large amounts of CO₂ usually accompany hydrocarbon generation during the thermal cracking of kerogen as a result of the decarboxylation of organic acids and esters.

4.2.2 C₁, C₁-C₅, C₂-C₅, and gas dryness

Figure 13 (a-c) compares C₁, total gas yields (C₁-C₅), C₂-C₅, and gas dryness (C₁/C₁-C₅) in the pyrolysed samples. In general, all the samples follow similar thermal evolution patterns. The total gas yields (C₁-C₅) increase with rising pyrolysis temperature. At the final temperature (500°C), the maximum C₁-C₅ yields obtained in Dahomey shale was 45.06mg/gTOC, while in Anambra and Bida shales, the maximum was 14.56mg/gTOC and 14.10mg/gTOC, respectively. The C₂-C₅ maximum yields in shales from the Bida and Anambra Basins were obtained at 400°C (4.56mg/gTOC and 2.14mg/gTOC, respectively), while in the Dahomey shale, the maximum was obtained at 450°C (20.41mg/gTOC). Beyond these temperatures (i.e., 400°C and 450°C), C₂-C₅ began to crack in all the samples. At the inflexion temperatures where C₂-C₅ begins to crack in all the samples, there was a corresponding rise in C₁-C₅ yields (Fig. 13), and this is similar to the earlier report of Tian et al³⁸. Further, gas dryness in the Bida and Anambra shales began to rise at 380°C, while in the Dahomey shale, gas dryness began to rise at 450°C and it continued until the final pyrolysis temperature. The rise in gas dryness at temperatures at which wet gas began to decline shows that methane generation is dependent on the secondary cracking of other gases (C₂-C₅, in this study).

4.2.3 C₆₊ and Gas-oil ratio (GOR)

The gas-oil ratio (GOR) obtained in each sample is presented in Table 2. The GOR was calculated by dividing C₁-C₅ (total gas yields) by C₆₊ (total oil; the sum of C₆-C₁₄, and C₁₅₊ hydrocarbons). Maximum C₆₊ yield in each sample was obtained at different pyrolysis temperatures. In the shale sample from the Anambra Basin, maximum C₆₊ was obtained at 400°C, with a yield of 6.63mg/gTOC (Table 2, Fig. 14). Beyond that temperature, C₆₊ yields began to decline and it continued to decline until the final pyrolysis temperature. However, in the Dahomey and Bida shales, maximum C₆₊ was obtained at 380°C (24.09mg/gTOC and 5.80mg/gTOC respectively), the C₆₊ yields also began to decline beyond 380°C and at the final pyrolysis temperature where 8.20mg/gTOC and 4.86mg/gTOC were obtained in both samples, respectively. Higher C₆₊ was obtained in the Dahomey shale than in the other two samples (Anambra and Bida shales), and this is consistent with the geochemical origin of the samples (Table 1). Toyin³⁹ reported ≤ 40% and ≤ 37% liptinites in the Anambra coal and Dahomey shale, respectively, these could also impact on the quantities of C₆₊ generated in the two samples. In addition, occurrence of exsudatinites which was linked to earlier hydrocarbon generation in the Dahomey shale was reported by Toyin⁴⁰.

³⁷ Huss and Burnham, 1982. Gas evolution during pyrolysis of various Colorado oil shales. FUEL, Vol 61, 1188-1196

³⁸ Tian, H., Xiao, X.M., Wilkins, R.W.T., Li, X.Q., Gan, H.J., 2007. Gas sources of the YN2 gas pool in the Tarim Basin-evidence from gas generation and methane carbon isotope fractionation kinetics of source rocks and crude oils. Marine and Petroleum Geology 24, 29-41.

³⁹ Toyin A., 2024. Geochemical characterization of Cretaceous source rocks from Nigerian Frontier Basins: Implications for identifying new petroleum systems, and further exploration activities. (Ph.D. Thesis Unpublished).

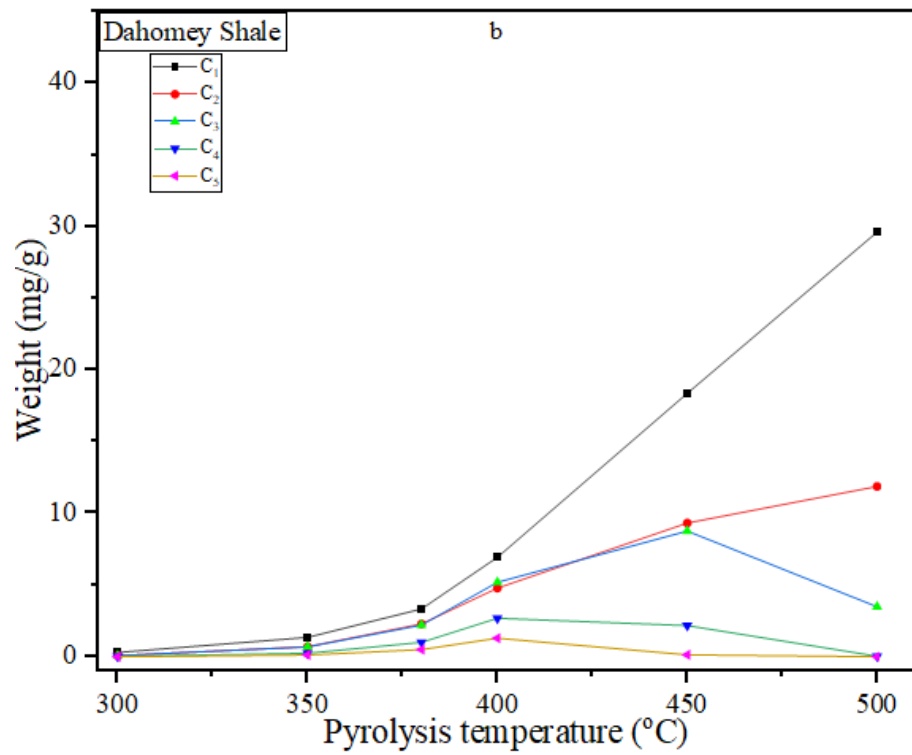
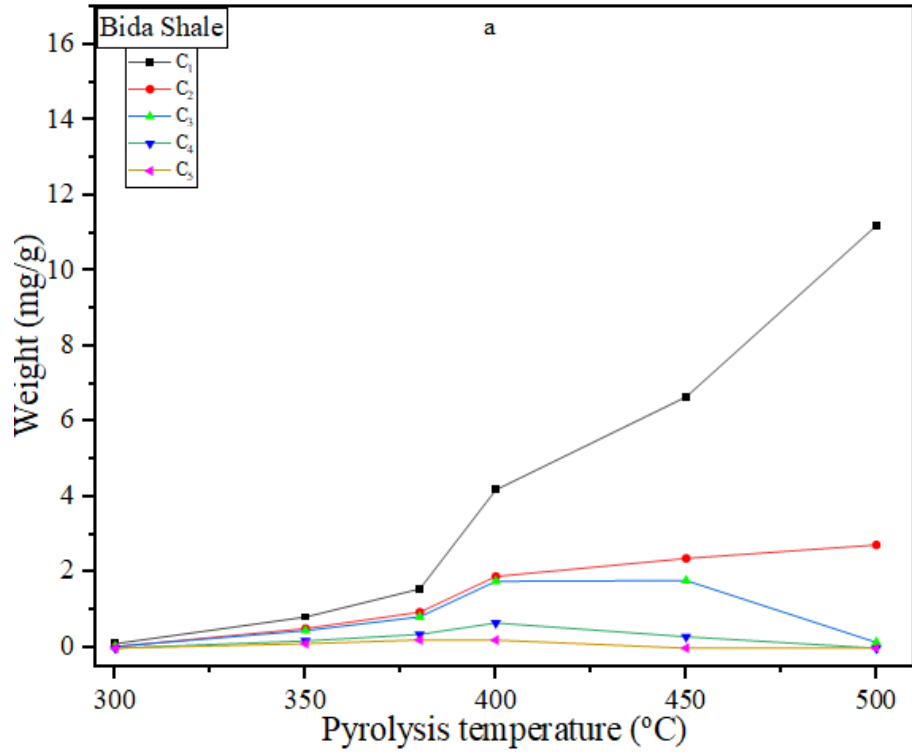
⁴⁰ Toyin Abdulkareem, Ningning Zhong, Falilat Omotolani Idris, Olabisi Adekeye, Shengbao Shi (2024). Geochemical evidence linking the Lower Cretaceous source rocks and biodegraded bitumen seeps and tar sands in the Gulf of Guinea Basin. Organic Geochemistry, 197, 104866.

However, the GOR in all the samples increases with increasing pyrolysis temperatures. A rapid rise in GOR was observed at temperatures at which C₆₊ began to crack in all the samples (Table 2). The highest GOR at 500°C was obtained in Dahomey shale, (5.50), followed by Bida shale (2.90) and the least was obtained in Anambra shale (2.52). The plot of GOR, C₁-C₅, C₆-C₁₄ and C₆₊ at each pyrolysis temperature for the pyrolysed source rock samples is shown in Fig. 14.

Table 2. Hydrocarbon and non-hydrocarbon gas yields (mg/gTOC) from the studied source rocks

Temp (°C)	Easy Ro (%)	C ₁	C ₂	C ₃	C ₄	C ₅	Total Gas (C ₁ -C ₅)	C ₂ -C ₅	Gas Dryness	C ₆ -C ₁₄	C ₁₅₊	Total Oil (C ₆₊)	GOR	CO ₂
Bida shale														
300	0.56	0.12	0.04	0.04	0.00	0.00	0.20	0.08	0.60	0.82	1.10	1.92	0.10	18.78
350	0.80	0.83	0.52	0.46	0.19	0.12	2.12	1.29	0.39	2.54	1.40	3.94	0.54	36.59
380	1.04	1.57	0.95	0.83	0.37	0.22	3.94	2.37	0.40	4.80	1.00	5.80	0.68	40.03
400	1.26	4.20	1.90	1.77	0.67	0.21	8.76	4.56	0.48	4.20	0.15	4.35	2.01	43.64
450	1.98	6.67	2.38	1.79	0.30	0.00	11.14	4.47	0.60	4.87	0.55	5.42	2.06	44.52
500	2.91	11.21	2.74	0.15	0.00	0.00	14.10	2.89	0.79	4.41	0.45	4.86	2.90	54.41
Dahomey shale														
300	0.56	0.30	0.08	0.08	0.02	0.00	0.47	0.17	0.64	0.18	3.65	3.83	0.12	48.54
350	0.80	1.36	0.70	0.69	0.24	0.13	3.12	1.76	0.43	1.17	3.95	5.12	0.61	80.61
380	1.04	3.34	2.29	2.22	1.00	0.49	9.34	6.00	0.36	20.39	3.70	24.09	0.39	90.78
400	1.26	6.94	4.80	5.20	2.69	1.29	20.91	13.97	0.33	14.06	2.60	16.66	1.25	89.05
450	1.98	18.38	9.33	8.77	2.18	0.13	38.80	20.41	0.47	12.49	0.95	13.44	2.89	103.55
500	2.91	29.62	11.89	3.49	0.04	0.00	45.06	15.43	0.66	7.40	0.80	8.20	5.50	116.06
Anambra shale														
300	0.56	0.19	0.06	0.04	0.00	0.00	0.29	0.10	0.66	1.55	1.50	3.05	0.10	11.96
350	0.80	1.30	0.54	0.30	0.08	0.26	2.48	1.18	0.52	0.52	0.15	0.67	3.72	36.19
380	1.04	2.08	0.86	0.50	0.13	0.21	3.77	1.69	0.55	2.38	0.60	2.98	1.27	40.35
400	1.26	5.77	1.42	0.62	0.07	0.02	7.91	2.14	0.73	3.58	3.05	6.63	1.19	58.40
450	1.98	8.41	1.32	0.28	0.00	0.03	10.04	1.62	0.84	2.40	3.70	6.10	1.65	73.10
500	2.91	13.06	1.44	0.06	0.00	0.00	14.56	1.51	0.90	2.83	2.95	5.78	2.52	87.50

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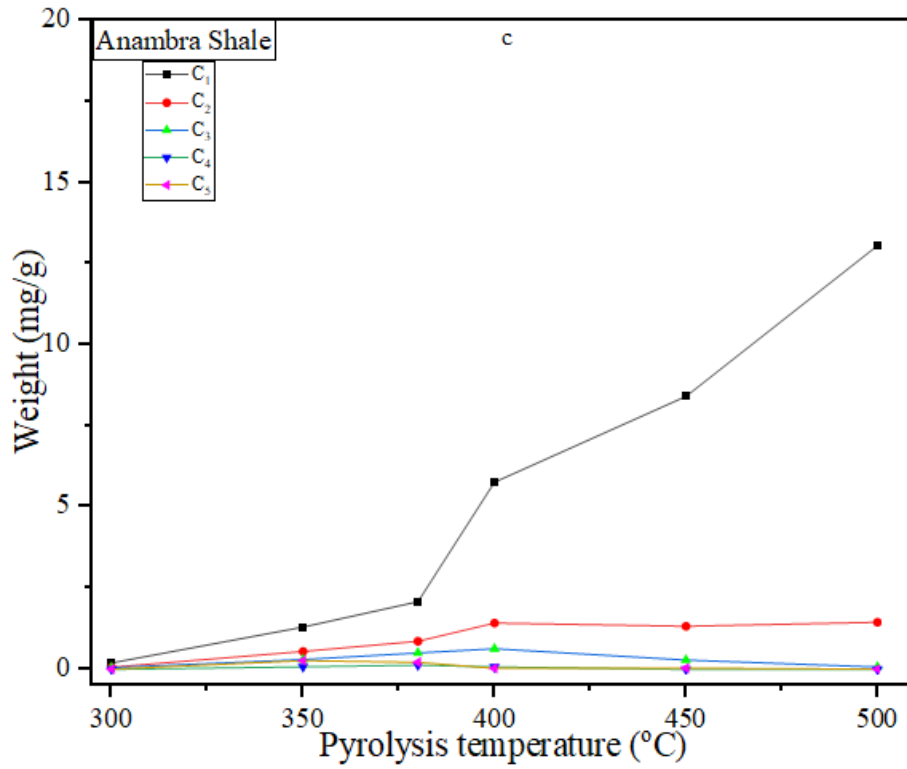
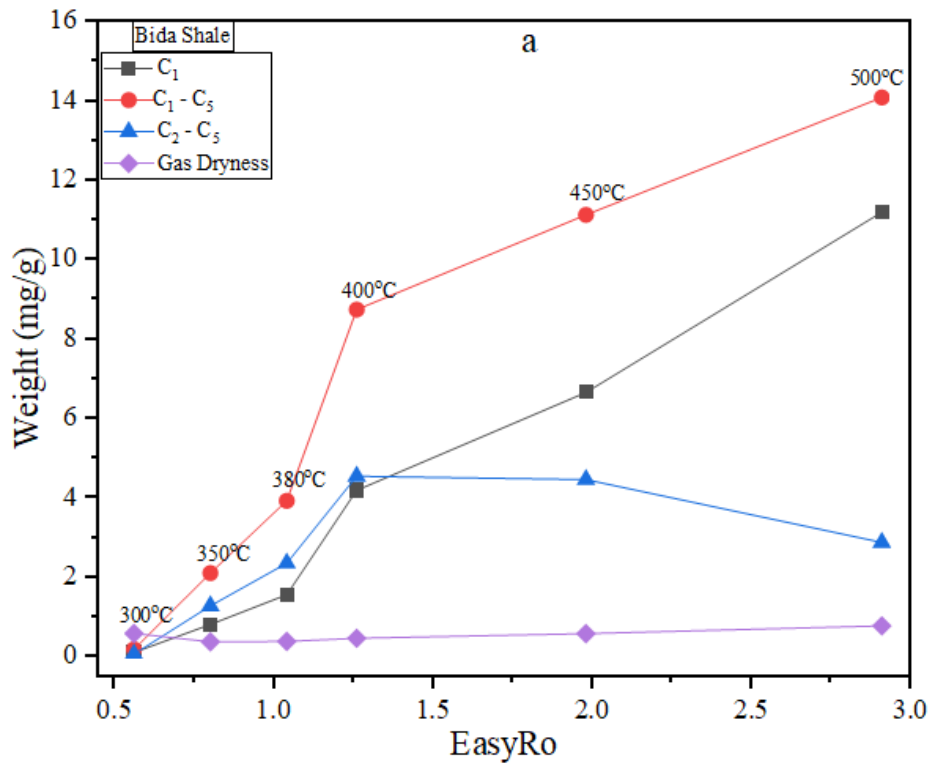
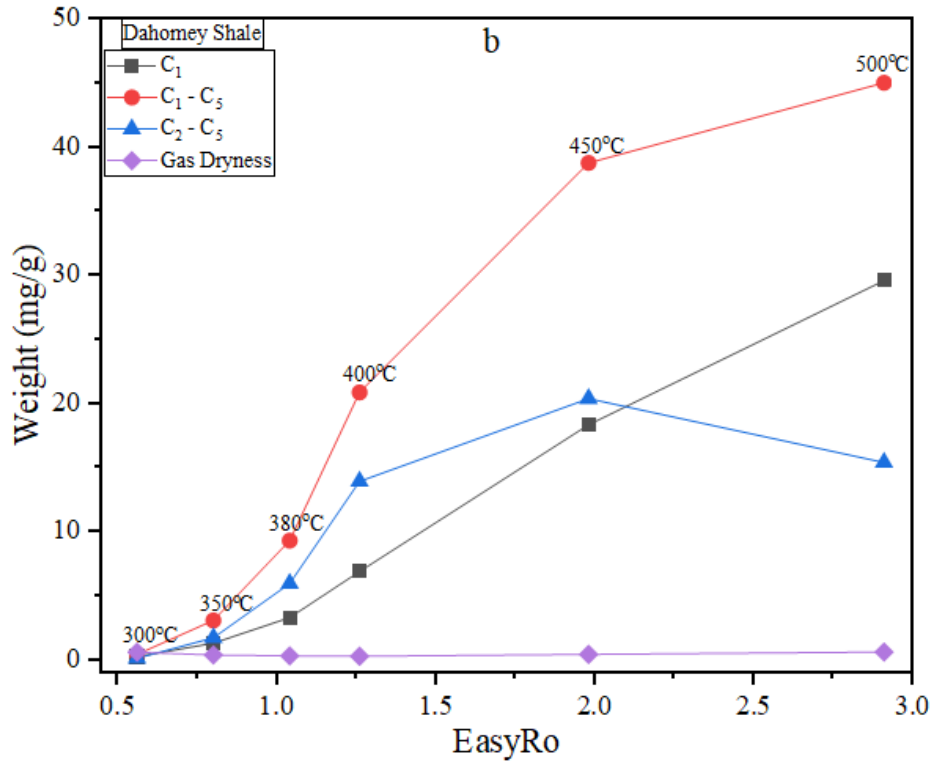


Figure 12: Plots of C₁ - 5 gas yields against pyrolysis temperatures for (a) Bida shale, (b) Dahomey shale (c) Anambra shale



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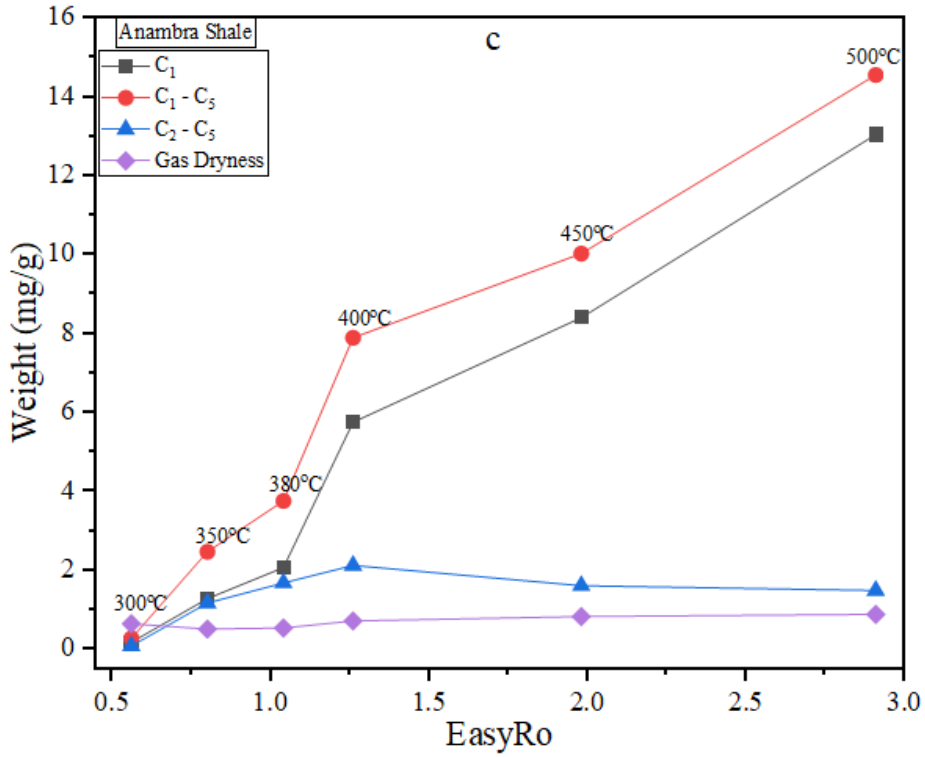
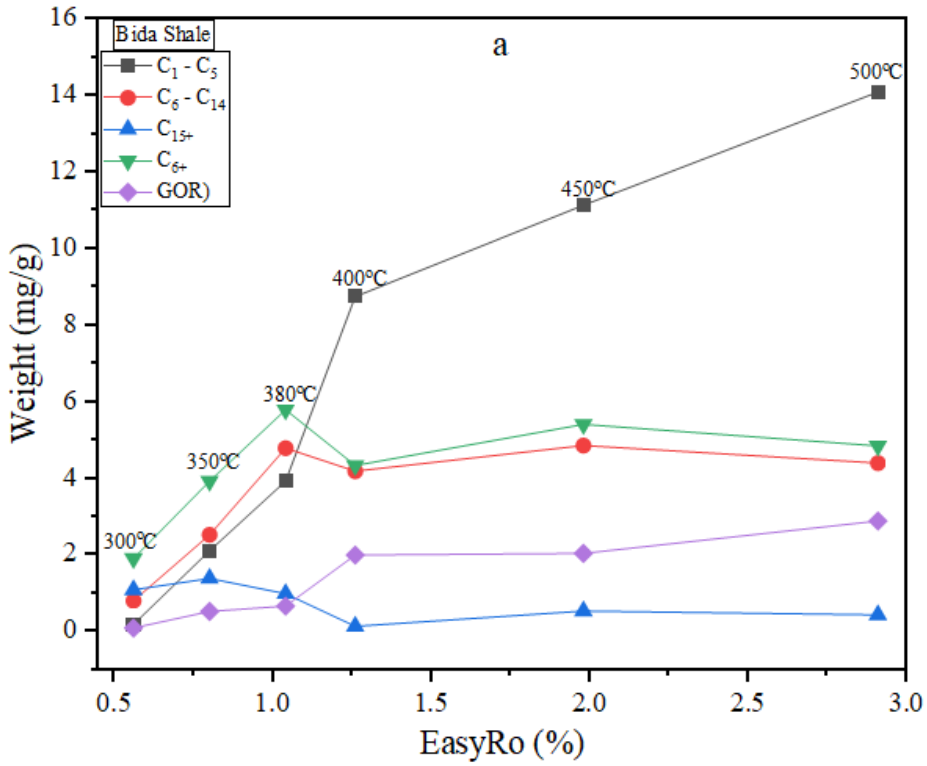


Figure 13: Plots of C₁, C₁ - C₅, C₂ - C₅, and gas dryness against EasyRo (%) for (a) Bida shale, (b) Dahomey shale (c) Anambra shale



Comparative Analysis of Hydrocarbon Generation in the Nigerian Frontier Basins: Insights from Late Cretaceous Hydrocarbon Source Rocks and Confined Pyrolysis Experiments

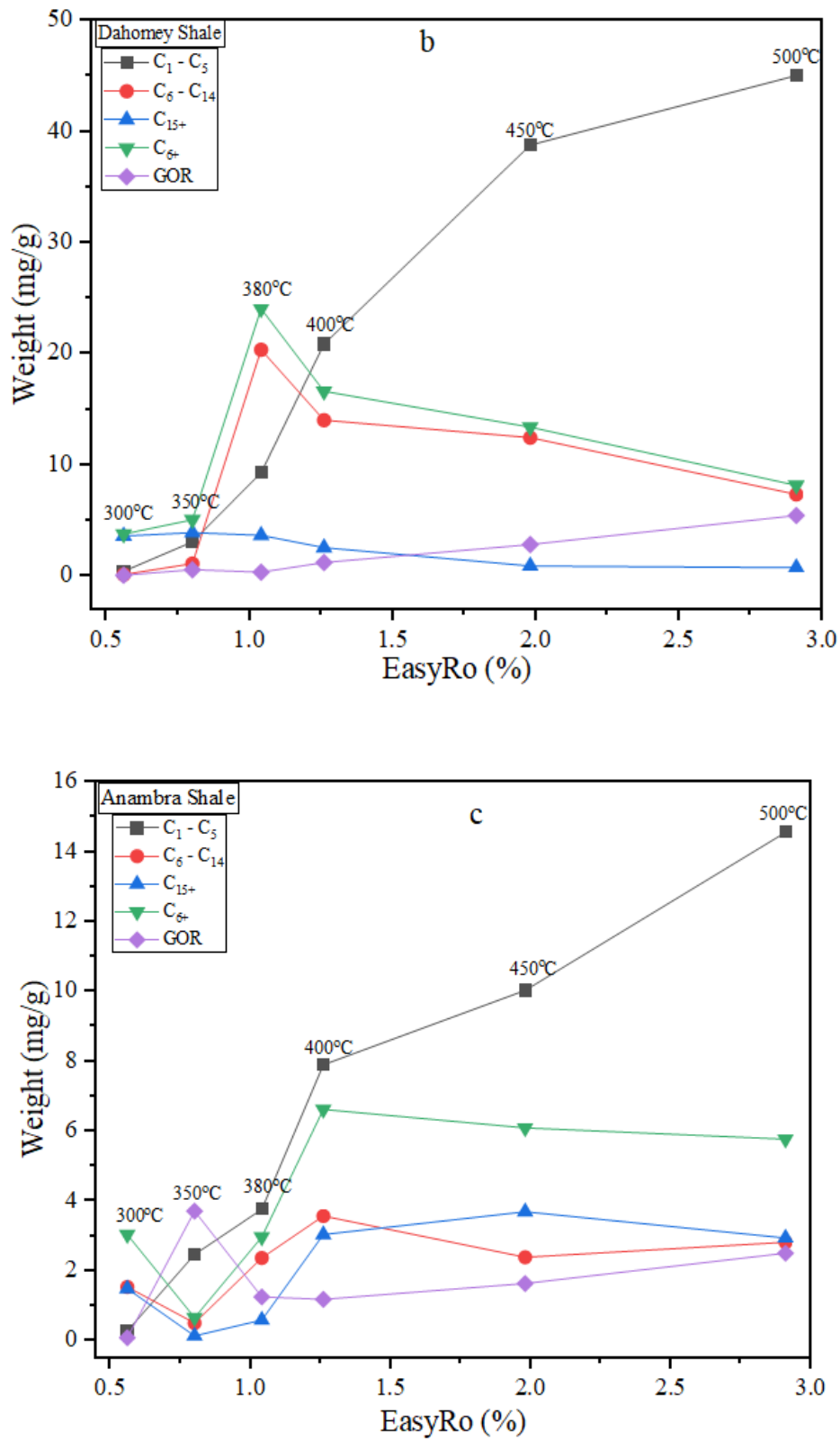


Figure 14. Plots of C₁ - C₅, C₆ - C₁₄, C₁₅₊, C₆₊ and GOR against EasyRo (%) for (a) Bida shale, (b) Dahomey shale (c) Anambra shale

4.4 Stable carbon isotopes of hydrocarbon gases

4.4.1 $\delta^{13}\text{C}_1$ - $\delta^{13}\text{C}_3$

The stable carbon isotopes of C_1 , C_2 and C_3 are considered in the present study and the values obtained in the pyrolyzed samples are presented in Table 3. The general isotopic trend shown by the gases is that they become enriched (heavy) with increasing pyrolysis temperatures. The values of $\delta^{13}\text{C}$ also become more positive with increasing carbon numbers from C_1 , C_2 to C_3 at similar stages of maturity. This observation is similar to that of Wang et al⁴¹. In the Bida shale, $\delta^{13}\text{C}_1$ becomes heavier from 380°C, (-36.5‰), and reaching -28.4‰ at 500°C. In the Dahomey shale, $\delta^{13}\text{C}_1$ also becomes heavier from 450°C (-34.6‰) and at 500°C, the value decreases to -32.7‰. However, in the Anambra shale, $\delta^{13}\text{C}_1$ becomes heavier from 350°C (-36.7‰) and at 500°C, -29.9‰ was obtained (Table 3, Fig. 15), at final pyrolysis temperature (500°C), the value of $\delta^{13}\text{C}_1$ was -32.7‰. The general trend shown by $\delta^{13}\text{C}_1$ in the present study (heavy at early and later stages of pyrolysis) is similar to those previously reported by some authors.^{38, 42, 43, 44, 38, 45} In addition, the decrease in $\delta^{13}\text{C}_1$ with increasing pyrolysis temperature is associated with a drop in gas dryness which occurred during an earlier stage of thermal cracking.⁴⁵ The decrease also indicates the generation of an early methane-enriched gas which results from the cracking of highly labile heteroatomic bonds such as C-O and C-S in source rocks.³⁸

Moreover, $\delta^{13}\text{C}_2$ and $\delta^{13}\text{C}_3$ in all the samples also become extremely enriched as the pyrolysis temperature increases, although $\delta^{13}\text{C}_3$ is richer (Fig. 15). This result is consistent with those previously reported by Tian et al³⁸. Earlier authors (e.g. Tilley and Muehlenbachs),⁴⁶ attributed the extremely heavy isotopes of C_2 and C_3 to their cracking at higher pyrolysis temperatures.

⁴¹ Wang Qingtao, Hong Lu, Paul Greenwood, Chenchen Shen, Jinzhong Liu, Ping'an Peng. 2013. Gas evolution during kerogen pyrolysis of Estonian Kukersite shale in confined gold tube system. *Organic Geochemistry* 65, 74–82.

⁴² Hill, R.J., Tang, Y.C., Kaplan, I.R., 2003. Insights into oil cracking based on laboratory experiments. *Organic Geochemistry* 34, 1651-1672.

⁴³ Cramer, B. S., Miller, K. G., Barrett, P. J., & Wright, J. D. (2011). Late Cretaceous–Neogene trends in deep ocean temperature and continental ice volume: Reconciling records of benthic foraminiferal geochemistry ($\delta^{18}\text{O}$ and Mg/Ca) with sea level history. *Journal of Geophysical Research: Oceans*, 116(C12).

⁴⁴ Tang, D., Hung, C. C., Warnken, K. W., & Santschi, P. H. (2000). The distribution of biogenic thiols in surface waters of Galveston Bay. *Limnology and Oceanography*, 45(6), 1289-1297.

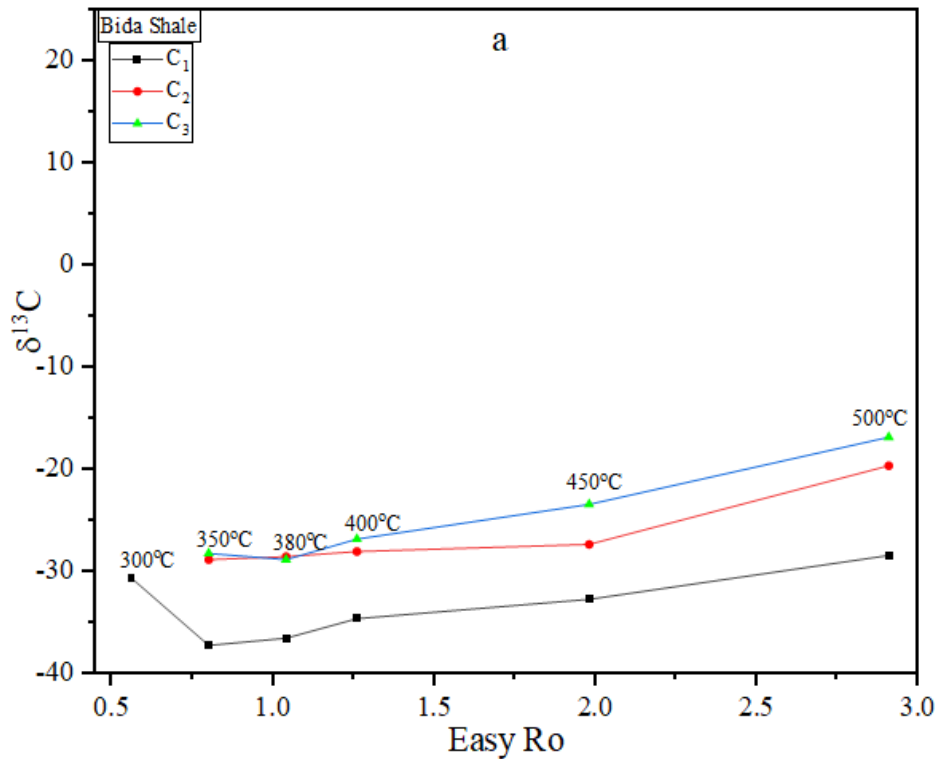
⁴⁵ Berner, U., Faber, E., Scheeder, G., & Panten, D. (1995). Primary cracking of algal and landplant kerogens: kinetic models of isotope variations in methane, ethane, and propane. *Chemical geology*, 126(3-4), 233-245.

⁴⁶ Tilley, B., & Muehlenbachs, K. (2006). Gas maturity and alteration systematics across the Western Canada Sedimentary Basin from four mud gas isotope depth profiles. *Organic Geochemistry*, 37(12), 1857-1868.

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Table 3: Stable carbon isotopes of hydrocarbon gases

Temp (°C)	EasyRo (%)	$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{13}C_3$	$\delta^{13}C_2 - \delta^{13}C_3$	$\ln C_1/C_2$	$\ln C_2/C_3$
Bida shale							
300	0.56	-30.6	-	-	-	1.16	-0.12
350	0.80	-37.2	-28.8	-28.2	-0.60	0.46	0.12
380	1.04	-36.5	-28.5	-28.8	0.30	0.50	0.14
400	1.26	-34.6	-28.0	-26.8	-1.10	0.79	0.07
450	1.98	-32.7	-27.3	-23.4	-3.90	1.03	0.28
500	2.91	-28.4	-19.6	-16.8	-2.80	1.41	2.89
Dahomey shale							
300	0.56	-33.6	-27.1	-26.3	-	1.39	-0.03
350	0.80	-35.7	-29.0	-27.1	-1.90	0.66	0.02
380	1.04	-36.0	-28.5	-27.6	-0.90	0.38	0.03
400	1.26	-36.6	-29.6	-28.3	-1.40	0.37	-0.08
450	1.98	-34.6	-27.8	-23.7	-4.10	0.68	0.06
500	2.91	-32.7	-24.2	-6.3	-17.90	0.91	1.22
Anambra shale							
300	0.56	-37.0	-29.9	-29.9	0.00	1.21	0.29
350	0.80	-36.7	-30.2	-29.1	-1.10	0.87	0.60
380	1.04	-36.5	-28.5	-28.1	-0.40	0.89	0.55
400	1.26	-34.3	-26.7	-22.8	-3.90	1.40	0.82
450	1.98	-32.4	-23.0	-13.9	-9.10	1.85	1.57
500	2.91	-29.9	-18.9	-	-	2.20	3.14



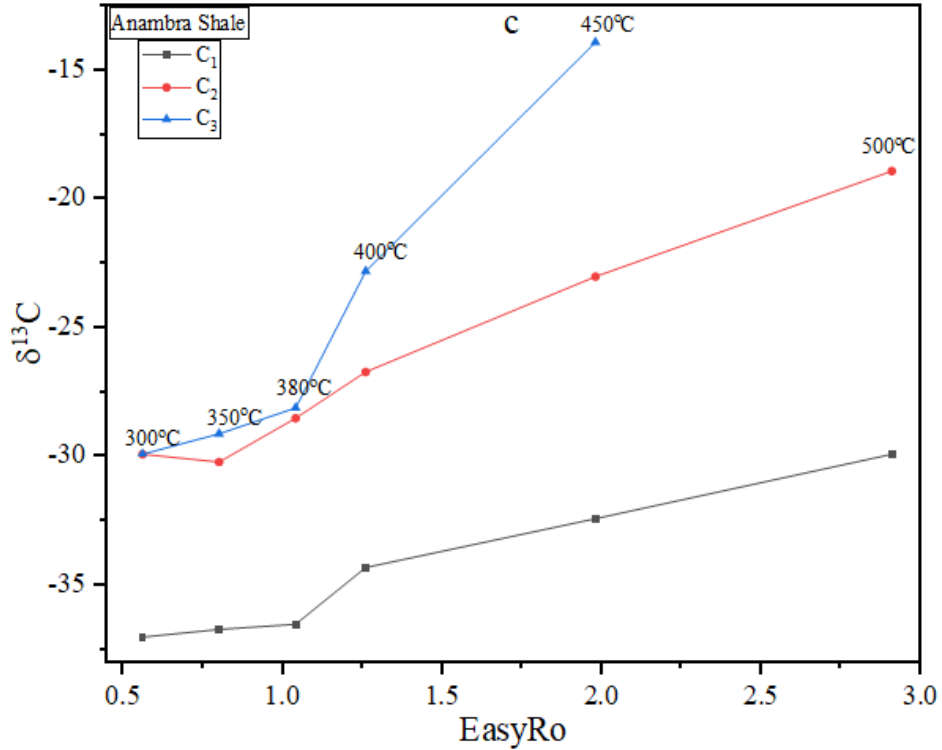
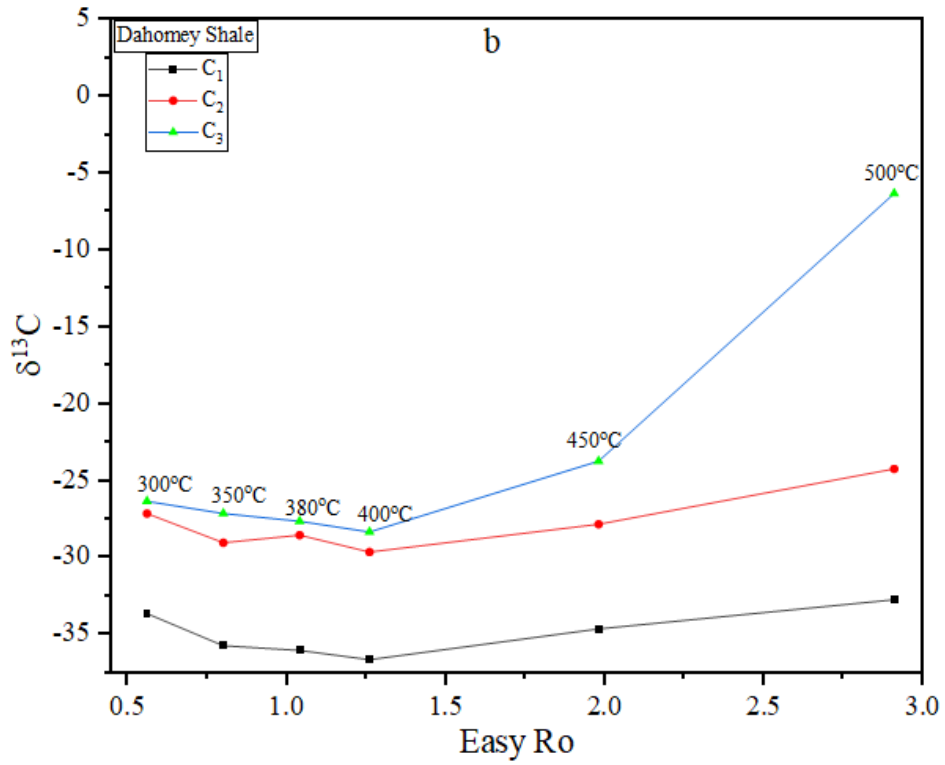


Figure 15. The plot of $\delta^{13}C_1$, $\delta^{13}C_2$ and $\delta^{13}C_3$ against EasyRo (%) for (a) Bida shale, (b) Dahomey shale (c) Anambra shale

5 Discussions

5.1 Gas evolution during pyrolysis experiment

The processes and mechanisms involved in natural gas evolution during the thermal transformation of kerogen and oil are well documented by earlier authors (e.g., ^{47, 48, 49}). Dominantly, primary gas formation from kerogen usually takes place at low temperatures, in contrast, at high temperatures, the formation of secondary gas occurs especially in petroleum reservoirs or in previously generated high molecular weight hydrocarbons during pyrolysis experiment ^{42, 35}. At different thermal maturity stages, proportions of C₁-C₃ in natural gas can be used to distinguish between methane sourced from kerogen or cracking of oil ⁵⁰. Further, the ratio of C₁/C₂ is believed to be significantly sensitive to thermal maturity as shown by increased methane production than ethane at higher maturity. Similar proportions of ethane and propane are produced when kerogen cracks and this leads to a relatively constant C₂/C₃ ratio. By contrast, in the secondary oil cracking stage, C₂/C₃ ratio increases as thermal maturity increases and this is due to further enhancement in C₂ production.

However, there are many documented parameters (e.g., plots of ln C₂/C₃ vs. ln C₁/C₂, δ¹³C₂-δ¹³C₃ vs. ln C₂/C₃) ^{42, 35, 50} and abundances of C₁ vs. C₂, i-C₄ vs. n-C₄ ⁵¹ that are being used to monitor stages of gas formation.

In the present study, the plot of ln C₂/C₃ against ln C₁/C₂ indicates three evolutionary stages of gas generation in the pyrolyzed hydrocarbon source rocks. During the first stage, there is a shift in the ratio of C₁/C₂ from higher to lower values at temperatures between 300°C and 350°C in the Bida and Anambra shales, 300°C in the Dahomey coaly-shale, whereas C₂/C₃ remains almost constant or slightly increases (Fig. 16). This trend can be attributed to preferential generation of C₃ and C₂ over C₁ at low pyrolysis temperatures and is consistent with the initial cracking of kerogen into hydrocarbon gases of higher molecular weight (C₂-C₅) than C₁ ⁴¹. During the second stage (at 350°C-450°C in the Bida and Anambra shales, and 380°C-450°C in the Dahomey coaly-shale), there is a slight increase in both ln C₁/C₂ and ln C₂/C₃, while during the third stage (450°C-500°C in all the samples), there is a rapid increase in ln C₁/C₂, while ln C₂/C₃ slightly increased. The third stage is characterized by an increased C₁ generation over C₂ and C₃ (C₁>C₂>C₃) and is classified as secondary oil cracking stage ⁵⁰.

⁴⁷ Vandenbroucke, M., Behar, F., & Rudkiewicz, J. L. (1999). Kinetic modelling of petroleum formation and cracking: implications from the high pressure/high temperature Elgin Field (UK, North Sea). *Organic Geochemistry*, 30(9), 1105-1125.

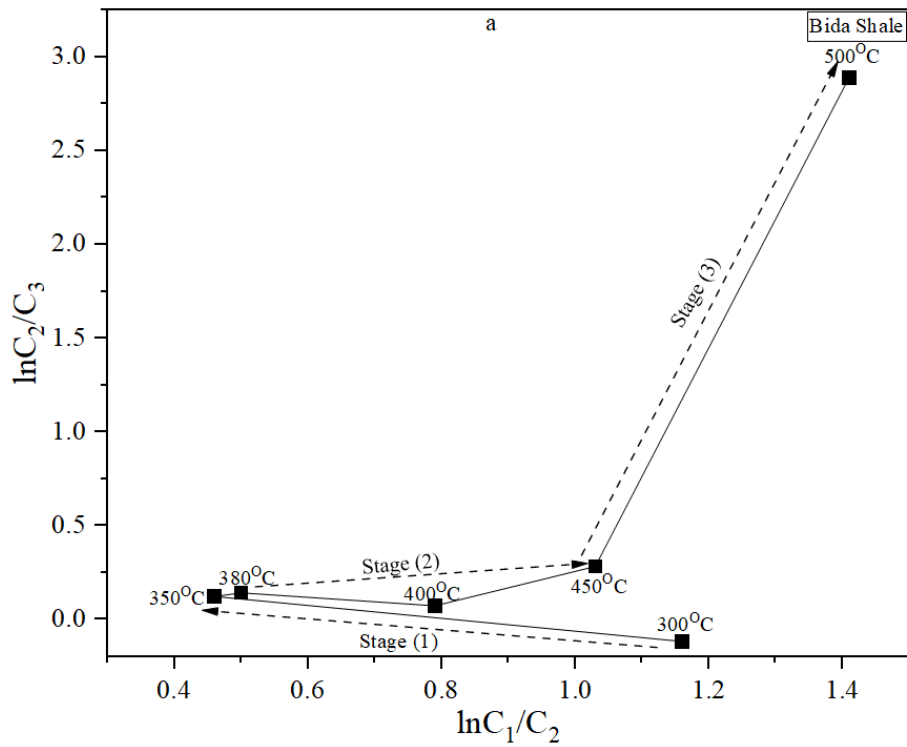
⁴⁸ Dieckmann, V., Schenk, H. J., Horsfield, B., & Welte, D. H. (1998). Kinetics of petroleum generation and cracking by programmed-temperature closed-system pyrolysis of Toarcian Shales. *Fuel*, 77(1-2), 23-31.

⁴⁹ Pepper, A. S., & Dodd, T. A. (1995). Simple kinetic models of petroleum formation. Part II: oil-gas cracking. *Marine and Petroleum Geology*, 12(3), 321-340.

⁵⁰ Prinzhofer, A. A., & Huc, A. Y. (1995). Genetic and post-genetic molecular and isotopic fractionations in natural gases. *Chemical Geology*, 126(3-4), 281-290.

⁵¹ Zhang Tongwei, Xun Sun, Kitty L. Milliken, Stephen C. Ruppel, and Daniel Enriquez (2017). Empirical relationship between gas composition and thermal maturity in Eagle Ford Shale, south Texas. *AAPG Bulletin*, v. 101, no. 8, pp. 1277-1307.

In addition, the plot of $\delta^{13}\text{C}_2-\delta^{13}\text{C}_3$ versus $\ln C_2/C_3$ was also employed to investigate gas formation processes during the pyrolysis experiment (Fig. 17). The plot shows that during the primary cracking of kerogen, $\delta^{13}\text{C}_2-\delta^{13}\text{C}_3$ remains almost constant or slightly increases while $\ln C_2/C_3$ also slightly increases. In the secondary cracking stage, $\delta^{13}\text{C}_2-\delta^{13}\text{C}_3$ decreases rapidly except in the Bida shale, where it decreases slightly (Fig. 17a), while $\ln C_2/C_3$ increases rapidly. Generally, secondary cracking begins at 450°C in all the samples.



Comparative Analysis of Hydrocarbon Generation in the Nigerian Frontier Basins: Insights from Late Cretaceous Hydrocarbon Source Rocks and Confined Pyrolysis Experiments

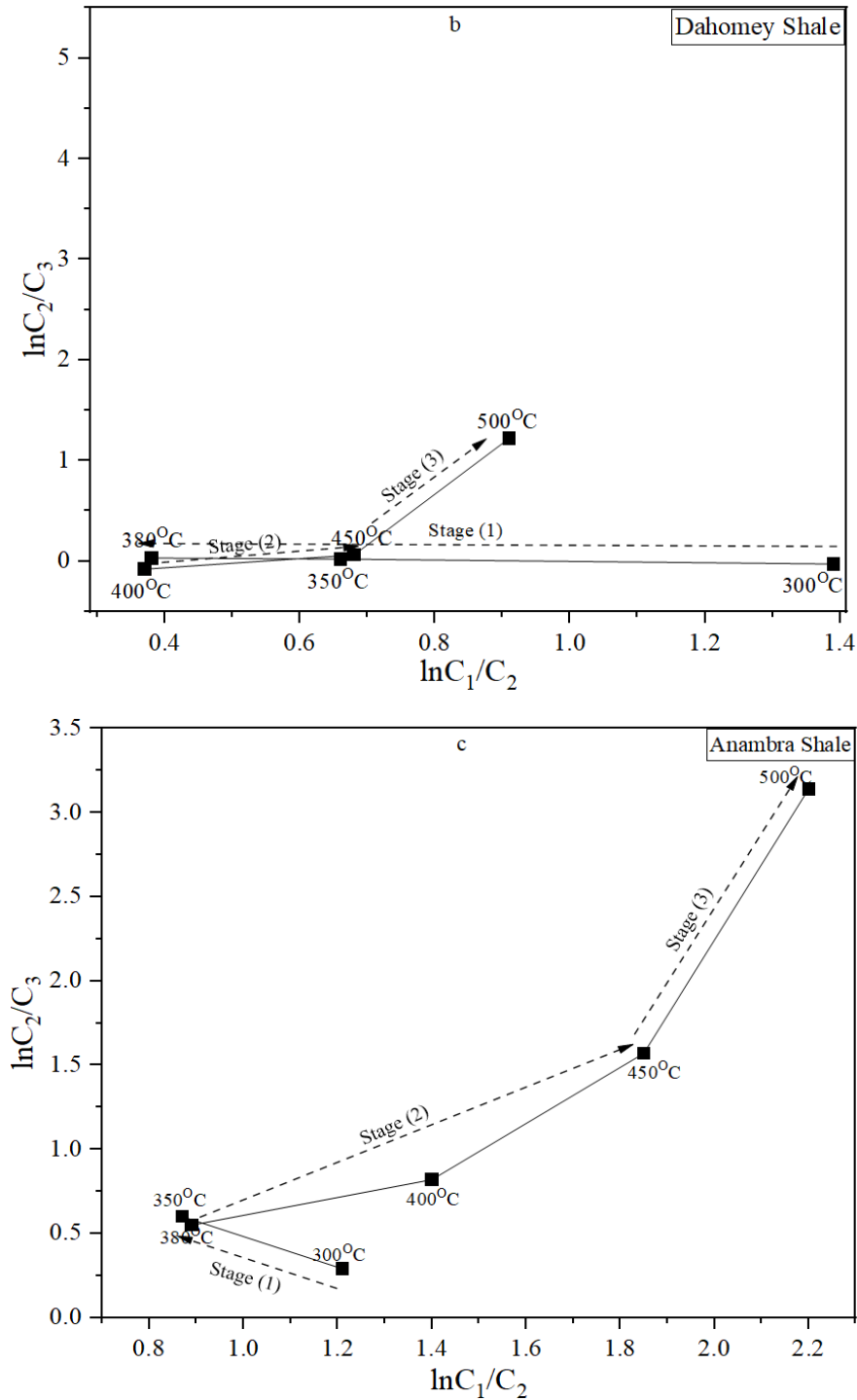
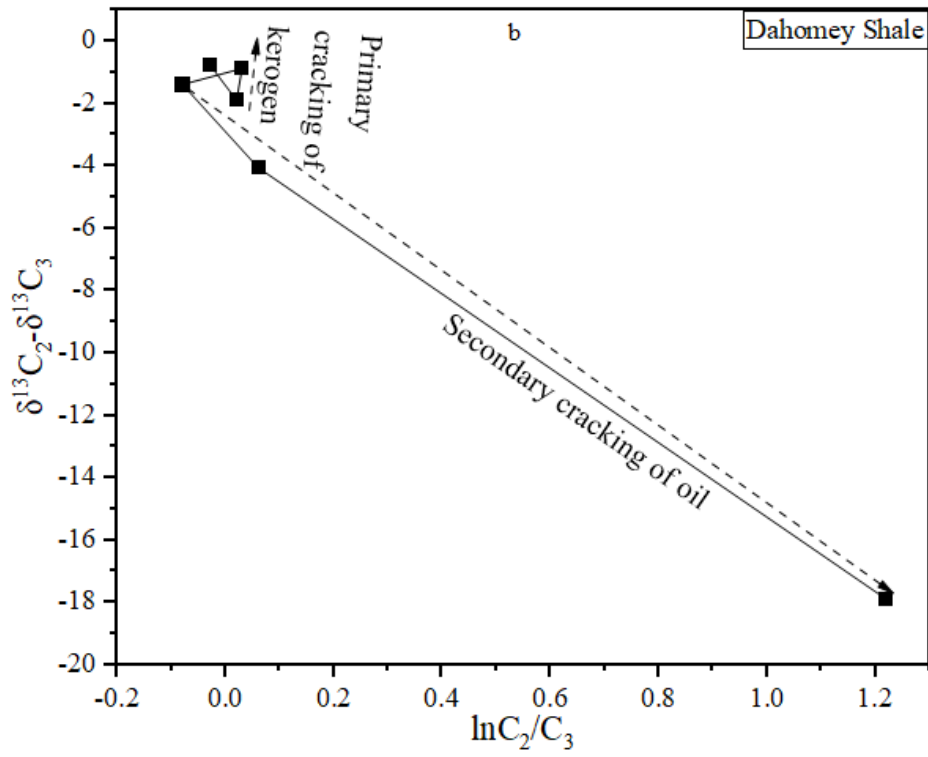
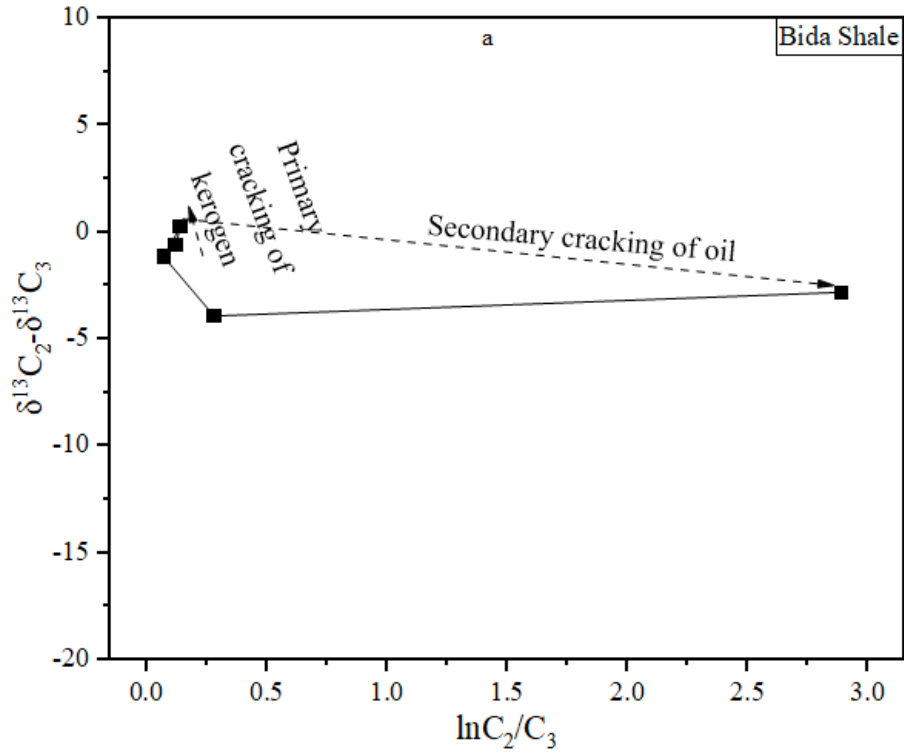


Figure 16. The plot of $\ln C_1/C_2$ against $\ln C_2/C_3$ shows three stages of hydrocarbon generation. In the first stage, C_1/C_2 shifts from higher to lower values, whereas C_2/C_3 remains almost constant. In the second stage, there was a slight increase in both $\ln C_1/C_2$ and $\ln C_2/C_3$. In the third stage, there was a rapid increase in $\ln C_1/C_2$, while $\ln C_2/C_3$ slightly increased.



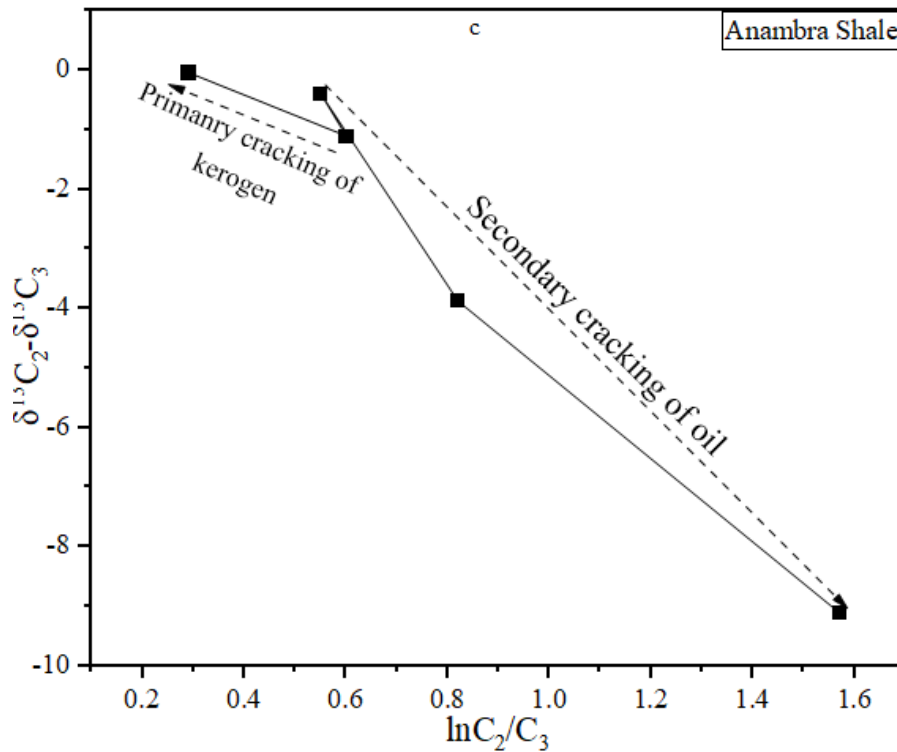
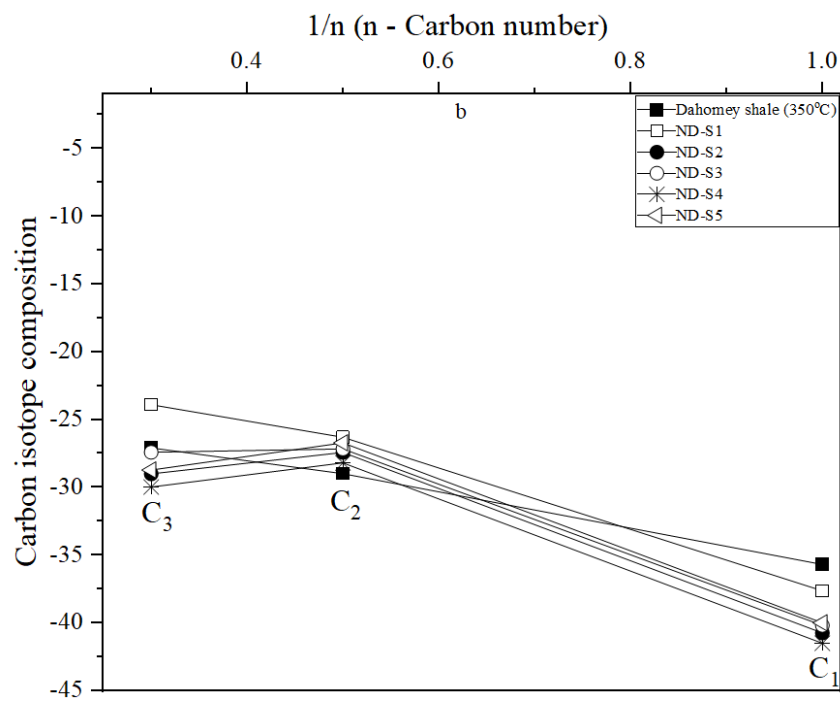
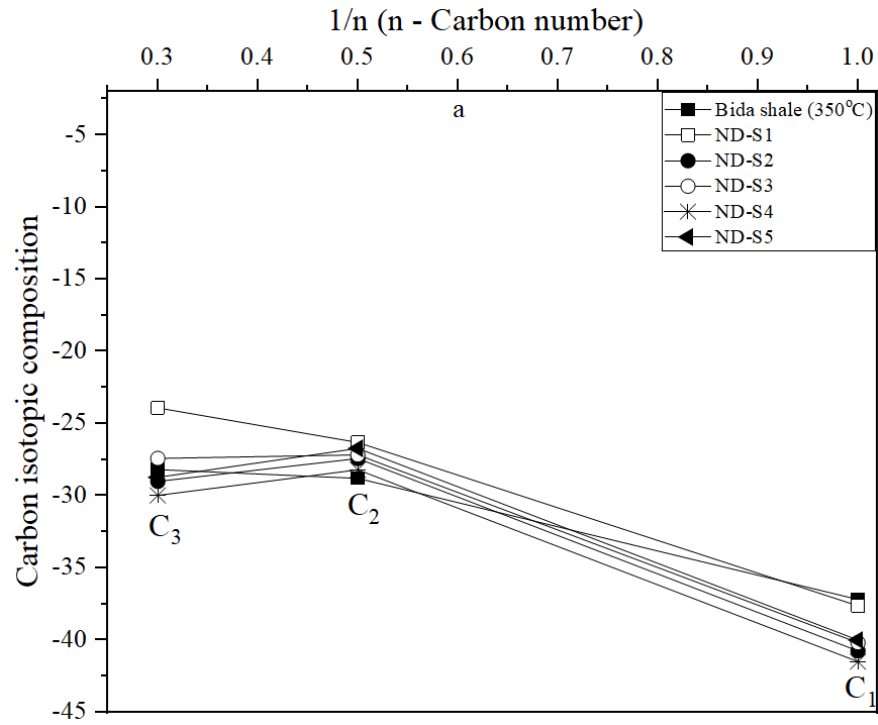


Figure 17. The plot of $\ln C_2/C_3$ against $\delta^{13}C_2 - \delta^{13}C_3$ indicates processes of hydrocarbon generation (i.e., primary, and secondary cracking stages). During the primary cracking stage, $\delta^{13}C_2 - \delta^{13}C_3$ remains almost constant or slightly increases while $\ln C_2/C_3$ also slightly increases. In the secondary cracking stage, $\delta^{13}C_2 - \delta^{13}C_3$ decreases rapidly except in the Bida shale, where it decreases slightly, while $\ln C_2/C_3$ increases rapidly.

5.2. Correlation of the generated gases to the Niger Delta gases

The natural gas plot of Chung et al.⁵² has been used to distinguish gases derived from a single source and those from mixtures of two or more sources. The plot is based on the isotopic compositions of C_1 through C_5 as a function of the reciprocal of their carbon numbers. In the present study, $\delta^{13}C$ of C_1 , C_2 , and C_3 from the generated gases at the pyrolysis temperature of 350°C (EasyRo%-0.8) were correlated to $\delta^{13}C$ of C_1 , C_2 , and C_3 of gases produced in the Niger Delta (Fig. 18). In the Bida shale, the generated gases, C_1 , C_2 , and C_3 are isotopically similar to those generated in the Niger Delta (Fig. 18a), while C_2 and C_3 generated by the Dahomey shale are isotopically similar to those of the Niger Delta, but the C_1 is heavier (Fig. 18b). However, in the Anambra shale, C_1 and C_3 are isotopically similar to those of the Niger Delta, while C_2 is lighter (Fig. 18 c).

⁵² Chung, H. M., Gormly, J. R., & Squires, R. M. (1988). Origin of gaseous hydrocarbons in subsurface environments: theoretical considerations of carbon isotope distribution. *chemical Geology*, 71(1-3), 97-104.



Comparative Analysis of Hydrocarbon Generation in the Nigerian Frontier Basins: Insights from Late Cretaceous Hydrocarbon Source Rocks and Confined Pyrolysis Experiments

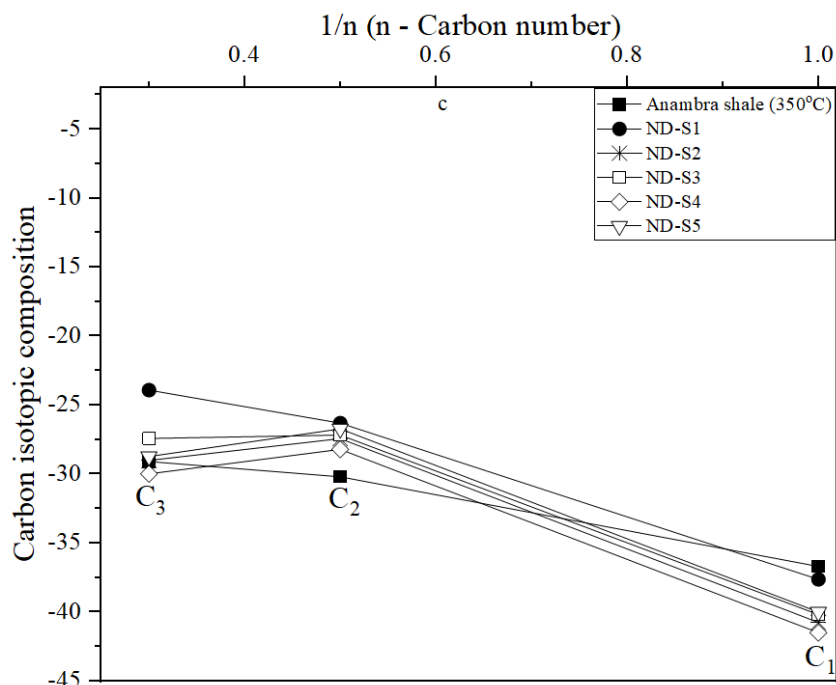


Figure 18. The plot of carbon isotopic composition of C₁, C₂ and C₃ against the reciprocal of carbon numbers to correlate the generated gases from this study with Niger Delta gas. (Niger Delta data were obtained from⁵³. C₁ and C₃ generated from the shale of the Anambra Basin are isotopically similar to those of the Niger Delta, but C₂ is heavier than that of the Niger Delta. C₁, C₂ and C₃ in the Bida shale are isotopically similar to those from the Niger Delta. C₂ and C₃ in the Dahomey shale are similar to those from the Niger Delta, but C₁ in the shale is heavier than that of the Niger Delta.

5.3 Isotopic significance of the generated gases

In studying gas origin, molecular compositions, carbon, and hydrogen isotopes of gases are essential. There are a large number of studies on gas origin (e.g.,^{50, 35, 54, 55, 56} etc). In many of the previous studies, the plot of $\delta^{13}\text{C}_1$ against $\delta^{13}\text{C}_2$ was used as a classification diagram for natural gas origin (e.g.,^{57, 58, 44}). In the present study, the pyrolyzed source rock samples show a similar range of $\delta^{13}\text{C}_1$. The values of $\delta^{13}\text{C}_1$ against $\delta^{13}\text{C}_2$ when plotted on the gas genetic diagram indicate a dominant contribution of terrestrially sourced organic matters in the pyrolysis products (Fig. 19).

⁵³ Botwe Takyi, Abrakasa Selegha, Udom J. Godwin, Kouadio Koffi Eugene. Correlation of natural gases from the X-field of the Niger Delta, Nigeria. *International Journal of Geography and Geology*, 2020, vol. 9, No. 2, pp. 93-100.

⁵⁴ Dai, L. Q., Zhao, Z. F., Zheng, Y. F., & Zhang, J. (2012). The nature of orogenic lithospheric mantle: geochemical constraints from postcollisional mafic-ultramafic rocks in the Dabie orogen. *Chemical Geology*, 334, 99-121.

⁵⁵ Dai, J., Ni, Y., Huang, S., Gong, D., Liu, D., Feng, Z., 2016. Origins of secondary negative carbon isotopic series in natural gas. *Nat. Gas. Geosci.* 27, 1-7.

⁵⁶ Milkov, A. V., & Etiope, G. (2018, June). Geochemistry of Shale Gases from around the World. In 80th EAGE Conference and Exhibition 2018 (Vol. 2018, No. 1, pp. 1-5). European Association of Geoscientists & Engineers.

⁵⁷ Rooney, M. A., Claypool, G. E., & Chung, H. M. (1995). Modeling thermogenic gas generation using carbon isotope ratios of natural gas hydrocarbons. *Chemical Geology*, 126(3-4), 219-232.

⁵⁸ Huang, D., Liu, B., Wang, T., Xu, Y., Chen, S., and Zhao, M., 1996. Genetic types of natural gases and their maturity discrimination in the east of Tarim Basin. *Sci. China* 39, 101-111.

5.4 Paleogeographic controls on the geochemistry of gases generated in the Nigerian Frontier Basins and Niger Delta

The Anambra, Bida and Dahomey Basins are parts of the West and Central African Rift Subsystem (WCARS) basins. The WCARS experienced different phases of marine transgressions in the past.⁵⁹ The first trans-Saharan transgression commenced in the Late Cenomanian, and it peaked in the Early Turonian. During these periods, the sea entered through the Benue rifts in Nigeria and the subsiding areas in North Africa. In the late Early Turonian, the central Sahara was land and the sea remained in the central part of the Benue rift, although the sea drifted forward during the minor Coniacian transgressive pulse. The Coniacian transgression penetrated only the eastern and central Niger Republic. For a short period, there was a link

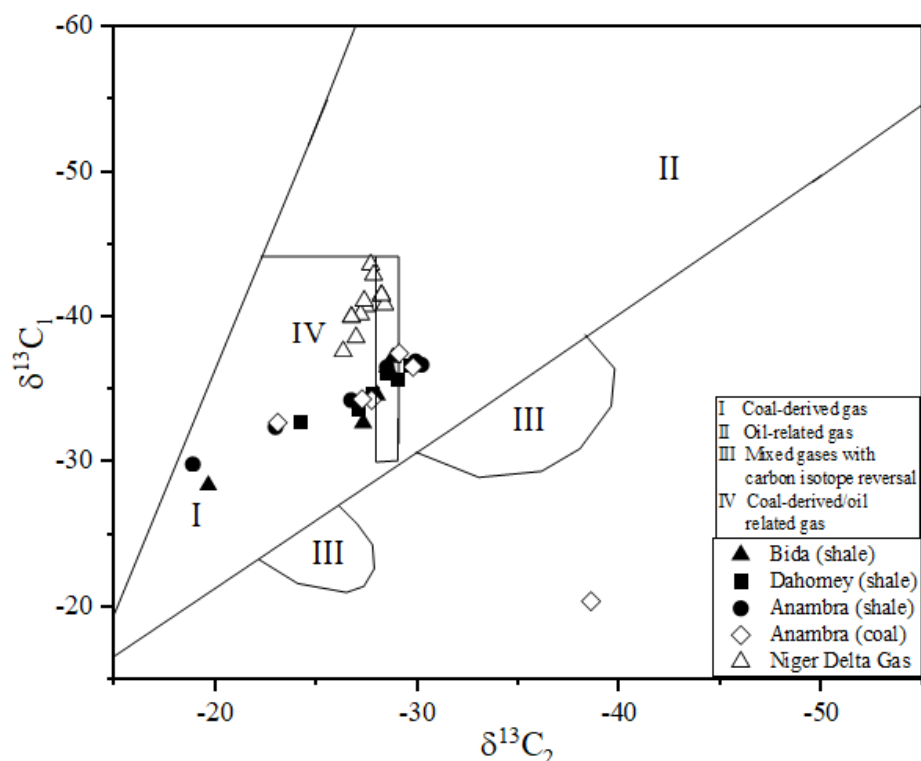


Figure 19. Plot of $\delta^{13}C_1$ against $\delta^{13}C_2$ indicating the origin of the generated gases from the pyrolysed source rocks. All the samples dominantly plot on coal-derived oil-related gas with a few plotting close to coal-derived gas. The diagram also shows that the generated gases from the source rocks are similar to those produced in the Niger Delta. (Niger Delta data were obtained from ⁵³)

between the Tethys and the South Atlantic during the Cenomanian-Turonian. This resulted in the deposition of organic-rich black shale during oceanic anoxic event II (OAE-II) worldwide. However, the most extensive epicontinental transgression in the WCARS basins commenced during the latest Campanian, and it reached its peak in the early Maastrichtian.

In Nigeria, water exchange between the Tethys and the South Atlantic occurred during the Cenomanian-Turonian, Maastrichtian, and Paleocene.⁵⁹ The waters move through the Benue Trough in eastern Nigeria and the Bida Basin in the west. The movements of waters during those

⁵⁹ Reyment, R.A., 1980. Biogeography of the Saharan Cretaceous and Paleocene Epicontinental 698 Transgressions". *Cretaceous Research*, 1, 299-327

periods resulted in the deposition of similar sedimentary facies across the Nigerian Frontier Basins and other African basins such as the Muglad Basin of Sudan, the Sirte Basin of Libya, and the Termit Basin of the Niger Republic^{60, 61}. In the Anambra and Dahomey Basins, deep marine waters penetrated most parts of the basins due to their closeness to the South Atlantic and lowland areas. In contrast, waters from marginal marine realms only penetrated the Bida Basin. As a result of this, there is a strong influence of marine waters on the nature of source rocks within the Dahomey and Anambra Basins. Since the Niger Delta Basin was used as an exchange point of waters (i.e., marginal, shallow, and deep-marine waters), between the Tethys and south-Atlantic,⁵⁹ marine and non-marine source rocks within the Niger Delta Basin are expected to have similar geochemical signatures to those in the Anambra, Bida and Dahomey Basins. Thus, the similarities in the gases generated from the pyrolyzed source rocks and those produced in the Niger Delta ($\delta^{13}\text{C}$ of C_1 , C_2 , and C_3) could be attributed to marine connections.

6. Conclusions

A comparative analysis of hydrocarbon generation potentials of Nigerian frontier basins was carried out to provide more insights into Late Cretaceous hydrocarbon source rocks using field studies, organic geochemical analyses as well as confined Pyrolysis Experiments. Based on the result of this study, the following are the conclusions:

- (1) The Cretaceous source rocks from the Nigerian Frontier Basins would generate oil and gas upon attaining an appropriate thermal maturity, in a similar manner to those in other WCARS basins.
- (2) Dahomey coaly-shale has the highest gas-to-oil ratio, and it also generates the highest amount of oil at low pyrolysis temperatures.
- (3) The composition of organic matter in the studied source rocks and the pyrolysis temperature control the gas-to-oil ratios.
- (4) There was a dominant contribution of terrestrially-sourced organic matter in the pyrolysis products.
- (5) The gases generated from the Anambra, Bida, and Dahomey Basins are isotopically similar to those of coal-derived oil-related gases.
- (6) The $\delta^{13}\text{C}$ of C_1 , C_2 and C_3 gases from the pyrolyzed source rocks are similar to those generated from the Niger Delta and it could be a result of marine connections.

Acknowledgements

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⁶⁰ Genik, G. J. (1992). Regional framework, structural and petroleum aspects of rift basins in Niger, Chad, and the Central African Republic (CAR). *Tectonophysics*, 213(1-2), 169-185.

⁶¹ Reymont, R. A. (1982). Phenotypic evolution in a Cretaceous foraminifer. *Evolution*, 1182-1199.